— CHAPTER 1 —

C_{20}-DITERPENOID ALKALOIDS

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I. Introduction

From the view point of their biogenesis, the alkaloids may be divided roughly into two broad categories: the *true alkaloids* and the *pseudo* (or *crypto)-alkaloids.* The former, in most cases, are derived from the α-amino acid precursors, while the latter appear to be the derivatives of generally occurring, nitrogen-free constituents, such as terpenes and steroids, *via* an amination process (*1*, *2*, *36*). Therefore, the definition of the diterpenoid alkaloids formulated by Pelletier (*3*) stressed the point that these bases are derived from tetracyclic or pentacyclic diterpenes in which the nitrogen atom of methylamine, ethylamine, or β-aminoethanol is linked to C-17 and C-19 in the C_{19}-diterpenoid alkaloids, and to C-20 and C-19 in the C_{20}-diterpenoid alkaloids, to form a substituted piperidine ring.

The prime and lasting attention of researchers to the diterpenoid alkaloids is due to the various bioactivities, structural complexity, and interesting chemistry.

The literature on the C_{20}-diterpenoid alkaloids reported before 1980 was reviewed in Volumes Ⅳ, Ⅶ, Ⅻ, and ⅩⅧ of this treatise, as well as other monographs, reports, and reviews (*3*~*58*). In 1992, we gave a systematic summing-up of the important chemical reactions of the diterpenoid alkaloids with literature coverage to the end of 1990 (*22*). Although a number of research papers involving various aspects of this field have been published since Pelletier's excellent chapter in Volume ⅩⅧ of this treatise, a systematic review in the research work during the past twenty years has not been published so far.

The number of known C_{20}-diterpenoid alkaloids, like other natural products, has grown markedly during 1980-2000, from 58 entries in 1980 to a present count of 281, with more distinctive diversity as compared with the C_{19}-diterpenoid alkaloids.

In this chapter, we thus wish to review, systematically and briefly, the C_{20}-diterpenoid alkaloids during the past twenty years, except for the literature

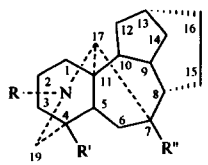
coverage on their chemistry, which starts from 1990 as a logical continuation of Volume 42 of this treatise.

In addition, liberal usage of figures and tables was adopted in order to save space.

II. Classification, Distribution, and Occurrence

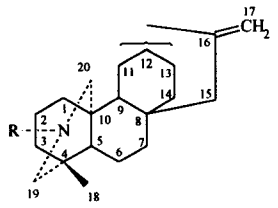
A. CLASSIFICATION

The criterion and change of the structural classification of C_{20}-diterpenoid alkaloids depend, to a large degree, on the research level and the number of known compounds available. In 1970, Pelletier (*7*) classified the C_{20}-diterpenoid alkaloids into two broad categories: the atisine-type (A) and veatchine-type (B), on the basis of the limited number of alkaloids (21) isolated at that time. When the number of alkaloids grew to a count of 58 by 1980, the C_{20}-diterpenoid alkaloids were divided



R'=H, OH, OR, CH_2-
R"=H, OH, OR

A (C_{18}, C_{19})



B (C_{20})

by Pelletier (*3, 4*) into four types: the atisine-type, veatchine–type, delnudine-type, and bisditerpenoid-type, listing the representative alkaloids such as atisine, denudatine, delnudine, hetidine, and hetisine for the atisine-type, and veatchine, garryfoline, ovatine, lindheimerine, and anopterimine for the veatchine-type. In the meantime, the atisine-type and the veatchine-type were subdivided by many scientists into the atisine-type and denudatine-type, delnudine-type, veatchine-type, napelline-type, and anopterine-type. In recent years, Russian scientists (*45*) have divided the diterpenoid alkaloids into four broad groups: atisanes (C_{20}), kauranes (C_{20}), aconanes (C_{18}/C_{19}), and the bisditerpenoid alkaloids ($C_{20}\times 2$). According to

their structural diversity, each of these groups was further subdivided into the types shown in Table I, and most of these types are compatible with the representative alkaloids reported by Pelletier in 1980 (*3*).

TABLE I

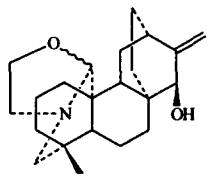
CLASSIFICATION OF C_{20}-DITERPINOID ALKALOIDS ACCORDING TO SULFANKHODZHAEV *ET AL.* (*45*)

group	type
atisane	atisine, dithydroatisine, ajaconine, denudatine, hetidine, coriphine, hetisine, isoatisine, spiradine D, spiramine A, brumonine, talasamine, vakognavine, albovionitine, delnudine
kaurane	veatchine, garryfoline, napelline, anopterine, anopterimine, lindheimerine
bisditerpenoid alkaloid	staphinine

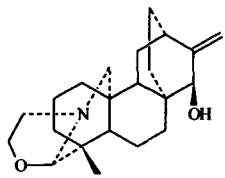
According to the above mentioned, two aspects may be pointed out as below:

a. The skeletal types of the C_{20}-diterpenoid alkaloids are fairly complex;

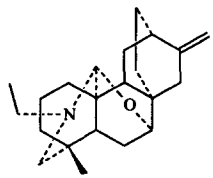
b. The classification of the C_{20}-diterpenoid alkaloids has not been very clear cut, especially in the types. For example, the three alkaloids atisine, isoatisine, and ajaconine, may be regarded as belonging to the same atisine-type, but are actually subdivided into three types, as shown in Table I. Their differentiation only depends on the different patterns of the *N,O*-mixed acetal systems. After carefully analyzing the structures of the known C_{20}-diterpenoid alkaloids with regard to the general features for classification, we now propose four criteria for this purpose.



atisine



isoatisine



ajaconine

1. With respect to the carbon skeleta, the C_{20}-diterpenoid alkaloids may be initially divided into four classes (Fig. 1):

1). Atisane-class (**A**): considered as the derivatives of aminated atisanes.

2). Kaurane-class (**B**): consided as the derivatives of aminated kauranes.

3). Rearranged-class (**C**): with a new heterocyclic skeleton formed by rearrangement of the hetisine- or denudatine-types.

4). Bisditerpenoid-class (**D**): with the carbon skeleton of 40 or 39 carbon atoms, i.e., by condensation of two C_{20}-diterpenoid alkaloids, or of one each of the C_{20}- and C_{19}-diterpenoid alkaloids.

2. In accordance with the number of skeletal rings and the positions of additional C-C or N-C or *seco* C-C/ C-N bonds, each class may included the types as shown in Fig. 1.

1). Atisane-class (A)

(1) Atisine-type (A Ⅰ): pentacyclic, the same as atisine;

(2) Denudatine-type (A Ⅱ): hexacyclic with an additional C-20-C-7 bond in the atisine-type;

(3) Spireine-type (AⅢ): hexacyclic with the additional N-C-21-C-7 linkage in the atisine-type;

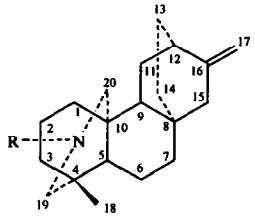
(4) Hetidine-type (AⅣ): hexacyclic with an additional C-20-C-14 bond in the atisine-type;

(5) Cardionidine-type (A Ⅴ): pentacyclic with a 6, 7-*seco* hetidine-type;

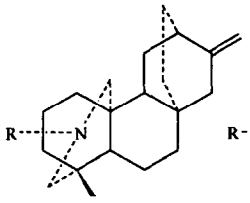
(6) Albovionitine-type (AⅥ): pentacyclic with a *N*, 20-*seco* hetidine-type;

(7) Hetisine-type (AⅦ): heptacyclic with an additional *N*-C-6 bond as compared with the hetidine-type, which is one of most complex entries in the atisane-class;

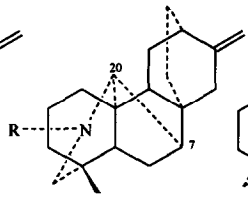
(8) Vakognavine-type (AⅧ): hexacyclic with a *N*, 19-*seco* hetisine-type;



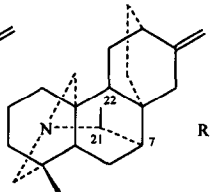
A



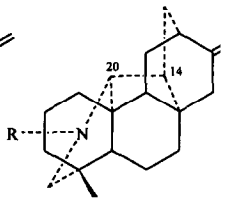
(A I)



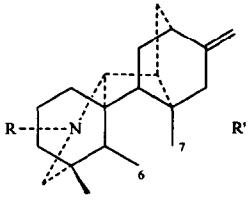
(A II)



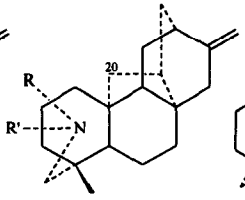
(AIII)



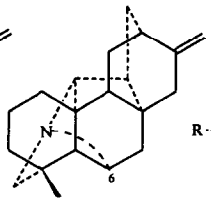
(AIV)



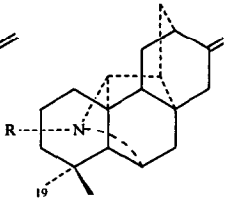
(A V)



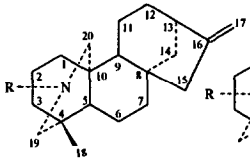
(AVI)



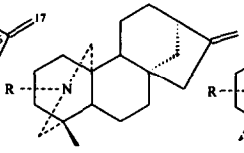
(AVII)



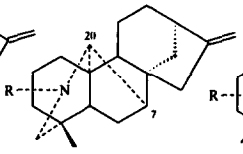
(AVIII)



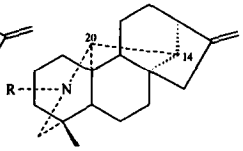
B



(B I)



(B II)



(BIII)

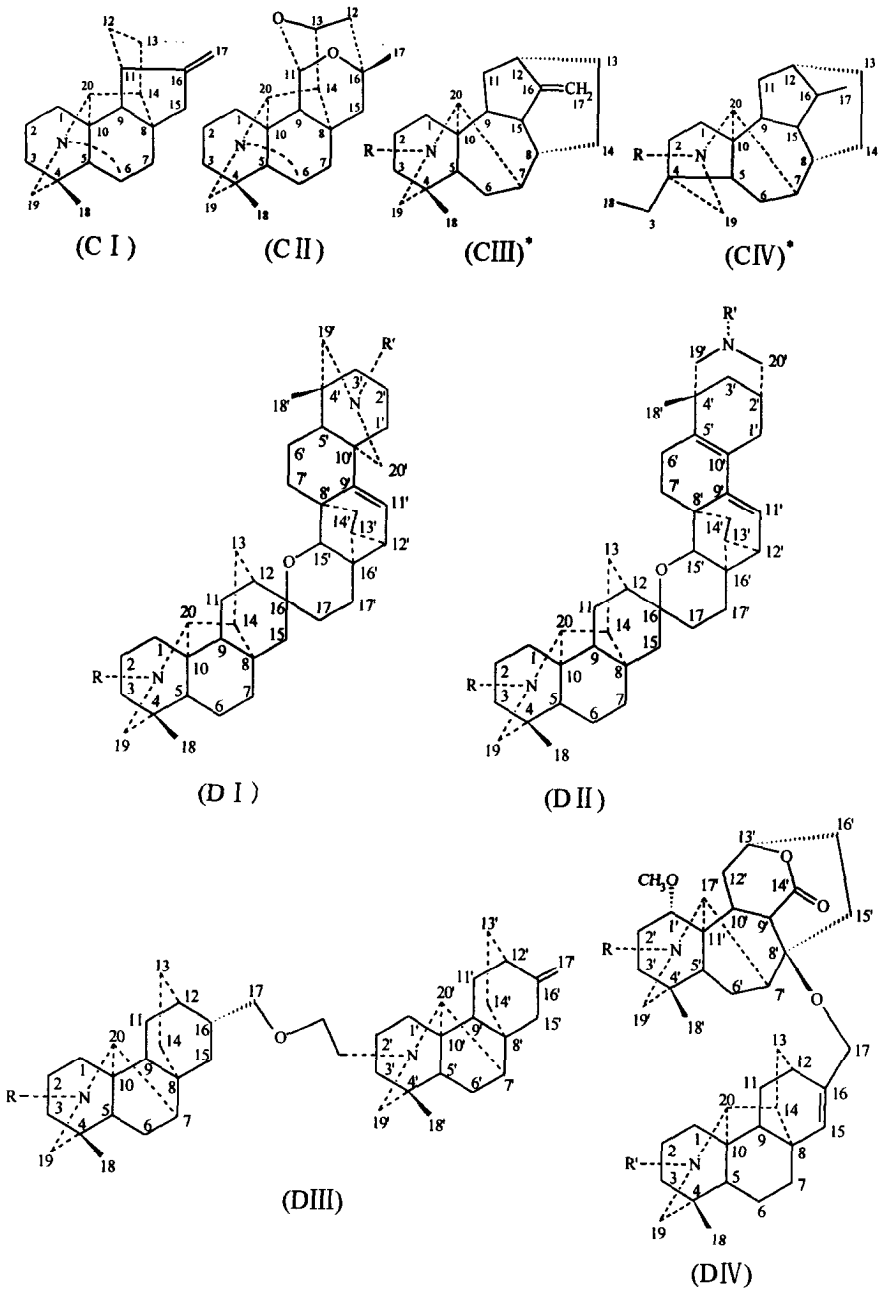


Fig. 1. Classes and types of C_{20}-diterpenoid alkaloids (* The numbering of carbon atoms adopted here differs from those given in the original papers)

2). Kaurane-class (B)

(9) Veatchine-type (B Ⅰ): pentacyclic, in which the carbon skeleton is the same as kaurane;

(10) Napelline-type (B Ⅱ): hexacyclic, with an additional C-20-C-7 bond in the kaurane-type;

(11) Anopterine-type (BIII): hexacyclic, with an additional C-20-C-14 bond in the veatchine-type;

3). Rearranged-class (C)

(12) Delnudine-type (C Ⅰ): heptacyclic, which may be considered as a rearrangement product of hetisine-type;

(13) Kusnesoline-type (C Ⅱ): pentacyclic, which was prepared first from hetisine by acid rearrangement, with "no name" (*365*), later isolated from *A. kusnezoffii* (*366*) and *A. racemulosum* var. *pengzhounense* (*367*), so renamed as "kusnezoline" (*367*).

(14) Actaline-type (CIII): hexacyclic, which may be considered as a B-homo-C-nor rearrangement of the denudatine-type;

(15) Racemulosine-type (CⅣ): hexacyclic, a novel skeleton recently isolated by us from *A. racemulosum* var. *pengzhounense* (*371*), which is considered as the A- nor- actaline-type and one of most complicated skeletal rearrangements.

4). Bisditerpenoid-class (D)

(16) Atisine-hetidine type (D Ⅰ): consists of one atisine-type and one hetidine-type *via* a condensation process;

(17) Rearranged atisine-hetidine type (D Ⅱ): consists of one rearranged atisine-type [C-20-C-10→C-20-C-2] and one hetidine-type;

(18) Denudatine-denudatine type (DIII): consists of two denudatine-type moieties;

(19) Heteratisine-denudatine type (DⅣ): consists of one lactone-type (C_{19}) and one denudatine-type.

3. According to the patterns of the nitrogen atom (amine, *N,O*-mixed acetal/ketal, lactam, imine, and *N*-oxide), each of the types may be subdivided into subtypes. For example, the atisine-type may include the following subtypes: amine-subtype (A I 1), *N,O*-mixed acetal/ketal-subtype (A I 2), imine-subtype (A I 3), and amide-lactam subtype (A I 4) (Fig. 2).

4. In the same subtype, alkaloids may be subdivided further into different groups, *which are responsible for their characteristic chemical and spectroscopic properties* (see Fig. 2). For example, the *N,O*-mixed acetal subtype in the atisine-type may include six groups: oxazolidine ring group (A I 2a), *N*-C-20-O-C-7 group (A I 2b), oxazolidine ring-[*N*-C-20-O-C-7] group (A I 2c), oxazolidine ring-lactam group (A I 2d), lactam-[*N*-C-20-O-C-7] group (A I 2e) and imine-[*N*-C-19-O-R] group (A I 2f).

The classification of the atisine-type diterpenoid alkaloids, is illustrated as shown in Fig. 2.

With the classification criteria mentioned above, the C_{20}-diterpenoid alkaloids may be divided into 4 classes, including 19 types, 34 subtypes, and 42 groups (Tables III~X XI).

Almost all of the C_{20}-diterpenoid alkaloids contain oxygenated groups. In contrast to the C_{19}-diterpenoid alkaloids, they possess the following distinctive features:

a). In most cases, they do not contain a methoxyl group, except for staphisine (*375*), staphigine (*376*), staphinine (*373*), staphisagnine (*372*), liangshanine (*315*), and vilmorinianine (*140*);

b). Except for a few examples they possess an exocyclic methylene, many of which have a secondary hydroxyl function in an allylic position;

c). Some alkaloids, in most cases, contain only the common ester groups, e.g., OAc and OBz. There are a few examples with other ester groups, such as cinnamate,

as in palmadine (*215*); propionate in acoridine (*231, 232*); isopropionate in 11-acetylcardionine (*272*); isobutyrate in guan-fu base Z (*228*), guan-fu base F

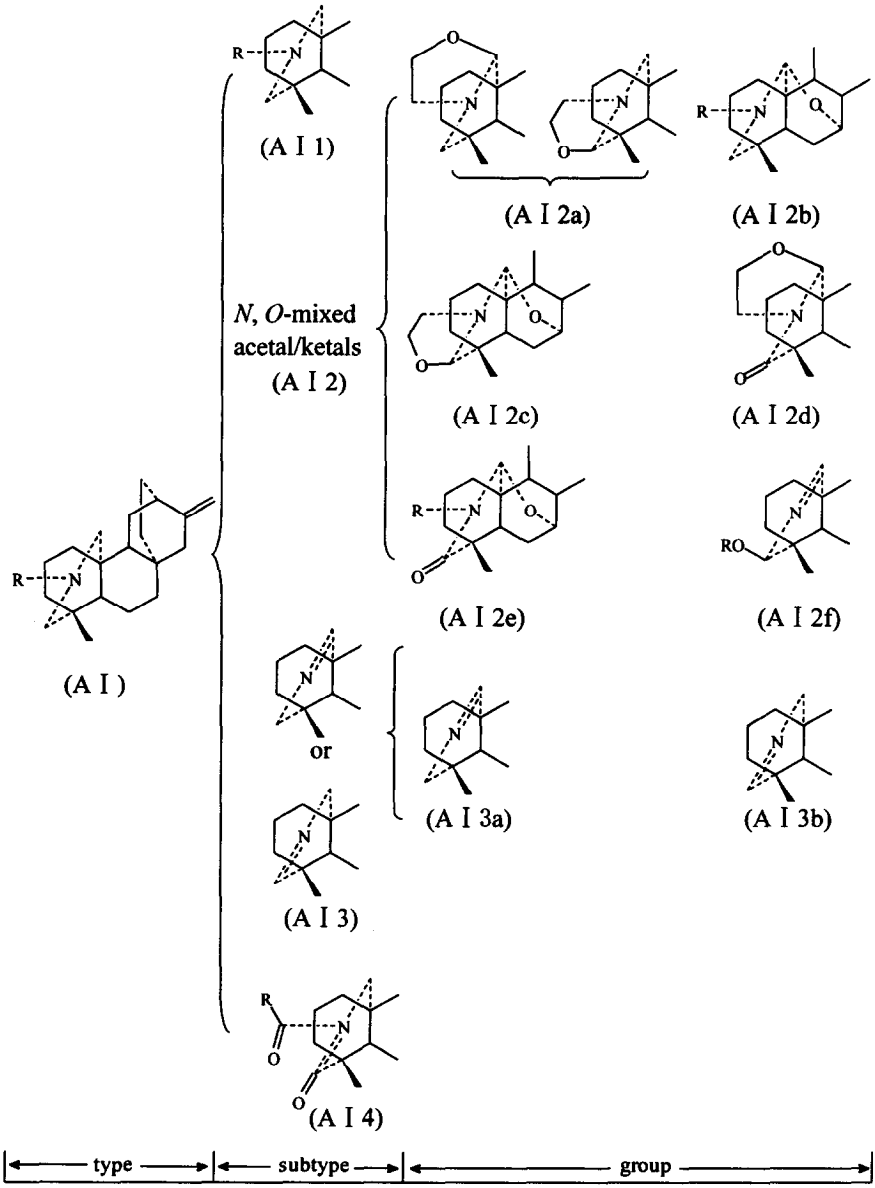


Fig. 2. Classification of atisine-type diterpenoid alkaloids (A I)

(*236*), cardiopidine (*254*), and cardionine (*272*); isopentanoate in cardiopine (*254*) and geyerinine (*273*), and tiglate in anopterine (*358*);

d). There are only a few atisine- and hetidine-type alkaloids which contain *N,O*-mixed acetal/ketal units;

e). Acorfine is the only alkaloid containing a chlorine atom to the present time.

The diterpenoid alkaloids were described as the *C_{19}- and C_{20}-diterpenoid* before 1989. We have suggested the use of the term *C_{18}-diterpenoid* differing from the "*C_{19}-diterpenoid*" (*157*). In accordance with Pelletier's recommendation (*393*), most scientists use the term *norditerpenoid* in place of *C_{19}-diterpenoid* and omit the descriptor C_{20} for *C_{20}-diterpenoid.* But, in some cases, the term *diterpenoid* is all embracing (C_{18}-, C_{19}-, C_{20}-), and sometimes specific only for the *C_{20}-diterpenoid.* In addition, the term *norditerpenoid* often includes both *nor* (C_{19}) and *bisnor* (C_{18}) alkaloids (*393*). In order to clarify the situation, we suggest here the restoration of the original terms "*C_{18}-, C_{19}- and C_{20}-diterpenoid alkaloids.*"

B. DISTRIBUTION

All of the known C_{20}-diterpenoid alkaloids have been isolated from eight genera of plants in five families (Table II). The richest sources are the plants of the two genera *Aconitum* and *Delphinium* in the Ranunculaceae and of the genus *Spiraea* in the Rosaceae. A sizable number of the C_{20}-diterpenoid alkaloids (47) were isolated from the several *Spiraea* plants due to the Chinese scientists Liang and Hao. In addition, one interesting advance in the field is that three known C_{20}-diterpenoid alkaloids acorientine, orientinine, and panicudine were identified from the epigeal parts of *Rumex pictus* (Polygonaceae) by the Egyptian scientist Salama (*263*) in 1997.

TABLE II
DISTRIBUTION IN PLANTS OF NATURAL C_{20}-DITERPENIOD ALKALOIDS

Plant	C_{20}-diterpenoid alkaloid*												
	A I (50)	A II (25)	AIII (1)	AIV (40)	A V (2)	AVI (1)	AVII (103)	AVIII (6)	B I (8)	B II (34)	BIII (5)	C (6)	D (10)
1. Ranunculaceae													
1) *Aconitum* sp.	8	17		22	1	1	52	2		34		4	4
2) *Delphinium* sp.	3	7		7	1		33	4				2	8
3) *Consolida* sp.	3						7						
4) *Thalictrum* sp.	1			1									
2. Rosaceae													
Spiraea sp.	34		1	13			11						
3. Garryaceae													
Garrya sp.									8				
4. Escalloniaceae													
Anopterus sp.											5		
5. Polygonaceae													
Rumex sp.							3						

* If one alkaloid occurs in several genera, it is counted as different entries.

C. OCCURRENCE

The naturally-occurring C_{20}-diterpenoid alkaloids reported to the end of 2000 are about 281 in number, mainly including the hetisine-type (103), the atisine-type (50), the hetidine-type (40), the napelline-type (34), and the denudatine-type (25) (Table II). With respect to the above mentioned classification criteria, these alkaloids are listed in Tables III~XXI, including the 8 atisane-type diterpenes (Table XXII) isolated from *Spiraea* plants. A code for each compound, with its structure, reference, molecular formula, molecular weight, melting point, $[\alpha]_D$ value, and plant source, is also presented, and the code possesses the following specifications (Fig. 3). In addition, the C_{20}-diterpenoid alkaloids listed in this chapter and their plant sources as well as code numbers, were cross-indexed as shown in Tables XXIII and XXIV.

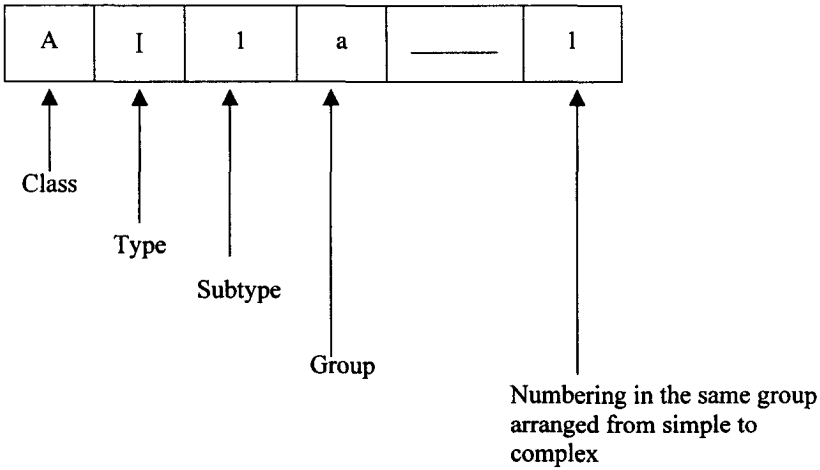
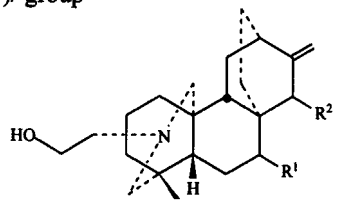


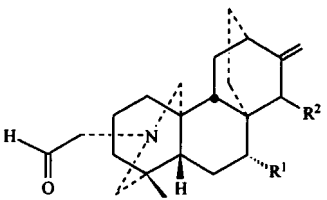
Fig. 3 Coding system for alkaloids in the Tables

TABLE III
ATISINE TYPE DITERPENOID ALKALOIDS (AI)

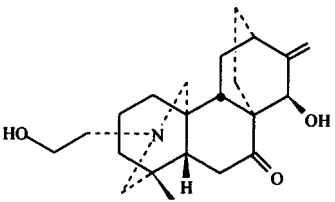
a. Amine subtype (A I 1)/ group



A I 1-1~AI1-2



A I 1-3~ A I 1-4

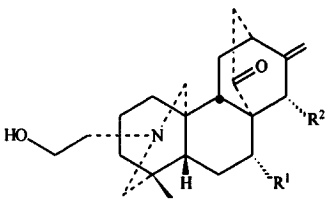


A I 1-5

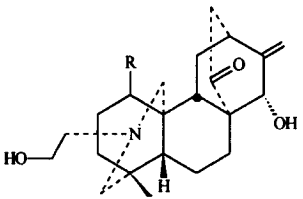
(Here and below, R is not specified when R=H)

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
A I 1-1 (dihydroatisine) R^2=βOH	$C_{22}H_{35}NO_2$	345	159-161	-44.5	*Aconitum heterophyllum*	*59~61, 77*
A I 1-2 (dihydroajaconine) R^1=αOH R^2=βOH	$C_{22}H_{35}NO_3$	361	99-100	-35	*Consolida amibigua*	*62, 63*
A I 1-3 (chellespontine) R^2=βOH	$C_{22}H_{33}NO_2$	343	227-230		*C. chellespontica*	*64*
A I 1-4 (spiratine A) R^1=OH R^2=αOH	$C_{22}H_{33}NO_2$	359		-6.25	*S. japonica* var. *acuta*	*419*
A I 1-5 (atidine)	$C_{22}H_{33}NO_3$	359	182.5-183.5	-47	*A. heterophyllum*	*65~67* *59~60*

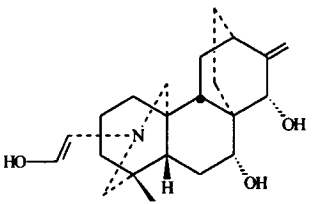
TABLE III (*continued*)



A I 1-6~A I 1-8

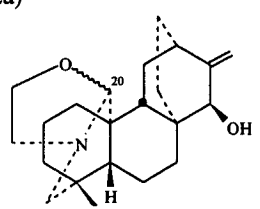


A I 1-9~A I 1-10

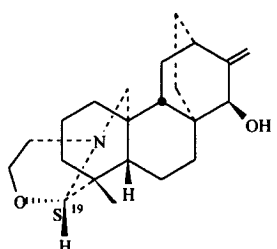


A I 1-11

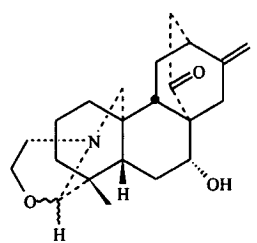
A I 1-6 (spiramine G) R^1=OH	$C_{22}H_{33}NO_3$	359	160-162	-16	*Spiraea japonica* var. *acuminata*	*68, 69*
A I 1-7 (spiramine H) R^2=OH	$C_{22}H_{31}NO_3$	359			*S. japonica* var. *acuminata*	*70, 88*
A I 1-8 (spiramine I) R^2=OAc	$C_{24}H_{33}NO_4$	401	168-170	-24	*S. japonica* var. *acuminata*	*70*
A I 1-9 (beiwusine A) R=αOH	$C_{22}H_{33}NO_4$	375		-34.1	*A. kusnezoffii*	*71*
A I 1-10 (beiwusine B) R=βOH	$C_{22}H_{33}NO_4$	375		-42.0	*A. kusnezoffii*	*71*
A I 1-11 (uncinatine)	$C_{23}H_{31}NO_3$	359			*Delphinium uncinatum*	*72*
b. Simple/complex *N,O*-mixed ketal subtype (A I 2)						
a). Oxazoliding ring group (A I 2a)						



A I 2a-1



A I 2a-2



A I 2a-3

A I 2a-1 (atisine)	$C_{22}H_{33}NO_2$	343	329-331(HCl)	+26.6	*A. heterophyllum*	*59, 73, 74*

TABLE III (*continued*)

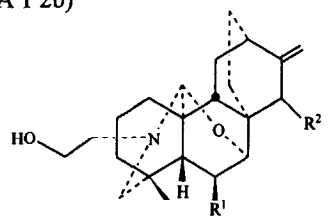
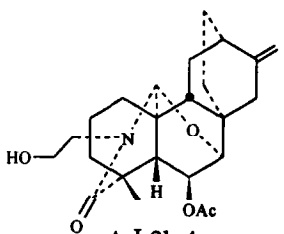
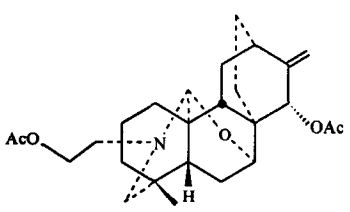
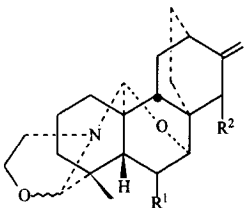
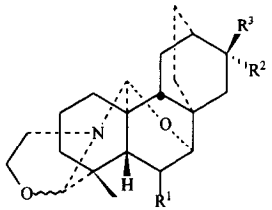
A I 2a-2 (isoatisine)	$C_{22}H_{33}NO_2$	343	152-153	-22	*A. coreanum; A. rotundifolum; A. zeravchanicum; A. heterophyllum*	*59, 60, 63, 73 76~78*
A I 2a-3 (spiramidines A(B))	$C_{22}H_{31}NO_3$	357			*S. japonica* var. *ovalifolia*	*75*
b). *N*-C-20-*O*-C-7 group (A I 2b)						
	 A I 2b-1~ A I 2b-3		 A I 2b-4		 A I 2b-5	
A I 2b-1 (ajaconine) R^2=βOH	$C_{22}H_{33}NO_3$	359	165-167	-99.9	*D. ajacis; D. consolida; C. ambigua; D. viresens; D. corolinianum; D. elatum*	*63, 79~84*
A I 2b-2 (deacetylspiramine F) R^2= αOH	$C_{22}H_{33}NO_3$	359	149-151	-134.5	*S. japonica* var. *ovalifolia*	*75*
A I 2b-3 (spiramine F) R^2=αOAc	$C_{24}H_{35}NO_4$	401	144-145	-101	*S. japonica* var. *acuminata*	*68*
A I 2b-4 (spiramine Y) R^1=OAc	$C_{24}H_{35}NO_5$	417		-152	*S. japonica* var. *acuta*	*85*
A I 2b-5 (spiramine E)	$C_{26}H_{37}NO_5$	443		-97	*S. japonica* var. *acuminata*	*68*

TABLE III (*continued*)

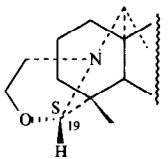
c). Oxazolidine ring—[*N*-C-20-*O*-C-7] group (A I 2c)

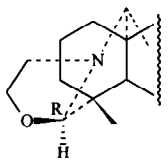


A I 2c-1~AI2c-6



A I 2c-7~A I 2c-12





A I 2c-1 (spiramine C) R^2=αOH (19*S*)	$C_{22}H_{31}NO_3$	357	160-162	-169.0	*S. japonica* var. *acuminata*	*86, 87*
A I 2c-2 (spiramine A) R^2= αOAc (19*S*)	$C_{24}H_{33}NO_4$	399	137.5-139	-130.1	*S. japonica* var. *acuminata* *S. japonica* var. *glabra*	*86~88*
A I 2c-3 (spiradine G) R^1=βOH (19*S*)	$C_{22}H_{31}NO_3$	357	168-170	-137	*S. japonica*	*89*
A I 2c-4 (spiradine F) R^1= βOAc (19*S*)	$C_{24}H_{33}NO_4$	399	114-140		*S. japonica* *S. japonica* var. *glabra*	*88, 89*
A I 2c-5 (spiramine D) R^2=αOH (19*R*)	$C_{22}H_{31}NO_3$	357	167-169	-149.9	*S. japonica* var. *acuminata*	*86, 87*
A I 2c-6 (spiramine B) R^2= αOAc (19*R*)	$C_{24}H_{33}NO_4$	399	129-131	-159.9	*S. japonica* var. *acuminata* *S. japonica* var. *glabra*	*86, 87*
A I 2c-7 (spiramine P) R^1= βOH R^2= CH_3 R^3= OH (19*S*)	$C_{22}H_{33}NO_4$	375	239-240	-44.3	*S. japonica* var. *acuminata*	*94*
A I 2c-8 (spiramine U) R^1= βOAc R^2= CH_3 R^3= OH (19*S*)	$C_{24}H_{35}NO_5$	415	216-218	-129.9	*S. japonica* var. *acuta*	*94, 90*
A I 2c-9 (thalicsiline) R^1= βOAc R^2= CH_3 R^3= OH (19*S*+19*R*)	$C_{24}H_{35}NO_5$	415	183-186	-11.4	*Thalictrum sessile*	*91, 92*

TABLE III (*continued*)

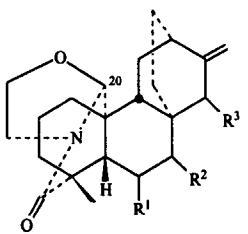
A I 2c-10 (spiramine Q) R^1= βOH R^2= OH R^3= CH_3 (19*S*)	$C_{22}H_{33}NO_4$	375	197-199	-70.0	*S. japonica* var. *incisa*	*93, 94*
A I 2c-11 (spiramine T) R^1= βOAc R^2=OH R^3= CH_3 (19*R*)	$C_{22}H_{35}NO_5$	417	183-185	-151.6	*S. japonica* var. *acuta*	*94, 90*
A I 2c-12 (spiramine W) R^1= βOH R^2=OH R^3= CH_3 (19*R*)	$C_{22}H_{33}NO_4$	375			*S. japonica* var. *acuta*	*95*
d). Oxazolidine ring—lactam group (A I 2d)						
 A I 2d-1~A I 2d-4						
A I 2d-1 (spiramine S) R^2=αOH R^3=αOAc	$C_{24}H_{33}NO_5$	415			*S. japonica* var. *acuminata*	*96*
A I 2d-2 (spiramine V) R^2=αOAc R^3=αOH (20*R*)	$C_{24}H_{33}NO_5$	415			*S. japonica* var. *acuminata*	*97*
A I 2d-3 (deacetyl spiramine S) R^2=R^3=αOH (20*R*)	$C_{22}H_{31}NO_4$	373	113-115	-74.4	*S. japonica* var. *ovalifolia*	*75*
A I 2d-4 (spiramide) R^1=βOAc R^2=αOAc (20*R*)	$C_{26}H_{35}NO_6$	457	276-278	-69.5	*S. japonica* var. *acuta*	*420*

TABLE III (*continued*)

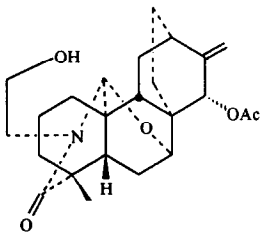
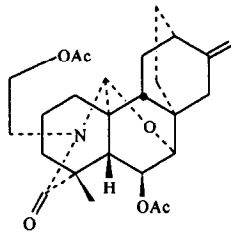
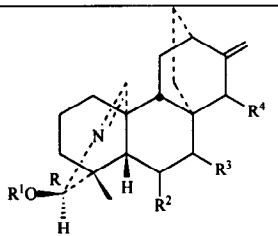
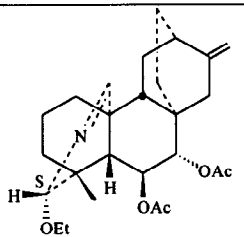
e). Lactam—[*N*-C-20-*O*-C-7] group (A I 2e)	 AI2e-1			 AI2e-2		
A I 2e-1 (spiramine R)	$C_{24}H_{33}NO_3$	415	190-192	-180.0	*S. japonica* var. *incisa*	*93*
A I 2e-2 (spiramine X)	$C_{24}H_{35}NO_6$	433	125-1227	-139.7	*S. japonica* var. *acuta*	*85*
f). Imine—[*N*-C-19-*O*-R] group (A I 2f)	 A I 2f-1~A I 2f-5			 A I 2f-6		
A I 2f-1 (19-*O*-deethyl spiramine N) R^3= R^4=αOH	$C_{20}H_{29}NO_3$	331		+17.99	*S. japonica* var. *ovalifolia*	*75*
A I 2f-2 (spiratine B) R^2= βOAc R^3= αOAc	$C_{24}H_{33}NO_5$	415		-129.48	*S. japonica* var. *acuta*	*419*
A I 2f-3 (spiramine N) R^1=Et R^3=R^4=αOH	$C_{22}H_{33}NO_3$	359		+44.4	*S. japonica* var. *acuminata*	*98*
A I 2f-4 (brunonine) R^1=Et R^3=αOH R^4=βOH	$C_{22}H_{33}NO_3$	359	208-209	+17.4	*D. brunonianum*	*99*

TABLE III (*continued*)

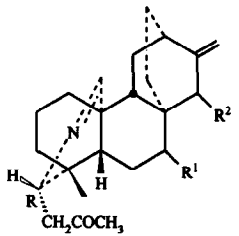
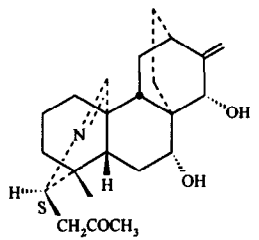
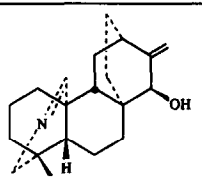
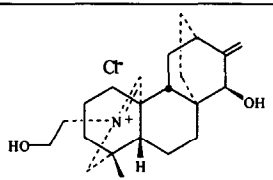
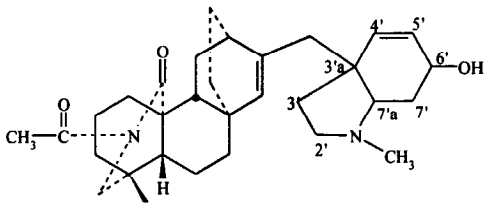
A I 2f-5 (spiramine O) R^1=Me R^3=R^4=αOH	$C_{21}H_{31}NO_3$	345		+11	*S. japonica* var. *acuminata*	*70*
A I 2f-6 (spiramine Z)	$C_{26}H_{37}NO_5$	443		+81.7	*S. japonica* var. *acuta*	*85*
	 AI2f-7~AI2f-9			 AI2f-10		
A I 2f-7 (spiramine J) R^1= R^2=αOH	$C_{23}H_{33}NO_3$	371	92-94	-95	*S. japonica* var. *acuminata*	*100*
A I 2f-8 (spiramine L) R^1=αOH R^2=αOAc	$C_{25}H_{35}NO_4$	413		-77	*S. japonica* var. *acuminata*	*100*
A I 2f-9 (spiramine M) R^1=αOAc R^2= αOH	$C_{25}H_{35}NO_4$	413		-55	*S. japonica* var. *acuminata*	*100*
A I 2f-10 (spiramine K)	$C_{23}H_{33}NO_3$	371		-18	*S. japonica* var. *acuminata*	*100*
c. Imine subtype (A I 3) / group	 A I 3-1		 A I 3-2			
A I 3-1 (azitine)	$C_{20}H_{29}NO_3$	299	178-179		*C. hellespontica*	*59, 64*
A I 3-2 (atisine chloride)	$C_{22}H_{34}NO_2Cl$	379/381	297		*A. coreanum,* *A. rotundifolium,* *A. zeravschanicum*	*77, 101, 102*

TABLE III (*continued*)

d. Amide—Lactam subtype (A I 4) / group



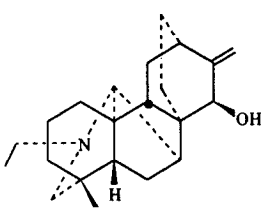
A I 4-1

A I 4-1 (coryphidine)	$C_{31}H_{44}N_2O_3$	492		*A. coreanum*	*103*

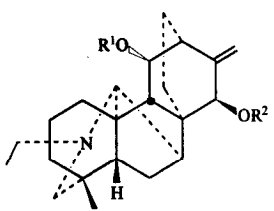
TABLE IV

DENUDATINE TYPE DITERPENOID ALKALOIDS (A II)

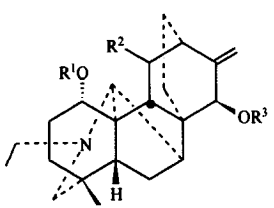
a. Amine subtype (A II 1) / group



A II 1-1



A II 1-2~A II 1-3



A II 1-4~A II 1-9

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
A II 1-1 (gymnandine)	$C_{22}H_{33}NO$	327			*A. gymnandrum*	*107*

TABLE IV (*continued*)

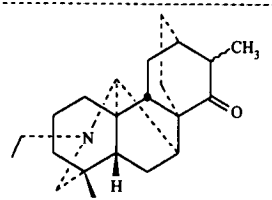
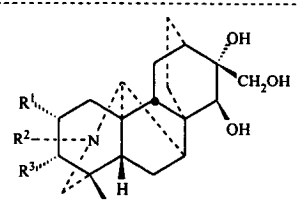
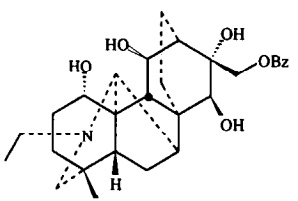
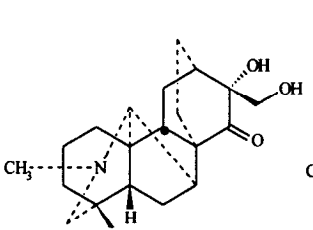
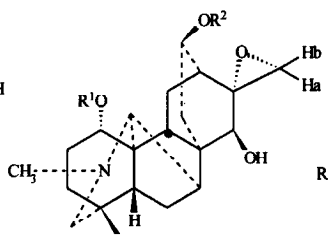
A II 1-2 (denudatine)	$C_{22}H_{33}NO_3$	343	249-251	+0.15	*D. denudatum*, *A. gymnandrum*, *A. jinyangense*, *A. kusnezoffii*, *A. vilmorrinianum* var. *albifidum*	*108~111, 113~115*
A II 1-3 (jynosine, 15-acetyl denudatine) R^2=Ac	$C_{24}H_{35}NO_3$	385	254-256	-37.4	*A. jinyangense*	*114*
A II 1-4 (lepenine) R^2=βOH	$C_{22}H_{33}NO_3$	359	199-201		*A. barbatum*	*113, 115, 117 118*
A II 1-5 (11α-hydroxylepenine) R^2=αOH	$C_{22}H_{33}NO_3$				*A. barbatum var. hispidum*	*116*
A II 1-6 (kirinine C) R^1=Ac R^2=βOH	$C_{22}H_{29}NO_4$	371	218-220		*A. kirinense*	*119*
A II 1-7 (lepetine, 11-acetyllepenine) R^2=βOAc	$C_{24}H_{35}NO_4$	401	130-131		*A. leucostomum*, *A. pseudohuilense*	*120, 117*
A II 1-8 (kirinine A) R^2=βOH R^3=Ac	$C_{24}H_{35}NO_4$	401	184-186		*A. kirinense*	*121, 122*
A II 1-9 (lepedine) R^1=CH_3 R^2=βOH	$C_{23}H_{35}NO_3$	373	156-158	-39.0	*A. pseudohuiliense*	*117*
						
	A II 1-10		A II 1-11~ A II 1-13		A II 1-14	
A II 1-10 (cordizine)	$C_{22}H_{35}NO$	327	122-124		*D. corymbosum*	*123*

TABLE Ⅳ (*continued*)

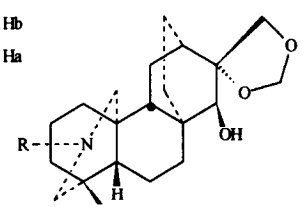
A II 1-11 (dictyzine, dictysine) R^2=CH_3	$C_{21}H_{31}NO_3$	347	184-186	-120	*D. corymbosum, D. dictyocarpum*	*124~130*
A II 1-12 (*N*-ethyl-des-*N*-methyldictyzine) R^2=Et	$C_{22}H_{35}NO_3$	361			*D. corymbosum*	*394~396*
A II 1-13 (macrocentrine) R^1= R^3=OH R^2=Et	$C_{22}H_{35}NO_5$	393	207-209		*D. macrocentrum*	*127*
A II 1-14 (lassiocarpine)	$C_{29}H_{39}NO_6$	497	141-143	-17.4	*A. kojimae* var. *lassiocarpium*	*131*



A II 1-15



A II 1-16~A II 1-18

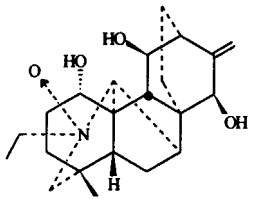


A II 1-19~A II 1-20

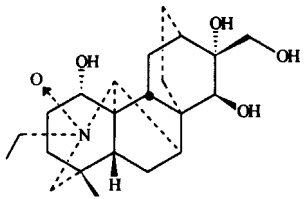
A II 1-15 (dehydrodictysine)	$C_{21}H_{31}NO_3$	345	145	-58	*D. dictyocarpum*	*125*
A II 1-16 (gomandonine)	$C_{21}H_{31}NO_4$	361	248-249	-42.5	*A. subcuneatum*	*132, 133*
A II 1-17 (gomandonine 13-*O*-acetate) R^2= Ac	$C_{23}H_{33}NO_5$	403			*A. delphinifolium*	*133*
A II 1-18 (yesoxine) R^1= R^2=Ac	$C_{25}H_{35}NO_6$	445	184	-37.5	*A. yesoense* var. *macroyesoense*	*133, 134*
A II 1-19 (corumdizinine) R=CH_3	$C_{22}H_{33}NO_3$	359	104-105		*D. corymbosum*	*135*
A II 1-20 (corumdizine) R=Et	$C_{23}H_{35}NO_3$	373			*D. corymbosum*	*136*

TABLE IV (*continued*)

b. *N*-oxide subtype/group (A II 2)



A II 2-1

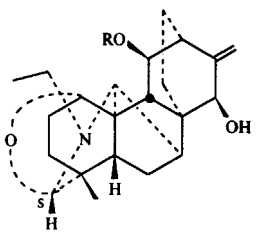


A II 2-2

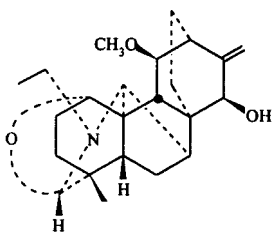
A II 2-1 (lepenine *N*-oxide)	$C_{22}H_{33}NO_4$	375			*A. kirinense*	*137*
A II 2-2 (paniculamine)	$C_{22}H_{35}NO_5$	395	222-224		*A. paniculatum*	*139*

c. *N,O*-mixed ketal subtype (A II 3)

a). C-1-O-C-19-*N* group (A II 3a)



A II 3a-1~A II 3a-2



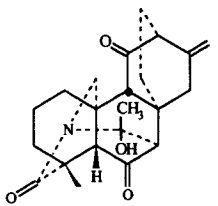
A II 3a-3

A II 3a-1 (kirinine B)	$C_{22}H_{31}NO_3$	357	157-158		*A. kirinense*	*119*
A II 3a-2 (11-acetyl-1, 19-epoxydenudatine) R=Ac	$C_{24}H_{33}NO_4$	399	202-203	+99.7	*A. barbatum*	*138*
A II 3a-3 (vilmorinianine)	$C_{23}H_{33}NO_3$	371		+60.0	*A. vilmorrianum* var. *albifedum*	*140*

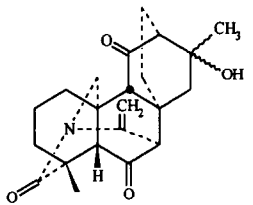
TABLE V

SPIREINE TYPE DITERPENOID ALKALOIDS/SUBTYPE/GROUP (AIII)

a. Spireine subtype (AIII1)/ group



or



AIII1-1 AIII1-2

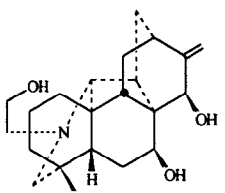
code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AIII1-1 /AIII1-2 (spireine, structures 1 or 2)	$C_{22}H_{27}NO_4$	369	230		*S. japonica*	*181, 185*

TABLE VI

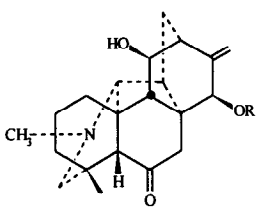
HETIDINE TYPE DITERPENOID ALKALOIDS (AIV)

a. Hetidine subtype (AIV1)

a). Amine group (AIV1a)

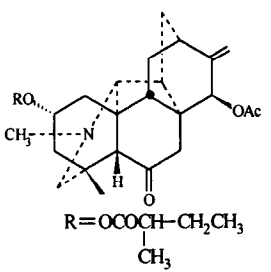


AIV1a-1



AIV1a-2~AIV1a-3

R=Vr=OCO-C_6H_4-$(OCH_3)_2$(3', 4')



AIV1a-4

TABLE VI (*continued*)

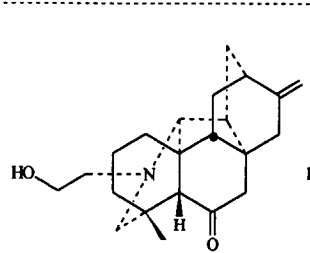
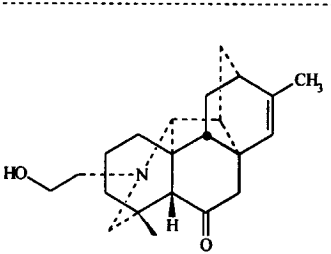
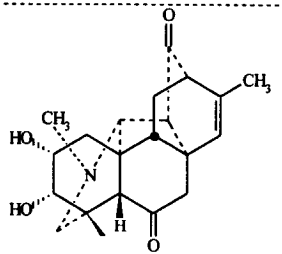
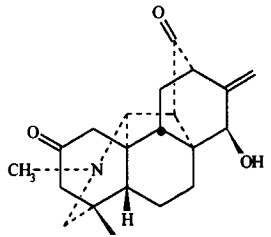
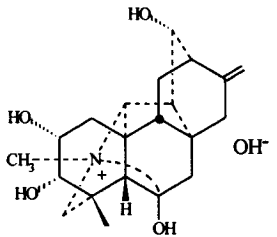
code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AIV1a-1 (trazonine)	$C_{22}H_{33}NO_3$	359	123-126	-5	*A. nasutum*	*141*
AIV1a-2 (yesonine)	$C_{21}H_{29}NO_3$	343		+2.4	*A. yesoense* var. *macroyesoense*	*142*
AIV1a-3 (yesoline) R=Vr	$C_{30}H_{37}NO_6$	507		-10.6	*A. yesoense* var. *macroyesoense*	*143*
AIV1a-4 (sczukitine)	$C_{28}H_{37}NO_6$	483	116-118	-66.6	*A. sczukinii*	*144*
						
	AIV1a-5		AIV1a-6		AIV1a-7	
AIV1a-5 (spirafine III)	$C_{22}H_{31}NO_2$	341	192-193	-46.07	*S. fritschiana* var. *parvifolia*	*145*
AIV1a-6 (spirafine II)	$C_{22}H_{31}NO_2$	341	155-156	-33.16	*S. fritschiana* var. *parvifolia*	*145*
AIV1a-7 (racemulodine)	$C_{21}H_{27}NO_4$	357	181-183	-24.9	*A. racemulosum* var. *pengzhounense*	*146*

TABLE VI (*continued*)

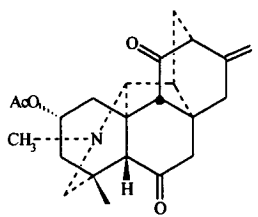


AIV1a-8

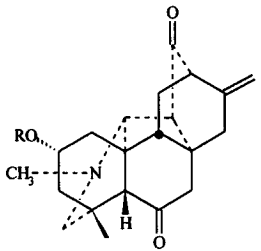


AIV1a-9

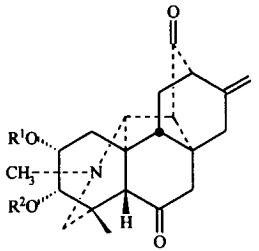
AIV1a-8 (delcarduchol)	$C_{21}H_{27}NO_3$	341			*D. carduchorum*	*147*
AIV1a-9 (vakhmadine)	$C_{21}H_{30}NO_4^+OH^-$	359	263-273	-37.8	*A. palmatum*	*148*



AIV1a-10



AIV1a-11~AIV1a-12



AIV1a-13~AIV1a-17

AIV1a-10 (panicutine)	$C_{23}H_{29}NO_4$	383			*A. paniculatum, D. denudatum*	*149~151*
AIV1a-11 (deacetylheterophylloidine)	$C_{21}H_{27}NO_3$	341	160-161	-59.9	*D. albiflorum*	*152, 153*
AIV1a-12 (heterophylloidine) R=Ac	$C_{23}H_{29}NO_4$	399		-82.0	*A. heterophyllum*	*150, 152~155*
AIV1a-13 (hetidine)	$C_{21}H_{27}NO_4$	357	218-221	-77.1	*D. albiflorum*	*66, 152*

TABLE VI (*continued*)

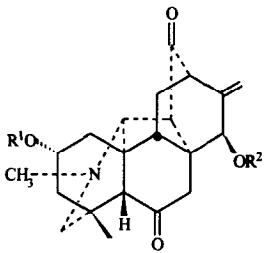
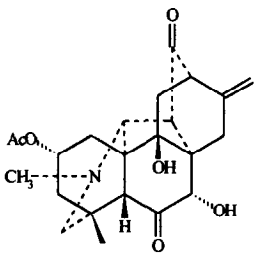
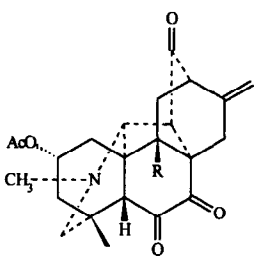
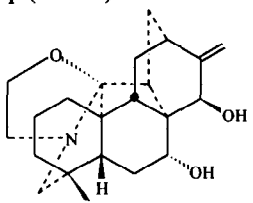
						156
AIV1a-14 (episcopalidine) R^1=Ac R^2=Bz	$C_{30}H_{33}NO_6$	503	210-220	-80.0	*A. contortum*	*157~160*
AIV1a-15 (contorine) R^1=Ac R^2=As	$C_{31}H_{35}NO_7$	533	238	-44.9	*A. contortum*	*161*
AIV1a-16 (contorsine) R^1=Ac R^2=OCCH-$(CH_3)_2$	$C_{27}H_{35}NO_6$	469	203-206	-88.1	*A. contortum*	*161*
AIV1a-17 (contortine) R^1=Ac R^2=OCCH-$(CH_3)CH_2CH_3$	$C_{28}H_{37}NO_6$	483	230-233	-82.1	*A. contortum*	*161*
						
	AIV1a-18~AIV1a-19		AIV1a-20		AIV1a-21~AIV1a-22	
AIV1a-18 (sczukidine)	$C_{21}H_{27}NO_4$	357	119-121	-87.1	*A. sczukinii*	*144, 162*
AIV1a-19 (sczukinine) R^1=Ac	$C_{23}H_{29}NO_5$	399	272-273	-107.9	*A. sczukinii*	*144, 162*
AIV1a-20 (miyaconitine)	$C_{23}H_{29}NO_6$	415	218	-87.5	*A. miyabei*	*164*
AIV1a-21 (vilmorrianone)	$C_{22}H_{27}NO_4$	397	253-255	-22	*A. vilmorrianum, D. denudatum*	*151, 163*
AIV1a-22 (miyaconitinone) R=OH	$C_{23}H_{27}NO_6$	413	285	-27.6	*A. miyabei*	*164~170*

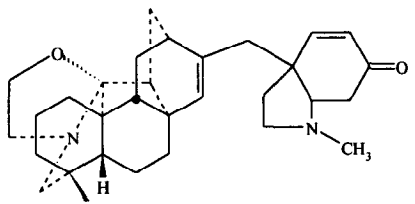
TABLE VI (*continued*)

b. *N,O*-Mixed ketal subtype (AIV2)

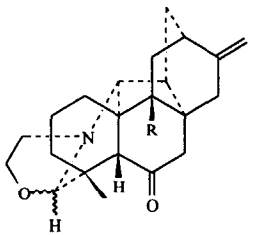
a). Oxazolidine ring group (AIV2a)



AIV2a-1

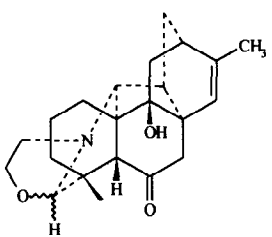


AIV2a-2

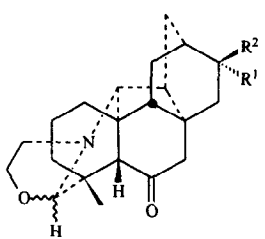


AIV2a-3~AIV2a-4

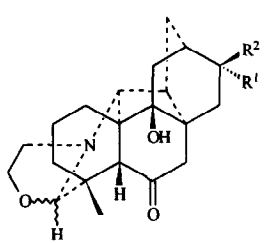
AIV2a-1 (septatisine, septedinine)	$C_{22}H_{31}NO_3$	357	160-161	+30.55	*A. septentrionale*	*141*
					A. nasutum	*171~173*
AIV2a-2 (coryphine)	$C_{31}H_{42}N_2O_2$	474	200	+150	*A. coreanum*	*174*
AIV2a-3 (spiradine D)	$C_{22}H_{29}NO_2$	339	134-135		*S. japonica*	*88, 175*
AIV2a-4 (spirasine II) R=OH	$C_{22}H_{29}NO_3$	355	230-231	-37.6	*S. japonica*	*176*



AIV2a-5



AIV2a-6~AIV2a-7

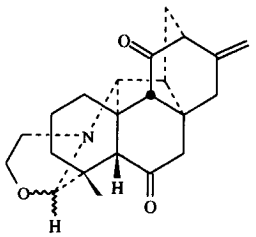


AIV2a-8~AIV2a-9

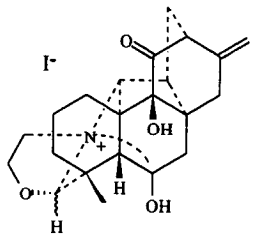
AIV2a-5 (spirasine I)	$C_{22}H_{29}NO_3$	355	244-246	-131	*S. japonica*	*176*

TABLE VI (*continued*)

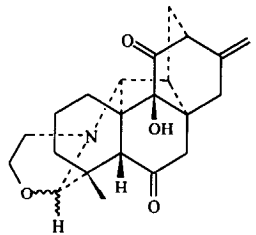
AIV2a-6 (spirasine V) R^1=OH R^2=CH_3 (19*S*)*	$C_{22}H_{31}NO_3$	343	177-179	-47	*S. japonica*	*177*
AIV2a-7 (spirasine VI) R^1= CH_3 R^2= OH (19*S*)*	$C_{22}H_{31}NO_3$	343	202-203	-107	*S. japonica*	*177*
AIV2a-8 (spirasine VII) R^1=OH R^2=CH_3	$C_{22}H_{31}NO_4$	359	191-193	-78	*S. japonica*	*176*
AIV2a-9 (spirasine VIII) R^1= CH_3 R^2= OH	$C_{22}H_{31}NO_4$	359	207-209	-57	*S. japonica*	*176*



AIV2a-10



AIV2a-11



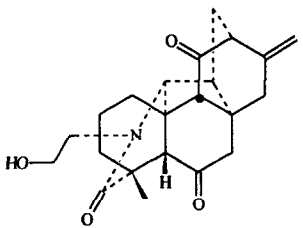
AIV2a-12

AIV2a-10 (spiredine)	$C_{22}H_{27}NO_3$	353	163	-21	*S. japonica*, *T. sessile*	*92, 178, 179*
AIV2a-11 (spireine*)	$C_{22}H_{27}NO_4$	369	230		*S. japonica*	*180, 181*
AIV2a-12 (spirasine III)	$C_{22}H_{27}NO_4$	369	210-212	-9	*S. japonica*, *S. japonica* var. *glabra*	*88, 92, 178*

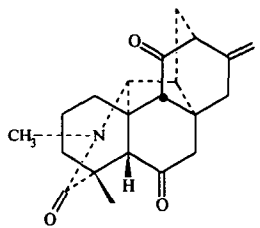
* solid state.

TABLE VI (*continued*)

b). Lactam subtype (AIV2b) / group



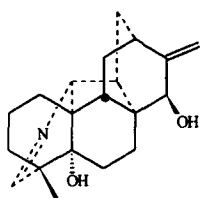
AIV2b-1



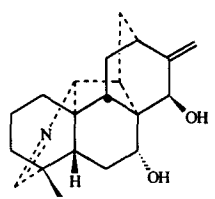
AIV2b-2

AIV2b-1 (thalicsessine)	$C_{22}H_{27}NO_2$	313	213-216	+113	*T. sessile*	*92, 182*
AIV2b-2 (carduchoron)	$C_{21}H_{25}NO_3$	399			*D. carduchorum*	*147*

c). Imine subtype (AIV3) / group



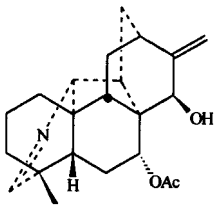
AIV3-1



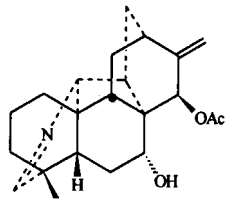
AIV3-2

AIV3-1 (tongolinine)	$C_{20}H_{27}NO_2$	313	233-234		*D. tongolense*	*183*
AIV3-2 (talassamine)	$C_{20}H_{27}NO_2$	313	208-210		*A. talassicum*	*184*

TABLE VI (*continued*)



AIV3-3



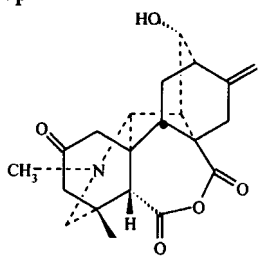
AIV3-4

AIV3-3 (talassimine)	$C_{22}H_{29}NO_3$	335	242-245	*A. talassicum*	*184*
AIV3-4 (talasssimidine)	$C_{22}H_{29}NO_3$	335	263-263	*A. talassicum*	*184*

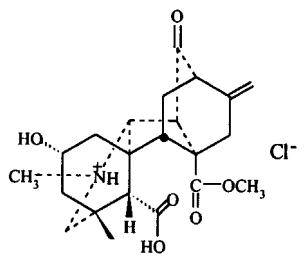
TABLE VII

CARDIONIDINE TYPE DITERPENOID ALKALOIDS (AV)

a. Cardionidine subtype (AV1) / group



AV1-1



AV1-1

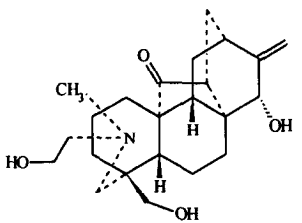
TABLE VI (*continued*)

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AV1-1 (cardionidine)	$C_{21}H_{25}NO_5$	371			*D. cardiopetalum*	*187*
AV1-2 (vilmoridine)	$C_{22}H_{29}NO_6$	403	238-240		*A. vilmorrianum*	*188*

TABLE VII

ALBOVIONITINE TYPE DITERPENOID ALKALOIDS (AVI)

a. Albovionitine (*N*, 20-*seco* hetidine) subtype (AVI1) / group



AVI1-1

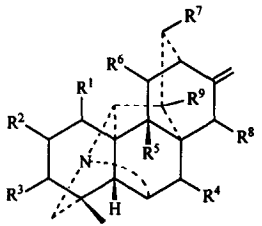
code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AVI1-1 (albovionitine)	$C_{23}H_{35}NO_4$	389	150-152		*A. alboviolaceum*	*189*

TABLE IX

HETISINE TYPE DITERPENOID ALKALOIDS (AVII)

a. Hetisine subtype (AVII1)

a). Amine group (AVII1a)



AVII1a-1~AVII1a-45

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AVII1a-1 (spirasine XI) R^7=βOH	$C_{20}H_{27}NO$	297	286-288	-23.8	*S. japonica* var. *fortunei*	*190*
AVII1a-2 (nominine) R^8=βOH	$C_{20}H_{27}NO$	297	250-251		*D. tongolense*	*191~193*
AVII1a-3 (zeraconine) R^8=β-OC_6H_4(p)-$CH_2CH_2N(CH_3)_2$	$C_{30}H_{40}N_2O$	444	130-131		*A. zeravschanium*	*191, 194*
AVII1a-4 (cossonidine, davisine) R^1=R^8=βOH	$C_{20}H_{27}NO_2$	313	243-245	+34.7	*D. cossonianum, D. cardiopetalum, D. davisii*	*195, 196*
AVII1a-5 (sanyonamine) R^2=αOH R^8=βOH	$C_{20}H_{27}NO_2$	313	276-278	+62.9	*A. sanyoense*	*197*
AVII1a-6 (kobusine) R^6=R^8=βOH	$C_{20}H_{27}NO_2$	313	272-274	+80	*A. talassicum, D. davisii*	*192, 195 196,198~201*
AVII1a-7 (hetisine, delatine) R^2=R^6=αOH R^7=βOH	$C_{20}H_{27}NO_3$	329	256-259	+109	*A. heterophyllum, D. cardinale, D. tongolense*	*202~211,186 148, 193 66, 80*

TABLE IX (*continued*)

AVII1a-8 (13-acetylhetisine) R^2=R^6=αOH R^7=βOAc	$C_{20}H_{27}NO_4$	345	273-280		*D. nuttallianum*	*202, 215*
AVII1a-9 (palmasine) R^2=R^6=αOH R^7=βO$_2$C-CH=CH-C$_6$H$_5$	$C_{29}H_{33}NO_4$	459	252-254		*A. palmatum*	*215*
AVII1a-10 (palmadine) R^2=αOH R^6=αOAc R^7=βO$_2$C-CH=CH-C$_6$H$_5$	$C_{31}H_{35}NO_5$	501	269-271	+11.2	*A. palmatum*	*215*
AVII1a-11 (hanamisine) R^1=βOAc R^2=αOBz R^8=βOH	$C_{29}H_{33}NO_5$	475			*A. sanyoense* var. *tonense*	*216*
AVII1a-12 (isohypognavine) R^2=αOBz R^6=R^8=βOH	$C_{27}H_{31}NO_4$	433	135		*A. majimai*, *A. japonicum*, etc.	*217, 218*
AVII1a-13 (torokonine) R^2=αOBz R^4=αOH R^5=R^8=βOH	$C_{27}H_{31}NO_5$	449	198.5-199	+71.7	*A. subcuneatum*	*132*
AVII1a-14 (souline F) R^2=R^4=R^6=βOH	$C_{20}H_{27}NO_3$	329	>350	+1.24	*D. souliei*	*219*
AVII1a-15 (crassicauline B) R^1=βOH R^4= αOH R^7=βOBz	$C_{27}H_{31}NO_4$	433			*A. crassicaule*	*220*
AVII1a-16 (ryosenaminol) R^2=αOH R^5=OH R^8=βOH	$C_{20}H_{27}NO_3$	329	287-290	+66.8	*A. ibukiense*	*221*
AVII1a-17 (ryosenamine) R^2=αOBz R^5=OH R^8=βOH	$C_{27}H_{31}NO_4$	433	213-215	+96.8	*A. ibukiense*	*221*
AVII1a-18 (delfissinol) R^4=R^6=R^7=αOH	$C_{20}H_{27}NO_3$	329		-39.1	*A. fissum* subsp. *anatolicum*	*223*
AVII1a-19 (delnuttine) R^4=αOH R^6=αOAc R^8=βOH	$C_{22}H_{29}NO_4$	371			*D. nuttalianum*	*224*

TABLE IX (*continued*)

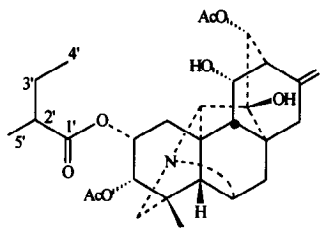
AVII1a-20 (deacetylhanamisine, hanamiyama base) R^1=R^8=βOH R^2=αOBz	$C_{27}H_{31}NO_4$	433	243-245	+130	*A. sanyoense; A. sanyoense* var. *tonense*	*216, 225*
AVII1a-21 (venudelphine) R^1=βOAc R^2=R^7=αOAc	$C_{26}H_{33}NO_6$	455			*D. venulosm*	*226*
AVII1a-22 (tangutisine) R^2=R^6=R^7=αOH R^9=βOH	$C_{20}H_{27}NO_4$	345	310-315		*A. tanguticum*	*227*
AVII1a-23 (guan-fu base Y) R^2=αOAc R^7=R^9=βOH R^6=αOH	$C_{22}H_{29}NO_5$	387	218-219		*A. coreanum*	*228, 229*
AVII1a-24 (guan-fu base Z, 2-isobutyryl-14-hydroxyhetisine) R^2=αOCOCH$(CH_3)_2$ R^6=αOH R^7=R^9=βOH	$C_{24}H_{33}NO_5$	415	230-231		*A. coreanum*	*228~231*
AVII1a-25 (acoridine) R^2=αOCOCH$_2$CH$_3$ R^6=αOH R^7=R^9=βOH	$C_{23}H_{31}NO_5$	401	204-206	+16	*A. coreanum*	*231*
AVII1a-26 (guan-fu base A) R^2=R^7=αOAc R^6=αOH R^9=βOH	$C_{24}H_{31}NO_6$	429	199	+49	*A. coreanum*	*229, 233*
AVII1a-27 (guan-fu base O) R^2=αOCOCH$_2$CH$_3$ R^6=αOH R^7=βOAc R^9=βOH	$C_{25}H_{33}NO_6$	443			*A. coreanum*	*235*
AVII1a-28 (guan-fu base F) R^2=αOCOCH$(CH_3)_2$ R^6=αOH R^7=βOAc R^9=βOH	$C_{26}H_{35}NO_6$	457	181-182	+58	*A. coreanum*	*236*
AVII1a-29 (zeravshanisine) R^2=αOAc R^6=αOH R^7=βOBz R^9=βOH	$C_{29}H_{33}NO_6$	491	287-289		*A. zeravschanicum*	*237*
AVII1a-30 (guan-fu base G) R^2=R^6=R^7=αOAc R^9=βOH	$C_{26}H_{33}NO_7$	471	178		*A. coreanum*	*229, 232, 233*

TABLE IX (*continued*)

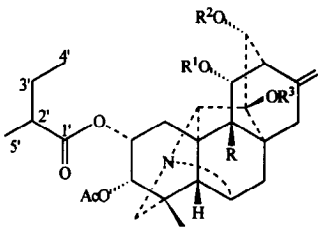
AVII1a-31 (hypognavinol) R^1=R^8=βOH R^2=αOH R^5=OH	$C_{20}H_{27}NO_4$	345	307-308	+67.7	*A. sanyoense*	*238~243*
AVII1a-32 (hypognavine) R^1=βOBz R^2=αOH R^5=OH R^8=βOH	$C_{27}H_{31}NO_5$	449	239-241	+127.1	*A. sanyoense*	*238~243* *221, 222*
AVII1a-33 (paniculatine) R^1=R^2=βOAc R^6=αOBz R^7=βOH	$C_{31}H_{35}NO_7$	533			*A. paniculatum*	*244, 245*
AVII1a-34 (1-*O*-acetylhypognavine) R^1=βOAc R^2=αOBz R^5=R^8=βOH	$C_{29}H_{33}NO_6$	491	127-128	+116.7	*A. sanyoense* var. *tonense*	*216*
AVII1a-35 (1, 15-di-*O*-acetylhypognavine) R^1=R^8=βOAc R^2=αOBz R^5= βOH	$C_{37}H_{38}NO_{14}$	560		+83	*A. snyoense* var. *tonesne*	*216*
AVII1a-36 (tadzhaconine) R^1=βOAc R^2=αOBz R^6= αOAc R^7=βOH	$C_{31}H_{35}NO_7$	533	236-237		*A. zeravschanium*	*246*
AVII1a-37 (3-epi-ignavinol) R^2=R^3=αOH R^5=OH R^8=βOH	$C_{20}H_{27}NO_4$	345	292-293.5	+49.1	*A. japonica* var. *montanum*	*247*
AVII1a-38 (ignavine) R^2=αOH R^3=βOBz R^5=OH R^8=βOH	$C_{27}H_{31}NO_5$	449	172-174	+58.3	*A. sayoense*, *A. japonicum*, *A. tasiromontanum*	*248~252*
AVII1a-39 (cossonine) R^2=βOBz R^3=R^7=αOAc R^6=αOH	$C_{31}H_{35}NO_7$	533	+45		*D. cossonianum*	*253*
AVII1a-40 (cardiopimine) R^1=βOAc R^2=αOH R^3=αOCOCH$(CH_3)_2$ R^6=αOAc R^7=αOBz	$C_{35}H_{45}NO_9$	619	-81.3		*D. cardiopetalum*	*254*
AVII1a-41 (cardiopidine) R^1=βOAc R^2=αOH R^3=αOCOCH$(CH_3)_2$ R^6=αOAc R^7=αOBz	$C_{36}H_{43}NO_9$	633			*D. cardiopetalum*	*254*

TABLE IX (*continued*)

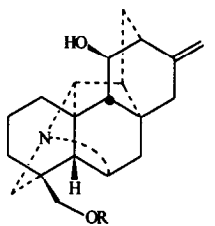
AVII1a-42 (cardiopinine) R^1=βOAc R^2=αOCOCH$(CH_3)_2$ R^3=αOH R^6=αOAc R^7=αOBz	$C_{35}H_{45}NO_9$	619	218-220	-26.6	*D. cardiopetalum*	*254*
AVII1a-43 (cardiopine) R^1=βOAc R^3=αOH R^2=αOCOCH$(CH_3)CH_2CH_3$ R^6=αOAc R^7=αOBz	$C_{36}H_{43}NO_9$	633	194-197	-26.3	*D. cardiopetalum*	*254*
AVII1a-44 (cardiodine) R^1=βOAc R^3=αOAc R^2=αOCOCH$(CH_3)CH_2CH_3$ R^6=αOAc R^7=αOBz R^9=βOH	$C_{38}H_{45}NO_{11}$	691			*D. cardiopetalum*	*254*
AVII1a-45 (13-acetyl-14-hydroxy-2-propionyl-hetisine) R^2=α-$OOCCH_2CH_3$ R^6=α-OH R^7=βOAc R^9=βOH	$C_{25}H_{33}NO_6$				*A. coreanum*	*255*



AVII1a-46



AVII1a-47~AVII1a-50



AVII1a-51~AVII1a-52

AVII1a-46 (13-*O*-acetyl-9-deoxyglanduline)	$C_{29}H_{39}NO_8$	529	154-156	+46.6	*C. glandulosa*	*256*
AVII1a-47 (glanduline) R=OH	$C_{27}H_{37}NO_8$	503	134-137	+24	*C. glandulosa*	*256*
AVII1a-48 (13-*O*-acetylglanduline) R^2=Ac R=OH	$C_{28}H_{39}NO_9$	545	110-115	+15.2	*C. glandulosa*	*256*

TABLE IX (*continued*)

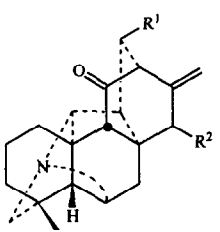
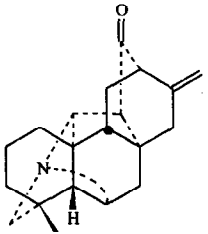
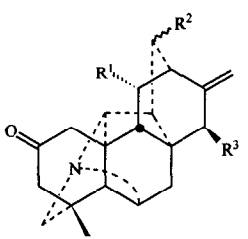
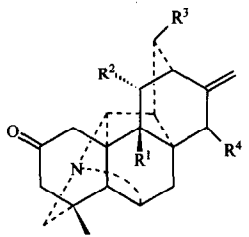
AVII1a-49 (14-*O*-acetyl-9-deoxyglanduline) R^3=Ac	$C_{29}H_{39}NO_8$	529	145-148	+20	*C. glandulosa*	*256*
AVII1a-50 (11, 13-*O*-diacetyl-9-glanduline) R^1=R^2=Ac	$C_{31}H_{41}NO_9$	571	195-198	+36	*C. glandulosa*	*256*
AVII1a-51 (davisinol)	$C_{20}H_{27}NO_2$	313		+27.5	*D. davisii*	*196*
AVII1a-52 (18-benzoyldavisinol) R=Bz	$C_{27}H_{31}NO_3$	417		+42.3	*D. davisii*	*196*
						
	AVII1a-53~AVII1a-55		AVII1a-56			
AVII1a-53 (spirasine IX)	$C_{20}H_{25}NO$	295	157-158	+135.5	*S. japonica* var. *fortunei*	*190, 159*
AVII1a-54 (spirasine X) R^1=αOH	$C_{20}H_{25}NO_2$	311	224-227	+51	*S. japonica*	*257*
AVII1a-55 (11-dehydrokobusine) R^2=βOH	$C_{20}H_{25}NO_2$	311	239-241		*A. talassicum*	*258, 192*
AVII1a-56 (spirasine IV)	$C_{20}H_{25}NO$	295		-95.7	*S. japonica* var. *fortunei*	*190, 159*

TABLE IX (*continued*)



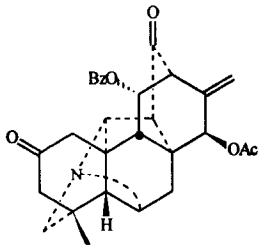
AVII1a-57~AVII1a-58



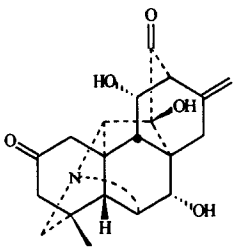
AVII1a-59~AVII1a-61

AVII1a-57 (hetisinone, 2-dehydrohetisine) R^1=OH R^2=βOH	$C_{20}H_{25}NO_3$	327	268-270	+40	*D. cardinale*, *D. denudatum*, *A. heterophyllum*	*204~214*, *66, 80*, *186*
AVII1a-58 (venulusine, venuluson) R^2=αOH R^3=βOH	$C_{20}H_{25}NO_3$	327		+27.3	*D. venulosum*	*259*
AVII1a-59 (fissumine) R^1=OAc R^3=αOH	$C_{22}H_{27}NO_4$	369		-33.8	*D. fissum* subsp. *anatolicum*	*223*
AVII1a-60 (cardiopetamine) R^2=αOBz R^3=R^4=βOH	$C_{27}H_{29}NO_5$	447		+45	*D. cardiopetalum*	*204, 260 261*
AVII1a-61 (15-acetylcardiopetamine) R^2=αOBz R^3=βOH R^4=βOAc	$C_{29}H_{31}NO_6$	489	236-238	+16	*D. cardiopetalum*	*204, 260 261*

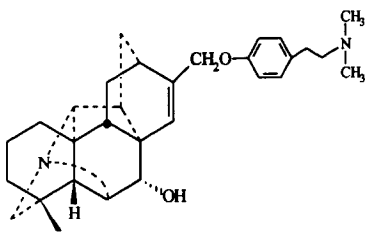
TABLE IX (*continued*)



AVII1a-62

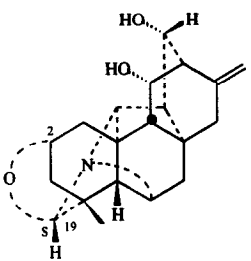


AVII1a-63



AVII1a-64

AVII1a-62 (15-acetyl-13-dehydro-cardiopetamine)	$C_{29}H_{29}NO_6$	487	253-255	-46	*A. napellus*	*204, 260 261*
AVII1a-63 (orientinine)	$C_{20}H_{23}NO_5$	357		-42	*A. orientale, Rumex pictus*	*262, 263*
AVII1a-64 (eraconine)	$C_{30}H_{40}N_2O$	444	130-131		*A. zeravschanicum*	*191, 194*
b. N,O-Mixed ketal subtype (AVII2)						
a). C-2-O-C-19-*N* group (AVII2a)						

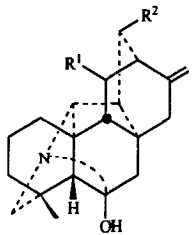


AVII2a-1

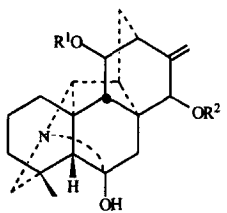
AVII2a-1(delatisine)	$C_{20}H_{25}NO_3$	327	274.5-276.5	+86	*D. elatum*	*264*

TABLE IX (*continued*)

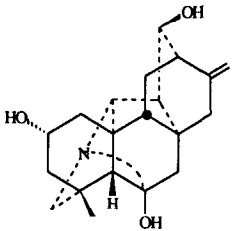
b). *N*-C(6)-OH group (AVII2b)



AVII2b-1~AVII2b-5



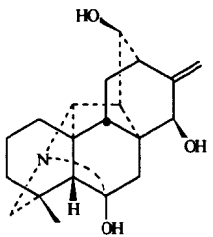
AVII2b-6~AVII2b-9



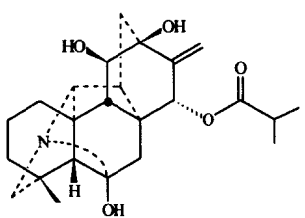
AVII2b-10

AVII2b-1 (spiradine B) R^1=OH			259-260		*S. japonica*	*265~267*
AVII2b-2 (venulol) R^1=αOH	$C_{20}H_{27}NO_2$	313		+19.7	*D. venulosum*	*259*
AVII2b-3 (spiradine C) R^1=OAc	$C_{22}H_{29}NO_3$	355	248-249		*S. japonica*	*265*
AVII2b-4 (spirasine XIV) R^2=αOH	$C_{20}H_{27}NO_2$	313	244-246	-18.8	*S. japonica*	*268*
AVII2b-5 (spiradine XV) R^2=βOH	$C_{20}H_{27}NO_2$	313	156-158	0	*S. japonica*	*268*
AVII2b-6 (pseudokobusine)	$C_{20}H_{27}NO_3$	329	268-270		*A. talaossicum;*	*141*
					A. yesoense;	*198~201*
					A. luciduscul um	*269*
AVII2b-7 (yesodine) R^2=CO—C(H)(CH$_3$)—CH$_2$CH$_3$	$C_{25}H_{35}NO_4$	413		-9.4	*A. yesoense* var. *macroyesoense*	*270*
AVII2b-8 (15-benzoylpseudokobusine) R^2=Bz	$C_{27}H_{31}NO_4$	433		-6.9	*A. yesoense* var. *macroyesoense*	*134* *271*
AVII2b-9 (15-veratroylpseudokobusine) R=Vr	$C_{29}H_{35}NO_6$	493		-6.7	*A. yesoense* var. *macroyesoense*	*134*
AVII2b-10 (tatsirine)	$C_{20}H_{27}NO_3$	329	260-263		*D. tatsienense*	*129*

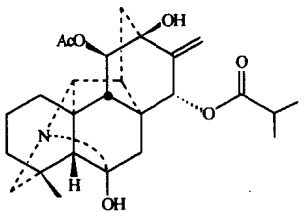
TABLE IX (*continued*)



AVII2b-11

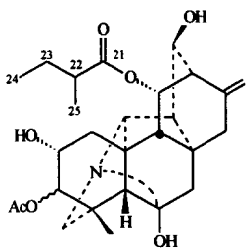


AVII2b-12

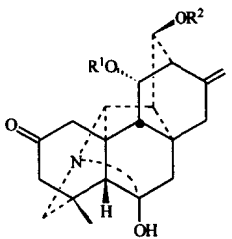


AVII2b-13

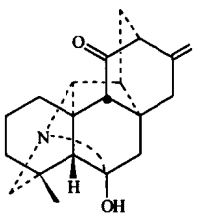
AVII2b-11 (acorientine)	$C_{20}H_{27}NO_3$	329		+13.5	*A. orientale,*	*262*
					Rumex pictus	*263*
AVII2b-12 (cardionine)	$C_{24}H_{33}NO_5$	415	235	+4.68	*D. cardiopetalum*	*272*
AVII2b-13 (11-acetylcardionine)	$C_{26}H_{35}NO_6$	457		-5.71	*D. cardiopetalum*	*272*



AVII2b-14



AVII2b-15~AVII2b-17

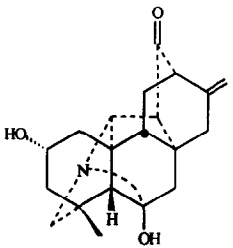


AVII2b-18

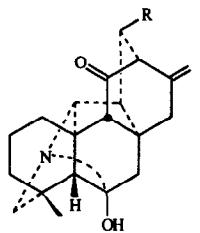
AVII2b-14 (geyerinine)	$C_{27}H_{38}NO_7$	487			*D. geyeri*	*273*
AVII2b-15 (delbidine)	$C_{20}H_{27}NO_4$	343	>360	+22.3	*D. occidentale*	*212*
AVII2b-16 (geyeridine) R^2=Ac	$C_{22}H_{27}NO_5$	385			*D. geyeri*	*273*

TABLE IX (*continued*)

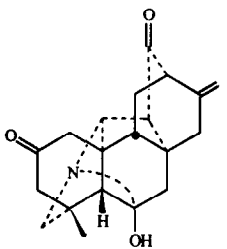
AVII2b-17 (geyerine) R^1=$COCH(CH_3)CH_2CH_3$	$C_{25}H_{33}NO_5$	427		+9.6	*D. geyeri*	*273*
AVII2b-18 (spiradine A)	$C_{22}H_{25}NO_2$	311	281-282		*S. japonica*	*265*



AVII2b-19

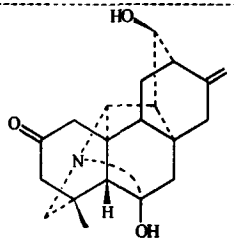


AVII2b-20~AVII2b-21

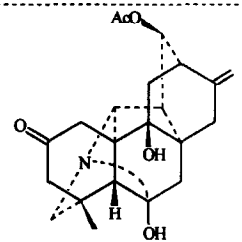


AVII2b-22

AVII2b-19 (panicudine)	$C_{22}H_{25}NO_3$	327	215-217		*A. paniculatum*	*274*
AVII2b-20 (spirasine XII) R=αOH	$C_{20}H_{25}NO_3$	327	226-228	+17.9	*S. japonica*	*268*
AVII2b-21 (spirasine XIII) R=βOH	$C_{20}H_{25}NO_3$	327	188-189	+25.7	*S. japonica*	*268*
AVII2b-22 (paniculadine)	$C_{20}H_{23}NO_3$	325			*A. paniculatum*	*275*



AVII2b-23

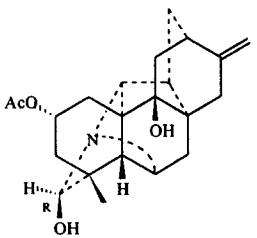


AVII2b-24

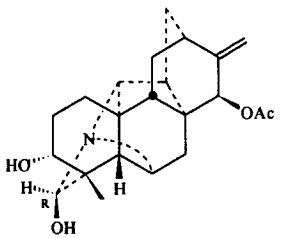
TABLE IX (*continued*)

AVII2b-23 (delnuttidine)	$C_{20}H_{25}NO_3$	327			*D. nuttalianum*	*224*
AVII2b-24 (delnuttaline)	$C_{22}H_{27}NO_5$	385	269-271		*D. nuttalianum*	*224, 276*

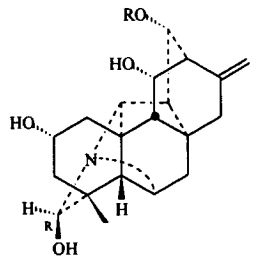
c) *N*-C-19-OH group (AVII2c)



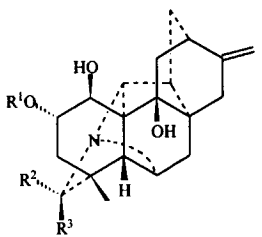
AVII2c-1



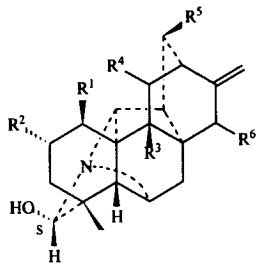
AVII2c-2



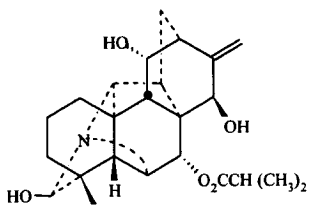
AVII2c-3~AVII2c-4



AVII2c-5~AVII2c-6



AVII2c-7- AVII2c-9



AVII2c-10

AVII2c-1 (acsinatine)	$C_{22}H_{29}NO_4$	371	251-253		*A. leucostomum*	*277, 278*
AVII2c-2 (andersobine)	$C_{22}H_{29}NO_4$	371	310		*D. andersonii*	*279*
AVII2c-3 (vakhmatine)	$C_{22}H_{27}NO_4$	345	170.5-174.5	-12.6	*A. palmatum*	*148*

TABLE IX (*continued*)

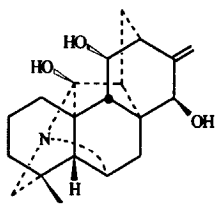
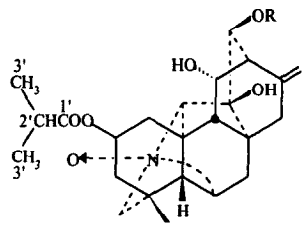
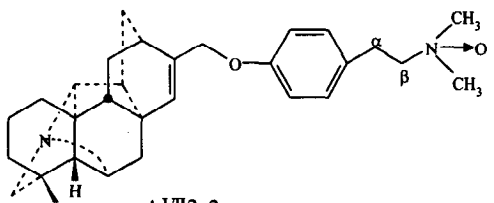
AVII2c-4 (13-*O*-acetylvakhmatine) R=Ac	$C_{22}H_{29}NO_5$	387		-20	*C. ambigua*	*280*
AVII2c-5 (septenine) R^1=Ac R^3=OH (19*S*)	$C_{22}H_{29}NO_5$	387	190-192		*A. setentrionale*	*281*
AVII2c-6 (septentriosine) R^2=OH (19*S*)	$C_{20}H_{27}NO_4$	345	260-262	+21	*A. setentrionale*	*282*
AVII2c-7 (2-acetylseptentriosine) R^2=OAc R^1=R^3=OH	$C_{22}H_{29}NO_5$	387	182-184	+6.4	*A. setentrionale*	*283*
AVII2c-8 (delgramine) R^1=R^4=αOH R^2=OBz	$C_{27}H_{31}NO_5$	449	173-175	+16.7	*D. grandiforum*	*284*
AVII2c-9 (talatizine) R^4=R^6==βOH	$C_{20}H_{27}NO_3$	329	246-246.5	+38	*A. talassicum*	*397, 398*
AVII2c-10 (ternatine) R^1=αOCOCH$(CH_3)_2$ R^2=αOH	$C_{24}H_{33}NO_6$	415	236-238		*D. ternatum*	*395*
d). *N*-C(20)-OH group (AVII2d)						
 AVII2d-1						
AVII2d-1 (orgetine)	$C_{20}H_{27}NO_3$	329	280-282	+40	*A. orientale*	*285*

TABLE IX (*continued*)

d. *N*-Oxide subtype (AVII3) / group



AVII3-1~AVII3-2



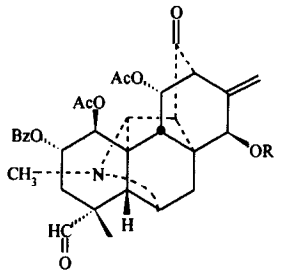
AVII3-3

AVII3-1 (guan-fu base Z *N*-oxide)	$C_{24}H_{33}NO_6$	431	317-319	*A. coreanum*	*286*
AVII3-2 (guan-fu base F *N*-oxide) R=Ac	$C_{26}H_{35}NO_7$	473	240-242	*A. coreanum*	*287*
AVII3-3 (eraconine *N*-oxide)	$C_{30}H_{40}N_2O_2$	460	94-95	*A. zeravechanicum*	*288, 194*

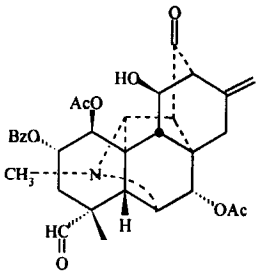
TABLE X

VAKOGNAVINE TYPE DITERPENOID ALKALOIDS (AⅧ)

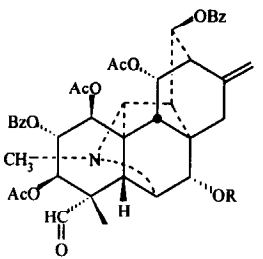
a. Vakognavine (*N*,19-*seco* hetisine) subtype (AⅧ1) / group



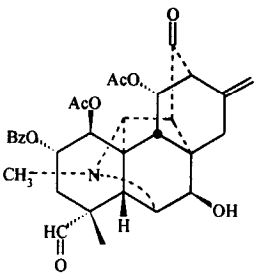
AⅧ1-1~AⅧ1-2



AⅧ1-3



AⅧ1-4~AⅧ1-5



AⅧ1-6

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
AⅧ1-1 (15-deacetylvakognavine)	$C_{32}H_{35}NO_9$	577	224.5-226.5	-73.4	*A. palmatum*	*215*
AⅧ1-2 (vakognavine) R=Ac	$C_{34}H_{37}NO_{10}$	619	298		*A. palmatum*	*215, 289~292*

TABLE X (*continued*)

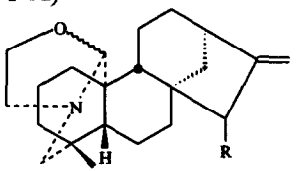
AⅧ1-3 (barbisine)	$C_{32}H_{34}NO_9$	577	251-254	-62.6	*D. barbeyi*	*293*
AⅧ1-4 (delgrandine)	$C_{41}H_{43}NO_{12}$	739	300-302	-130.2	*D. grandiflorum*	*294*
AⅧ1-5 (acetyldelgrandine) R=Ac	$C_{43}H_{45}NO_{13}$	696	274-275	-113.0	*D. grandiflorum*	*294*
AⅧ1-6 (barbaline)	$C_{34}H_{37}NO_{11}$	635	297	-17.2	*D. barbeyi*	*295*

TABLE XI

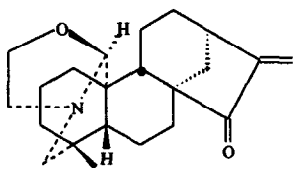
VEATCHINE TYPE DITERPENOID ALKALOIDS (B Ⅰ)

a. N, O-Mixed ketal subtype (B Ⅰ 1) / group

a). Oxazoliding ring group (B Ⅰ 1a)



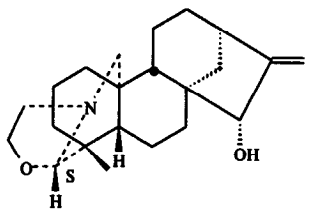
B Ⅰ 1a-1~B Ⅰ 1a-3



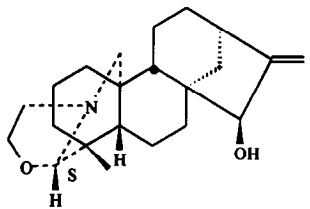
B Ⅰ 1a-4

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
B Ⅰ 1a-1 (veatchine) R=αOH	$C_{22}H_{33}NO_2$	343	122-126	-69	*Garrya veatchii*	*296, 297, 299~304, 73, 77*
B Ⅰ 1a-2 (garryfoline) R=βOH	$C_{22}H_{33}NO_2$	343	124-126	-46	*G. laurifolia*, *G. ovata* var. *lindheimeri*	*305~309*
B Ⅰ 1a-3 (ovatine) R=βOAc	$C_{24}H_{35}NO_3$	385	113-114	-79.4	*G. ovata* var. *lindheimeri*	*302, 305~308*
B Ⅰ 1a-4 (cuauchichicine)	$C_{22}H_{33}NO_2$	343	152-154	-69	*G. laurifolia;* *G. ovata* var. *lindheimeri*	*302, 305~308* *306, 307, 310~313*

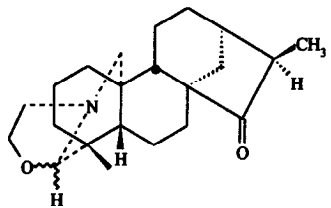
TABLE XI (*continued*)



B I 1a-5



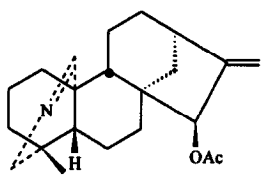
B I 1a-6



B I 1a-7

B I 1a-5 (garryine)	$C_{22}H_{33}NO_2$	343	74-82	-84.2	*G. veatchii*	*77, 296 297, 299~304*
B I 1a-6 (isogarryine)	$C_{22}H_{33}NO_2$	343	140-144	-57	*G. laurifolia*	*302, 305~307 309, 311~314*
B I 1a-7 (isocuauchichicine)	$C_{22}H_{33}NO_2$	343	132-134	-79.3	*G. laurifolia*	*302, 306~308, 310*

b. Imine subtype (B I 1b) / group



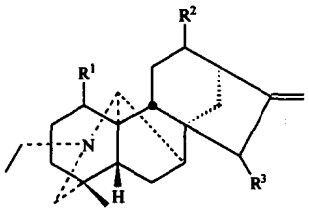
B I 1b-1

B I 1b-1 (lindheimerine)	$C_{22}H_{31}NO_2$	341	-113.8		*G. ovata* var. *lindheimeri*	*305*

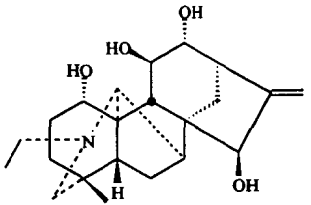
TABLE XII

NAPELLINE TYPE DITERPENOID ALKALOIDS (B II)

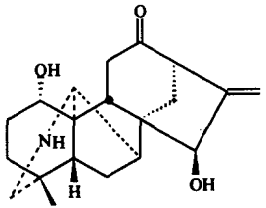
a. Amine subtype (B II 1)/ group



B II 1-1~B II 1-8



B II 1-9

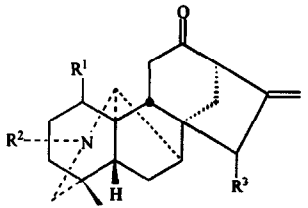


B II 1-10

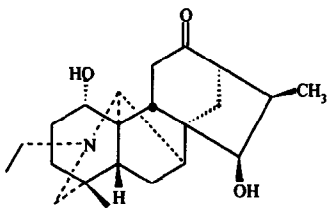
code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
B II 1-1 (liangshanine) R^1=αOCH$_3$ R^2=R^3=βOH	$C_{23}H_{35}NO_3$	373		-16.4	*A. liangshanium*	*315*
B II 1-2 (12-epi-lucidusucline) R^1=αOH R^2=βOH R^3=βOAc	$C_{24}H_{35}NO_4$	401	160-164	-100	*A. liangshanium*	*315*
B II 1-3 (napelline, luciculine) R^1= R^2=αOH R^3=βOH	$C_{22}H_{33}NO_3$	359	116-117	-13	*A. napellus, A. karakolicum*	*316~329*
B II 1-4 (12-epi-napelline) R^1=αOH R^2= R^3=βOH	$C_{22}H_{33}NO_3$	359	72-72.5	-40.2	*A. karakolicum*	*316, 330 331*
B II 1-5 (1-epi-napelline) R^1=R^3=βOH R^2= αOH	$C_{22}H_{33}NO_3$	359	87-89	-11.7	*A. flavum*	*316*
B II 1-6 (12-acetylnapelline) R^1=αOH R^2=αOAc R^3=βOH	$C_{24}H_{35}NO_4$	401	205-206		*A. karakolicum, A. soongaricum*	*333*
B II 1-7 (lucidusculine) R^1=R^2=αOH R^3=βOAc	$C_{24}H_{35}NO_4$	399	170-171	-95	*A. luciduscul um, A. yeosoense*	*201, 316 328, 329, 334~339*

TABLE XII (*continued*)

B II 1-8 (12-acetyllucidusculine) R^1=αOH R^2=αOAc R^3=βOAc	$C_{26}H_{37}NO_5$	443	132-134	-94.1	*A. yeosoense* var. *macroyesoense*	*134, 316, 318*
B II 1-9 (turpelline)	$C_{22}H_{33}NO_4$	375			*A. turczanmowii*	*340*
B II 1-10 (norsongorine)	$C_{20}H_{27}NO_3$	329			*A. soongoricum*	*341, 342*



B II 1-11~B II 1-14

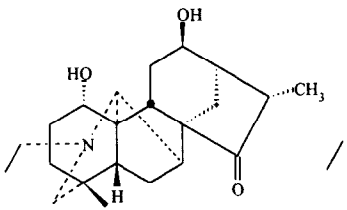


B II 1-15

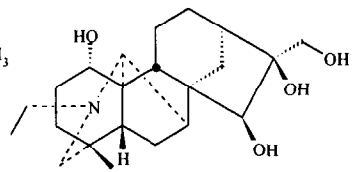
B II 1-11 (songorine, shimaburo base I, bullatine G, napellonine) R^1=αOH R^3=βOH R^2=Et	$C_{22}H_{31}NO_3$	357	201-203	-140	*A. baicalense, A. barbatum, A. gekanovskyi, A. firmum, A. karakolicum, A. monticola, A. septentrionale, A. soongaricum, A. volubile*	*153, 261, 321~323, 325~328, 331~333, 341~343*
B II 1-12 (15-acetylsongorine) R^1=αOH R^3=βOAc R^2=Et	$C_{24}H_{33}NO_4$	399	176-178	-172	*A. firmum, S. soongaricum*	*345*
B II 1-13 (liangshanone) R^1=αOCH_3 R^2=Et R^3=βOH	$C_{23}H_{33}NO_3$	371		-101	*A. liangshanium*	*315*

TABLE XII (*continued*)

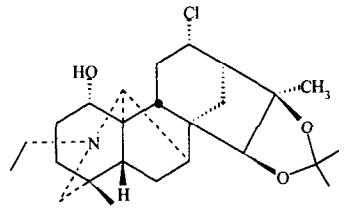
B II 1-14 (finetianine) R^1=βOH R^2=CH_3 R^3=βOH	$C_{21}H_{29}NO_3$	343	238-240		*Aconitum* spp.	*298*
B II 1-15 (dehydrosongorine)	$C_{22}H_{33}NO_3$	359	202-204		*A. karakolicum*	*341, 346*



B II 1-16



B II 1-17

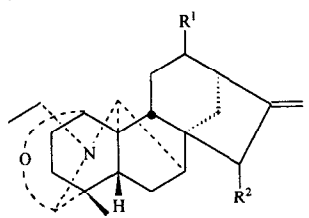


B II 1-18

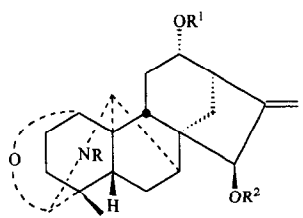
B II 1-16 (karakomine)	$C_{22}H_{33}NO_3$	359		-18.7	*A. karakolicum*	*347*
B II 1-17 (chuanfunine)	$C_{22}H_{35}NO_5$	393			*A. karmichael*	*348*
B II 1-18 (acofine)	$C_{25}H_{36}NO_3Cl$	435	159-160		*A. karakolicum*	*349*

b. *N,O*-Mixed ketal subtype (B II 2)/ group

a) C-1-*O*-C-19-*N* group (B II 2a)



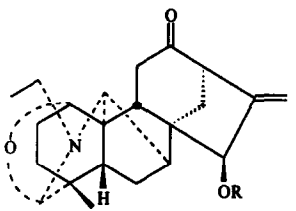
B II 2a-1~B II 2a-6



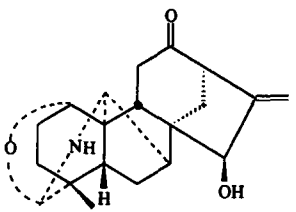
B II 2a-7~B II 2a-8

TABLE XII (*continued*)

B II 2a-1 (dehydronapelline, dehydroluciculine) R^1=αOH R^2=βOH	$C_{22}H_{31}NO_3$	357	103.5-105	+78.3	*A. yesoense* var. *maoroyeoense*	*134, 142 316*
B II 2a-2 (12-epi-19-dehydronapelline) R^1=R^2=βOH	$C_{22}H_{31}NO_3$	357		+45	*A. napellus*	*331*
B II 2a-3 (dehydrolucidusculine) R^1= αOH R^2=βOAc	$C_{24}H_{33}NO_4$	399	186-189	+2.6	*A. yesoense* var. *macroyesoense*	*134, 331a*
B II 2a-4 (12-epi-acetyldehydronapelline) R^1= βOAc R^2=βOH	$C_{24}H_{33}NO_4$	399		+25	*A. napellus*	*331*
B II 2a-5 (12-acetyldehydrolucidusculine) R^1= αOAc R^2=βOAc	$C_{26}H_{35}NO_5$	441		+9.3	*A. yesoense var. macroyesonese*	*134*
B II 2a-6 (12-epi-acetyldehydrolucidusculine) R^1=R^2=βOAc	$C_{26}H_{35}NO_5$	441			*A. pendulum*	*350*
B II 2a-7 (subdesculine) R^1=Ac R=Et	$C_{24}H_{33}NO_4$	399			*A. japonicum*	*351*
B II 2a-8 (*N*-deethyldehydrolucidusculine) R^2=Ac	$C_{22}H_{29}NO_4$	371		-9.6	*A. yesoense* var. *macroyesoense*	*331a*



B II 2a-9~B I 2a-10



B II 2a-11

TABLE XII (*continued*)

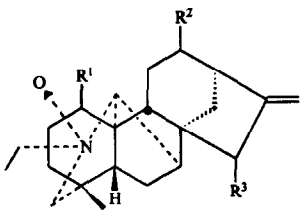
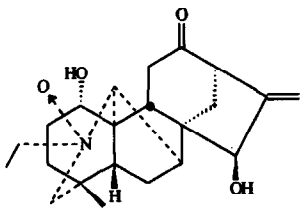
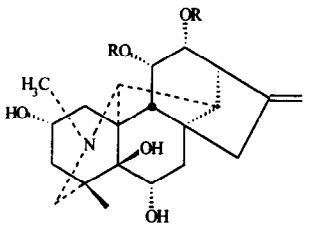
B II 2a -9 (songoramine)	$C_{22}H_{29}NO_3$	355	20-212	*A. karakolicum;* *A. monticola;* *A. soongaricum*	*261* *331* *341*
B II 2a -10 (15-acetylsongoramine) R=Ac	$C_{24}H_{31}NO_4$	397		*A. soongaricum*	*352*
B II 2a -11(norsongoramine)	$C_{20}H_{25}NO_3$	327	286-288	*A. tamarae*	*353*
c. *N*-Oxide subtype (B II 3)/ group					
 B II 3-1~B II 1-4					
 B II 3-5					
B II 3-1 (napelline *N*-oxide, flavamine) R^1=R^2=αOH R^3=βOH	$C_{22}H_{33}NO_4$	375	197-199	*A. soongaricum,* *A. flavum*	*142, 354*
B II 3-2 (12-epi-napelline *N*-oxide) R^1=αOH R^2=R^3=βOH	$C_{22}H_{33}NO_4$	375		*A. baicalense*	*355*
B II 3-3 (12-acetylnapelline *N*-oxide) R^1=αOH R^2=αOAc R^3=βOH	$C_{24}H_{35}NO_5$	417	235	*A. soongaricum*	*356*
B II 3-4 (flavadine) R^1=R^2=αOH R^3=βOAc	$C_{24}H_{35}NO_3$	401	198-200	*A. flavum*	*142, 354*
B II 3-5 (songorine *N*-oxide)	$C_{24}H_{31}NO_4$	373	253-255	*A. monticola*	*357*

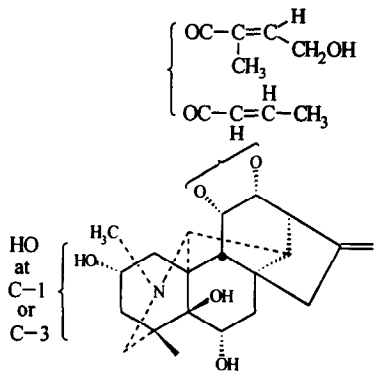
TABLE XIII

ANOPTERINE TYPE DITERPENOID ALKALOIDS (BIII)

a. Amine subtype (BIII1) / group



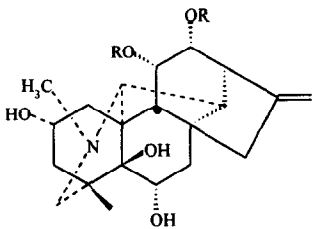
BIII1-1: R=COC(H)=C(H)–CH$_3$



BIII1-2

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
BIII1-1 (anopterine)	$C_{31}H_{43}NO_7$	541	222-223	-12	*Anopterus glandulosus;* and *A. macleayanus*	*358~362*
BIII1-2 (dihydroxyanopterine)	$C_{31}H_{43}NO_9$	573	242-244	-9	*Anopterus macleayanus*	*359, 360*

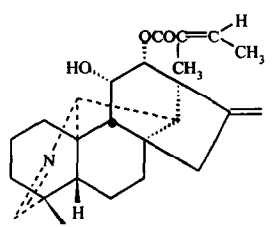
TABLE XIII (*continued*)



BIII1-3: R=COC(H)=C(H)–CH$_3$ C_1/C_3-OH

BIII1-3 (hydroxyanopterine)	$C_{31}H_{43}NO_8$	557	247-249	-14	*Anopterus glandulosus*, and *A. macleayanus*	*358* *360*

b. Imine subtype (BIII2) / group

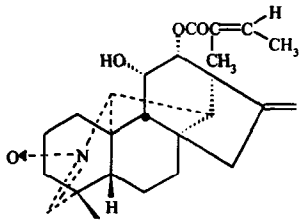


BIII2-1

BIII2-1 (anopterimine)	$C_{25}H_{33}NO_3$	395	235-238	+106	*Anopterus macleayanus*	*358*

TABLE XIII (*continued*)

c. Imine *N*-oxide subtype (BIII3) / group



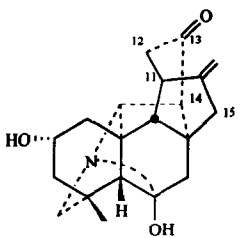
BIII2b

BIII3-1 (anopterimine *N*-oxide)	$C_{25}H_{33}NO_4$	411	233-235	+95	*Anopterus macleayanus*	*358*

TABLE XIV

DELNUDINE TYPE DITEERPENOID ALKALOIDS/SUBTYPE/GROUP (C I)

a. Delnudine sutype (C I 1) / group



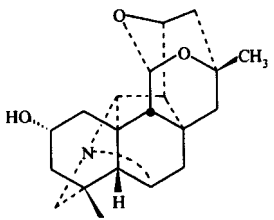
C I 1-1

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
C I 1-1 (delnudine)	$C_{20}H_{25}NO_3$	327	235-237		*D. denudatum*	*363, 364*

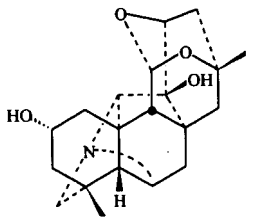
TABLE X V

KUSNESOLINE TYPE DITERPENOID ALKALOIDS (C II)

a. kusnesoline subtype (C II 1) / group



C II 1-1



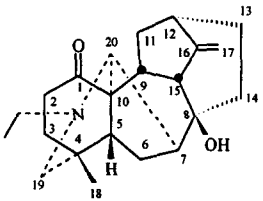
C II 1-2

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
C II 1-1 (kusnesoline, no name)	$C_{20}H_{27}NO_3$	329	279-279.5	+9.1	*A. kusnezoffii; A. racemulosum* var. *pengzhouense*	*365~367*
C II 1-2 (guan-fu base K)	$C_{20}H_{27}NO_4$	345	242	+50	*A. coreanum*	*368*

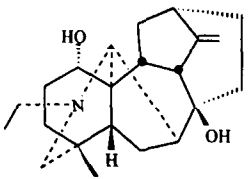
TABLE XVI

ACTALINE TYPE DITERPENOID ALKALOIDS (CIII)

a. Actaline subtype (CIII1) / group



CIII1-1



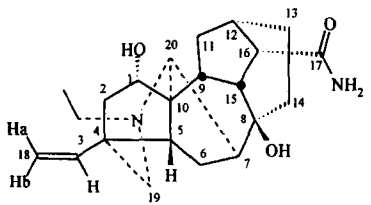
CIII1-2

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
CIII1-1 (actaline)	$C_{22}H_{31}NO_2$	341	125-127		*A. talassicum*	*369*
CIII1-2 (ajabicine)	$C_{22}H_{33}NO_2$	343			*D. ajacis*	*370*

TABLE XVII

RACEMULOSINE TYPE DITERPENOID ALKALOIDS (CIV)

a. Racemulosine subtype (CIV1) / group



CIV1-1

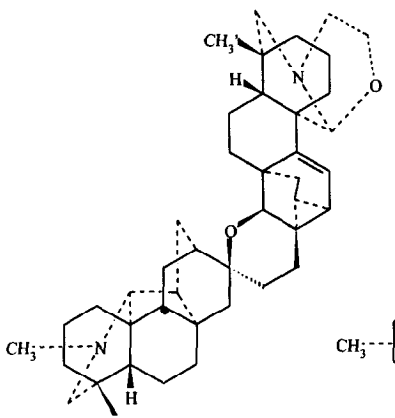
TABLE XVII (*continued*)

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
CIV 1-1 (racemulosine)	$C_{22}H_{32}N_2O_3$	372	228-230	-19.2	*A. racemulosum* var. *pengzhouense*	*371*

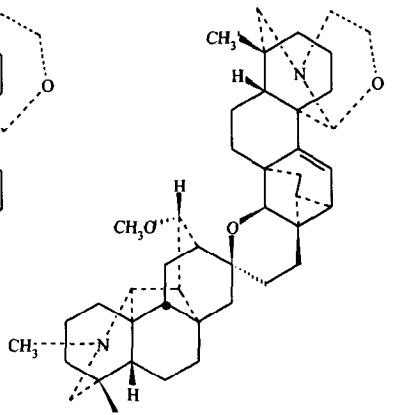
TABLE XVIII

ATISINE-HETIDINE TYPE BOSDITERPENOID ALKALOIDS (D I)

A. Atisine-hetidine subtype(D I 1) / group



D I 1-1



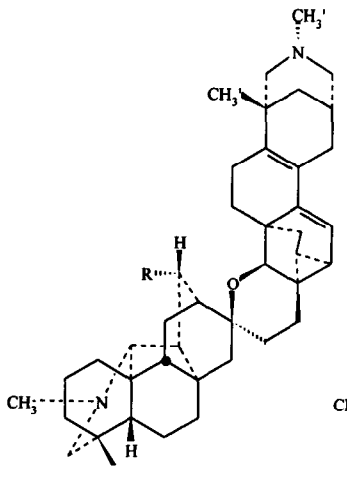
D I 1-2

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
D I 1-1 (staphisagrine)	$C_{43}H_{60}N_2O_2$	636	229-231	-105.6	*D. staphisagria*	*372*
D I 1-2 (staphisagnine)	$C_{44}H_{62}N_2O_3$	666		-104.5	*D. staphisagria*	*372*

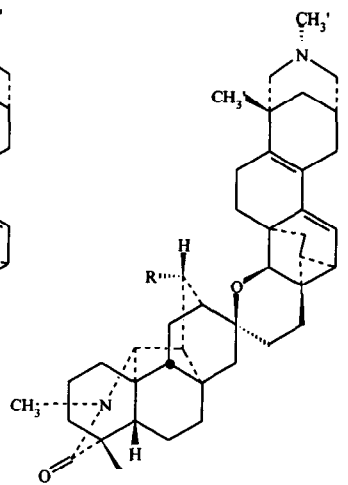
TABLE X IX

REARRANGED ATISINE-HETIDINE TYPE BISDITERPENOID ALKALOIDS (D II)

a. Rearranged atisine-hetidine subtype (D II 1) / group



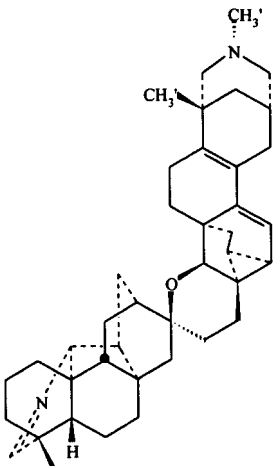
D II 1-1~D II 1-2



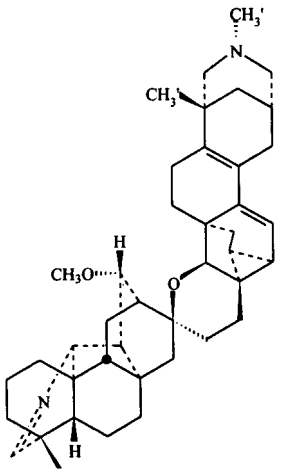
D II 1-3~D II 1-4

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
D II 1-1 (staphidine)	$C_{42}H_{58}N_2O$	606	213-216	-160	*D. staphisagria*	*373, 374*
D II 1-2 (staphisine) R=OCH_3	$C_{43}H_{60}N_2O_2$	636	200-208	-148.4	*D. staphisagria*	*373, 375*
D II 1-3 (staphirine)	$C_{42}H_{56}N_2O_2$	620		-126	*D. staphisagria*	*374, 376*
D II 1-4 (staphigine) R=OCH_3	$C_{43}H_{60}N_2O_3$	650	225-227	-116	*D. staphisagria*	*374, 376*

TABLE XIX (*continued*)



D II 1-5



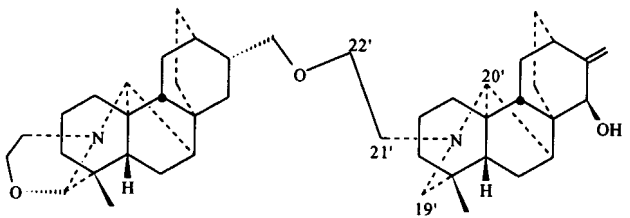
D II 1-6

D II 1-5 (staphimine)	$C_{41}H_{54}N_2O$	590	-58.5	*D. staphisagria*	*373, 374*
D II 1-6 (staphinine)	$C_{42}H_{56}N_2O_2$	620	-57.5	*D. staphisagria*	*373, 374*

TABLE X X

DENUDATINE-DENUDATINE TYPE BISDITERPENOID ALKALOIDS (DIII)

a. Denudatine-denudatine subtype (DIII1) / group



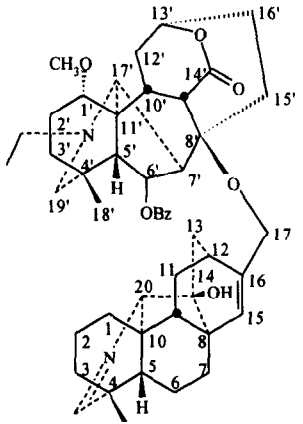
DIII1-1

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
DIII1-1 (pukeensine)	$C_{44}H_{64}N_2O_3$	668			*A. pukeense*	*377*

TABLE X X I

HETERATISINE-HETIDINE TYPE BISDITERPENOID ALKALOIDS (DIV)

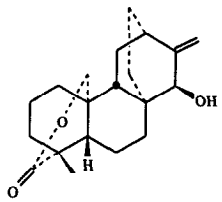
A. Heteratinine-hetidine subtype (DIV1) / group



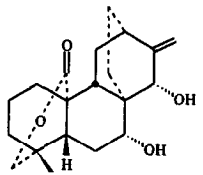
DIV1-1

code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
DIV1-1 (tangirine)	$C_{49}H_{62}N_2O_7$	790			*A. tanguticum*	*378*

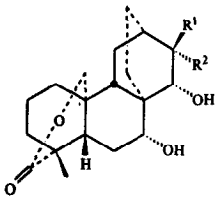
TABLE X X II (A I ')
ATISANE TYPE DITERPENES



A I '-1

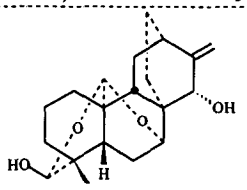


A I '-2

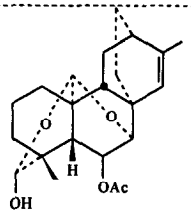


A I '-3~A I '-4

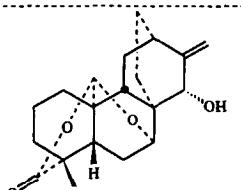
code (name)	formula	MW	mp	$[\alpha]_D$	plant	*ref*
A I '-1 (atisenol)	$C_{20}H_{28}O_3$	316	161-163	-23.8	*A. heterophyllum*	*104*
A I '-2 (spiramilactone)	$C_{20}H_{28}O_4$	332	222-224	-36	*S. japonica* var. *incisa*	*112*
A I '-3 (spiramilactone C) $R^1+R^2=CH_2$	$C_{20}H_{28}O_4$	332	172-174	-50	*S. japonica* var. *acuta*	*105, 106*
A I '-4 (spiramilactone D) R^1=OH $R^2=CH_3$	$C_{20}H_{30}O_5$	350	225-227	-52	*S. japonica* var. *acuta*	*105, 106*



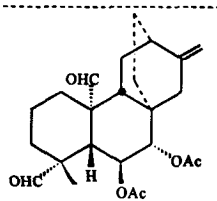
A I '-5



A I '-6



A I '-7



A I '-8

A I '-5 (spiraminol)	$C_{20}H_{28}O_4$	332	184-186	-115	*S. japonica* var. *acuminata*	*98*
A I '-6 (spiramacetal)	$C_{22}H_{30}O_5$	347	148-150	-75	*S. japonica* var. *acuta*	*105, 106*
A I '-7 (spiramilactone B)	$C_{20}H_{26}O_4$	330	215-217		*S. japonica* var. *stellaris*	*106*
A I '-8 (spiramadol)	$C_{24}H_{32}O_6$	417	208-210	-19	*S. japonica* var. *acuta*	*105, 106*

TABLE XXIII
OCCURRENCE OF NATURAL C_{20}-DITERPENOID ALKALOIDS IN PLANT SPECIES

Plant	Alkaloid	*Ref.*
I. Ranunculaceae		
A. *Aconitum* spp.		
1) *A. alboviolaceum* kom	albovionitine	*189*
2) *A. altaicum* Stein	napelline	*380*
3) *A. baicalense*	12-epinapelline *N*-oxide	*355*
(A. czekanovskyi)	napelline	*355*
	songorine	*379, 383*
4) *A. barbatum* Pers	11-acety1-1, 19-epoxydenudatine	*138*
	lepenine	*117, 381*
	lepetine	*381*
	songorine	*355, 382*
5) *A. barbatum* var. *hispidum* Ledeb	11-hydcoxylepenine	*116*
6) *A. contortum* Finet et Gagnep	episcopalidine	*161, 157*
	contorine	*161*
	contorsine	*161*
	contortine	*161*
7) *A. carael* Debx	chuanfunine	*346*
8) *A. coreanum* (Levl) Raipaies	acoridine	*231, 232*
	14-acetyl-14-hydroxy-2-propionyl hetisine	*255*
	atisine chloride	*102*
	coriphine	*174*
	coryphidine	*103*
	guan-fu base A	*233*
	guan-fu base F	*236*
	guan-fu base F *N*-oxide	*287*
	guan-fu base G	*229, 232, 233*
	guan-fu base K	*359*
	guan-fu base O	*235*
	guan-fu base Y	*228, 229*
	guan-fu base Z	*228, 230, 231*
	guan-fu base Z *N*-oxide	*287*
	isoatisine	*78*
9) *A. crassicaule* W. T. Wang	crassicauline B	*220*
10) *A. delphinifolium*	gomandonine 11-O-acetate	*133*
11) *A. flavum* Hand-Mazz	1-epinapelline	*310*
	flavadine	*354, 143*
	flavamine	*143*

TABLE XXIII (*continued*)

12)	*A. finetianum* W. T. Wang	finetianine	*298*
13)	*A. firmum* Reicheb	15-acetylsongorine	*345*
		songorine	*345*
		tadzhaconine	*345*
14)	*A. gymnandrum* Maxim	gymnandine	*107*
15)	*A. heterophyllum* Stapf	atidine	*60, 66*
		atisine	*60, 66*
		dehydroatisine	*61, 100*
		heterophylloidine	*154*
		hetisine	*66, 100*
		hetisinone	*66*
		isoatisine	*63, 73, 76, 77*
16)	*A. ibukiense* Nakai	ryosenamine	*221, 222*
		ryosenaminol	*221, 222*
17)	*A. japonica* Thung	ignavine	*249*
		isohypognavine	*218*
		subdesculine	*351*
18)	*A. japonica* var. *montanum*	3-epi-ignavinol	*247*
19)	*A. jinyanyense* W. T. Wang	denudatine	*114*
		jynosine	*114*
20)	*A. karakolicum* Rapaics (*A. soongaricum*)	12-acetylnapelline	*333*
		acofine	*349*
		dehydrosongorine	*341*
		12-epinapelline	*316, 330*
		karakonine	*347*
		napelline	*322*
		songoramine	*331*
		songorine	*341, 321, 332* *333*
21)	*A. kirinense* Nakai	lepenine *N*-oxide	*137*
		kirinine A	*121*
		kirinine B	*119*
		kirinine C	*119*
22)	*A. kojimae* var. *lassiocarpium* W. Z. Wang	lassiocarpine	*131*
23)	*A. kusnezoffii* Reichb	beiwusine A	*71*
		beiwusine B	*71*
		denudatine	*113, 115*
		kusnezoline (no name)	*366*

TABLE X XIII (*continued*)

24)	*A. liangshanicum* W. Z. Wang	12-epi-lucidusculine	*315*
		liangshanine	*315*
		liangshanone	*315*
25)	*A. lucidusculum* Nakai	lucidusculine	*315*
26)	*A. leucostomum* Worosch	11-acetyllepenine	*120*
		acsinatine	*277, 278*
27)	*A. magimai*	isohypognavine	*217*
28)	*A. miyabei* Nakai	miyaconitine	*164*
		miyaconitinone	*73,164*
29)	*A. monticola* Stein	norsongorine	*385*
		songoramine	*332*
		songorine	*343, 385*
		songorine *N*-oxide	*357*
30)	*A. napellus L*	15-acetyl-13-dehydrocardio-pe tamine	*385*
		cardiopetamine	*385*
		12-epi-acetyldehydronapelline	*331*
		12-epi-19-dehydronapelline	*331*
		napelline	*321*
		songoramine	*261*
31)	*A. nasutum* Fisch et Reichb	pseudokobusine	*142*
		septatisine	*173*
		trabzonine	*142*
32)	*A. orientale Mill*	acorientine	*262*
		orgetine	*285*
		orientinine	*259*
33)	*A. palmatum* Don	15-deacetylvakhognavine	*215*
		palmadine	*215*
		palmasine	*215*
		vakhmadine	*148*
		vakhmatine	*148*
		vakognavine	*215, 289~292*
34)	*A. paniculatum* Lam	panicudine	*274*
		paniculadine	*275*
		paniculamine	*139*
		paniculatine	*244, 245*
		panicutine	*149*
35)	*A. pendulum* Busch	12-epiacetyldehydro-luciduscu line	*350*
36)	*A. pseudohuiliense* Chang et Wang	lepedine	*107*
		lepenine	*107*
		lepetine	*107*
37)	*A. pukeense*	pukeensine	*377*

TABLE XXIII (*continued*)

38)	*A. racemulosum* var. *pengzhouense* W. J. Zhang et G. H. Chen	kusnezoline	*367*
		racemulodine	*146*
		racemulosine	*371*
39)	*A. rotundifolium* Kar. et Kir	atisine chloride	*77, 102*
		isoatisine	*59, 60, 78*
40)	*A. sachalinense*	kobusine	*199*
41)	*A. sanyoense* Nakai	deacetylhanamisine	*216*
		hypognavine	*243, 239*
		hypognavinol	*238~243*
		ignavine	*249*
		nominine	*192, 191*
		sanyonamine	*197*
42)	*A. sanyoense* var. *onense* Nakai	1-O-acetylhypognavine	*216*
		deacetylhanamisine	*216*
		1, 15-di-O-acetylhypognavine	*216*
		hanamisine	*215*
43)	*A. septentrionale* Koelle	2-acetylseptontriosine	*283*
		septatisine	*171*
		septenine	*281*
		septentriosine	*282*
44)	*A. soongaricum* Stapf	12-acetylnapelline	*332*
		12-acetylnapelline *N*-oxide	*356*
		15-acetylsongoramine	*352*
		15-acetylsongorine	*345*
		napelline	*386*
		napelline *N*-oxide	*387*
		norsongorine	*341*
		songoramine	*341*
		songorine	*341*
45)	*A. subcuneatum* Nakai	gomandonine	*132*
		torokonine	*132*
46)	*A. talassicum* M. Pop	12-acetyldehydrolucidusculine	*134*
		actaline	*369*
		N-deethyldehydrolucidusculine	*334*
		11-dehydrokobusine	*192*
		dehydrolucidusculine	*334*
		kobusine	*198, 200*
		talassamine	*184*
		talassimidine	*187*
		talatizine	*397*
		talassimine	*184*
47)	*A. tanguticum* (Marrin Stapf)	tangirine	*378*

TABLE XXIII (*continued*)

	W. T. Wang		
48)	*A. tassiromontanum*	ignavine	*252*
		tangutisine	*227*
		lepenine	*388*
49)	*A. turczanmowii* Worosch	turpelline	*340*
50)	*A. vilmorrianum* Kom	vilmoridine	*188*
		vilmorianone	*163*
51)	*A. vilmorriaum* var. *altifidum*	denudatine	*140*
		vilmorianine	*140*
		napelline	*380*
52)	*A. volubile* Pall. ex Koelle	songorine	*380*
53)	*A. yesoense*	lucidusculine	*328*
		pseudokobusine	*198, 199*
54)	*A. yesoense* var. *macroyesoense* (Nakai) Tamura	12-acetyllucidusculine	*134*
		15-benzoylpseudokobusine	*134, 271*
		dehydronapelline	*134, 142*
		zeraconine	*191*
		zeraconine *N*-oxide	*288*
55)	*A. zeravschanicum* Steinb	zeravshanisine	*237*
		atidine	*389*
		atisine chloride	*78*
		isoatisine	*78*
		nominine	*78*
		tadzhaconine	*390*
		zeraconine	*78, 191*
		zeraconine *N*-oxide	*191*
		zeravschanine	*238*
B.	*Delphinium* spp.		
1)	*D. ajacis* L	ajabicine	*370*
		ajaconine	*81*
2)	*D. albiflorum DC*	dehydroheterophylloidine	*152*
		hetidine	*66, 156*
3)	*D. andersonii* Gray	andersobine	*279*
4)	*D. barbeyi* Huth	barbaline	*295*
		barbisine	*293*
5)	*D. brunonianum* Royle	brunonine	*99*
6)	*D. Cardinale* Hook	hetisine	*208*
		hetisinone	*186*
7)	*D. cardiopetalum* DC	11-acetylcardionine	*272*
		15-acetylcardiopetamine	*260*
		cardiodine	*254*
		cardionidine	*187*

TABLE XXIII (*continued*)

		cardionine	*272*
		cardiopetamine	*260*
		cardiopidine	*254*
		cardiopimine	*254*
		cardiopine	*254*
8)	*D. carduchorum* Chowdhuri ex. Davis	carduchorum	*147*
		delcarduchol	*147*
9)	*D. consolida*	ajaconine	*81*
10)	*D. corolinianum*	ajaconine	*83*
11)	*D. corumbosum* Regel	cordizine	*123*
		corymdizine	*136*
		corymdizinine	*135*
		dictysine	*124*
	D. corymbosum auct. (*D. turketanicum*)	cordizine	*49*
		N-ethyl-des-*N*-methyl dictyzine	*394*
		corumdizine	*49*
		corumdizinine	*49*
		dictysine	*391*
12)	*D. cossonianum* Bath	cossonidine	*195*
		cossonine	*253*
13)	*D. davisii* Munz	18-benzoyldavisinol	*196*
		davisine	*196*
		davisinol	*196*
		kobusine	*196*
14)	*D. delevayi Franch* var. *pogonanthum* (H-M) Wang	ajaconine	*80*
		hetisine	*80*
		hetisinone	*80*
15)	*D. denudatum* Wall	delnudine	*363*
		denudatine	*108*
		hetisinone	*213*
		panicutine	*151*
		vilmorrianone	*151*
16)	*D. dictyocarpum* DC	dehydrodictysine	*151*
		dictysine	*125, 392*
17)	*D. elatum L*	ajaconine	*79*
		delatisine	*264*
18)	*D. fissum* subsp. *anatolicum*	delfissinol	*223*
		fissumine	*223*
19)	*D. geyeri*	geyeridine	*273*
		geyerine	*273*
		geyerinine	*273*

TABLE X XIII (*continued*)

20)	*D. grandiforum* L	acetyldelgrandine	*294*
		delgrandine	*294*
		delgramine	*284*
21)	*D. macroceantrum* Oliv	macrocentrine	*127*
22)	*D. nuttalianum* Pritz	13-acetylhetisine	*202, 203*
		delnuttaline	*224, 276*
		delnuttidine	*224*
		delnuttine	*224*
23)	*D. occidentale* Swats	delbidine	*212*
24)	*D. souliei* Franch	souline F	*219*
25)	*D. staphisagria* L	staphidine	*373*
		staphigine	*374, 376*
		staphimine	*374, 376*
		staphinine	*374, 376*
		staphirine	*374, 376*
		staphisagnine	*372*
		staphisagrine	*372*
		staphisine	*375, 373*
26)	*D. tamarae*	norsongoramine	*353*
27)	*D. tatsiense* Franch	tatsirine	*129*
28)	*D. ternatum*	ternatine	*395*
29)	*D. tongolense* Franch	hetisine	*193*
		nominine	*193*
		tongolinine	*183*
30)	*D. uncinatum*	uncinatine	*72*
31)	*D. venubosum*	venudelphine	*226*
		venulol	*259*
		venuluson	*259*
C. *Consolida* spp.			
1)	*C. amibigua* L. P. W. Ball et. V. H. Heywood	13-*O*-acetylvakhamatine	*280*
		ajaconine	*81*
		dihydroajaconine	*62*
2)	*C. chellespontica*	chellespontine	*64*
3)	*C. glandulosa* (Boiss et Huet) Bornm	13-O-acetyl-9-deoxyglanduline	*256*
		14-O-acetyl-9-deoxyglanduline	*256*
		13-O-acetylglanduline	*256*
		11, 13-diacetyl-9-deoxy-glandulin e	*256*
		glanduline	*256*
D. *Thalictrum* spp.			
1)	*T. sessile* Hayata	spirasine III	*92*

TABLE XXIII (*continued*)

	thalicsiline	*91*
	thalicsessine	*92, 182*
II. Rosaceae		
Spiraea spp.		
1) *S. fritschiana* var. *parvifolia*	spirafine II	*145*
	spirafine III	*145*
2) *S. japonica* L	spiradine A	*265*
	spiradine B	*178, 179*
	spiradine C	*265*
	spiradine D	*175*
	spiradine F	*89*
	spiradine G	*89*
	spiramine X	*85*
	spiramine Y	*85*
	spirasine I	*176*
	spirasine II	*176*
	spirasine III	*178*
	spirasine III	*92, 178*
	spirasine V	*177*
	spirasine VI	*177*
	spirasine VII	*176*
	spirasine VIII	*176*
	spirasine XII	*268*
	spirasine XIII	*268*
	spirasine XIV	*268*
	spirasine XV	*268*
	spiredine	*178, 179*
	spireine	*185*
	spireine*	*180, 181*
3) *S. japonica* var. *acuminata* Franch	spiramine A	*86~88*
	spiramine B	*86~88*
	spiramine C	*86~88*
	spiramine D	*86~88*
	spiramine E	*68, 69*
	spiramine F	*68, 69*
	spiramine G	*68, 69*
	spiramine H	*70*
	spiramine I	*70*
	spiramine N	*98*
	spiramine O	*70*
	spiramine S	*96, 97*

TABLE XXIII (*continued*)

	spiramine V	*96, 97*
4) *S. japonica* var. *acuta* Yu	spiramine J	*101*
	spiramide	*420*
	spiramine K	*101*
	spiramine L	*101*
	spiramine M	*101*
	spiramine P	*94*
	spiramine Q	*90*
	spiramine T	*90*
	spiramine W	*95*
	spiramine Z	*85*
	spiratine A	*419*
	spiratine B	*419*
5) *S. japonica* var. *fortunei* (Planchon) Rohd	spirasine III	*88*
	spirasine IV	*190*
	spirasine IX	*190*
	spirasine X	*257*
	spirasine XI	*190*
6) *S. japonica* var. *glabra* (Regel) koidz	spiradine D	*88*
	spiradine F	*88*
	spiramine H	*88*
	spirasine III	*88*
	spiratine A	*430*
	spiratine B	*430*
7) *S. japonica* var. *incisa* Yu	spiramine Q	*93*
	spiramine R	*93*
8) *S. japonica* var. *ovalifolia* Franch	deacetylspiramine F	*75*
	deacetylspiramine S	*75*
	19-*O*-deethylspiramine N	*75*
	spiramide	*54*
	spiramidine A (B)	*75*
III. Garryaceae		
Garry spp.		
1) *G. laurifolia*	cuauchichicine	*313*
	garryfoline	*313*
	isocuauchichicine	*302, 307, 308*
	isogarryfoline	*313, 314*
2) *G. ovata* var. *lindheimeri* Tor	cuauchichicine	*306*
	garryfoline	*311*
	lindheimerine	*313*
	ovatine	*305*
3) *G. veatchii*	garryine	*299~304*
	veatchine	*299~304*

TABLE X X III (*continued*)

IV. Escalloniaceae		
Anopterus spp.		
1) *A. glandulosus*	anopterine	*301, 359*
	hydroxyanopterine	*358, 360*
2) *A. macleayanus*	anopterimine	*358*
	anopterine *N*-oxide	*358*
	dihydroxyanopterine	*358*
	hydroxyanopterine	*358, 360*
V. Polygonaceae		
Rumex spp.		
1) *R. pictus*	acorientine	*262*
	orientinine	*263*
	panicudine	*274*

TABLE X X IV

C_{20}-DITERPENOID ALKALOIDS AND THEIR CODE NUMBER INDEX

Alkaloid	code number
11-acetylcardionine	AVII2b-13
15-acetylcardiopetamine	AVII1a-61
15-acetyl-13-dehydrocardiopetamine	AVII1a-62
13-*O*-acetyl-9-deoxyglanduline	AVII1a-46
14-*O*-acetyl-9-deoxyglanduline	AVII1a-49
acetyldelgrandine	A V 4-5
12-acetyldehydrolucidusculine	B II 2a-5
11-acetyl-1, 19-epoxydenudatine	A II 3a-2
13-acetylhetisine	AVII1a-8
13-acetyl-14-hydroxy-2-propinylhetisine	AVII1a-45
1-*O*-acetylhypognavine	AVII1a-34
13-*O*-acetylglanduline	AVII1a-48
11-acetyllepenine	A II 1-7
12-acetyllusidusculine	B II 1-8
12-acetylnapelline	B II 1-6
12-acetylnapelline *N*-oxide	B II 3-3
2-acetylseptentrisosine	AVII2c-7
15-acetylsongoramine	B II 2a-10
15-acetylsongorine	B II 1-12
13-*O*-acetylvakhnatine	AVII2c-4

TABLE XXIV (*continued*)

acofine	BII 1-18
acoridine	AVII1a-25
acorientine	AVII2b-11
acsinatine	AVII2c-1
actaline	CIII1-1
ajabicine	CIII1-2
ajaconine	AI 2b-1
albovionitine	AVI1-1
andersobine	AVII2c-2
anopterimine	BIII2-1
anopterimine *N*-oxide	BIII3-1
anopterine	BIII1-1
atidine	AI 1-5
atisenol	AI '-1
atisine	AI 2a-1
atisine chloride	AI 3-2
azitine	AI 3-1
barbaline	AVIII1-6
barbisine	AVIII1-3
beiwusine A	AI 1-9
beiwusine B	AI 1-10
18-benzoyldavisinol	AVII1a-52
15-benzoylpseudokobusine	AVII2b-8
brunonine	AI 2f-4
bullatine G	BII 1-11
cardiodine	AVII1a-44
cardionidine	AV 1-1
cardionine	AVII2b-12
cardiopetamine	AVII1a-60
cardiopidine	AVII1a-41
cardiopine	AVII1a-43
cardiopimine	AVII1a-40
cardiopinine	A1a-42
carduchoron	AIV2b-2
chellespontine	AI 1-3
chuanfunine	BII 1-17
contorine	AIV1a-15

TABLE XXIV (*continued*)

contorsine	AIV1a-16
contortine	AIV1a-17
cordizine	AII1-10
corumdizine	AII1-20
corumdizinine	AII1-19
coryphidine	AI4-1
coryphine	AIV2a-2
cossonidine	AVII1a-4
cossonine	AVII1a-39
crassicauline B	AVII1a-15
cuauchichicine	BI1a-4
davisine	AVII1a-4
davisinol	AVII1a-51
deacetylhanamisine	AVII1a-20
deacetylheterophylloidine	AIV1a-11
deacetylspiramine F	AI2b-2
15-deacetylvakognavine	AVIII1-1
deacetylspiramine S	AI2d-3
N-deethyldehydroluciduscuiline	BII2a-8
19-*O*-deethyl spiramine N	AI2f-1
dehydrodictysine	AII1-15
2-dehydrohetisine	AVII1a-57
11-dehydrokobusine	AVII1a-55
dehydroluciculine	BII2a-1
dehydrolucidusiculine	BII2a-3
dehydronapelline	BII2a-1
dehydrosongorine	BII1-15
delatine	AVII1a-7
delatisine	AVII2a-1
delbidine	AVII2b-15
delcarduchol	AIII1a-8
delfissinol	AVII1a-18
delgrandine	AVII4-4
delgramine	AVII2c-8
delnudine	CI1-1
delnuttaline	AVII2b-24
delnuttidine	AVII2b-23
delnuttine	AVII1a-19
denudatine	AII1-2

TABLE XXIV (*continued*)

11, 13-*O*-diacetyl-9-deoxyglanduline	AVII1a-50
1, 15-di-*O*-acetylhypognavine	AVII1a-35
dictisine	A II 1-11
dictyzine	A II 1-11
dihydroajaconine	A I 1-2
dihydroatisine	A I 1-1
dihydrodictysine	A II 1-13
dihydroxyanopterine	BIII1-2
12-epi-acetyldehydrolucidusculine	B II 2a-6
12-epi-acetyldehydronapelline	B II 2a-4
12-epi-19-dehydronapelline	B II 2a-2
3-epi-ignavinol	AVII1a-37
12-epi-lucidusculine	B II 1-2
1-epi-napelline	B II 1-5
12-epi-napelline	B II 1-4
12-epi-napelline *N*-oxide	B II 3-2
episcopalidine	AIV 1a-14
eraconine	AVII1a-64
eraconine *N*-oxide	AVII3-3
N-ethyl-des-*N*-methyldictyzine	A II 1-12
finetianine	B II 1-14
fissumine	AVII1a-59
flavadine	B II 3-4
flavamine	B II 3-1
garryfoline	B I 1a-2
garryine	B I 1a-5
geyeridine	AVII2b-16
geyerinine	AVII2b-14
geyerine	AVII2b-17
glanduline	AVII1a-47
gomandonine	A II 1-16
gomandonine-13-*O*-acetate	A II 1-17
guan-fu base A	AVII1a-26
guan-fu base F	AVII1a-28
guan-fu base G	AVII1a-30
guan-fu base K	C II 1-2
guan-fu base O	AVII1a-27

TABLE XXIV (*continued*)

guan-fu base Y	AVII1a-23
guan-fu base Z	AVII1a-24
guan-fu base F *N*-oxide	AVII3-2
guan-fu base Z *N*-oxide	AVII3-1
gymnandine	A II 1-1
hanamisine	AVII1a-11
hanamiyama base	AVII1a-20
heterophylloidine	AIV1a-12
hetidine	AIV1a-13
hetisine	AVII1a-7
hetisinone	AVII1a-57
hydroxyanopterine	BIII1-3
11α-hydroxylepenine	A II 1-5
hypognavine	AVII1a-32
hypognavinol	AVII1a-31
ignavine	AVII1a-38
isoatisine	A I 2a-2
isocaunchichicine	B I 1a-7
isogarryine	B I 1a-6
isohypognavine	AVII1a-12
jynosine	A II 1-3
karakomine	B II 1-16
kirinine A	A II 1-8
kirinine B	A II 3a-1
kirinine C	A II 1-6
kobusine	AVII1a-6
kusnezoline	C II 1-1
lassiocarpine	A II 1-14
lepedine	A II 1-9
lepenine	A II 1-4
lepenine *N*-oxide	A II 2-1
lepetine	A II 1-7
liangshanine	B II 1-1
liangshanone	B II 1-13
lindheimerine	B I 1b-1
luciculine	B II 1-3

TABLE XXIV (*continued*)

lucidusculine	BII 1-7
macroceatrine	AII 1-13
miyaconitine	AIV 1a-20
miyaconitinone	AIV 1a-22
napelline	BII 1-3
napelline *N*-oxide	BII 3-1
napellonine	BII 1-11
nominine	AVII 1a-2
no name	CII 1-1
norsongoramine	BII 2a-11
norsongorine	BII 1-10
no name	CII 1-1
orgetine	AVII 2d-1
orientinine	AVII 1a-63
ovatine	BI 1a-3
palmadine	AVII 1a-10
palmasine	AVII 1a-9
panicudine	AVII 2b-19
paniculadine	AVII 2b-22
paniculamine	AII 2-2
paniculatine	AVII 1a-33
panicutine	AIV 1a-10
pseudokobusine	AVII 2b-6
pukeensine	DIII 1-1
racemulodine	AIV 1a-7
racemulosine	CIV 1-1
ryosenamine	AVII 1a-17
ryosenaminol	AVII 1a-16
sanyonamine	AVII 1a-5
sczukidine	AIV 1a-18
sczukinine	AIV 1a-19
sczukitine	AIV 1a-4
septatisine	AIV 2a-1
septedinine	AIV 2a-1

TABLE XXIV (*continued*)

septenine	AVII2c-5
septentriosine	AVII2c-6
shimaburo base I	B II 1-11
songoramine	B II 2a-9
songorine	B II 1-11
songorine *N*-oxide	B II 3-5
souline F	AVII1a-14
spiradine A	AVII2b-18
spiradine B	AVII2b-1
spiradine C	AVII2b-3
spiradine D	AIV2a-3
spiradine F	A I 2c-4
spiradine G	A I 2c-3
spirafine II	AIV1a-6
spirafine III	AIV1a-5
spiramacetal*	A I '-6
spiramadol*	A I '-8
spiramide	A I 2d-4
spiramidines A (B)	A I 2a-3
spiramilactone*	A I '-2
spiramilactone B	A I '-7
spiramilactone C*	A I '-3
spiramilactone D*	A I '-4
spiraminol*	A I '-5
spiramine A	A I 2c-2
spiramine B	A I 2c-6
spiramine C	A I 2c-1
spiramine D	A I 2c-5
spiramine E	A I 2b-5
spiramine F	A I 2b-3
spiramine G	A I 1-6
spiramine H	A I 1-7
spiramine I	A I 1-8
spiramine J	A I 2f-7
spiramine K	A I 2f-10
spiramine L	A I 2f-8
spiramine M	A I 2f-9
spiramine N	A I 2f-3
spiramine O	A I 2f-5
spiramine P	A I 2c-7

TABLE XXIV (*continued*)

spiramine Q	AI2c-10
spiramine R	AI2e-1
spiramine S	AI2d-1
spiramine T	AI2c-11
spiramine U	AI2c-8
spiramine V	AI2d-2
spiramine W	AI2c-12
spiramine X	AI2e-2
spiramine Y	AI2b-4
spiramine Z	AI2f-6
spirasine I	AIV2a-5
spirasine II	AIV2a-4
spirasine III	AIV2a-12
spirasine IV	AVII1a-56
spirasine V	AIV2a-6
spirasine VI	AIV2a-7
spirasine VII	AIV2a-8
spirasine VIII	AIV2a-9
spirasine IX	AVII1a-53
spirasine X	AVII1a-54
spirasine XI	AVII1a-1
spirasine XII	AVII2b-20
spirasine XIII	AVII2b-21
spirasine XIV	AVII2b-4
spirasine XV	AVII2b-5
spiratine A	AI1-4
spiratine B	AI2f-2
spiredine	AIV2a-10
spireine (structure 1)	AIII-1
spireine (structure 2)	AIII-2
spireine*	AIV2a-11
staphidine	DII1-1
staphigine	DII1-4
staphimine	DII1-5
staphinine	DII1-6
staphirine	DII1-3
staphisagnine	DI1-2
staphisagrine	DI1-1
staphisine	DII1-2
subdesculine	BII2a-7

TABLE XXIV (*continued*)

tadzhaconine	AVII1a-36
talassamine	AIII3-2
talassimidine	AIV3-4
talassimine	AIV3-3
talatizine	AVII2c-9
tangirine	DIV1-1
tangutisine	AVII1a-22
tatsirine	AVII2b-10
ternatine	AVII2c-10
thalicsessine	AIV2b-1
thalicsiline	A I 2c-9
tongolinine	AIV3-1
torokonine	AVII1a-13
trabzonine	AIV1a-1
turpelline	B II 1-9
uncinatine	A I 1-11
vakhmadine	AIV1a-9
vakhmatine	AVII2c-3
vakognavine	AVIII1-2
veatchine	B I 1a-1
venudelphine	AVII1a-21
venulusine	AVII1a-58
venuluson	AVII1a-58
venulol	AVII2b-2
15-veratroylpseudokobusine	AIV2b-9
vilmoridine	A V 1-2
vilmorinianine	A II 3a-3
vilmorrianone	AIV1a-21
yesodine	AVII2b-7
yesoline	AIV1a-3
yesonine	AIV1a-2
yesoxine	A II 1-18
zeraconine	AVII1a-3
zeravshanisine	AVII1a-29

* atisane type diterpenes

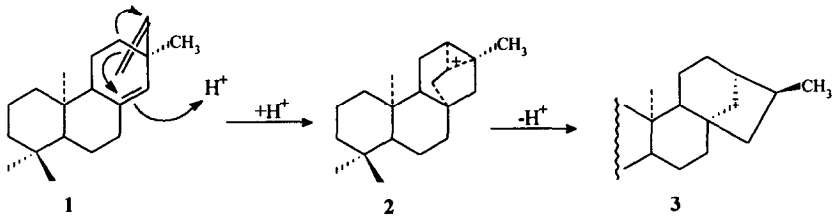
III. Biosynthesis and Biogenesis

Only a few papers (*399~401*) on the biosynthesis of the C_{20}-diterpenoid alkaloids have been reported. Edwards (*10*) reviewed early investigations in this field. Two excellent reviews were made by Benn (*36*) and by some Tashkent scientists (*45*). At the present time, the biogenetic hypotheses for these alkaloids are based on some biochemical reactions, chemical transformations, and the massive phytochemical data.

A. ATISINE-TYPE AND VEATCHINE-TYPE ALKALOIDS

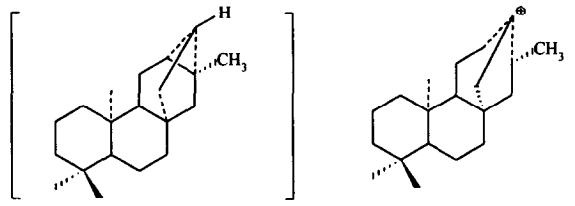
1. Formation of Skeleta

Pelletier *et al.* (*4*) pointed out that the C_{20}-diterpenoid alkaloids were derived biogenetically from kauranes. Wenkert (*402*) hypothesized that compound **1** was a precursor of the atisinoids, which formed **2**, a common precursor for the skeleton of

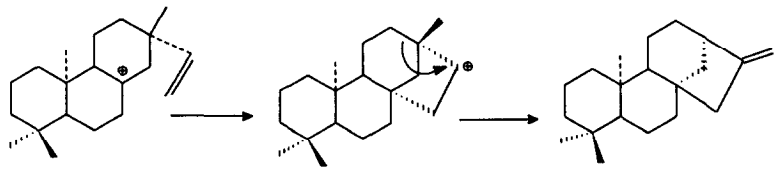


1 **2** **3**

Scheme 1



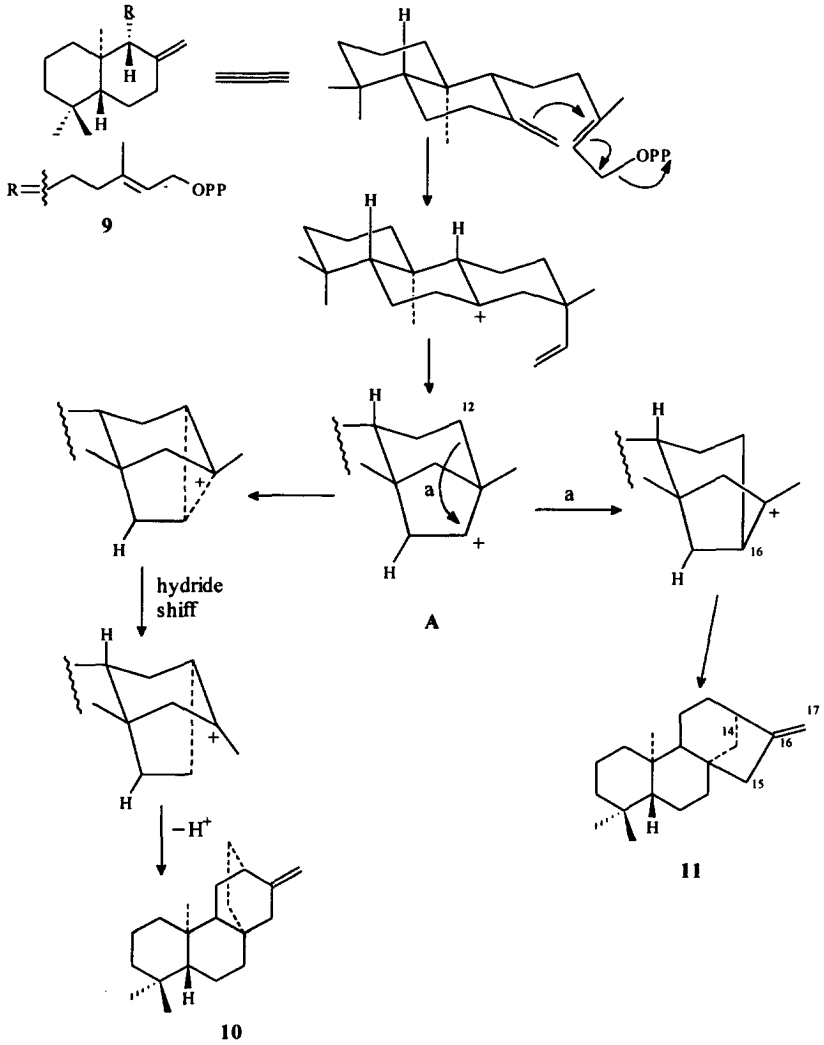
4 **5**



6 **7** **8**

Scheme 2

both the atisinoids and veatchinoids (Scheme 1). Another way to form the atisine alkaloids is through a number of stages *via* the nonclassical cyclic cation **4** (*402*). Walley (*403*) considered that cation **2** gave **5**, a precursor of the atisinoids, *via* a 1, 3-hydride shift. Birch (*404*) suggested that the kaurane skeleton was formed first from the intermediate **6**, and then the atisane skeleton by rearrangement (Scheme 2).



Scheme 3

Modern biosynthetic studies showed that GGPP was cycliced to give *ent*-CPP (*ent*-copalyl diphosphate) (**9**), leading to the naturally-occurring tetracyclic diterpenes *ent*-atisir-16-ene (**10**) (atisane-type) and *ent*-kaur-16-ene (**11**) (kaurane-type) by further cyclization (Scheme 3) (*405*). This fact indicated that the atisane and kaurane skeletons were derived from the bicyclic diterpene GGPP, and that the key intermediate **A** was a common precursor for the atisine- and veatchine-type alkaloids, not by the sequential conversion as speculated by Birch (*404*).

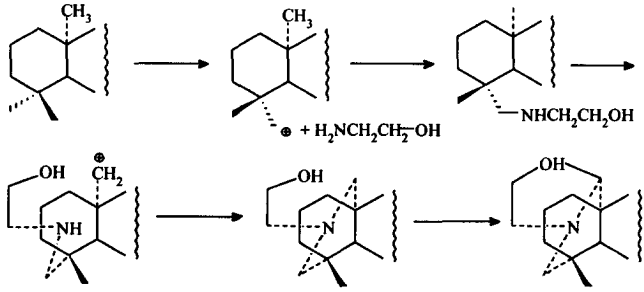
2. Source of the Nitrogen Atom

According to Pelletier (*4*), the nitrogen atom in the diterpenoid alkaloids is biogenetically derived from methylamine, ethylamine, and β-aminoethanol, which is formed the corresponding *N*-methyl, *N*-ethyl, and *N*-ethanol groups. But Benn (*36*) has pointed out that the *N*-methyl and *N*-ethyl groups possibly came from *S*-adenosylmethionine and the reactions (addition, elimination, and reduction) of acetaldehyde (C_2 unit) with the secondary amines or alanine (*401*), respectively. Similarly, the *N*-ethanol group was considered to come from serine (*36*). Chinese scientists Hao *et al.* (*406, 407*) deduced that the *N*-ethanol group was derived from the β-aminoethanol widely distributed in plants as convincingly supported by his successful biomimetic synthesis.

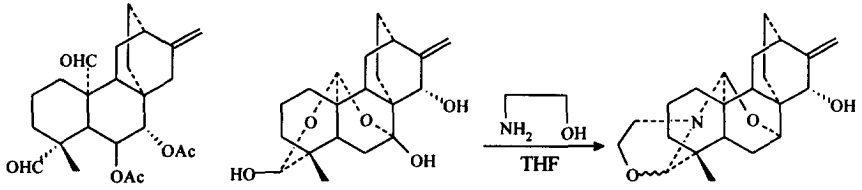
3. Introduction Points of the Nitrogen Atom

The introduction point of the nitrogen atom during the biosynthesis of the C_{20}-diterpenoid alkaloids has not been clarified so far. Wenkert (*402*) pointed out that this introduction might occur just prior to, or right after, the construction of the skeleta. Walley (*403*) suggested a process for the introduction of the nitrogen atom as depicted in Scheme 4. In recent years, Hao and his colleagues have isolated a large number of atisines, hetidines, and hetisines (Tables III, VII, IX), including 7 atisane-type diterpenes (Table XII) from several *Spiraea* plants. Comparison of

these alkaloids suggested that the 19,20-aldehyde-containing spiramidol (**12**) or spiraminol (**13**), isolated from *Spiraea japonica* var. *acuta* and *Spiraea japonica* var. *acuminata,* respectively, was a biogenetic precursor for the *Spiraea* alkaloids, since the synthesis of spiramines C (**14**) and D (**15**), two atisine-type alkaloids from *Spiraea japonica* var. *acuminata*, starting from **13** and ethanolamine, could be accomplished *via* a so-called double Mannich condensation (Scheme 5) (*406, 407*).



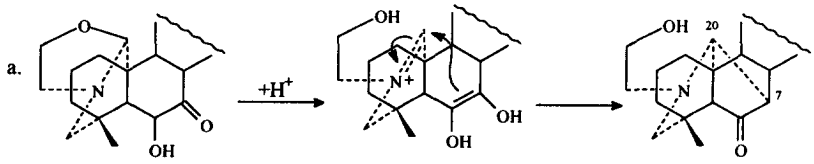
Scheme 4

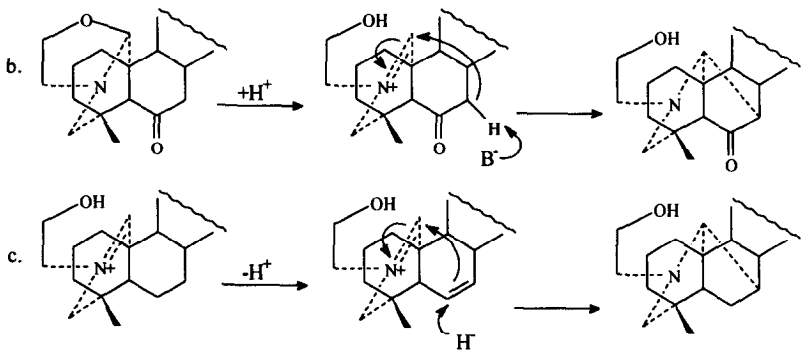


Scheme 5

B. DENUDATINE-TYPE AND NAPELLINE-TYPE ALKALOIDS

These alkaloids were considered biogenetically to arise from the atisine and veatchine alkaloids, respectively. Formation of the C-20-C-7 bond may proceed by Mannich condensation (Scheme 6, a) (*408*), or Schiff's base (Scheme 6, b) (*409*), or by Prins cyclization with the participation of a hydride (Scheme 6, c) (*10*).

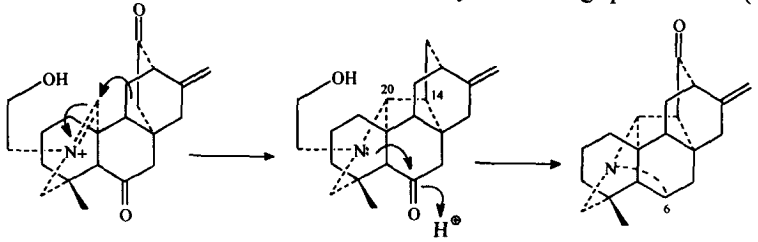




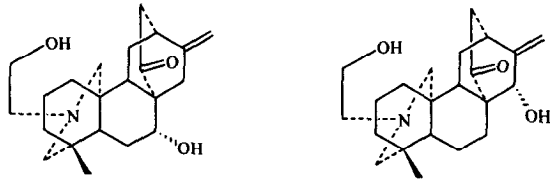
Scheme 6

C. HETIDINE-TYPE AND HETISINE-TYPE ALKALOIDS

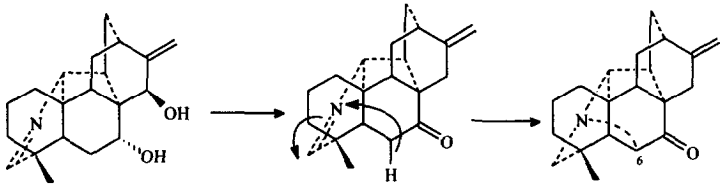
These two alkaloids may be derived biogenetically from the atisine-type alkaloids (*410*), as exemplified by miyaconitine and miyaconitinone, and proposed by Japanese scientists (*164*). The process of the formation of the C-14-C-20 and *N*-C-6 bonds is shown in Scheme 7. The 14-carbonyl-containing spiramines G (**16**)



Scheme 7



16 **17**



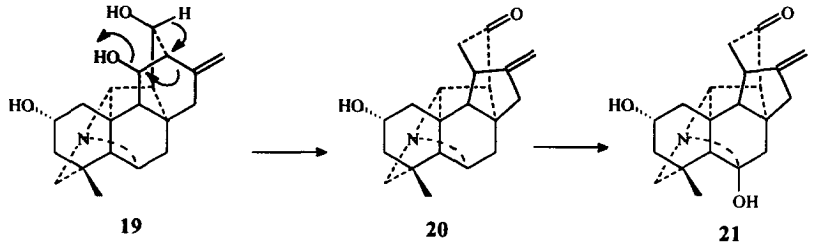
18

Scheme 8

(*68, 69*) and H (**17**) (*70*), two atisine-type alkaloids from *Spiraea japonica* var. *acuminata*, were assumed by Hao *et al.* (*406, 407*) to be precursors for the formation of the C-20-C-14 bonds in the hetidine-type alkaloids. Similarly, talassamine (**18**) may be an intermediate in the formation of the *N*-C-6 bonds in the hetisine-type alkaloids (Scheme 8) (*184*).

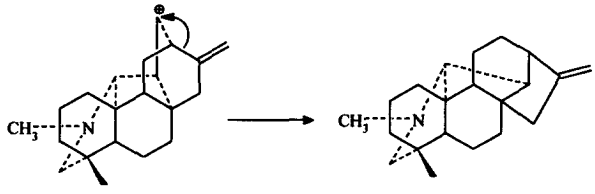
D. DELNUDINE-TYPE AND ANOPTERINE-TYPE ALKALOIDS

Delnudine (**21**), from *Delphinium denudatum* (*363, 364*), is the only member of the delnudine-type alkaloids. Its biosynthesis may be carried out *via* a rearrangement of hetisine (Scheme 9) (*364*). The anopterine-type alkaloids **23** may be derived from the hetisine-type intermediate **22** instead of the veatchine-type alkaloids (Scheme 10) (*358*).



19 **20** **21**

Scheme 9



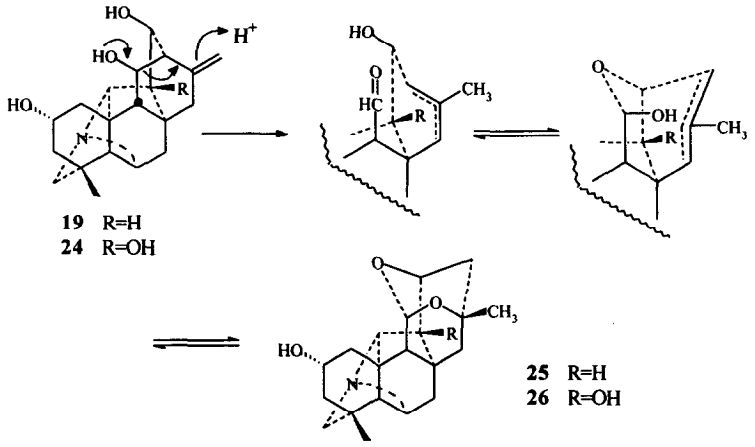
22 **23**

Scheme 10

E. KUSNEZOLINE-TYPE, ACTALINE-TYPE AND RACEMULOSINE-TYPE ALKALOIDS

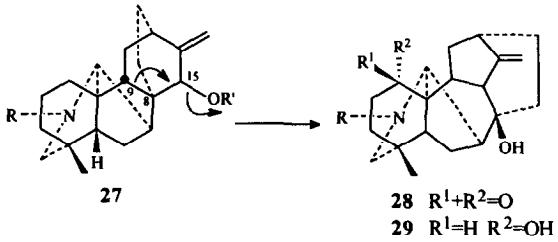
Kusnezoline (**25**) (*365~367*) and guan-fu base K (**26**) (*368*) are the only reported members of kusnezoline-type alkaloids. The former was prepared first by Pelletier (*365*) from the rearangement of hetisine (**19**). Kusnezoline was isolated

later by us (*366, 367*) from *A. kusnezollum* and *A. racemulosum* var. *pengzhounese,* and guan-fu base K was isolated by Liu (*368*) from *A. coreanum.* They may be derived from the rearrangement of the corresponding hetisine (**19**) and guan-fu base A (**24**) (Scheme 11) (*365*).



Scheme 11

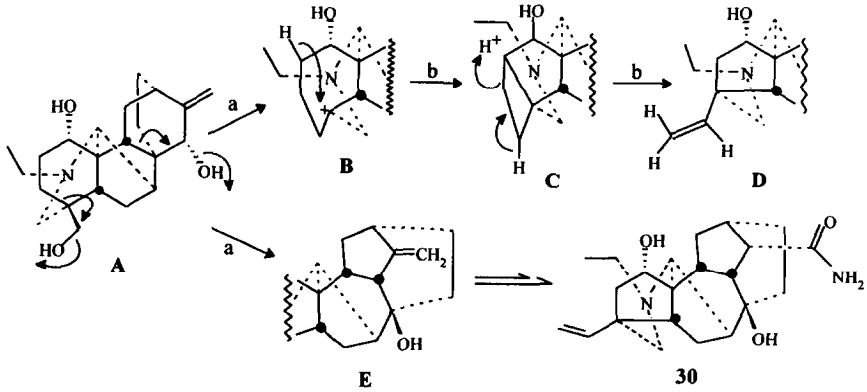
Actaline (**28**) and ajabicine (**29**) are the only known members of the actaline-type alkaloids, which may be produced biogenetically by a Wagner-Meerwein rearrangement of the denudatine-type alkaloid **27** or its derivatives (Scheme 12). This kind of skeletal transformation lends support to the view that the C_{18}/C_{19}-diterpenoid alkaloids, usually with a typical framework like that of **28** and **29**, are biogenetically derived from the C_{20}-diterpenoid alkaloids.



Scheme 12

Racemulosine (**30**), a novel skeletal C_{20}-diterpenoid alkaloid, recently isolated

by us (*371*) from *A. racemulosum* var. *pengzhounese* grown in Sichuan Province, China, may be formed by an A-nor-rearrangement of the actaline-type, or by an A-nor-B-homo-C-nor-rearrangement of the denudatine-type alkaloids (Scheme 13).

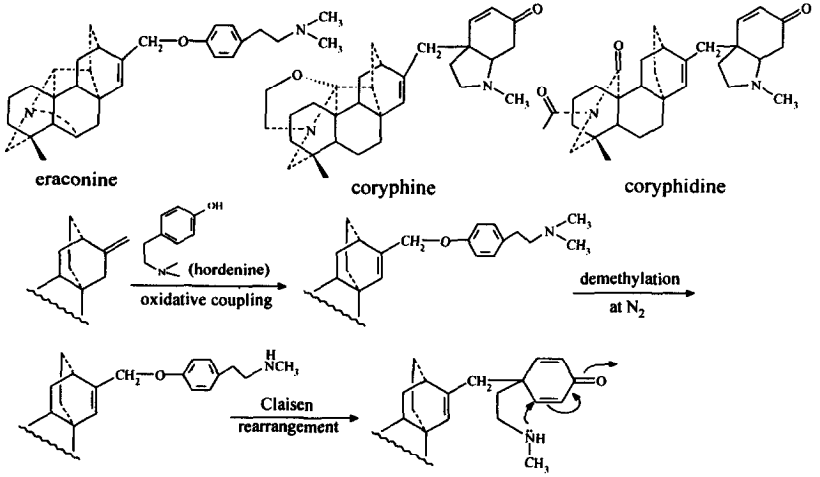


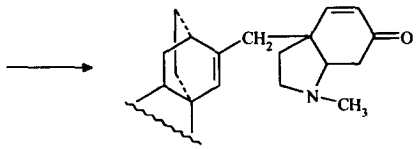
a. Wagner-Meerwein rearrangement; b. ring rupture

Scheme 13

F. ERACONINE, CORYPHINE AND CORYPHIDINE

There is a close relationship among the three alkaloids, the first one from *A. zeravschanicum* (*191*), and the latter two from the same plant, *A. coreanum* (*174, 103*). The formation of the side-chains in their molecules may be seen in Scheme 14 (*174*).

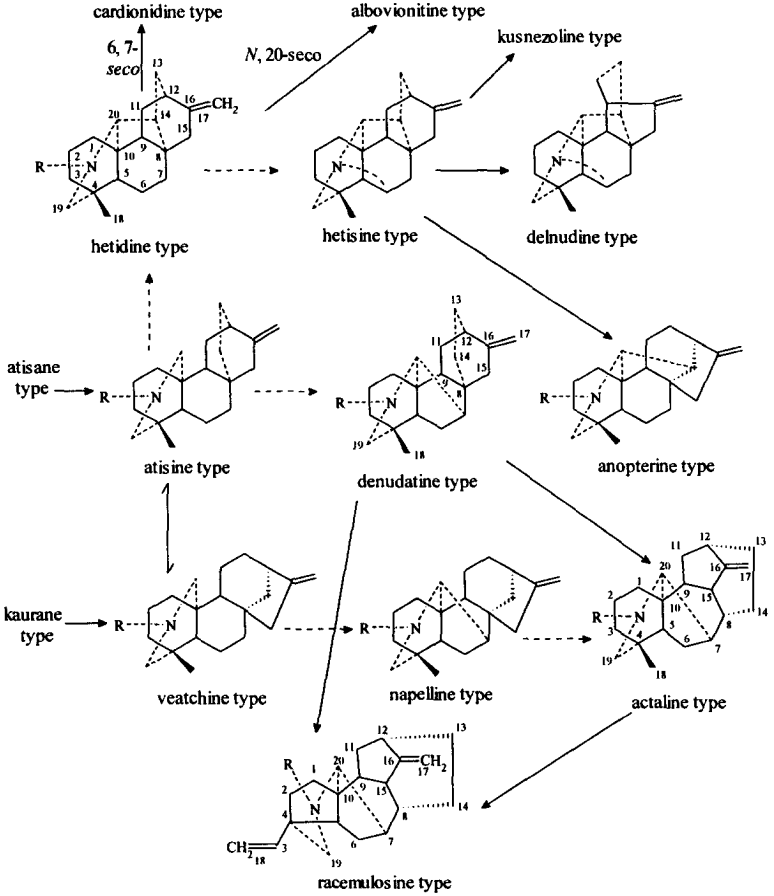




Scheme 14

G. BIOGENETIC RELATIONSHIPS AMONG C_{20}-DITERPENOID ALKALOIDS

In 1976, the Japanese scientist Ichinohe (*411*) pointed out first the biogenetic



Scheme 15. Possible biogenetic relationships among the known, naturally-occurrining, C_{20}-diterpenoid alkaloid

relationship among the diterpenoid alkaloids on the basis of a systematic analysis of the chemical and biochemical data and various hypotheses. Tashkent scientists Sultankhodzhaev and Nishanov (*45*) have proposed a scheme for the biogenesis of the diterpenoid alkaloids. A summation of the biosynthesis and biogenesis of the C_{20}-diterpenoid alkaloids, with some new entries, is presented in Scheme 15.

Ⅳ. Spectroscopy

A. CD SPECTROSCOPY

There are only a few, but very useful reports, for the location of the carbonyl groups or confirming the absolute configurations at C-15 in C_{20}-diterpenoid alkaloids using CD spectroscopy (Table X X V). In 1982, Sakai *et al.* (*192, 197, 222*) studied the CD spectra of some C_{20}-diterpenoid alkaloids having 15- and 11-keto groups. Yu *et al.* (*159*) and Pelletier *et al.* (*150*) reported later the valuable results of the CD spectra of the 6-, 11/13-carbonyl-containing C_{20}-diterpenoid alkaloids.

The features of the CD spectra of these alkaloids are summarized as below.

1. The 11,13-carbonyl-containing C_{20}-Diterpenoid Alkaloids

Because of the presence of a β,γ-unsaturated ketone system, as in spiradine A (**33**) (*159*) and spirasine Ⅳ (**37**) (*159*), the π–π^* transition near 300 nm contributed by the 11- and 13-keto groups in the molecules usually exhibits both positive and negative Cotton effects, respectively, as depicted in Figs. 4 and 5. At this time, the extended octant rule (*412*) generally can be applied.

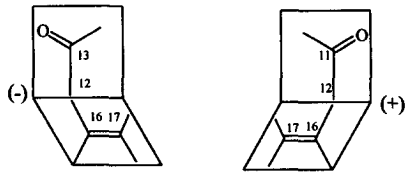


Fig. 4. Correlation between chirality and sign of Cotton effect for chiral β, γ-unsaturated ketones (C-11 and C-13) of C_{20}-diterpenoid alkaloids

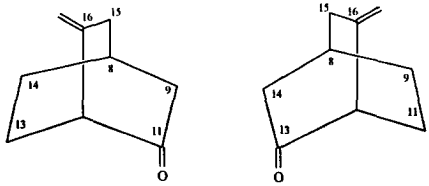


Fig. 5. Enantiotopic relationships beween the C-11 and C-13 ketones in the β, γ-unsaturated ketone systems of C_{20}-diterpenoid alkaloids

2. The 6, 11- and the 6, 13-carbonyl-containing C_{20}-Diterpenoid Alkaloids

In addition to a Cotton effect near 300 nm contributed by the 11- or 13-keto groups, a negative, weak n–π* Cotton effect centered at near 180 nm contributed by the 6-keto group, as in spiredine (**44**) (*52*), may be observed. But, acidification of the alkaloids, such as spiredine (**44**) and episcopalidine (**46**), leads to the disappearance of this Cotton effect due to transannular *N*-C-16 bond formation (*155, 413*).

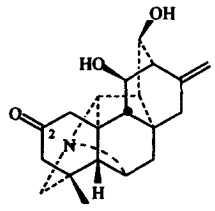
3. The 15-carbonyl –containing C_{20}-Diterpenoid Alkaloids

In fact, there is an *α, β*-unsaturated system in these alkaloids, as in **39** (*197*), which therefore display a strong positive π–π* Cotton effect near 250 nm and a weak positive n–π* Cotton effect near 350 nm. In this case, the octant rule generally cannot be applied, except for predicting the wavelength of the π–π* Cotton band according to Woodward-Fieser's rule (*414~417*).

4. The 15-OBz-containing C_{20}-Diterpenoid Alkaloids

The benzoyl group at C-15 in these alkaloids, as **49** (*32*), is consistent with a

chiroptical method for determining the absolute configuration of allylic secondary alcohol(s) (*414~417*).



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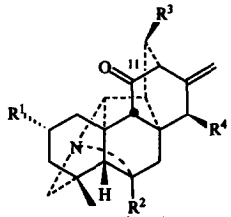
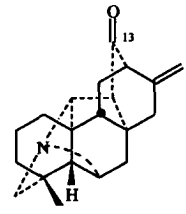
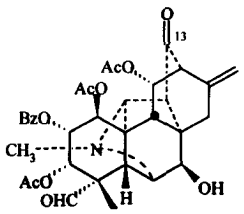


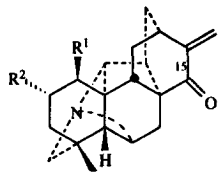
32 R^1=R^2=R^3=H R^4=OH
33 R^1=R^3=R^4=H R^2=OH
34 R^1=R^3=R^4=H R^2=OAc
35 R^1=R^2=R^3=R^4=H
36 R^1=R^3=OH R^2=R^4=H



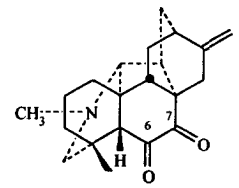
37



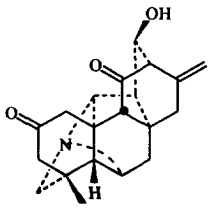
38



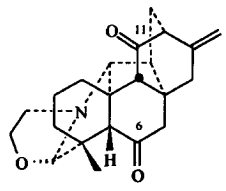
39 R^1=R^2=H
40 R^1=H R^2=OH
41 R^1=βOAc R^2=OBz



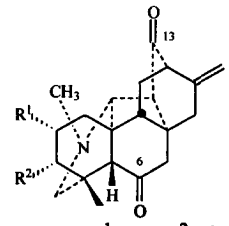
42



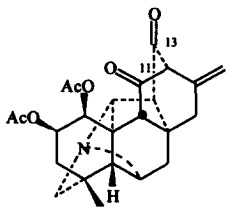
43



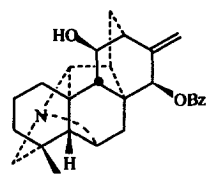
44



45 R^1=OH R^2=H
46 R^1=OAc R^2=OBz
47 R^1=OAc R^2=H



48



49

Table X X V

CD SPECTRA OF C_{20}-DITERPENOID ALKALOIDS

a. 2-keto

2-ketohetisine (**31**) (*150*): CD (MeOH); $[\theta]_{210}$+1863.9, $[\theta]_{220}$-1700.4, $[\theta]_{225}$ -17985 (max), $[\theta]_{255}$-66.4, $[\theta]_{287.5}$-294.3, $[\theta]_{320}$-32.7

b. 11-keto

1) 11-dehydrokobusine (**32**) (*192*): CD (MeOH) nm ($\triangle\varepsilon$): 262 (0), 305 (3.33), 313 (2.64), 335 (0)

2) spiradine A (**33**) (*159*): CD (MeOH) nm ($\triangle\varepsilon$): 270 (0), 305 (4.35), 313 (3.96, sh), 330 (0)

3) spiradine A acetate (**34**) (*150*): see CD curve in ref. [150]

4) spirasine IX (**35**) (*159*): CD (MeOH) nm ($\triangle\varepsilon$): 260 (0), 304 (3.35), 312 (3.13, sh), 337 (0)

5) 11-ketohetisine (**36**) (*150*): see CD curve in ref. [150]

c. 13-keto

1) spirasine IV(**37**) (*159*): CD (EtOH) nm ($\triangle\varepsilon$): 257 (0), 303 (-4.53), 313 (- 4.37, sh), 332 (0)

2) barbaline (**38**) (*295*): CD (EtOH) nm (ε): 270 (-30200, min), 300 (-127000), 303 (-353200), 309 (-359800, max), 320 (-24900, sh)

d. 15-keto (α, β-unsaturated ketone)

1) (**39**) (*197*): very similar to **40**

2) (**40**) (*197*): CD (dioxane) nm ($\triangle\varepsilon$): 235 (2.03), 260 (0.40), 330 (0.13, sh), 337 (0.19, sh), 353 (0.30), 368 (0.26), 388 (0.10, sh)

3) acetylhypognavine (**41**) (*222*): CD (dioxane) nm ($\triangle\varepsilon$): 340 (0.32), 353 (0.43), 368 (0.42), 388 (0.16, sh)

e. 6, 7-diketo

vilmorrianone (**42**) (*163*): CD: ~305 nm; CE: (-)

Table X X V (*continued*)

f. 2, 11-diketo

2, 11-diketohetisine (**43**) (*150*): CD (MeOH): $[\theta]_{213}$ −11472.5, $[\theta]_{260}$ 130, $[\theta]_{300}$6955, $[\theta]_{310}$ 6955, $[\theta]_{330}$ 97.5

g. 6, 11-diketo

spiredine (**44**) (*159*): CD (EtOH) nm (△ε): 257 (0), 281 (-0.77), 297 (0), 315 (1.38), 350 (0); After acidification with HCl, 260 (0), 305 (1.79), 313 (1.77, sh), 338 (0)

h. 6, 13-diketo

1) deacetylheterophylloidine (**45**) (*150*): see CD curve in ref. [150]

2) episcopalidine (**46**) (*159*): 300 (-6.60); After acidifying with HCl, 303 (-4.52), 310 (-4.20, sh), 332 (0)

3) panicutine (**47**) (*150*): CD nm (△ε): 301 (-2.9)

i. 11, 13-diketo

dehydropaniculatine (**48**) (*244*): CD (EtOH) nm/[θ]: 215.0/(+13690, min), 229.0/(+26482, max), 251.5/(-4264, min), 267.5/(-2020), 300.0/(-12568, min), 303.5/ (-12231, max), 308.5/(-12904, min)

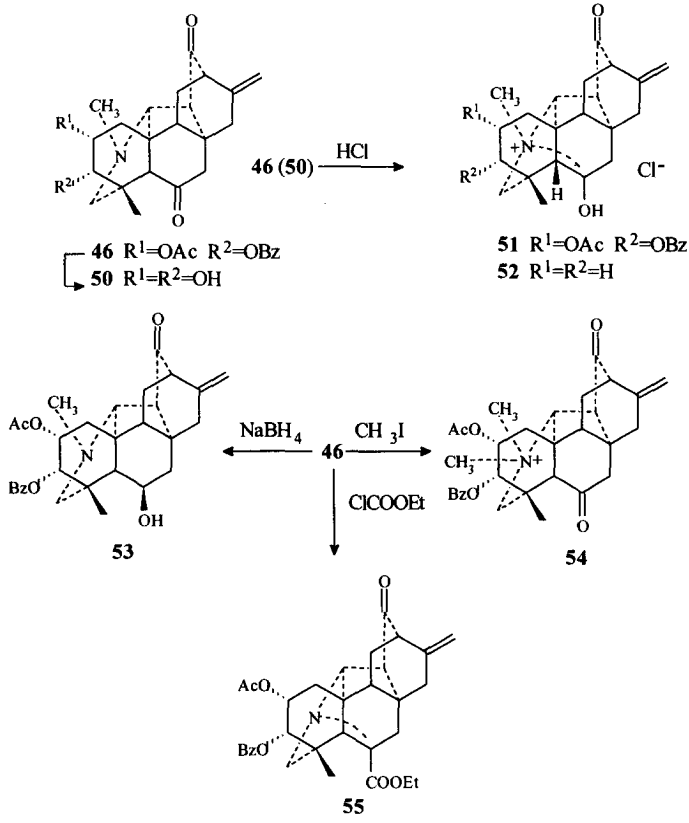
j. 15-OBz

(**49**) (*192*): CD (MeOH) nm (△ε): 225.5 (+4.96)

B. IR SPECTROSCOPY

The IR spectra of the C_{20}-diterpenoid alkaloids are mainly used for identification purposes, and sometimes for the analysis functional groups. In 1970, Ichinohe *et al.* (*164*) first reported the presence of the transannular effect based on the IR spectra, which was confirmed later by us with the IR and ^{13}C NMR spectra of episcopalidine (**46**) and its analogues (*418, 155*). The IR of episcopalidine (**46**) showed three absorption bands at 1730, 1710, and 1690 cm^{-1}. The first two were contributed by the ester carbonyls and one of the two keto groups, while the last one

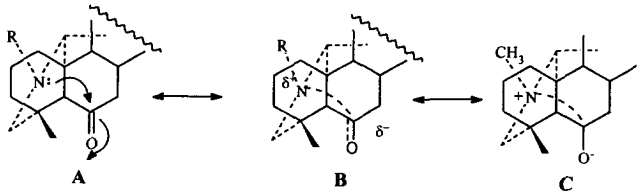
was purely ketonic. The IR spectrum of the aminoalcohol **50** from **46** exhibited only two carbonyl absorption bands at 1718 cm^{-1} and 1690 cm^{-1}, so that the absorption band at 1690 cm^{-1} in the IR spectra of **50** and **46** could be assigned to the 6- or 13-keto groups. After various treatments of **46** or **50** with HCl, CH_3I, ClCOOEt or $NaBH_4$ shown in Scheme 16, the disappearance of the original absorption band at 1690 cm^{-1} showed that the absorption bands at 1710 cm^{-1} in **46** and 1718 cm^{-1} in **50** may be assigned to the 13- keto group, and at 1690 cm^{-1} to the 6-keko group.



Scheme 16

The fact that the 6-keto groups in **46** and **50** possessed an absorption band at lower than 1700 cm^{-1} is a powerful evidence for the presence of a transannular

effect. The effect in the hetidine-type alkaloids having the 6-keto groups, e. g. hetidine (**50**), miyaconitine (*164*). episcopalidine (**46**) (*157*), is depicted in canonical forms in Scheme 17 (*177*). As one consequence of this lone-pair donation, the IR frequency of C-6 carbonyl is lowered to *ca.* 1690 cm^{-1}.



Scheme 17. Transannular effect in hetidine-type alkaloids with a 6-carbonyl group

C. ^{1}H NMR SPECTROSCOPY

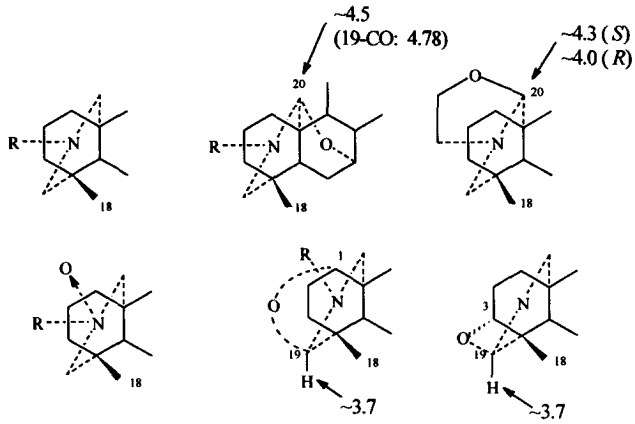
In 1968, Pelletier *et al.* (*60*) studied the ^{1}H NMR spectra of forty-four C_{20}-diterpenoid alkaloids and their derivatives. Several reviews (*29, 31*) were reported later. Only a minority of the characteristic signals in the ^{1}H NMR spectra of the 274 naturally-occurring C_{20}-diterpenoid alkaloids reported so far (Tables XXVII, XXIX~XLII) have been assigned. The structural complexity caused by the various patterns of the nitrogen atom leads to very complicated ^{1}H NMR spectra. Careful examination of the ^{1}H NMR data of the C_{20}-diterpenoid alkaloids enabled us to discern the relationships between the δ values of some signals, especially the H_3-18, H-19, or the H-20, and, the structural types or groups (Table X X VI). These features are useful for differentiation of the various types or groups among the C_{20}-diterpenoid alkaloids. Thus, the signals H_3-18, H-19, and H-20 may be considered as diagnostic tools for the structural analysis of C_{20}-diterpenoid alkaloids.

1. The H_3-18, H-19 and H-20. A tabulation of the δ value ranges of H_3-18, H-19, and H-20 in the ^{1}H NMR spectra of these alkaloids is given in Table X X VI.

TABLE X X VI

CHARACTERISTIC δ VALUE RANGES OF H_3-18, H-19, AND H-20 IN THE ^{1}H NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS

1. H_3-18 at δ 0.6~0.8



2. H_3-18 at δ~0.9-1.1

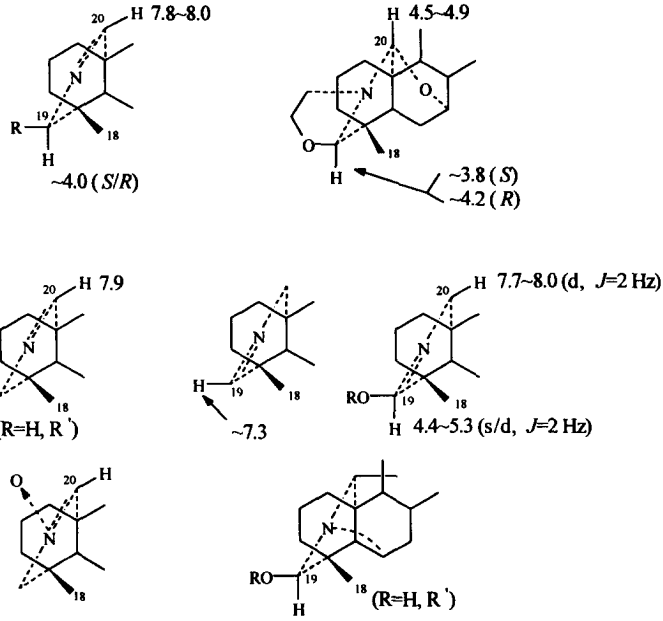
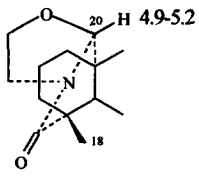
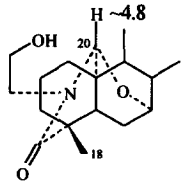
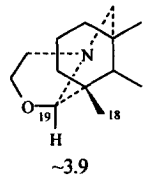


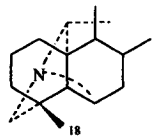
TABLE XXVI (*continued*)

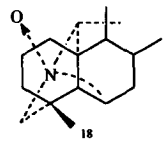
3. H_3-18 at δ~1.0-1.2



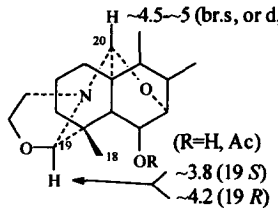




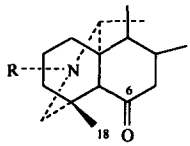


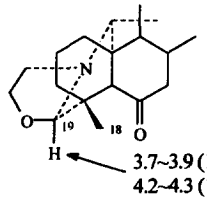


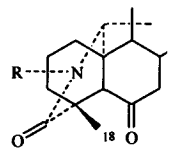
4. H_3-18 at δ1.1~1.4

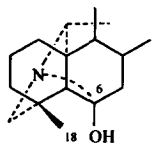


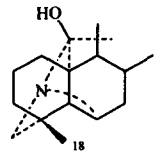
5. H_3-18 at δ1.3-1.5



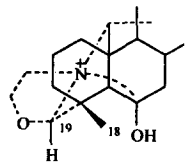




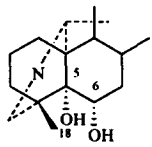




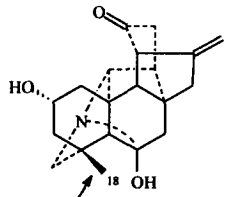
only orgentine (*285*)



6. H_3-18 at δ~1.6



anopterine-type



1.63 delnudine

From Table X X VI, we may conclude as follows:

a. The structures, including the subtypes or groups, are deduced roughly on the basis of the δ value ranges of the H_3-18 and H-19 or H-20;

b. The chemical shifts of H_3-18 in the hetisine-type alkaloids (A Ⅷ1a) are little affected by substituent groups (OH, O_2CR) at C-2 or C-3, or by the carbonyl at C-2;

c. In the ^1H NMR spectra of hetisine-type alkaloids (A Ⅶ2b), the δ values of H_3-18, in a few cases, e.g., delnuttidine (*224*) and delnuttaline (*230*), will appear downfield at 1.7 ppm;

d. In the ^1H NMR spectra of the amine-subtype (B Ⅱ 1) of napelline, the δ values of H_3-18 of some alkaloids having a 1α-methoxyl group, e.g., liangshanine (*315*) and liangshanone (*315*), may be located at about 1.0 ppm;

e. The δ values of H_3-18 in the ^1H NMR spectra of some alkaloids, e.g., *N*-deethyldehydrolucidusculine (*334*) and norsongoramine (*353*), in the B Ⅱ group of the napellines, may appear close to 1.12 ppm.

2. Exocyclic methylene $\Delta^{16(17)}$

The chemical shifts of H_2-17 are influenced slightly by the types of C_{20}-diterpenoid alkaloids. In general, the influences derived from the neighboring groups are very important. The δ values for the 15-non-oxygenated cases and the 15-oxygenated cases (OH, OAc, OBz) are generally at δ 4.8~5.4 and δ 4.3~5.1, respectively

3. The 16α- and 16β-OH epimers

The δ values for the 16-CH_3 in the ^1H NMR spectra of both epimers having no

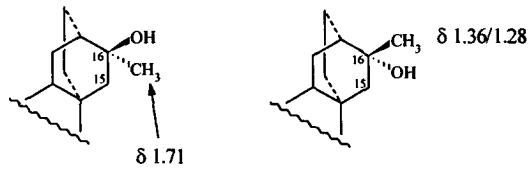


Fig. 6.

oxygenated substituents at C-15 are very different, leading easily to differentiation (Fig. 6).

4. The ^1H NMR data of the known naturally-occurring C_{20}-diterpenoid alkaloids are presented in Tables XXVII, XXIX~XLV according to their structural types (groups).

TABLE X X Ⅶ

^{1}H NMR DATA OF ATISINE TYPE DITERPENOID ALKALOIDS (A Ⅰ)

code (name) (*ref*)	δ_H
A Ⅰ 1-1 (dihydroatisine) (*60*)	0.70 (3H, s, H_3-18), 2.46 (2H, t, *J*=5.5 Hz, H_2-21), 3.66 (2H, t, *J*=5.5 Hz, H_2-22), 5.08 (2H, m, H_2-17)
A Ⅰ 1-2 (dihydroajaconine) (*62*)	0.80 (3H, s, H_3-18), 5.12 (2H, m, H_2-17)
A Ⅰ 1-3 (chellespontine) (*64*)	0.84 (3H, s, H_3-18), 3.93 (1H, br.s, H-15α), 5.10, 5.37 (each 1H, br.s, H_2-17), 9.43 (2H, s, CHO)
A Ⅰ 1-4 (spiratine A) (*419*)	1.08 (3H, s, H_3-18), 4.16, 4.19 (each 1H, m, H_2-21), 4.04, 5.05 (each 1H, br.s, H_2-17), 8.73 (1H, s, H-22)
A Ⅰ 1-5 (atidine) (*60, 67*)	0.77 (3H, s, H_3-18), 2.46 (2H, t, *J*=5.5 Hz, H_2-21), 3.67 (2H, t, *J*=5.5 Hz, H_2-21), 4.53 (1H, br.s, H-15α), 5.04, 5.17 (each, 1H, m, H_2-17)
A Ⅰ 1-6 (spiramine G) (*68, 69*)	0.80 (3H, s, H_3-18), 1.67 (1H, m, H-11), 1.95 (1H, m, H-11), 2.19 (1H, dd, *J*=3, 20 Hz, H-13α), 2.25 (1H, dt, *J*=2.7 Hz, H-15α), 2.31 (1H, dt, *J*=3, 20 Hz, H-13β), 2.12, 2.20, 2.45, 2.52 (each 1H, 2×ABq, H_2-20 and H_2-19), 2.40 (2H, m, H_2-21), 2.70 (1H, m, H-12), 3.07 (1H, dt, *J*=2.5, 11 Hz, H-15β), 3.20 (1H, ddd, *J*=6, 8, 11 Hz, H-7β), 3.48 (1H, d, *J*=8 Hz, OH), 3.60 (2H, m, H_2-22), 4.29, 4.74 (each 1H, m, H_2-17)
A Ⅰ 1-7 (spiramine H) (*70*)	0.78 (3H, s, H_3-18), 1.65 (1H, m, H-11α), 1.86 (1H, m, H-11β), 2.20 (1H, dd, *J*=3, 20 Hz, H-13α), 2.30 (1H, dt, *J*=3, 20 Hz, H-13β), 2.20, 2.21, 2.42, 2.50 (each 1H, d, *J*=11 Hz, H_2-19 and H_2-20), 2.62 (1H, dt, *J*=3, 13 Hz, H-7α), 2.79 (1H, m, H-12), 3.56 (2H, dq, *J*=6, 11 Hz, H_2-22), 3.93 (1H, br.s, H-15β), 5.16 (2H, br.s, H_2-17)
A Ⅰ 1-8 (spiramine I) (*70*)	0.79 (3H, s, H_3-18), 2.02 (3H, s, OAc), 2.80 (1H, m, H-12), 3.60 (2H, dq, *J*=6, 11 Hz, H_2-22), 5.08, 5.16 (each 1H, br.s, H_2-17), 5.40 (1H, br.s, H-15β)
A Ⅰ 1-9 (beiwasine A) (*71*)	0.76 (3H, s, H_3-18), 3.49 (1H, dd, *J*=4, 9.6 Hz, H-1β), 3.59 (2H, dt, *J*=1, 2, 11 Hz, H_2-22), 4.00 (1H, br.s, H-15β), 5.13 (2H, s, H_2-17)
A Ⅰ 1-10 (beiwasine B) (*71*)	0.78 (3H, s, H_3-18), 3.55 (2H, m, H_2-22), 3.74 (1H, d, *J*=2.6 Hz, H-1α), 3.99 (1H, s, H-15β), 5.14 (2H, d, *J*=1.4 Hz, H_2-17)

TABLE XXVII (*continued*)

A I 1-11 (uncinatine) (*72*)	1.70 (1H, m, H-1α), 2.80 (1H, br.d, *J*=14 Hz, H-1β), 1.80 (1H, ddd, *J*=3, 10, 12 Hz, H-2α), 1.20 (1H, dd, *J*=3, 12 Hz, H-2β), 1.87 (1H, dd, *J*=5, 14 Hz, H-3α), 2.10 (1H, ddd, *J*=5, 12, 14 Hz, H-3β), 1.72 (1H, dd, *J*=2, 14 Hz, H-5β), 1.24 (1H, dd, *J*=2, 12 Hz, H-6α), 1.60 (1H, m, H-6β), 3.90 (1H, d, *J*=5 Hz, H-7β), 2.20 (1H, d, *J*=3 Hz, H-9β), 2.00 (1H, dd, *J*=3, 12 Hz, H-11α), 1.50 (1H, m, H-11β), 2.40 (1H, d, *J*=3 Hz, H-12α), 1.80 (1H, m, H-13α), 2.05 (1H, m, H-13β), 1.90 (1H, m, H-14), 4.20 (1H, d, *J*=3 Hz, H-15β), 5.02 (1H, br.s, H-17α), 5.12 (1H, br.s, H-17β), 1.07 (3H, s, H_3-18), 3.60 (1H, d, *J*=10 Hz, H-19α), 3.45 (1H, d, *J*=10 Hz, H-19β), 4.15 (1H, d, *J*=20 Hz, H-20), 7.08 (1H, d, *J*=8.5 Hz, H-21), 6.75 (1H, d, *J*=8.5 Hz, H-22)
A I 2a-2 (isoatisine) (*60*, *78*)	1.00 (1.19) (3H, s, H_3-18), 2.71 (2H, br.s, H_2-20), 3.47 (3H, m), 3.86 (1H, br.s), 4.87, 4.98 (each 1H, br.s, H_2-17)
A I 2a-3 (spiramidines A(B)) (*75*)	1.22 (1H, m, H-1β), 1.43 (1H, m, H-1α), 1.45 (1H, m, H-2β), 2.28 (1H, m, H-2α), 1.91 (1H, m, H-3α), 1.97 (1H, m, H-3β), 0.89, 0.71 (1H, m, H-15), 1.43 (1H, m, H-6α), 1.58 (1H, m, H-6β), 3.03 (1H, d, *J*=2.5 Hz, H-7), 1.50 (1H, m, H-9), 1.58 (1H, m, H-11β), 1.98 (1H, m, H-11α), 2.86 (1H, m, H-12), 2.16 (1H, m, H-13α), 2.23 (1H, m, H-13β), 2.24 (1H, dd, *J*=2.5, 8.0 Hz, H-15), 2.99 (1H, s, H-15), 4.69 (4.62), 4.87 (4.83) (each 1H, br.s, H_2-17), 1.04 (1.01) (3H, s, H_3-18), 3.70 (3.89) (1H, br.s, H-19), 2.65 (1H, m, H-20α), 3.40 (1H, m, H-20β), 3.41 (1H, m, H-21β), 3.46 (1H, m, H-21α), 3.75 (2H, m, H_2-22)
A I 2b-1 (ajaconine) (*99*)	0.74 (3H, s, H_3-18), 4.17 (1H, d, *J*=8 Hz, H-7β), 4.57 (1H, s, H-20), 5.02, 5.13 (each 1H, d, *J*=2 Hz, H_2-17)
A I 2b-3 (spiramine F) (*68*, *69*)	0.60 (1H, m, H-5β), 0.61 (3H, s, H_3-18), 1.68 (1H, m, H-6β), 1.71 (3H, s, OAc), 1.78 (1H, m, H-6α), 2.35 (1H, m, H-12), 3.13 (2H, m, H_2-19), 4.49 (1H, br.s, H-20), 2.86, 3.42 (each 1H, m, H_2-21), 3.53 (1H, d, *J*=5 Hz, H-17β), 3.75 (2H, m, H_2-22), 4.49 (1H, br.s, H-20), 5.02, 5.23 (each 1H, br.s, H_2-17), 5.38 (1H, br.s, H-15β)

TABLE XXVII (*continued*)

A I 2b-4 (spiramine Y) (*85*)	1.37, 1.70 (each 1H, m, H_2-1), 1.48, 1.75 (each 1H, m, H_2-2), 1.55, 1.61 (each 1H, m, H_2-3), 1.50 (1H, br.s, H-5), 5.13 (1H, t, *J*=4.6 Hz, H-6α), 3.73 (1H, d, *J*=4.8 Hz, H-7β), 1.44 (1H, m, H-9), 2.08, 2.38 (each 1H, m, H_2-11), 2.35 (1H, m, H-12), 1.36, 1.90 (each, 1H, m, H_2-13), 1.35, 1.85 (each 1H, m, H_2-14), 1.33, 1.77 (each 1H, m, H_2-15), 4.66, 4.82 (each 1H, br.s, H-17), 1.13 (3H, s, H_3-18), 4.78 (1H, d, *J*=1.6 Hz, H-20), 3.20, 3.63 (each 1H, m, H_2-21), 3.79 (2H, m, H_2-22), 2.04 (3H, s, OAc)
A I 2b-5 (spiramine E) (*68, 69*)	0.63 (3H, s, H_3-18), 1.68 (3H, s, OAc), 1.73 (1H, m, H-6β), 1.75 (3H, s, OAc), 1.80 (1H, m, H-6α), 2.55 (1H, m, H-12), 2.16, 2.60 (each, 1H, d, *J*=11 Hz, H_2-19), 2.64, 2.98 (each 1H, d, *J*=6, 13.5 Hz, H_2-21), 3.60 (1H, d, *J*=5 Hz, H-7β), 4.16 (2H, t, *J*=6 Hz, H_2-22), 4.51 (1H, br.s, H-20), 5.03, 5.28 (each 1H, t, *J*=1.5 Hz, H_2-17), 5.46 (1H, br.s, H-15β)
A I 2c-1 (spiramine C) (*87*)	0.67 (1H, m, H-5), 1.22 (3H, s, H_3-18), 1.52 (1H, m, H-6α), 2.22 (1H, m, H-12), 2.62 (1H, ddd, *J*=4, 5, 15 Hz, H-6β), 3.00, 3.25 (each 1H, m, H_2-21), 3.79 (1H, br.s, H-15), 3.36, 3.83 (each 1H, m, H_2-22), 3.80 (1H, d, *J*=5 Hz, H-7β), 3.88 (1H, s, H-19), 4.49 (1H, d, *J*=2 Hz, H-20, 4.90, 4.93 (each 1H, br.s, H_2-17)
A I 2c-2 (spiramine A) (*86~88*)	0.62 (1H, ddd, *J*=2.4, 13 Hz, H-5), 1.18 (3H, s, H_3-18), 1.65 (3H, s, OAc), 1.80 (1H, dd, *J*=13, 15 Hz, H-6α), 2.23 (1H, m, H-12), 2.63 (1H, ddd, *J*=4, 5.15 Hz, H-6β), 3.01, 3.24 , 3.37, 3.81 (each 1H, m, H_2-21, H_2-22), 3.54 (1H, d, *J*=5 Hz, H-7), 3.87 (1H, s, H-19), 4.47 (1H, d, *J*=1.8 Hz, H-20), 5.04, 5.30 (each 1H, br.s, H_2-17), 5.46 (1H, br.s, H-15)
A I 2c-3 (spiramine G) (*89*)	1.17 (3H, s, H_3-18), 3.32 (1H, d, *J*=5 Hz), 3.80 (1H, s), 4.46 (1H, s), 4.58, 4.72 (each 1H, br.s, H_2-17)
A I 2c-4 (spiramine F) (*88*)	1.10 (3H, s, H_3-18), 2.04 (3H, s, OAc), 3.21 (1H, m, H-22), 3.31, 3.46 (each 1H, m, H_2-21), 3.63 (1H, d, *J*=5 Hz, H-7β), 3.70 (1H, dd, *J*=8, 15 Hz, H_2-22), 3.88 (1H, s, H-19β), 4.57 (1H, s, H-20), 4.65, 4.82 (each br.s, H_2-17), 5.67 (1H, dd, *J*=3, 5 Hz, H-6α)

TABLE XXVII (*continued*)

A I 2c-5 (spiramine D) (*87*)	0.77 (1H, m, H-5), 0.99 (3H, s, H_3-18), 1.52 (1H, m, H-6α), 1.84 (1H, ddd, *J*=4, 5, 15 Hz, H-6β), 2.61 (1H, m, H_2-21), 2.71, 3.04 (each 1H, m, H_2-21), 3.66, 3.74 (each 1H, m, H_2-22), 3.79 (1H, br.s, H-15), 3.86 (1H, d, *J*=5 Hz, H-7), 4.29 (1H, s, H-19), 4.72 (1H, d, *J*=2 Hz, H-20), 4.91, 4.94 (each 1H, br.s, H_2-17)
A I 2c-6 (spiramine B) (*87*)	0.75 (1H, ddd, *J*=2, 4, 13 Hz, H-5), 0.97 (3H, s, H_3-18), 1.66 (3H, s, OAc), 1.85 (2H, m, H_2-6), 2.59 (1H, m, H-20), 2.70, 3.02 (each 1H, m, H_2-21), 3.61 (1H, d, *J*=5 Hz, H-7), 3.65, 3.73 (each 1H, m, H_2-22), 4.27 (1H, s, H-19), 4.69 (1H, d, *J*=2 Hz, H-20), 5.04, 5.30 (each 1H, br.s, H_2-17), 5.46 (1H, br.s, H-15β)
A I 2c-7 (spiramine P) (*94*)	1.32, 1.21 (each 1H, m, H_2-1), 1.39, 2.26 (each 1H, m, H_2-2), 1.40, 1.52 (each 1H, m, H_2-3), 1.38 (1H, br.s, H-5), 5.09 (1H, dd, *J*=2.1, 4.9 Hz, H-6β), 3.70 (1H, d, *J*=4.9 Hz, H-7), 2.03 (1H, dd, *J*=2.9, 10.5 Hz, H-9), 1.23, 1.60 (each 1H, m, H_2-11), 1.83 (1H, m, H-12), 1.48, 1H, d, *J*=5 Hz, H-7), 1.48, 2.65 (each 1H, m, H_2-13), 1.50, 2.12 (each 1H, m, H_2-14), 1.89 (1H, d, *J*=12.4 Hz, H-15), 3.06 (1H, dd, *J*=3.2, 12.4 Hz, H-15), 1.71 (3H, s, H_3-17), 1.40 (3H, s, H_3-18), 3.91 (3H, s, H_3-19), 4.64 (1H, s, H-20), 3.18, 3.38 (each 1H, m, H_2=21) 3.40, 3.75 (each 1H, m, H_2-22)
A I 2c-8 (spiramine U) (*94*)	1.18, 1.68 (each 1H, m, H_2-1), 1.40, 2.03 (each 1H, m, H_2-2), 1.20, 1.46 (each 1H, m, H_2-3), 1.08 (1H, d, *J*=2 Hz, H-5), 5.61 (1H, dd, *J*=2, 4.9 Hz, H-6α), 3.53 (1H, d, *J*=4.9 Hz, H-7), 1.53 (1H, m, H-9), 1.31, 1.50 (each 1H, m, H_2-11), 1.51 (1H, m, H-12), 1.38, 1.91 (each 1H, m, H_2-13), 1.21, 1.80 (each 1H, m, H_2-14), 1.28 (1H, d, *J*=12.4 Hz, H-15), 1.90 (1H, dd, *J*=3.4, 12.4 Hz, H-15), 1.36 (3H, s, H_3-17), 1.07 (3H, s, H_3-18), 3.83 (1H, s, H_3-19), 4.54 (1H, s, H-20), 3.17, 3.26 (each 1H, m, H_2-21), 3.43, 3.63 (each 1H, m, H_2-22), 2.00 (3H, s, OAc)
A I 2c-9 (thalicsiline) (*91*, *92*)	0.94 (3H, s, H_3-18), 1.30 (1.31) (3H, s, H_3-17), 4.58 (4.82) (1H, s, H-20), 2.06 (3H, s, OAc), 2.05 (1H, s, H-6), 5.32 (5.67) (1H, d, *J*=2.4 Hz), 3.86 (4.11) (1H, s, H-19), 3.00-4.10 (5H, m, oxazolidine ring)
A I 2c-10 (spiramine Q) (*93*, *94*)	1.15 (3H, s, H_3-18), 1.28 (3H, s, H_3-17), 2.70 (1H, br.s, OH), 3.18, 3.60 (each 1H, m, H_2-22), 3.28, 3.46 (each 1H, m, H_2-21), 3.30 (1H, d, *J*=5 Hz, H-7), 3.50 (1H, br.s, OH), 3.84 (1H, s, H-19), 4.52 (1H, s, H-20), 4.56 (1H, br.s, H-6)

TABLE XXVII (*continued*)

A I 2c-11 (spiramine T) (*94*)	0.88 (3H, s, H_3-18), 1.27 (3H, s, H_3-17), 2.02 (3H, s, OAc), 2.96, 2.99 (each 1H, m, H_2-21), 3.55 (1H, d, *J*=4.6 Hz, H-7β), 3.79, 3.82 (each 1H, m, H_2-22), 4.05 (1H, br.s, H-19), 4.77 (1H, br.s, H-20), 5.26 (1H, m, H-6α)
A I 2c-12 (spiramine W) (*95*)	1.20 (3H, s, H_3-18), 1.74 (3H, s, H_3-17), 3.09, 3.20 (each 1H, m, H_2-21), 3.40, 3.87 (each 1H, m, H_2-22), 3.70 (1H, d, *J*=4.9 Hz, H-7β), 3.87 (H, s, H-22), 4.22 (H, s, H-19), 4.94 (1H, s, H-20), 5.09 (1H, dd, *J*=2.1, 4.9 Hz, H-6α)
A I 2d-1 (spiramine S) (*96*)	1.09 (3H, s, H_3-18), 2.02 (3H, s, OAc), 3.68 (1H, m, H-7β), 4.91 (1H, br.s, H-20), 4.98, 5.04 (each 1H, br.s, H_2-17), 5.22 (1H, d, *J*=1.76 Hz, H-15β)
A I 2d-2 (spiramine V) (*97*)	1.09 (3H, s, H_3-18), 1.91 (3H, s, OAc), 3.90 (1H, br.s, H-15β), 4.81 (1H, m, H-7β), 4.91 (1H, s, H-20), 4.98, 5.04 (each 1H, br.s, H_2-17)
A I 2d-3 (deacetylspiramine S) (*75*)	0.89 (2H, m, H_2-1), 1.30, 1.40 (each 1H, m, H_2-2), 1.42, 1.84 (each 1H, m, H_2-3), 1.52 (1H, d, *J*=9.6 Hz, H-5), 1.75, 1.95 (each 1H, m, H_2-6), 3.73 (1H, dd, *J*=5.9, 8.6 Hz, H-9), 1.42, 1.69 (each 1H, m, H_2-11), 2.36 (1H, m, H-12), 1.30, 1.41 (each 1H, m, H_2-13), 1.42, 1.68 (each 1H, m, H_2-14), 3.93 (1H, s, H-15), 5.06, 5.09 (each 1H, br.s, H_2-17), 1.21 (3H, s, H_3-18), 5.11 (1H, s, H-20), 3.28 (1H, dt, *J*=2.6 Hz, H-21), 3.90 (1H, m, H-21), 3.87 (1H, m, H-22), 4.18 (1H, dt, *J*=3.2 Hz, H-22)
A I 2d-4 (spiramide) (*420*)	0.95 (1H, ddd, *J*=4.6, 4.8, 13.3 Hz, H-1β), 2.41 (1H, br.dd, *J*=3.2, 13.3 Hz, H-1α), 1.39 (1H, m, H-2α), 1.46 (1H, m, H-2β), 1.43 (1H, m, H-3β), 1.78 (1H, m, H-3α), 1.84 (1H, d, *J*=11.6 Hz, H-5), 5.33 (1H, dd, *J*=9.9, 11.6 Hz, H-6), 4.76 (1H, d, *J*=9.9 Hz, H-7), 1.48 (1H, m, H-9), 1.73, (1H, m, H-11), 2.09 (1H, ddd, *J*=2.4, 7.2, 13.5 Hz, H-11), 2.25 (1H, br.s, H-12), 1.52 (1H, dd, *J*=7.8, 12.1 Hz, H-13), 1.65 (1H, br.d, *J*=12.1 Hz, H-13), 1.60 (1H, dd, *J*=6.5, 12.8 Hz, H-14), 1.89 (1H, br.d, *J*=12.8 Hz, H-14), 1.98 (1H, br.d, *J*=16.0 Hz, H-15), 2.20 (1H, br.d, *J*=6.4 Hz, H-15), 4.60, 4.77 (each 1H, *J*=1.2 Hz, H_2-17), 1.15 (3H, s, H_3-18), 5.06 (1H, s, H-20), 3.29 (1H, ddd, *J*=3.7, 8.2, 11.2 Hz, H-21), 3.97 (1H, ddd, *J*=8.2, 8.2, 11.2 Hz, H-21), 3.84 (1H, dt, *J*=8.2, 8.2, 11.2 Hz, H-22), 4.15 (1H, ddd, *J*=3.7, 8.2, 11.2 Hz, H-22), 1.92, 1.98 (each 3H, s, OAc×2)

TABLE XXVII (*continued*)

A I 2e-1 (spiramine R) (*93*)	1.09 (3H, s, H_3-18), 1.99 (3H, s, OAc), 2.42 (1H, m, H-12), 3.22, 3.60 (each 1H, m, H_2-21), 3.46 (1H, d, *J*=4 Hz, H-7), 3.75, 3.90 (each 1H, m, H_2-22), 4.77 (1H, d, H-20), 5.01 (2H, *J*=3 Hz, H_2-17), 5.17 1H, br.s, H-15)
A I 2e-2 (spiramine X) (*85*)	1.38, 1.68 (each 1H, m, H_2-1), 1.46, 1.74 (each 1H, m, H_2-2), 1.52, 1.58 (each 1H, m, H_2-3), 1.49 (1H, br.s, H-5), 5.12 (1H, t, *J*=3 Hz, H-6α), 3.65 (1H, d, *J*=3.8 Hz, H-7), 1.40 (1H, m, H-9), 2.07, 2.36 (each 1H, m, H_2-11), 2.33 (1H, m, H-12), 1.37, 1.87 (each 1H, m, H_2-13), 1.40, 1.90 (each 1H, m, H_2-14), 1.29, 1.79 (each 1H, d, *J*=12.4 Hz, H-15), 4.66, 4.82 (each 1H, br.s, H_2-17), 1.13 (3H, s, H_3-18), 4.78 (1H, d, *J*=1.8 Hz, H-20), 3.28, 4.01 (each 1H, m, H_2-21), 4.18 (2H, m, H_2-22), 2.02 (3H, s, OAc)
A I 2f-1 (19-*O*-deethyl spiramine N) (*75*)	1.04 (1H, m, H-1β), 2.46 (1H, m, H-1α), 1.41 (1H, m, H-2α), 1.76 (1H, m, H-2β), 0.99 (1H, m, H-3β), 1.61 (1H, m, H-3α), 1.21 (1H, d, *J*=14.0 Hz, H-5), 1.65 (1H, m, H-6α), 2.34 (1H, m, H-6β), 3.90 (1H, dd, *J*=4.1, 7.4 Hz, H-7), 1.27 (1H, d, *J*=5.4 Hz, H-9), 1.56 (1H, m, H-11β), 2.02 (1H, d, *J*=13.0 Hz, H-11α), 2.31 (1H, d, *J*=16.0 Hz, H-12), 1.15 (1H, m, H-13α), 1.62 (1H, m, H-13β), 1.18 (1H, m, H-14α), 1.76 (1H, m, H-14β), 4.26 (1H, d, *J*=4.1 Hz, H-15), 5.11, 5.33 (each 1H, s, H_2-17), 1.10 (3H, s, H_3-18), 5.30 (1H, s, H-19), 7.99 (1H, s, H-20)
A I 2f-2 (spiratine B) (*419*)	0.98 (3H, s, H_3-18), 1.96 (3H, s, 6-OAc), 2.00 (3H, s, 7-OAc), 4.74 (1H, d, *J*=8.0 Hz, H-7), 4.62, 4.79 (each 1H, br.s, H_2-17), 5.11 (1H, s, H-19), 5.20 (1H, t, *J*=8.0 Hz, H-6), 7.76 (1H, br.s, H-20)
A I 2f-3 (spiramine N) (*98*)	0.95 (3H, s, H_3-18), 1.25 (3H, t, *J*=7.0 Hz, 3H-22), 2.41 (1H, m, H-12β), 3.65 (1H, dd, *J*=5.0, 11.0 Hz, H-7β), 4.00 (1H, dd, *J*=1.5 Hz, H-15β), 3.67, 4.11 (each 1H, dq, *J*=7.0, 11.0 Hz, H_2-21), 4.45 (1H, d, *J*=2.0 Hz, H-19), 5.03, 5.05 each 1H, br.s, H_2-17)
A I 2f-4 (brunonine) (*99*)	0.97 (3H, s, H_3-18), 4.30 (br.s, H-19), 8.03 (1H, H-20), 1.27 (3H, t, *J*=7.2 Hz, OCH_2CH_3), 3.67, 4.14 (each 1H, dq, *J*=7.2, 10.8 Hz, OCH_2CH_3)
A I 2f-5 (spiramine O) (*70*)	0.96 (3H, s, H_3-18), 3.60 (1H, m, H-7β), 4.00 (1H, br.s, H-15β), 4.35 (1H, d, *J*=2 Hz, H-19α), 5.05 , 5.07 (each 1H, br.s, H_2-17), 7.85 (1H, br.s, H-20)

TABLE XXVII (*continued*)

A I 2f-6 (spiramine Z) (*85*)	1.09, 1.66 (each 1H, m, H_2-1), 0.98, 1.94 (each 1H, m, H_2-2), 1.34 (2H, m, H_2-3), 1.52 (1H, d, *J*=10.2 Hz, H-5), 5.08 (1H, t, *J*=10.2 Hz, H-6α), 4.65 (1H, d, *J*=10.2 Hz, H-7β), 1.50 (1H, m, H-9), 1.78 (2H, m, H_2-11), 2.27 (1H, m, H-12), 1.52, 1.58 (each 1H, H_2-13), 1.48, 1.56 (each 1H, m, H_2-14), 1.92, 2.19 (each 1H, d, *J*=17.2 Hz, H_2-15), 4.54, 4.71 (each 1H, s, H_2-17), 0.84 (3H, s, H_3-18), 4.56 (1H, s, H-19), 7.74 (1H, s, H-20), 3.59, 4.03 (each 1H, m, O*C*H_2CH$_3$), 1.13 (3H, t, *J*=7.0 Hz, OCH$_2$*C*H_3), 1.95 (3H, s, 6-OAc), 1.89 (3H, s, 7-OAc)
A I 2f-7 (spiramine J) (*100*)	0.90 (3H, s, H_3-18), 2.21 (3H, s, CO*C*H_3), 2.73 (2H, oct, *J*=7, 17 Hz, -*C*H_2O), 3.59 (1H, dd, *J*=5, 11 Hz, H-7β), 3.94 (1H, dd, *J*=2.5, 7 Hz, H-19), 3.98 (1H, br.s, H-15β), 5.03, 5.06 (each 1H, br.s, H_2-17), 7.94 (1H, d, *J*=2.5 Hz, H-20)
A I 2f-8 (spiramine L) (*100*)	0.89 (3H, s, H_3-18), 2.13 (3H, s, OAc), 2.22 (3H, s, -CO*C*H_3), 2.72 (2H, octa, *J*=8, 17 Hz, *C*H_2CO), 3.55 (1H, dd, *J*=5, 11 Hz, H-7β), 3.93 (1H, dd, *J*=3, 8 Hz, H-19), 4.95, 5.02 (each 1H, br.s, H_2-17), 5.36 (1H, d, *J*=2 Hz, H-15β), 7.94 (1H, d, *J*=2.5 Hz, H-20)
A I 2f-9 (spiramine M) (*100*)	0.88 (3H, s, H_3-18), 2.03 (3H, s, OAc), 2.24 (3H, s, -CO*C*H_3), 2.60 (2H, octa, *J*=8, 17 Hz, *C*H_2CO), 3.98 (1H, s, H-15β), 3.93 (1H, dt, *J*=2.5, 7 Hz, H-19), 4.83 (1H, dd, *J*=5, 11 Hz, H-7β), 4.94, 5.02 (each 1H, br.s, H_2-17), 7.96 (1H, d, *J*=2 Hz, H-20)
A I 2f-10 (spiramine K) (*100*)	0.89 (3H, s, H_3-18), 2.29 (3H, s, CO*C*H_3), 2.59 (1H, dd, *J*=11, 15 Hz, *CH*CO), 2.51 (1H, dd, *J*=3, 15 Hz, *CH*CO), 3.66 (1H, dd, *J*= 5, 11 Hz, H-7β), 3.95 (1H, tt, *J*=1, 11 Hz, H-19), 3.98 (1H, br.s, H-15β), 5.02, 5.06 (each 1H, br.s, H_2-17), 7.83 (1H, d, *J*=1 Hz, H-20)
A I 3-1 (azitine) (*64*)	1.02 (3H, s, H_3-18), 2.40 (1H, m, H-12), 3.41, 3.42 (2H, H_2-19), 3.70 (1H, br.s, H_2-17), 7.90 (1H, s, H-20)
A I 3-2 (azitine chloride) (*101*, *102*)	1.03 (3H, s, H_3-18), 3.56-3.57 (3H, m, H-19, H-15), 3.90, 4.14 (each 1H, m, H-21, H-22), 5.00 (2H, H_2-17), 8.65 (1H, br.s, H-20)
A I 4-1 (coryphidine) (CD_3OD_3) (*103*)	0.87 (3H, s, H_3-18), 1.92 (3H, m, NCO*C*H_3), 2.31 (3H, s, *N*CH$_3$), 2.95 (1H, ddd, *J*=1.8, 7.0, 8.2 Hz, H-7'), 3.14, 3.45 (each 1H, d, *J*=13.2 Hz, H_2-19), 4.17 (1H, tdd, *J*=1.8, 5.5, 10.8 Hz, H-6'), 5.53-5.60 (3H, m, H-4', 5', 15)

TABLE XXVIII
^{1}H NMR DATA OF ATISANE TYPE DITERPENES

code (name) (*ref*)	δ_H
A I ' -1 (atisenol) (*104*)	1.21 (3H, s, H_3-18), 2.22 (2H, br.s, H_2-20), 3.70 (1H, t, H-15α), 5.20 (1H, m, H-17)
A I ' -2 (spiramilactone) (*112*)	0.89 (3H, s, H_3-18), 3.65 (1H, dd, *J*=4.3, 11.0 Hz, H-7), 3.90 (1H, br.s, H-15), 4.02, 4.18 (each 1H, ABq, *J*=11.7 Hz, H_2-19), 4.18 (1H, dd, *J*=2.2, 11.7 Hz)
A I ' -3 (spiramilactone C) (*105*)	1.28 (3H, s, H_3-18), 3.87 (1H, dd, *J*=4.0, 11.4 Hz, H-7β), 4.17 (1H, br.s, H-15β), 4.26 (1H, d, *J*=12.1, H-20), 4.94 (1H, dd, *J*=2.0, 12.1 Hz, H-20), 5.12 (1H, d, *J*=1.4 Hz, H-17), 5.34 (1H, d, *J*=1.5 Hz, H-17)
A I ' -4 (spiramilactone D) (*105*)	1.28 (3H, s, H_3-18), 1.47 (3H, s, H_3-17), 3.40 (1H, d, *J*=9.0 Hz, H-7β), 4.04 (1H, s, H-15β), 4.04 (1H, d, *J*=11.3, H-20), 4.45 (1H, dd, *J*=2.0, 11.3 Hz, H-20)
A I ' -5 (spiraminol) (*98*)	0.87 (3H, s, H_3-18), 3.90 (1H, d, *J*=5.0 Hz, H-7β), 3.98 (1H, br.s, H-15β), 5.04, 5.06 (each 1H, br.s, H_2-17), 5.30 (1H, d, *J*=2.0 Hz, H-20)
A I ' -6 (spiramacetal) (*105*)	1.17 (3H, s, H_3-18), 1.75 (3H, s, OAc), 2.15 (3H, s, H_3-17), 4.35 (1H, d, *J*=5.3 Hz, H-7β), 5.47 (1H, d, *J*=1.6 Hz, H-19), 5.69 (1H, s, H-20), 5.79 (1H, dd, *J*=1.5, 5.3 Hz, H-6α), 6.00 (1H, s, H-15)
A I ' -7 (spiramlactone B) (*106*)	1.23 (3H, s, H_3-18), 3.91 (1H, d, *J*=4.6 Hz, H-7β), 3.99 (1H, br.s, H-15β), 5.08, 5.10 (each 1H, br.s, H_2-17), 5.63 (1H, d, *J*=2.7 Hz, H-20)
A I ' -8 (spiramdol) (*105*)	1.06 (3H, s, H_3-18), 2.00, 2.02 (each 3H, s, 2×OAc), 4.60, 4.76 (each 1H, d, *J*=2 Hz, H_2-17), 4.78 (1H, d, *J*=9.8 Hz, H-7β), 6.00 (1H, dd, *J*=9.8, 11.7 Hz, H-6α), 9.60 (1H, s, H-20), 9.84 (1H, s, H-19)

TABLE XXIX

^{1}H NMR DATA OF DENUDATINE TYPE DITERPENOID ALKALOIDS (A II)

code (name) (*ref*)	δ_H
A II 1-1 (gymnanadine) (*107*)	0.68 (3H, s, H_3-18), 1.02 (3H, t, *J*=7 Hz, NCH_2CH_3), 3.38 (1H, br.s, OH), 4.29 (1H, t, *J*=2 Hz, H_2-15), 4.92, 5.07 (each 1H, br.s, H_2-17)
A II 1-2 (denudatine) (*115*)	1.13 (1H, dt, *J*=13.6, 4.0, 4.0 Hz, H-1α), 0.98 (1H, dt, *J*=13.6, 13.6, 5.5 Hz, H-1β), 0.59 (1H, m, H-2α), 1.56 (1H, m, H-2β), 0.75 (1H, dt, *J*=13.8, ~4.0, 3.8 Hz, H-3α), 0.39 (1H, dt, *J*=13.8, 13.8, 3.5 Hz, H-3β), 0.37 (1H, m, H-5), 0.37 (1H, m, H-6α), 1.98 (1H, dd, *J*=13.8, 7.9 Hz, H-6β), 1.23 (1H, d, *J*=7.9 Hz, H-7), 0.53 (1H, d, *J*=9.6 Hz, H-9), 2.87 (1H, dd, *J*=9.6, 4.9 Hz, H-11), 1.30 (1H, brs, *J*<1.0 Hz, H-12), 0.61 (1H, m, H-13), 0.84 (1H, t, *J*=12.0 Hz, H-13), 0.25 (1H, m, H-14), 1.03 (1H, m, H-14), 3.35 (1H, d, *J*=6.1 Hz, H-15), 3.88 (1H, d, *J*=6.1 Hz, HO-15), 4.09, 4.37 (each 1H, dd, *J*=~3.4, 2.2 Hz, H_2-17), 0.90 (3H, s, H_3-18), 1.42, 1.66 (each 1H, ABq, *J*=11.1 Hz, H_2-19), 2.51 (1H, s, H-20), 1.58, 1.69 (each 1H, m, H_2-22), 0.23 (3H, t, *J*=7.2 Hz, H_3-23)
A II 1-2 (denudatine) (*113*)	1.84 (2H, m, H_2-1), 1.12 (1H, m, H-3β), 1.50 (1H, m, H-3α), 1.06 (1H, d, *J*=8.3 Hz, H-5), 2.74 (1H, dd, *J*=8.3, 13.8 Hz, H-6β), 1.08 (1H, dd, *J*=5.3, 13.8 Hz, H-6α), 1.95 (1H, dd, *J*=5.27 Hz, H-7), 1.25 (1H, d, *J*=9.6 Hz, H-9), 3.59 (1H, dd, *J*=4.4, 9.6 Hz, H-11), 2.00 (1H, m, H-12), 1.31(1H, m, H-13α), 1.57 (1H, m, H-13β), 0.97 (1H, m, H-14β), 1.80 (1H, m, H-14α), 4.05 (1H, ddd, *J*= 1.9, 2.4, 5.6 Hz, H-15), 5.07 (1H, dd, *J*=1.9, 2.7 Hz, H-17a), 4.79 (1H, dd, *J*=2.4, 2.7 Hz, H-17b), 0.67 (3H, s, H_3-18), 2.16 (1H, dd, *J*=1.9, 10.8 Hz, H-19a), 2.41 (1H, d, *J*=10.8 Hz, H-19b), 3.26 (1H, s, H-20), 2.37 (2H, m*, NCH_2CH_3), 0.97 (3H, t, *J*=7.3 Hz, NCH_2CH_3), 4.19 (1H, d, *J*=4.4 Hz, 11-OH), 4.88 (1H, d, *J*=5.9 Hz, 15-OH)
A II 1-3 (jinosine, 15- acetyl denudatine) (*114*)	0.78 (3H, s, H_3-18), 1.02 (3H, t, *J*=7 Hz, NCH_2CH_3), 2.25 (3H, s, OAc), 3.38 (1H, s, H-20), 3.74 (1H, m, H-11α), 4.95 (2H, d, *J*=2 Hz, H_2-17), 5.37 (1H, t, *J*=2 Hz, H-15α)

TABLE XXIX (*continued*)

A II 1-4 (lepenine) (*115*, *113*)	4.15 (1H, dd, *J*=6.7, 10.0 Hz, H-1β), 2.73 (1H, HO-1), 1.78 (1H, m, H-2β), 2.32 (1H, m, H-2α), 1.58 (1H, dd, *J*=2.8, 4.3 Hz, H-3α), 1.28 (1H, d, *J*=13.4 Hz, H-3β), 1.32 (1H, d, *J*=8.6 Hz, H-5), 1.25 (1H, m, H-6α), 2.73 (1H, dd, *J*=8.6, 13.7 Hz, H-6β), 2.17 (1H, d, *J*=7.0 Hz, H-7), 1.26 (1H, dd, *J*=7.8, 9.0 Hz, H-9), 4.43 (1H, dd, *J*=4.0, 9.0 Hz, H-11), 2.73 (1H, s, HO-11), 2.18 (1H, m, H-12), 1.46 (1H, m, H-13α), 1.72 (1H, m, H-13β), 1.11 (1H, m, H-14α), 1.93 (1H, m, H-14β), 4.27 (1H, dd, *J*=6.2, 7.8 Hz, H-15), 2.33 (1H, HO-15), 5.02 (1H, s, H-17α),5.24 (1H, s, H-17β), 0.69 (3H, s, H_3-18), 2.49 (1H, ABq, *J*=11.0 Hz, H-19β), 3.66 (1H, s, H-20), 2.40, 2.52 (each 1H, dd, *J*=7.1, 14.0 Hz, NCH_2CH_3), 1.04 (3H, t, *J*=7.1 Hz, NCH_2CH_3)
A II 1-5 (11α-hydroxylepenine) (*116*)	4.13 (1H, dd, *J*=7.0, 10.9 Hz, H-1), 1.71, 2.40 (each 1H, m, H_2-2), 1.33 (1H, m, H-3a), 1.58 (1H, dt, *J*=2.4, 2.7 Hz, H-3b), 1.35 (1H, d, *J*=7.7 Hz, H-5), 1.26 (1H, m, H-6a), 2.76 (1H, br.d, *J*=6.1, 13.7 H, H-6b), 2.14 (1H, d, *J*=5.1 Hz, H-7), 1.34 (1H, d, *J*=9.4 Hz, H-9), 4.42 (1H, br.d, *J*=9.4 Hz, H-11), 2.10 (1H, br.s, H-12), 1.44, 1.70 (each 1H, m, H_2-13), 1.08, 1.96 (each 1H, m, H_2-14), 4.22 (1H, t, *J*=2.1 Hz, H-15), 4.93, 5.18 (each 1H, t, *J*=2.1 Hz, H_2-17), 0.71 (3H, s, H_3-18), 2.29 (1H, dd, *J*=1.9, 12.4 Hz, H-19a), 2.55 (1H, d, *J*=12.4 Hz, H-19b), 3.74 (1H, br.s, H-20), 2.45, 2.59 (each 1H, dq, *J*=7.2, 12.1 Hz, H_2-21), 1.07 (3H, t, *J*=7.2 Hz, H_3-22)
A II 1-6 (kirinine C) (*119*)	5.30 (1H, dd, *J*=7.2, 10.8 Hz, H-1β), 1.30 (1H, m, H-2α), 1.98 (1H, m, H-2β), 1.23 (1H, m, H-3α), 1.51 (1H, m, H-3β), 1.43 (1H, M, H-5), 1.20 (1H, m, H-6α), 2.91 (1H, ddd, *J*=1.3, 7.8, 14.0 Hz, H-6β), 2.17 (1H, m, H-7), 1.35 (1H, d, *J*=9.2 Hz, H-9), 3.84 (1H, dd, *J*=1.4, 9.2 Hz, H-11), 2.15 (1H, m, H-12), 1.48 (1H, m, H-13α), 1.69 (1H, m, H-13β), 1.96 (1H, m, H-14α), 1.25 (1H, m, H-14β), 4.28 (1H, br.s, H-15), 5.22 (2H, t, *J*=2.0 Hz, H_2-17), 0.98 (3H, s, H_3-18), 7.25 (1H, s, H-19), 4.67 (1H, br.s, OH), 1.86 (1H, br.s, OH), 1.81 (1H, br.s, OH), 2.05 (3H, s, OAc)
A II 1-7 (11-acetyllepenine) (*120*)	0.70 (3H, s, H_3-18), 1.05 (3H, t, *J*=7.5 Hz, NCH_2CH_3), 2.08 (3H, s, OAc), 3.85 (1H, dd, *J*=5.0 Hz, H-1β), 4.32 (1H, d, *J*=2.2 Hz, H-15α), 4.97, 5.23 (each 1H, d, *J*=2.2 Hz, H_2-17), 5.52 (1H, d, H-11α)

TABLE XXIX (*continued*)

A II 1-8 (kirinine A) (*122, 121*)	4.11 (1H, dt, *J*=6.9, 10.8 Hz, H-1β), 1.82, 2.35 (each 1H, m, H_2-2), 1.32, 1.64 (each 1H, m, H_2-3), 1.37 (1H, d, *J*=7.6 Hz, H-5), 1.25 (1H, m, H-6α), 2.74 (1H, dd, *J*=7.6, 13.0 Hz, H-6β), 2.21 (1H, m, H-7), 1.37 (1H, d, *J*=9.5 Hz, H-9), 4.40 (1H, dd, *J*=7.0, 8.6 Hz, H-11), 2.21 (1H, m, H-12), 1.47, 1.72 (each 1H, m, H_2-13), 1.14, 1.94 (each 1H, m, H_2-14), 5.35 (1H, t, *J*=2.2 Hz, H-15α), 4.88 (1H, t, *J*=2.2 Hz, H-17a), 4.93 (1H, t, *J*=2.2 Hz, H-17b), 0.64 (3H, s, H_3-18), 2.23, 2.50 (each 1H, m, H_2-19), 3.62 (1H, br.s, H-20), 2.30-2.50 (2H, m, NCH_2CH_3), 0.96 (3H, t, *J*=7.2 Hz, NCH_2CH_3), 2.10 (3H, s, OAc), 2.50 (1H, br.s, OH), 2.08 (1H, d, *J*=7.7 Hz, OH)
A II 1-9 (lepedine) (*117*)	0.71 (3H, s, H_3-18), 1.07 (3H, t, *J*=7 Hz, *N*-CH_2CH_3), 3.60 (1H, s, H-20), 3.95 (1H, d, *J*=9 Hz, H-11), 4.11 (1H, s, H-15), 4.88, 5.13 (each 1H, s, H_2-17), 3.31 (3H, s, 1-OCH_3)
A II 1-10 (cordizine) (*123*)	0.64 (3H, ds, H_3-18), 0.97 (3H, t, *J*=7.0 Hz, NCH_2CH_3), 1.16 (3H, d, *J*=8.0 Hz, H_3-17), 3.20 (1H, br.s, H-20)
A II 1-11 (dictyzine, dictysine) (*130*)	1.40 (1H, m, $J_{2\alpha,\,1\beta}$=14.4 Hz, $J_{2\alpha,\,1\beta}$=8.0 Hz, H-1β), 1.88 (1H, m, d, *J*=12.5 Hz, H-1α), 2.23 (1H, m, $J_{2\alpha,\,2\beta}$=12.7 Hz, H-2β), 1.43 (1H, m, $J_{2\alpha,\,2\beta}$=12.7 Hz, $J_{2\alpha,\,1\beta}$=8.8 Hz, H-2α), 1.20 (1H, m, $J_{3\beta,\,2\alpha}$=7.5 Hz, H-3β), 1.54 (1H, m, $J_{3\alpha,\,3\beta}$=12.0 Hz, $J_{3\alpha,\,2\alpha}$=4.1 Hz, H-2α, $J_{3\alpha,\,2\beta}$=2.2 Hz, H=3α), 1.10 (1H, br.d, *J*=7.8 Hz, H-5), 2.68 (1H, dd, *J*=7.8, 13.2 Hz, H-6β), 1.18 (1H, m, H-6α), 2.10 (1H, br.d, *J*=5.4 Hz, H-7), 1.82 (1H, m, H-9), 1.60 (1H, m, H-1β), 1.23 (1H, m, H-11α), 1.61 (1H, m, H-12), 1.27 (1H, m, H-13β), 1.96 (1H, m, H-13α), 1.13 (1H, m, H-14β), 1.96 (1H, m, H-14α), 3.38 (1H, s, H-15), 3.98 (1H, d, *J*=11.7 Hz, H-17 pro *R*), 3.58 (1H, d, *J*=11.7 Hz, H-17 pro *S*), 0.70 (3H, s, H_3-18), 2.29 (1H, ABq, *J*=11.2 Hz, H-19α), 2.42 (1H, ABq, *J*=11.2 Hz, H-19β), 3.30 (1H, s, H-20), 2.26 (3H, s, NCH_3)
A II 1-13 (macrocontrine) (*127*)	0.81 (3H, s, H_3-18), 1.11 (3H, t, *J*=7 Hz, NCH_2CH_3), 3.52, 4.00 (each 1H, ABq, *J*=11.5 Hz, H_2-17), 3.90 (1H, s, H-15)*, 3.76 (1H, br.m, W1/2=~10 Hz, H-2β)*, 3.19 (1H, d, *J*=4.5 Hz, H-3β)*

TABLE XXIX (*continued*)

A II 1-14 (lassiocarpine) (*131*)	4.83 (1H, dd, *J*=5.7, 10.9 Hz, H-1), 2.00, 2.85 (each 1H, m, H_2-2), 1.54 (1H, d, *J*=12.2 Hz, H-3α), 1.38 (1H, m, H-3β), 1.58 (1H, d, *J*=7.3 Hz, H-5), 3.61 (1H, dd, *J*=7.3, 13.6 Hz, H-6), 1.37 (1H, m, H-6), 2.28 (1H, s-like, H-7), 2.53 (H, d, *J*=8.9 Hz, H-9), 5.53 (1H, d, *J*=8.9 Hz, H-11), 2.65 (1H, br.s, H-12), 1.76 (1H, s-like, H-13), 2.62 (1H, m, H-13), 1.77, 2.28 (each 1H, m, H_2-14), 4.66 (1H, d, *J*=3.4 Hz, H-15), 5.77, 5.63 (each 1H, d, *J*=11.4 Hz, H-17), 0.72 (3H, s, H_3-18), 2.27, 2.56 (each 1H, ABq, *J*=10.9 Hz, H_2-19), 4.15 (1H, s, H-20), 2.39, 2.55 (each 1H, m, NCH_2CH_3), 1.05 (3H, t, *J*=7.6 Hz, NCH_2CH_3), 8.26 (2H, d, *J*=7.6 Hz); 7.25 (2H, dd, *J*=7.6, 7.6 Hz), 7.42 (1H, dd, J=7.6, 7.6 Hz) (OBz)
A II 1-15 (dehydrodictysine) (*125*)	0.64 (3H, s, H_3-18), 1.40, 1.48 (3H, s, 3×OCH_3), 2.18 (3H, s, NCH_3), 3.14 (1H, s, H-20), 3.75, 3.91 (each 1H, d, *J*=10 Hz, H_2-17)
A II 1-16 (gomandonine) (*132*)	0.71 (3H, s, H_3-18), 2.25 (3H, s, NCH_3), 2.66 (1H, d, *J*=6.3 Hz, H-17b), 3.47 (1H, brd, J_1=8.2 Hz, J_2=13.8 Hz, H-6β), 3.63 (1H, d, *J*=6.3 Hz, H-17a), 3.89 (1H, br.s, H-20), 4.13 (1H, dd, *J*=6.3, 10.9 Hz, H-1), 4.37 (1H, dd, *J*=4.4, 8.4 Hz, H-13), 5.00 (1H, s, H-15)
A II 1-17 (gomandonine 13-*O*-acetate) (*133*)	0.70 (3H, s, H_3-18), 2.06 (3H, s, OAc), 2.27 (3H, s, NCH_3), 2.48 (1H, d, *J*=4.5 Hz, H-17a), 3.12 (1H, d, *J*=4.5 Hz, H-17b), 3.51 (1H, br.s, H-20), 3.84 (1H, dd, *J*=6.5, 9.5 Hz, H-1), 4.18 (1H, br.s, H-15), 4.91 (1H, dd, *J*=4.0, 8.8 Hz, H-13)
A II 1-18 (yesoxine) (*134*)	0.71 (3H, s, H_3-18), 2.06 (6H, s, 2×OAc), 2.30 (3H, s, NCH_3), 2.42 (1H, d, *J*=4.9 Hz), 3.10 (1H, d, *J*=4.9 Hz), 4.21 (1H, s), 4.85 (1H, dd, *J*=4.3, 8.3 Hz), 5.05 (1H, dd, *J*=6.3, 10.9 Hz)
A II 1-19 (corumdizinine) (*135*)	0.61 (3H, s, H_3-18), 2.13 (3H, s, NCH_3), 3.17 (1H, brs, H-20), 3.37, 4.32 (each 1H, d, *J*=8.0 Hz, H_2-17), 3.91 (1H, s, H-15α), 4.49, 4.88 (each 1H, s, CH_2O_2)
A II 1-20 (corumdizine) (*136*)	0.64 (3H, s, H_3-18), 0.96 (3H, t, *J*=7.0 Hz, NCH_2CH_3), 3.26 (1H, br.s, H-20), 3.40, 4.35 (each 1H, d, *J*=8.0 Hz, H_2-17), 3.92 (1H, s, H-15α), 4.51, 4.93 (each 1H, s, CH_2O_2)
A II 2-1 (lepenine *N*-oxide) (*137*)	0.77 (3H, s, H_3-18), 1.32 (3H, t, *J*=7 Hz, NCH_2CH_3), 4.91, 5.15 (each 1H, br.s, H_2-17)
A II 2-2 (paniculamine) (*139*)	0.82 (3H, s, H_3-18), 1.33 (3H, t, *J*=7.5 Hz , NCH_2CH_3), 2.78 (1H, q, *J*=7.5 Hz, H-21), 3.00-4.00 (1H, m, H-21), 3.11, 3.36 (each 1H, d, *J*=13 Hz, H_2-19), 3.67, 3.90 (each 1H, d, *J*=12 Hz, H_2-17), 3.97-4.10 (3H, m, H-1, H-15, H-20)

TABLE XXIX (*continued*)

A II 3a-1 (kirinine B) (*119*)	4.19 (1H, d, *J*=5.3 Hz, H-1β), 1.24 (1H, m, H-2α), 1.83 (1H, m, H-2β), 1.56 (1H, m, H-3α), 1.63 (1H, m, H-3β), 1.61 (1H, m, H-5), 1.67 (1H, m, H-6α), 2.35 (1H, ddd, *J*=2.0, 8.5, 12.6 Hz, H-6β), 1.84 (1H, m, H-7), 1.28 (1H, d, *J*=9.6 Hz, H-9), 3.74 (1H, dd, *J*=6.8, 9.6 Hz, H-11), 2.21 (1H, dd, *J*=5.2, 5.3 Hz, H-12), 1.47 (1H, m, H-13α), 1.71(1H, m, H-13β), 1.97 (1H, ddd, *J*=7.0, 11.7, 14.0 Hz, H-14α), 1.21 (1H, m, H-14α), 1.21 (1H, m, H-14β), 4.28 (1H, dt, *J*=2.0, 2.0, 6.8 Hz, H-15), 5.04 (1H, t, *J*=2.0 Hz, H-17a), 5.23 (1H, t, *J*=2.0 Hz, H-17b), 0.78 (3H, s, H_3-18), 3.68 (1H, s, H-19), 3.04 (1H, dd, *J*=2.1, 4.1 Hz, H-20), 2.63-2.69 (2H, m, NCH_2CH_3), 0.99 (3H, t, *J*=7.3 Hz, NCH_2CH_3), 1.76 (1H, d, *J*=6.8 Hz, OH), 1.40 (1H, d, *J*=6.8 Hz, OH)
A II 3a-2 (11-acetyl-1, 19-epoxydenudatine) (*138*)	4.00 (1H, d, *J*=5.3 Hz, H-1), 1.46 (1H, m, H-2a), 1.78 (1H, m, *J*=5.3 Hz, H-2b), 1.24 (1H, m, H-3a), 1.52 (1H, m, H-3b), 1.20 (1H, ddd, *J*=1.3, 3.0, 8.4 Hz, H-5), 2.45 (1H, ddd, *J*=1.5, 8.4, 12.5 Hz, H-6a), 1.67 (1H, ddd, *J*=3.0, 5.1, 12.5 Hz, H-6b), 1.88 (1H, dd, *J*=1.6, 5.1 Hz, H-7), 1.72 (1H, d, *J*=10.5 Hz, H-9), 4.84 (1H, dd, *J*=0.9, 10.5 Hz, H-11), 2.33 (1H, m, *J*=0.9 Hz, H-12), 1.50 (1H, m, H-3a), 1.87 (1H, m, H-13b), 1.28 (1H, m, H-14a), 2.07 (1H, ddd, *J*=6.9, 11.6, 13.9 Hz, H-14b), 4.31 (1H, ddd, *J*=2.1, 2.4, 6.9 Hz, H-15), 5.24 (1H, dd, *J*=1.1, 2.1 Hz, H-17a), 5.00(1H, dd, *J*=1.1, 2.4 Hz, H-17b), 0.81 (3H, s, H_3-18), 3.69 (3H, s, H_3-19), 2.68 (1H, dd, *J*=7.2, 11.8 Hz, NCH_2CH_3), 1.01 (3H, t, *J*=7.2 Hz, NCH_2CH_3), 2.00 (3H, s, OAc), 2.34 (1H, d, *J*=6.9 Hz, OH)
A II 3a-3 (vilmorinianine) (*140*)	0.83 (3H, s, H_3-18), 1.00 (3H, t, *J*=6.8 Hz, NCH_2CH_3), 2.41 (1H, d, *J*=6.9 Hz, H-15), 3.26 (1H, d, *J*=10.4 Hz, H-11α), 3.31 (3H, s, CH_3O-11), 2.66 (2H, dd, *J*=6.8, 12 Hz, NCH_2), 3.69 (1H, s, H-19), 4.04 (1H, d, *J*=5.2 Hz, H-1β), 4.25 (1H, br.s, H-15), 3.04 (1H, br.s, H-20), 5.00, 5.23 (each 1H, d, *J*=2.1 Hz, H_2-17)

TABLE X X X

^{1}H NMR DATA OF HETIDINE TYPE DITERPENOID ALKOLOIDS (AIV)

code (name) (*ref*)	δ_H
AIV1a-1 (trabzonine) (*141*)	1.84 (2H, m, H_2-1), 1.52 (2H, m, H_2-2), 1.33 (1H, H-3α), 1.30 (1H, H-3β), 1.18 (1H, H-5), 2.16 (1H, H-6α), 1.93 (1H, H-6β), 4.24 (1H, H-7), 1.55 (1H, H-9), 1.92 (1H, H-11α), 1.56 (1H, H-11β), 2.26 (1H, H-12), 1.62 (1H, H-13α), 1.49 (1H, H-13β), 2.11 (1H, H-14), 4.52 (1H, H-15), 4.98 (1H, H-17a), 4.87 (1H, H-15b), 0.97 (3H, H_3-18), 2.73 (1H, H-19α), 2.13 (1H, H-19β), 2.35 (1H, H-20), 2.86 (1H, H-21a), 2.51 (1H, H-21b), 3.17 (1H, H-22a), 3.54 (1H, H-22b)
AIV1a-2 (yesonine) (*142*) *	1.47 (3H, s, H_3-18), 2.46 (3H, s, NCH_3), 3.95 (1H, s, H-15), 4.08 (1H, d, *J*=5.0 Hz, H-11), 5.15, 5.26 (each 1H, s, H_2-17)
AIV1a-3 (yesoline) (*143*) *	1.45 (3H, s, H_3-18), 2.45 (3H, s, NCH_3), 3.92, 3.93 (each 3H, s, $OCH_3\times2$), 4.16 (1H, d, *J*=5.0 Hz, H-11), 5.23, 5.41 (each 1H, s, H_2-17), 5.66 (1H, s, H-15), 6.86 (1H, d, *J*=8.6 Hz); 7.52 (1H, d, *J*=2.0 Hz); 7.59 (1H, dd, *J*=2.0, 8.6 Hz) (aromatic protons)
AIV1a-4 (sczukitine) (*144*)	1.50 (1H, dd, *J*=5, 15.0 Hz, H-1), 2.00 (1H, d, *J*=15 Hz, H-1), 5.14 (1H, ds, W1/2=10 Hz, H-2), 1.66 (1H, s, H-5), 2.28 (1H, d, *J*=18.4 Hz, H-7), 2.79 (1H, d, *J*=18 Hz, H-7), 2.13 (1H, dd, *J*=2, 10 Hz, H-9), 1.87, 2.05 (each 1H, m, H_2-11), 2.99 (1H, d, *J*=3 Hz, H-12), 2.81 (1H, d, *J*=3 Hz, H-14), 5.57 (1H, s, H-15), 5.02 (1H, d, *J*=2 Hz, H_2-17), 1.47 (3H, s, H_3-18), 2.57, 2.72 (each 1H, d, *J*=11 Hz, H_2-19), 2.40 (3H, s, N*CH*$_3$), 2.06 (3H, s, OAc), 1.16 (3H, d, *J*=6.7 Hz); 2.38-2.43 (1H, m); 1.70 (2H, m); 0.93 (3H, t, *J*=7.0 Hz) (OC-*CH*(*CH*$_3$)-*CH*$_2$-*CH*$_3$)
AIV1a-5 (spirafine III) (*145*)	1.77 (2H, m, H_2-1), 1.57 (2H, m, H_2-2), 1.25 (2H, m, H_2-3), 1.57 (1H, s, H-5), 2.66 (1H, dd, *J*=1.5, 11.9 Hz, H_2-7), 1.57 (1H, s, H-9), 2.02 (2H, m, H_2-11), 2.13 (1H, m, H-12), 1.62 (2H, m, H_2-13), 1.62 (2H, m, H_2-14), 2.19 (2H, s, H_2-15), 4.49, 4.66 (each 1H, br.s, H_2-17), 1.49 (3H, s, H_3-18), 2.66 (2H, ABq, *J*=11.9 Hz, H_2-19), 2.20 (1H, s, H-20), 3.05 (2H, m, H_2-21), 3.72 (2H, m, H_2-22)

* The star marks in Tables XXX and XXXIII indicate no assignments or the reassignments by us.

TABLE X X X (*continued*)

AIV1a-6 (spirafine II) (*145*)	1.63 (2H, m, H_2-1), 1.52 (2H, m, H_2-2), 1.25 (2H, m, H_2-3), 1.52 (1H, s, H-5), 2.06, 2.84 (each 1H, ABq, H_2-7), 1.53 (1H, s, H-9), 1.85 (2H, m, H_2-11), 2.19 (1H, m, H-12), 1.85 (2H, m, H_2-13), 1.85 (1H, m, H_2-14), 5.25 (1H, s, H_2-15), 1.76 (3H, s, H_3-17), 1.50 (3H, s, H_3-18), 2.67, 3.45 (each 1H, ABq, *J*=11.9 Hz, H_2-19), 2.33 (1H, s, H-20), 3.05 (2H, m, H_2-21), 3.73 (2H, m, H_2-22)
AIV1a-7 (racemuldine) (*146*)	1.82 (1H, dd, *J*=4.4, 14.2 Hz, H-1β), 2.14 (1H, dd, *J*=2.0, 14.2 Hz, H-1α), 3.92 (1H, hept, W1/2=2.0 Hz, H-2β), 3.35 (1H, d, *J*=5.6 Hz, H-3), 1.85 (1H, s, H-5), 2.79 (2H, br.s, H_2-7), 1.76 (1H, dt, *J*=2.0, 10.4 Hz, H-9), 1.55 (1H, ddd, *J*=2.0, 10.4, 14.0 Hz, H-11β), 1.99 (1H, ddd, *J*=1.6, 3.0, 14.0 Hz, H-11α), 2.98 (1H, m, W1/2=5.7 Hz, H-12), 2.30 (1H, d, *J*=2.8 Hz, H-14), 5.50 (1H, s, H-15), 1.86 (3H, d, *J*=2.0 Hz, H_3-17), 1.16 (3H, s, H_3-18), 1.88, 2.64 (each 1H, ABq, *J*=12.4 Hz, H_2-19), 3.06 (1H, d, *J*=3.2 Hz, H-20), 2.45 (3H, s, NCH_3)
AIV1a-8 (delcarduchol) (*147*)	3.26 (1H, d, *J*=13 Hz, H-1α), 1.30 (1H, d, *J*=13 Hz, H-1β), 2.90 (1H, d, *J*=12 Hz, H-3α), 1.90 (1H, d, *J*=12 Hz, H-3β), 1.86 (1H, br.s, H-5), 2.85 (1H, m, H-6α), 1.60 (1H, m, H-6β), 2.75 (1H, m, H-7α), 1.65 (1H, m, H-7β), 2.04 (1H, dd, *J*=4, 7 Hz, H-9), 1.80 (1H, m, H-11α), 2.35 (1H, m, H-11β), 2.60 (1H, br.s, *J*=3 Hz, H-12), 1.65 (1H, m, H-14), 3.95 (1H, br.s, H-15α), 4.97, 5.01(each 1H, t, *J*=1.5 Hz, H_2-17), 1.00 (3H, s, H_3-18), 2.16 (1H, d, *J*=13 Hz, H-19α), 1.98 (1H, d, *J*=13 Hz, H-19β), 2.97 (1H, br.s, H-20), 2.37 (3H, s, NCH_3)
AIV1a-9 (vakhmadine) (*148*) (D_2O)	1.40 (3H, s, H_3-18), 2.58 (3H, s, NCH_3), 2.97, 4.05 (each 1H, d, *J*=11.7 Hz, H_2-19),3.33 (1H, d, *J*=4.3 Hz, H-3β), 3.93 (1H, d, *J*=11.0 Hz, H-13β), 3.97 (1H, m, H-2β), 4.22 (1H, s, H-20), 4.59, 4.73 (each 1H, s, H_2-17)
AIV1a-10 (panicutine) (*149*)	1.48 (3H, s, H_3-18), 1.45-1.55 and 1.7~1.8 (each 1H, AB, ABX, $\Delta\delta_{AB}$=90 Hz, H_2-3), 1.60 (1H, s, H-9), 1.55~1.6 and 2.0~2.05 (each 1H, 2m, AB, ABX, $\Delta\delta_{AB}$=150 Hz, H_2-1), 1.80-1.9 and 2.0-2.1 (each 1H, 2m, AB, ABX, $\Delta\delta_{AB}$=70 Hz, H_2-3), 1.99-2.07 (2H, m, H_2-14), 2.05 (3H, s, OAc), 2.26 and 2.69 (each 1H, ABq, *J*=18 Hz, $\Delta\delta_{AB}$=160 Hz, H_2-7), 2.35 (3H, s, NCH_3), 2.35, 2.49 (each 1H, ABq, *J*=16 Hz, H_2-15), 2.50 (1H, d, W1/2=5 Hz, H-20), 2.54, 2.68 (each 1H, ABq, *J*=10 Hz, H_2-19), 2.60 (1H, s, H-5), 2.92 (1H, m, W1/2=7 Hz, H-12), 4.82, 4.98 (each 1H, W1/2=4 Hz, H_2-17), 5.14 (1H, m, W1/2=10 Hz, H-2)

TABLE X X X (*continued*)

AIV1a-11 (deacetylheterophylloidine) (*153*)	2.02 (1H, dd, *J*=4.4, 13.8 Hz, H-1α), 1.61 (1H, dd, *J*=5.5, 13.8 Hz, H-1β), 3.92 (1H, br.s, W1/2=5.0 Hz, H-2β), 1.80 (1H, m, H-3α), 1.72 (1H, m, H-3β), 1.85 (1H, s, H-5), 2.41 (2H, m, H_2-7), 1.91 (1H, m, H-9), 2.07 (1H, m, H-11α), 1.85 (1H, m, H-11β), 2.92 (1H, br.d, W1/2=7.5 Hz, H-12), 2.60 (1H, br.t, W1/2=6.0 Hz, H-14), 2.35 (1H, ABq, *J*=18.1 Hz, H-15α), 2.49 (1H, ABq, *J*=18.1 Hz, H-15β), 4.76 (1H, br.s, W1/2=5.0 Hz, H-17a), 4.94 (1H, br.s, W1/2=5.0 Hz, H-17b), 1.08 (3H, s, H_3-18), 2.10 (1H, ABq, *J*=8.0 Hz, H-19α), 2.40 (1H, ABq, *J*=8.0 Hz, H-19β), 3.21 (1H, s, H-20), 2.45 (3H, s, NCH_3), 6.62 (1H, br.s, H-2)
AIV1a-12 (heterophyllidine) (*150, 153, 154*)	1.50 (3H, s, H_3-18), 2.06 (3H, s, OAc), 2.57 (3H, s, NCH_3), 4.72, 4.99 (each 1H, br.s, H_2-17), 5.16 (1H, m, W1/2=11 Hz, H-2β)
AIV1a-13 (hetidine) (*152*)	2.15 (1H, dd, *J*=3.5, 15.4 Hz, H-1α), 1.73 (1H, dd, *J*=3.5, 14.5 Hz, H-1β), 3.95 (1H, br.t, *J*=3.5, 3.5, 3.5 Hz, H-2β), 3.36 (1H, d, *J*=5.3 Hz, H-3β), 1.83 (1H, s, H-5), 2.48 (2H, m, H_2-7), 1.92 (1H, m, H-9), 2.07 (1H, m, H-11α), 1.83 (1H, m, H-11β), 2.95 (1H, br.d, W1/2=7.0 Hz, H-12), 2.61 (1H, br.d, W1/2=3.0 Hz, H-14), 2.38, 2.49 (each 1H, ABq, *J*=18.0 Hz, H_2-15), 4.79 (1H, br.s, W1/2=7.0 Hz, H-17a), 4.96 (1H, br.s, W1/2=7.0 Hz, H-17b), 1.18 (3H, s, H_3-18), 1.94, 2.73 (each 1H, ABq, *J*=12.4 Hz, H_2-19), 3.17 (1H, br.d, W1/2=3.0 Hz, H-20), 2.47 (3H, s, NCH_3)
AIV1a-14 (episcopalidine) (*158, 157*)	1.58 (3H, s, H_3-18), 1.78 (1H, ABX, J_{ab}=16 Hz, 4.5 Hz, H-1β), 2.02 (1H, ABX, J_{AX}=16 Hz, J_{BX}=2.2 Hz, H-1α), 2.04 (3H, s, OAc), 2.44 (3H, s, *N*CH_3), 2.76 (1H, ABq, *J*=18 Hz, H-7), 2.12 (1H, ABq, *J*=18 Hz, H-7), 2.52 (1H, ABq, *J*=12 Hz, H-9), 2.76 (1H, s, H-5), 2.92 (1H, d, *J*=3 Hz, H-20), 3.30 (1H, ABq, *J*=12 Hz, H-19), 4.82 (1H, t, *J*=2.2 Hz, H-17), 4.88 (1H, d, *J*=4.5 Hz, H-3β), 4.98 (1H, t, *J*=7.2 Hz, H-17), 5.53 (1H, ddd, *J*=2.2, 4.5, 4.5 Hz, H-2β), 7.44, 7.58, 7.97 (5H, m, Ar-H)
AIV1a-15 (contorine) (*161*)*	1.57 (3H, s, H_3-18), 2.44 (3H, s, NCH_3), 2.04 (3H, s, OAc), 3.30 (1H, ABq, *J*=12.1 Hz, H-19), 3.86 (3H, s, OCH_3-4"), 4.83 (1H, ddd, *J*=0.7, 2.2, 2.2 Hz, H-17), 4.85 (1H, d, *J*=4.5 Hz, H-3β), 5.51 (1H, ddd, *J*=2.3, 4.5, 4.5 Hz, H-2β), 4.99 (1H, t, *J*=2.3 Hz, H-17), 6.92, 7.93 (each 1H, AA', BB', *J*=9.0 Hz, H_2-2", 6", H_2-3", 5")

TABLE XXX (*continued*)

AIV1a-16 (contorsine) (*161*)*	1.50 (3H, s, H_3-18), 2.07 (3H, s, OAc), 2.42 (3H, s, NCH_3), 1.15, 1.16 [each 3H, d, *J*=7.0 Hz, CH-*(CH_3)$_2$*], 2.46, 3.16 (each 1H, ABq, *J*=11.7 Hz, H_2-19), 4.62 (1H, d, *J*=4.5 Hz, H-3β), 4.82, 4.98 (each 1H, t, *J*=2.5 Hz, H_2-17), 5.41(1H, ddd, *J*=2.3, 4.5, 4.5 Hz, H-2β)
AIV1a-17 (contortine) (*161*)*	0.89 (3H, t, *J*=7.4 Hz, *CH_3*-CH_2), 1.13 (3H, d, *J*=7.0 Hz, CH-*CH_3*), 1.52 (3H, s, H_3-18), 2.07 (3H, s, OAc), 2.45 (3H, s, NCH_3), 2.50, 3.21 (each 1H, ABq, *J*=12.0 Hz, H_2-19), 4.64 (1H, d, *J*=4.4 Hz, H-3β), 4.83, 4.98 (each 1H, t, *J*=2.0 Hz, H_2-17), 5.41 (1H, ddd, *J*=2.3, 4.4, 4.4 Hz, H-2β)
AIV1a-18 (sczukidine) (*162, 144*) (pyridine-d_5)	1.49 (1H, dd, *J*=4, 14 Hz, H-1), 2.15 (2H, d, *J*=14 Hz, H-1), 4.26 (1H, br.s, W1/2=10 Hz, H-2), 1.57 (1H, dd, *J*=4.6, 15 Hz), 1.86 (2H, d, *J*=14 Hz, H_2-3), 1.78 (1H, s, H-5), 2.82 (1H, d, *J*=19 Hz), 3.37 (2H, d, *J*=19 Hz, H_2-7), 2.02 (1H, d, *J*=10 Hz, H-9), 1.76 (1H, m), 2.08 (2H, dd, *J*=4, 10 Hz, H_2-11), 3.13 (1H, d, *J*=4 Hz, H_2-12), 3.15 (1H, s, H-14), 4.53 (1H, s, H-15), 5.26, 5.52 (1H, s, H_2-17), 1.54 (3H, s, H_3-18), 2.46, 3.71 (each 1H, d, *J*= 11 Hz, H_2-19), 3.40 (1H, s, H-20), 2.30 (3H, s, NCH_3)
($CDCl_3$)	1.49 (1H, dd, *J*=5, 15 Hz, H-1), 2.02 (1H, d, *J*=15 Hz, H-1), 5.19 (1H, br.s, W1/2=10 Hz, H-2), 1.46 (1H, dd, *J*=5, 15 Hz, H-3), 1.78 (1H, m, H-3), 1.46 (1H, s, H-5), 2.73, 3.44 (each 1H, ABq, *J*=13 Hz, H_2-7), 2.07 (1H, d, *J*=11 Hz, H_2-9), 1.68 (1H, d, *J*=11 Hz, H_2-11), 1.99 (1H, m, H-11), 3.14 (1H, d, *J*=3 Hz, H-12), 3.09 (1H, d, *J*=2 Hz, H-14), 4.54 (1H, s, H-15), 5.28, 5.58 (each 1H, s, H_2-17), 1.59 (3H, s, H_3-18), 2.52, 2.63 (each 1H, ABq, *J*= 12 Hz, H_2-19), 2.82 (1H, s, H-20), 2.26 (3H, s, NCH_3), 1.99 (3H, s, OAc)
AIV1a-19 (sczukinine) (*162, 144*)	1.50 (1H, dd, *J*=5, 15 Hz, H-1), 2.00 (1H, d, *J*=15 Hz, H-1), 5.14 (1H, br.s, W1/2=10 Hz, H-2), 1.60 (1H, dd, *J*=5, 15 Hz, H-3), 1.66 (1H, m, H-5), 2.28, 2.79 (each 1H, ABq, *J*=18 Hz, H_2-7), 2.13 (1H, dd, *J*=2, 10 Hz, H-9), 1.87, 2.05 (each 1H, m, H_2-11), 2.99 (1H, d, *J*=3 Hz, H-12), 2.81 (1H, d, *J*=3 Hz, H-14), 5.57 (1H, s, H-15), 5.02, 5.17 (each 1H, d, *J*=2 Hz, H_2-17), 1.47 (3H, s, H_3-18), 2.57, 2.72 (each 1H, ABq, *J*=11 Hz, H_2-19), 2.69 (1H, br.s, W1/2=8 Hz, H-20), 2.40 (3H, s, NCH_3), 2.06 (3H, s, OAc), 1.16 (3H, d, *J*=6.7 Hz, CH-*CH_3*), 2.38-2.43 (1H, m, *C*HCH_3), ~1.70 (2H, m, *CH_2*CH_3), 0.93 (3H, t, *J*=7.0 Hz, *CH_2*CH_3)

TABLE X X X (*continued*)

AIV1a-20 (miyaconitine) (*164*)	1.55 (3H, s, H_3-18), 2.14 (3H, s, OAc), 2.40 (3H, s, NCH_3), 3.97 (1H, s, OH), 4.81 (1H, br.s, W1/2=10 Hz, H-2β), 4.95 (2H, br.d, H_2-17)
AIV1a-21 (vilmorrianone) (*163*)	1.42 (3H, s, H_3-18), 2.08 (3H, s, OAc), 2.28 (3H, s, NCH_3), 2.43, 2.83 (each 1H, d, *J*=12 Hz, H_2-15), 2.53, 3.11 (each 1H, br.d, *J*=20 Hz, H_2-19), 2.96 (1H, d, *J*=2 Hz, H-20), 3.00 (1H, s, H-5), 4.96, 5.06 (each 1H, br.s, H_2-17), 5.23 (1H, m, H-2)
AIV1a-22 (miyaconitinone) (*164*)	1.38 (3H, s, H_3-18), 2.28 (3H, s, NCH_3), 4.97 (2H, br.d, H-2β)
AIV2a-1 (septatisine) (*171~173*)	0.90 (1H, ddd, *J*=5.4, 13.3, 13.3 Hz, H-1β), 2.20 (1H, m, H-1α), 1.45 (1H, m, H-2β), 1.55 (1H, m, H-2α), 1.11 (1H, ddd, 5.1, 13.2, 13.2 Hz, H-3β), 1.25 (1H, m, H-5), 2.10 (1H, m, H-6β), 2.28 (1H, ddd, *J*=8.7, 13.3, 13.4 Hz, H-6α), 4.21 (1H, dd, *J*=7.7, 8.7 Hz, H-7), 1.45 (1H, m, H-9), 1.55 (1H, m, H-1β), 2.10 (1H, m, H-11α), 2.20 (1H, br.s, H-12), 1.36 (1H, dddd, *J*=2.0, 2.2, 12.2, 13.4 Hz, H-13β), 1.98 (1H, m, H-13α), 2.01 (1H, m, H-14), 4.49 (1H, br.s, H-15), 4.83 (1H, dd, *J*=1.2, 2.1 Hz, H-17a), 4.94 (1H, dd, *J*=1.2, 2.1 Hz, H-17b), 1.00 (3H, s, H_3-18), 2.35, 2.58 (each 1H, ABq, *J*=11.4 Hz, H_2-19), 2.81 (1H, ddd, *J*=12.4, 6.9, 2.2 Hz, H-21α), 3.03 (1H, ddd, *J*=12.4, 12.1, 8.6 Hz, H-21β), 3.78 (1H, ddd, *J*=13.6, 8.6, 2.2 Hz, H-22α), 3.56 (1H, ddd, *J*=13.6, 8.6, 2.2 Hz, H-22β)
AIV2a-2 (coriphine) (*174*)	1.00 (3H, s, H_3-18), 2.26 (3H, s, NCH_3), 2.42, 2.61 (each 1H, d, *J*=11.4 Hz, H_2-19), 2.60 (2H, m, H_2-2), 2.84 (1H, ddd, *J*=2.0, 7.0, 12.3 Hz, H-7a), 3.02, 3.10 (each 1H, dt, *J*=3.9 Hz, H_2-21), 3.55, 3.78 (each 1H, s, H_2-22), 5.38 (1H, s, H-15), 5.87 (1H, d, *J*=10 Hz, H-5'), 6.60 (1H, dd, *J*=1.8, 10 Hz, H-4')
AIV2a-3 (spiradine D) (*88*, *175*)	1.46 (1.50) (3H, s, H_3-18), 3.69 (4.21) (1H, s, H-19), 4.54, 4.70 (each 1H, t, *J*=2 Hz, H_2-17)
AIV2a-4 (spirasine II) (*176*)	1.40 (1.43) (3H, s, H_3-18), 3.20-4.07 (4H, m), 3.92 (4.20), (1H, s, H-19), 4.52, 4.62 (each 1H, br.s, H_2-17)
AIV2a-5 (spirasine I) (*176*)	1.46 (1.49), (3H, s, H_3-18), 1.86 (3H, s, H_3-17), 3.00-4.0 (4H, m), 3.82 (4.29) (1H, s, H-19), 5.29 (1H, br.s, H-15)
AIV2a-6 (spirasine V) (*177*)	1.32 (3H, s, H_3-17), 1.44 (3H, br.s, H_3-18), 3.4-4.25 (5H, m)

TABLE XXX (*continued*)

AIV2a-7 (spirasine VI) (*177*)	1.33 (3H, s, H_3-17), 1.48 (3H, br.s, H_3-18), 3.40-4.15 (4H, m), 3.95 (4.25) (1H, s, H-19), 1.47 (1.51) (3H, s, 3H-18, after addition of D_2O) (Ist ^1H nmr showed a pair of epimer at C-19)
AIV2a-8 (spirasine VII) (*176*)	1.33 (3H, s, H_3-17), 1.48 (3H, br.s, H_3-18), 3.40-4.24 (5H)
AIV2a-9 (spiraedine XIII) (*176*)	1.40 (3H, s, H_3-17), 1.40 (1.44) (H_3, br.s, H_3-18), 3.00-4.00 (4H, m), 3.71 (4.22) (1H, s, H-19)
AIV2a-10 (spiredine) (*178*)	1.48 (1.52) (3H, s, H_3-17), 3.84 (4.25) (1H, s, H_3-19), 4.85, 5.02 (1H, br.s, H_2-17)
AIII2a-11 (spireine*) (*181*)	1.44 (1.47) (3H, s, H_3-18), 2.05 (2.47) (1H, d, J=9 Hz), 4.81, 4.97 (1H, br.s, H_2-17)
AIV2a-12 (spirasine III) (*178, 92*)	1.49 (1.53) (3H, s, H_3-18), 3.00-4.00 (4H, m), 3.90 (4.29) (1H,.s, H_3-19), 4.87, 5.03 (each, 1H, br.s, H_2-17)
AIV2b-1 (thalicsessine) (*182, 92*)	1.50 (3H, s, H_3-17), 2.85 (1H, t, J=5.1 Hz, OH), 3.45 (1H, ddd, J=3.4, 5.1, 14 Hz, H-21), 3.62 (1H, ddd, J=3.4, 8.0, 14.1 Hz, H-21), 3.87 (1H, m, H-22ax, changed to ddd, J=3.4, 5.1, 11.4 Hz, on addition of D_2O), 3.88 (1H, m, H-22eq, changed into ddd, J=3.4, 8.0, 14.1 Hz, on addition of D_2O), 4.85 (1H-d, J=2.4 Hz, H-17eq), 5.00 (1H, d, J=2.4 Hz, H-17e)
AIV2b-2 (carduchoron) (*147*)	2.01 (1H, dd, J=5, 12 Hz, H-1α), 1.60 (1H, brd, J=12 Hz, H-1β), 1.75 (1H, m, H-2α), 1.40 (1H, m, H-2β), 1.85 (1H, m, H-3α), 1.40 (1H, m, H-3β), 2.50 (1H, m, H-5), 2.75 (1H, d, J=18 Hz, H-7α), 2.25 (1H, d, J=18 Hz, H-7β), 1.66 (1H, s, H-9), 2.30 (1H, br.s, H-12), 1.90 (1H, m, H-13α), 1.40 (1H, m, H-13β), 1.80 (1H, m, H-14), 2.26 (1H, d, J=14 Hz, H-15α), 2.38 (1H, d, J=14 Hz, H-15β), 4.78, 4.97 (each 1H, br.s, H_2-17), 1.50 (3H, s, H_3-18), 2.02 (1H, d, J=3 Hz, H-20), 2.50 (3H, s, NCH_3)
AIV3-1 (tongolinine) (*183*)	1.05 (3H, s, H_3-18), 4.94 (2H, m, H_2-17), 7.41 (1H, s, H-19)
AIV3-2 (talassamine) (*184*)	1.00 (3H, s, H_3-18), 3.22 (1H, br.s, H-20), 3.94 (1H, q, J=10, 7 Hz, H-7), 4.53 (1H, t, J=1.5 Hz), 4.81, 4.92 (each 1H, s, H_2-17), 7.31 (1H, br.s, H-19)
AIV3-3 (talassimine) (*184*)	0.98 (3H, s, H_3-18), 1.99 (3H, s, OAc), 3.24 (1H, br.s, H-20), 4.20 (1H, t, J=1.5 Hz, H-15), 4.83, 4.92 (each 1H, s, H_2-17), 5.18 (1H, q, J=10, 7 Hz, H-7), 7.32 (1H, br.s, H-19)
AIV3-4 (talassimidine) (*184*)	1.00 (3H, s, H_3-18), 2.12 (3H, s, OAc), 3.25 (1H, br.s, H-20) 3.47 (1H, q, J=7, 10 Hz, H-17), 4.61, 4.86 (each 1H, d, J=2 Hz, H_2-17), 5.84 (1H, t, J=1.5 Hz, H-15), 7.33 (1H, br.s, H-19)

TABLE XXXI

^{1}H NMR DATA OF CARDIONIDINE TYPE DITERPENOID ALKALOIDS (AV)

Code (name) (*ref*)	δ_H
AV1-1 (cardionidine) (*187*)	1.25 (3H, s, H_3-18), 2.03 (3H, s, NCH_3), 2.07, 3.07 (each 1H, d, *J*=14.0 Hz, H-1β, H-1α), 2.10, 2.70 (each 1H, d, *J*=11.4 Hz, H_2-19), 3.37 (1H, dd, *J*=2.4, 7.0 Hz, H-9), 2.70, 2.85 (each 1H, dt, *J*=2.0, 17.0 Hz, H_2-15), 3.0 (1H, dd, *J*=2.4, 9.8 Hz, H-14), 3.29 (1H, s, H-20), 4.25 (1H, dd, *J*=2.4, 9.8 Hz, H-13β), 4.76, 4.89 (each 1H, br.s, H_2-17)
AV1-2 (vilmoridine) (*188*)	1.18 (3H, s, H_3-18), 2.72 (3H, d, *J*=3 Hz, NCH_3), 3.86 (3H, s, OAc), 4.20 (1H, br.m, H-2β), 4.86, 4.96 (each 1H, br.s, H_2-17), 16.5 (1H, br.s, COOH)

TABLE XXXII

^{1}H NMR DATA OF ALBORIONITINE TYPE DITERPENOID ALKALOIDS (AVI)

Code (name) (*ref*)	δ_H
AVI1-1 (albovionitine) (*189*)	2.08 (1H, t, *J*=4.5 Hz, H-1α), 1.11 (1H, dd, *J*=13.5, 4.5 Hz, H-1β), 1.03 (1H, m, W1/2=13 Hz, H-2α), 1.07 (1H, m, W1/2=5 Hz, H-2β), 2.40 (1H, t, H-3α), 1.75 (1H, dd, H-3β), 1.28 (1H, dd, *J*=5, 11 Hz, H-5), 1.26 (1H, dt, H-6α), 1.78 (1H, m, H-6β), 2.16 (1H, m, H-7α), 1.53 (1H, dd, *J*=3, 11 Hz, H-7β), 1.90 (1H, br.d, *J*=12 Hz, H-9), 1.70 (1H, m, H-11α), 1.85 (1H, br.d, *J*=12 Hz, H-11β), 2.29 (1H, br.s, H-12), 1.71 (1H, m, H-13α), 2.00 (1H, br.d, H-13β), 2.04 (1H, d, H-14), 4.12 (1H, br.s, H-15), 4.95, 5.04 (each 1H, br.s, H_2-17), 3.23, 4.00 (each 1H, br.d, H_2-18), 2.53, 3.12 (each 1H, d, *J*=10 Hz, H_2-19), 2.67 (2H, m, H_2-21), 3.70 (2H, m, H_2-22), 2.37 (3H, s, NCH_3)

TABLE XXXIII

^{1}H NMR DATA OF HETISINE TYPE DITERPENOID ALKALOIDS (AVII)

Code (name) (*ref*)	δ_H
AVII1a-1 (spirasine XI) (*190*)	1.13 (3H, s, H_3-18), 2.86, 3.06 (each 1H, ABq, *J*=11.5 Hz, H_2-19), 4.13 (1H, dd, *J*=3.0, 9.4 Hz, H-13β), 4.68, 4.85 (each 1H, br.s, H_2-17)
AVII1a-2 (nominine) (*191*)	1.08 (3H, s, H_3-18), 0.87 (3H, d, *J*=7.0 Hz, CH-*CH*$_3$), 3.79 (1H, brs, W1/2=7.0 Hz, H-6), 2.97 (1H, s, H-20), 2.73, 3.03 (each 1H, ABq, *J*=12 Hz, H_2-19)
AVII1a-3 (zeraconine) (*191*)	0.90 (3H, s, H_3-18), 2.19 (6H, s, 2×NCH_3), 3.10 (1H, br.s), 4.38 (2H, br.s), 5.69 (1H, br.s), 6.68, 6.95 (each 1H, d, *J*=8.5 Hz, Ar-H)
AVII1a-4 (cossonidine, davisine) (*195*, *196*)	4.19 (1H, br.s, W1/2=6 Hz, H-1α), 1.77 (1H, m, H-2β), 1.79 (1H, m, H-2α), 1.25 (1H, m, H-3α), 1.74 (1H, m, H-3β), 1.89 (1H, s, H-5), 3.40 (br.s, W1/2=6 Hz, *H*-6), 1.68 (1H, dd, *J*=3.1, 13.2 Hz, H-7α), 2.02 (1H, dd, 2.4, 13.2 Hz, H-7β), 2.01 (1H, d, *J*=11.5 Hz, H-9), 1.76 (1H, m, H-11β), 1.92 (1H, dd, *J*=4.2, 14.2 Hz, H-11α), 2.21 (1H, m, W1/2=8 Hz, H-12), 1.07 (1H, dt, *J*=2.7, 13.2, H-13α), 1.80 (1H, m, H-13β), 1.90 (1H, H-14), 4.00 (1H, s, H-15), 4.94, 4.97 (each 1H, s, H_2-17), 1.02 (3H, s, H_3-18), 2.39, 2.56 (each 1H, ABq, *J*=12.5 Hz, H_2-19), 2.49 (1H, s, H-20)
AVII1a-5 (sanyonamine) (*197*)	1.06 (3H, s, H_3-18), 2.77, 3.50 (each 1H, ABq, *J*=12.5 Hz, H_2-19), 3.63 (1H, br.s, H-6), 4.07 (1H, s, H-15), 4.31 (1H, br.s, H-2), 4.96, 4.98 (each 1H, s, H_2-17)
AVII1a-6 (kobusine) (*195*, *196*)	1.40 (1H, m, H-1β), 1.80 (1H, m, H-1α), 1.40~1.50 (1H, m, H-2β), 1.70 (1H, m, H-2α), 1.48 2H, m, H_2-3), 1.72 (1H, s, H-5), 3.14 (2H, br.s, H_2-6), 1.57 (1H, d, H-7β), 1.65 (1H, d, H-7α), 1.38 (1H, s, H-9), 4.01 (1H, d, *J*=4.8 Hz, H-11), 2.28 (1H, d, *J*=4.8 Hz, H-12), 0.91 (1H, m, H-13β), 1.90 (1H, m, H-13α), 1.78 (1H, m, H-14), 2.10 (1H, m, H-15), 4.83 (2H, d, *J*=1.8 Hz, H_2-17), 3.28, 3.43 (each 1H, ABq, *J*=10.8 Hz, H_2-18), 2.23, 2.55 (each 1H, ABq, *J*=12.5 Hz, H_2-19), 2.40 (1H, s, H-20)

TABLE XXXIII (*continued*)

AVII1a-7 (hetisine) (*167, 205*)	1.14 (3H, s, H_3-18), 1.84 (each 1H, dd, *J*=4, 16 Hz, H_2-7), 2.02 (2H, s, H_2-15), 2.13 (1H, dd, *J*=2.5, 9 Hz, H-14), 2.07 (1H, br.s, H-9), 2.40 (1H, d, *J*=2.5 Hz, H-12), 2.87, 3.87 (each 1H, ABq, *J*=11 Hz, H_2-19), 3.94 (1H, br.s, H-6), 4.14 (1H, t, H-13), 4.16 (1H, dd, H-11), 4.27 (1H, d, *J*=9 Hz, H-20), 4.60, 4.70 (each 1H, H_2-17)
AVII1a-8 (13-acetylhetisine) (*202*)	0.97 (3H, s, H_3-18), 2.18 (3H, s, OAc), 4.11 (1H, br.s, W1/2=~10 Hz), 4.20 (1H, d, *J*=9 Hz), 4.24 (2H, br.s, H-2 and H-11), 4.75, 4.92 (each 1H, br.s H_2-17), 5.20 (1H, dt, *J*=2, 10.5 Hz, H-13)
AVII1a-9 (palmasine) (*215*)	0.98 (3H, s, H_3-18), 3.38 (1H, br.s, H-6), 3.82 (1H, s, H-20), 4.24 (1H, br.m, W1/2=10.5 Hz, H-2β), 4.70, 4.91 (each 1H, s, H_2-17), 6.57, 7.79 (each 1H, d, *J*=16.0 Hz); 6.61, 7.86 (each 1H, *J*=16.1 Hz); 7.39 (3H, m); 7.49 (2H, m) [cinnamoyl group], 4.32 (1H, d, *J*=8.4 Hz, H-11β), 5.21 (1H, d, *J*=9.3 Hz, H-13α)
AVII1a-10 (palmadine) (*215*)	0.99 (3H, s, H_3-18), 2.02 (3H, s, OAc), 3.27 (1H, br.s, H-6), 3.84 (1H, s, H-20), 4.24 (1H, br.m, W1/2=10.8 Hz, H-2β), 4.82, 5.00 (each 1H, s, H_2-17), 2.20 (1H, d, *J*=8.6 Hz, H-9), 2.42 (1H, d, *J*=9.7 Hz, H-14), 5.19 (2H, d, *J*=9.5 Hz, H-11β and H-13α); 6.61, 7.86 (each 1H, d, *J*=16.1 Hz); 7.39 (3H, m); 7.53 (2H, m) (cinnamoyl group)
AVII1a-13 (torokonine) (*132*)	1.11 (3H, s, H_3-18), 2.60, 3.11 (each 1H, d, *J*=12.5 Hz, H_2-19), 2.96 (1H, s, H-20), 3.41 (1H, br.s, H-6), 4.42 (1H, d, *J*=2.6 Hz, H-7), 4.53 (1H, br.s, H-15), 5.00, 5.03 (each 1H, t, *J*=1.3 Hz, H_2-17), 5.52 (1H, m, H-2), 7.47-8.02 (5H, m, Ar-H)
AVII1a-14 (souline F) (*219*) (pyridine-d_5)	2.34, 2.47 (each 1H, t, *J*=13 Hz, H_2-15), 3.24, 4.02 (each 1H, d, *J*=12 Hz, H_2-19), 4.28 (1H, br.s, H-2β), 4.57 (1H, d, *J*=8 Hz, H-6β), 4.70 (1H, d, *J*=8 Hz, H-7α), 5.11, 5.26 (each 1H, s, H_2-17)
AVII1a-15 (crassicaulie B) (*220*)	1.10 (3H, s, H_3-18), 3.58 (1H, d, *J*=3 Hz, *CH*-OH), 4.27 (1H, m), 4.65, 4.76 (each 1H, s, H_2-15), 5.34 (1H, m, H-13), 7.55, 7.67, 8.06 (5H, m, Ar-H)
AVII1a-17 (ryosenamine) (*221, 222*)	1.06 (3H, s, H_3-18), 2.62, 3.04 (each 1H, ABq, *J*=13 Hz, H_2-19), 3.31 (1H, br.s, H-20), 3.33 (1H, br.s, H-6), 4.12 (1H, s, H-15), 4.97, 5.00 (each 1H, s, H_2-17), 5.52 (1H, m, H-2), 7.43-8.03 (5H, m, Ar-H)

TABLE XXXIII (*continued*)

AVII1a-18 (delfissinol) (*223*)	2.72, 3.07 (each 1H, ABq, J=12.5 Hz, H_2-19), 4.16 (1H, br.d, J=7 Hz, H-11), 4.26 (1H, br.d, J=8.6 Hz, H-13), 4.48 (1H, t, J=5 Hz, H-7), 4.68, 4.86 (each 1H, br.s, H_2-17)
AVII1a-19 (delnuttine) (*224*) ($CDCl_3$-CD_3OD)	0.93 (3H, s, H_3-18), 1.20 (1H, m, H-1β), 1.33-1.40 (4H, m, H-1α, H-2β, H-3β, H-13β), 1.50 (1H, s, H-5), 1.50-1.55 (1H, m, H-2α), 1.73 (1H, m, H-13α), 1.99 (3H, s, OAc), 2.39 (1H, br.d, J=10.5 Hz, H-14), 2.58 (1H, s, H-20), 3.20 (1H, br.s, H-6), 3.87 (1H, d, J=2.8 Hz, H-7β), 4.37 (1H, s, H-15α), 4.97, 5.02 (each 1H, br.s, H-17), 5.18 (1H, d, J=8.3 Hz, H-11β)
AVII1a-20 (deacetylhanamisine, hanamiyama base) (*216*) (pyridine-d_5)	1.00 (3H, s, H_3-18), 2.68, 3.21 (each 1H, ABq, J=12.1 Hz, H_2-19), 3.45 (1H, s, H-20), 3.47 (1H, br.s, H-6), 4.32 (1H, s, H-15), 4.68 (1H, s, H-1), 5.01, 5.21 (each 1H, d, J=1.5 Hz, H_2-17), 5.88 (1H, m, H-2)
AVII1a-21 (venudelphine) (*226*)	1.05 (3H, s, H_3-18), 1.98, 2.01, 2.09 (each 3H, s, 3×OAc), 2.55, 2.82 (each 1H, ABq, J=12.5 Hz, H_2-19), 3.32 (1H, br.s, H-6), 3.86 (1H, s, H-20), 4.82, 4.99 (each 1H, br.s, H_2-17), 5.07 (1H, dt, J=1.5, 1.5, 10 Hz, H-13β), 5.31 (1H, dd, J=3.5, 5 Hz, H-2β), 5.72 (1H, d, J=3.5 Hz, H-1α)
AVII1a-22 (tangutisine) (*227*) (CD_3OD+D_2O)	1.16 (3H, s, H_3-18), 1.62 (1H, dd, J=4.3, 15.4 Hz, H-3β), 1.76 (1H, dd, J=4.1, 15.4 Hz, H-1β), 1.77 (1H, br.d, J=15.3 Hz, H-7β), 1.92 (1H, br.d, J=1.7, 15.4 Hz, H-3α), 2.10 (1H, dd, J=3.4, 15.3 Hz, H-7α), 2.06, 2.26 (each 1H, ABq, J=18.1 Hz, H_2-15), 2.31 (1H, d, J=8.8 Hz, H-9), 2.19 (1H, s, W1/2=4.0 Hz, H-5), 2.55 (1H, d, J=1.0, 3.0 Hz, H-12), 3.01, 3.74 (each 1H, ABq, J=11.6 Hz, H_2-19), 4.05 (1H, br.s, W1/2=6.8 Hz, H-13β), 4.21 (1H, br.s, W1/2=10.4 Hz, H-2β), 4.33 (1H, ddd, J=<1.0, 1.8, 8.8 Hz, H-11β), 4.50 (1H, W1/2=3.9 Hz, H-20), 4.78, 4.99 (each 1H, br.s, W1/2=7.0 Hz, H_2-17)
AVII1a-23 (gua-fu base Y, 2-acetyl-14-hydroxyhetisine) (*229*, *228*)	2.91 (1H, ddd, J=2.2, 15.9 Hz, H-1α), 1.86 (1H, dd, J=4.6, 15.8 Hz, H-1β), 5.14 (1H, ddd, W1/2=9.5 Hz, H-3α), 1.86 (1H, m, H-3α), 1.59 (1H, dd, J=4.9, 15.5 Hz, H-3β), 1.55 (1H, s, H-5), 3.13 (1H, br.s, H-6), 1.82 (1H, dd, J=3.3, 13.9 Hz, H-7α), 1.39 (1H, dd, J=2.4, 13.9 Hz, H-7β), 1.99 (1H, d, J=8.9 Hz, H-9), 4.23 (1H, br.d, J=9 Hz, H-11), 2.51 (1H, d, J=8.9 Hz, H-12), 4.07 (1H, dd, J=2.4, 2.4 Hz, H-13), 2.08 (1H, ddd, J=2.0, 2.0, 17.9 Hz, H-15α), 1.99 (1H, ddd, J=2.5, 2.5, 17.9 Hz, H-15β), 4.70, 4.89 (each 1H, t, J=1~3 Hz, H_2-17), 1.02 (3H, s, H_3-18), 2.57, 2.98 (1H, ABq, J=12 Hz, H_2-19), 3.55 (1H, d, J=1.2 Hz, H-20)

TABLE XXXIII (*continued*)

AVII1a-24 (gua-fu base Z) (*230*, *228*)	2.85 (1H, d, *J*=15.7 Hz, H-1α), 1.86 (1H, m, H-1β), 5.13 (1H, m, H-2), 1.77 (1H, m, H-3α), 1.59 (1H, dd, *J*=4.1, 15.4 Hz, H-3β), 1.52 (1H, s, H-5), 3.11 (1H, br.s, H-6), 1.80 (1H, m, H-7α), 1.37 (1H, dd, *J*=2.2, 13.9 Hz, H-7β), 1.98 (1H, m, H-9), 4.22 (1H, d, *J*=8.7 Hz, H-11), 2.47 (1H, m, H-12), 4.04 (1H, br.s, H-13), 2.00 (2H, m, H_2-15), 4.68, 4.86 (each 1H, br.s, H_2-17), 1.01 (3H, s, H_3-18), 2.52, 2.95 (each 1H, ABq, *J*=12.2 Hz, H_2-19), 3.53 (1H, s, H-20)
AVII1a-25 (acoridine) (*231*)	0.86 (3H, s, H_3-18), 1.07 (3H, t, NCH_2CH_3), 1.33 (1H, d, *J*=3, 14 Hz, H-7), 1.48 (1H, s, H-5), 1.64 (1H, dd, *J*=4, 15.5 Hz, H-3β), 1.70-1.90 (3H, m, H-1β, H-3α, H-7), 1.90-2.00 (1H, s, H-9), 2.28 (2H, q, *J*=7.5 Hz, NCH_2CH_3), 2.42 (1H, br.s, H-12), 2.84 (1H, d, *J*=16 Hz, H-1α), 2.48, 2.91 (each 1H, d, *J*=12 Hz, H_2-19), 3.05 (1H, br.s, H-6), 3.46 (1H, s, H-20), 3.98 (1H, br.s, H-13), 4.15 (1H, d, *J*=9 Hz, H-11), 4.60, 4.99 (each 1H, br.s, H_2-17), 5.08 (1H, br.s, H-2)
AVII1a-26 (guan-fu base A) (*233*)	0.96 (3H, s, H_3-18), 1.94, 2.00 (each 3H, s, 2×OAc), 2.52, 2.92 (each 1H, 2×OH), 3.38 (1H, s, H-20), 4.20 (1H, d, *J*=8.0 Hz, H-11), 4.60 (1H, br.s, *CH*-OAc), 5.06 (1H, m, *CH*-OAc), 4.79, 4.85 (each, 1H, br.s, H_2-17)
AVII1a-27 (guan-fu base O) (*235*)	3.14 (1H, br.d, *J*=16.0 Hz, H-1α), 1.82 (1H, dd, *J*=4.9, 16.0 Hz, H-1β), 5.19 (1H, m, W1/2=11 Hz, H-2), 1.90 (1H, br.d, *J*=15.5 Hz, H-3α), 1.60 (1H, dd, *J*=4.6, 15.5 Hz, H-3β), 1.69 (1H, br.s, H-5), 3.19 (1H, br.s, H-6), 1.84 (1H, br.d, *J*=11.0 Hz, H-7α), 1.45 (1H, br.d, *J*=11.0 Hz, H-7β), 2.04 (1H, d, *J*=8.9 Hz, H-9), 4.22 (1H, br.d, *J*=8.9 Hz, H-11), 2.56 (1H, br.s, H-12), 4.91 (1H, br.s, H-13), 2.08 (2H, s, H_2-15), 4.73, 4.91 (each 1H, br.s H_2-17), 1.01 (3H, s, H_3-18), 2.55, 2.92 (each, 1H, ABq, *J*=11.0 Hz, H_2-19), 3.45 (1H, s, H-20), 2.37 (2H, q, *J*=7.5 Hz, H_2-2'), 1.13 (3H, t, *J*=7.5 Hz, 3H-3'), 2.01 (3H, s, 3H-2'')
AVII1a-28 (guan-fu base F) (*236*)	0.96 (3H, s, H_3-18), 1.09 (3H, d, *J*=6.5 Hz, $CH(CH_3)_2$), 1.33 (1H, dd, *J*=2, 14 Hz, H-7β), 1.49 (1H, s, H-5), 1.56 (1H, dd, *J*=4, 15.5 Hz, H-3β), 1.97 (3H, s, OAc), 1.64-2.06 (6H, m, H_2-15, H-9, H-1β, H-7α, H-3α), 2.40 (1H, m, H-2'), 2.55 (1H, d, *J*=4 Hz, H-12), 2.47, 2.83 (each 1H, ABq, *J*=12 Hz, H_2-19), 2.88 (1H, d, *J*=16 Hz, H-1α), 3.07 (1H, br.s, H-6), 3.32 (1H, s, H-20), 4.19 (1H, d, *J*=9 Hz, H-11), 4.68, 4.89 (each 1H, br.s, H_2-17), 4.99 (1H, br.s, H-13), 5.12 (1H, br.s, H-2β)

TABLE XXXIII (*continued*)

AVII1a-29 (zeravshanisine) (*237*)	0.90 (3H, s, H_3-18), 1.13 (3H, s, OAc), 2.40, 2.67 (each 1H, ABq, *J*=12 Hz, H_2-19), 3.23 (1H, s, H-20), 4.34 (1H, d, *J*=9 Hz, H-11β), 4.70, 4.88 (each 1H, br.s, H_2-17), 5.46 (1H, br.s, H-13α), 7.35-8.10 (5H, m, Ar-H)
AVII1a-30 (guanfu base G) (*229*, *233*)	0.96 (3H, s, H_3-18), 1.96 (6H, s, 2×OAc), 2.02 (3H, s, OAc), 3.30 (1H, s, H-20), 3.05 (1H, br.s, OH), 4.80 (1H, br.s, C*H*-OAc), 5.04 (2H, m, 2×C*H*-OAc), 4.88, 4.94 (each 1H, br.s, H_2-17)
AVII1a-33 (paniculatine) (*244*)	5.84 (1H, d, *J*=3 Hz, H-1), 5.55 (1H, m, W1/2=9 Hz, H-2), 1.78~1.84, 1.88~1.97 (each 1H, m, H_2-3), 2.05 (H, s, H-5), 3.29 (1H, W1/27 Hz, H-6), 1.63-1.70, 1.77-7.83 (each 1H, m, H_2-7), 2.26, 2.27 (1H, H-9), 5.37 (1H, m, H-11), 4.19 (1H, m, W1/2=16 Hz, H-13), 2.08, 2.35 (each 1H, ABq, *J*=20 Hz, $\Delta\delta_{AB}$=100 Hz, H_2-15), 4.77, 4.90 (each 1H, br.s, H_2-17), 1.03 (3H, s, H_3-18), 2.51, 2.88 (each 1H, ABq, *J*=15 Hz, H_2-19), 4.30 (1H, s, H-20), 1.63 (1H, br.s, H-13), 2.03 (6H, s, 2×OAc), 7.46, 7.58, 8.13 (5H, m, Ar-H)
AVII1a-34 (1-*O*-acetyl-hypognavine) (*216*)	1.10 (3H, s, H_3-18), 2.13 (3H, s, OAc), 2.72 (1H, s, H-5), 3.18 (1H, s, H-20), 3.47 (1H, br.s, H-6), 4.07 (1H, s, H-15), 5.02, 5.05 (each 1H, br.s, H_2-17), 5.26 (1H, m, H-2), 5.44 (1H, d, *J*=2.0 Hz, H-1), 7.44-8.00 (5H, m, Ar-H)
AVII1a-35 (1,15-di-*O*-acetyl-hypognavine) (*216*)	1.09 (3H, s, H_3-18), 2.13 (6H, s, 2×OAc), 2.37 (1H, s, H-5), 2.58, 2.93 (each 1H, ABq, *J*=12.4 Hz, H_2-19), 3.21 (1H, s, H-20), 3.41 (1H, br.s, H-6), 4.98, 5.10 (each 1H, s, H_2-17), 5.24 (1H, m, H-2), 5.46 (1H, d, *J*=2.0 Hz, H-1), 5.56 (1H, s, H-15), 7.44-8.00 (5H, m, Ar-H)
AVII1a-36 (tadzhaconine) (*246*)	0.94 (3H, s, H_3-18), 1.93, 1.94 (each 1H, s, 2×OAc), 2.39 (1H, d, *J*=12.9 Hz, H-19b), 2.79 (1H, d, *J*=12.0 Hz, H-19a), 3.18(1H, br.s, H-6), 4.08 (1H, br.d, *J*=9.0 Hz, H-13), 4.21 (1H, s, H-20), 4.67, 478 (each 1H, s, H_2-17), 5.26 (1H, d, *J*=9.0 Hz, H-11β), 5.46 (1H, m, H-2β), 5.77 (1H, d, *J*=3.0 Hz, H-1α), 7.28-8.12 (5H, m, Ar-H)
AVII1a-37 (3-epi-iganbinol) (*247*)	1.14 (3H, s, H_3-18), 3.37 (1H, d, *J*=4.6 Hz, H-3), 3.98 (1H, t, H-15α), 4.08 (1H, m, H-2), 4.99 (2H, d, *J*=1.7 Hz, H_2-17)

TABLE X X XIII (*continued*)

AVII1a-39 (cossonine) (*253*)	3.24 (1H, dd, H-1α), 1.81 (1H, dd, H-1β), 5.10 (2H, m, H-2α, H-3β), 5.21 (1H, d, H-3β), 1.84 (1H, s, H-5), 3.14 (1H, br.s, H-6), 1.77 (1H, dd, H-7α), 1.57 (1H, dd, H-7β), 1.96 (1H, dd, H-9), 4.22 (1H, d, H-11β), 2.39 (1H, d, H-12), 2.31 (1H, dd, H-14), 2.01 (1H, d, H-15α), 2.18 (1H, d, H-15β), 4.68, 4.86 (1H, each 1H, br.s, H_2-17), 1.01 (3H, s, H_3-18), 2.51, 2.82 (each 1H, ABq, H_2-19), 3.01 (1H, s, H-20), 1.86 (3H, s, OAc), 2.20 (3H, s, H-13α), 7.41, 7.53, 7.96 (5H, m, Ar-H)
AVII1a-40 (cardiopimine) (*254*)	6.04 (1H, d, *J*=3.2 Hz, H-1α), 4.28 (1H, dd, *J*=3.2, 4.7 Hz, H-2β), 4.91(1H, d, *J*=4.7 Hz, H-3β), 2.21 (1H, s, H-5), 3.33 (1H, br.s, W1/2=6.3 Hz, H-6), 1.61, 1.91 (each 1H, dd, *J*=3.2, 13.8 Hz, H-2α, H_2-7α), 2.30 (1H, dd, *J*=2.2, 9.6 Hz, H-9), 5.41 (1H, d, *J*=9.6 Hz, H-13β), 2.55 (1H, m, H-12), 5.33 (1H, dt, *J*=3.0, 9.6 Hz, H-13β), 2.55 (1H, m, H-14), 2.15, 2.39 (each 1H, br.d, *J*=17.5 Hz, H_2-15), 4.85, 5.10 (each 1H, br.s, H_2-17), 1.01 (3H, s, H_3-18), 2.41, 3.43 (each 1H, ABq, *J*=2.6 Hz, H_2-19), 3.95 (1H, s, H-20), 2.55 (1H, m, H-2'), 1.12 (3H, d, *J*=6.8 Hz, H-3'), 1.15 (3H, d, *J*=6.8 Hz, 3H-4'), 7.50, 7.57, 8.23 (5H, m, Ar-H), 1.97, 2.02 (each 3H, 2×OAc)
AVII1a-41 (cardiopidine) (*254*)	6.05 (1H, d, *J*=3.2 Hz, H-1α), 4.28 (1H, dd, *J*=3.4, 4.6 Hz, H-2β), 4.94 (1H, d, *J*=4.8 Hz, H-3β), 2.20 (1H, s, H-5), 3.27 (1H, br.s, W1/2=6.5 Hz, H-6), 1.70, 1.89 (each 1H, dd, *J*=1.2, 13.6 Hz, H-2α, H_2-7α), 2.30 (1H, dd, *J*=2.2, 9.6 Hz, H-9), 5.41 (1H, d, *J*=9.2 Hz, H-11β), 2.53 (1H, d, *J*=2.5 Hz, H-12), 5.36 (1H, dt, *J*=2.0, 9.5 Hz, H-13β), 2.50 (1H, dd, *J*=2.1, 9.0 Hz, H-14), 2.15, 2.40 (each 1H, br.d, *J*=18.0 Hz, H_2-15), 4.85, 5.01 (each 1H, br.s, H_2-17), 0.99 (3H, s, H_3-18), 2.40, 3.39 (each 1H, d, *J*=12 Hz, H-6 and H-19α), 3.91 (1H, s, H-20), 2.65 (1H, m, H-2'), 1.25 (2H, m, H-3'), 0.87 (3H, t, *J*=7.4 Hz, H_3-4'), 1.12 (3H, t, *J*=6.9 Hz, H_3-5'), 7.50, 7.56, 8.23 (5H, m, Ar-H), 1.97, 2.02 (each 3H, s, 2×OAc)

TABLE XXXIII (*continued*)

AVII1a-42 (cardiopinine) (*254*)	6.08 (1H, d, *J*=2.9 Hz, H-1α), 5.59 (1H, dd, *J*=2.8, 5.1 Hz, H-2β), 3.85 (1H, d, *J*=5.1 Hz, H-3β), 2.16 (1H, s, H-5), 3.32 (1H, br.s, W1/2=6.4 Hz, H-6), 1.69, 1.90 (each 1H, dd, *J*=3.2, 13.4 Hz, H_2-7), 2.30 (1H, dd, *J*=2.0, 9.6 Hz, H-9), 5.43 (1H, d, *J*=10.4 Hz, H-11β), 2.40 (1H, d, *J*=2.6 Hz, H-12), 5.48 (1H, dt, *J*=2.0, 10.0 Hz, H-13β), 2.53 (1H, dd, *J*=2.2, 9.9 Hz, H-14), 2.19, 2.39 (each 1H, br.d, *J*=17.5 Hz, H_2-15), 4.84, 4.97 (each 1H, br.s, H_2-17), 1.14 (3H, s, H_3-18), 2.35, 3.10 (each 1H, d, *J*=12.8 Hz, H_2-19), 3.67 (1H, s, H-20), 1.25 (1H, sept, *J*=6.6 Hz, H-2'), 0.95 (3H, d, *J*=7.0 Hz, H-3'), 0.90 (3H, d, *J*=7.0 Hz, H-4'), 7.47, 7.55, 8.15 (5H, m, Ar-H), 1.99, 2.05 (each 3H, s, 2×OAc)
AVII1a-43 (cardiopine) (*254*)	6.09 ((1H, d, *J*=2.9 Hz, H-1α), 5.60 (1H, dd, *J*=2.9, 5.2 Hz, H-2β), 3.87 (1H, d, *J*=5.0 Hz, H-3β), 2.15 (1H, s, H-5), 3.30 (1H, br.s, W1/2=6.0 Hz, H-6), 1.66, 1.86 (each 1H, dd, *J*=3.6, 13.6 Hz, H-6β and H-7α), 2.33 (1H, dd, *J*=2.1, 9.6 Hz, H-9), 5.42 (1H, d, *J*=9.5 Hz, H-11β), 2.38 (1H, d, *J*=2.7 Hz, H-12), 5.51 (1H, dt, *J*=2.6, 9.7 Hz, H-13β), 2.53 (1H, dd, *J*=1.9, 9.9 Hz, H-14), 2.18, 2.39 (each 1H, dt, *J*=2.1, 17.8 Hz, H_2-15), 4.87, 4.97 (each 1H, br.s, H_2-17), 1.14 (3H, s, H_3-18), 2.37, 3.10 (each 1H, d, *J*=12.8 Hz, H_2-19), 3.67 (1H, s, H-20), 1.10 (1H, m, H-2'), 1.08 (2H, m, H_2-3'), 0.57 (3H, t, *J*=7.5 Hz, H_3-4'), 0.85, 8.14 (3H, d, *J*=6.5 Hz, H-7, 2, 5'), 7.47, 7.57 (t, *J*=7.0, 7.4 Hz, Ar-H), 2.00, 2.06 (each 3H, s, 2×OAc)
AVII1a-44 (cardiodine) (*254*)	6.08 (1H, d, *J*=3.2 Hz, H-1α), 5.70 (1H, dd, *J*=3.1, 5.0 Hz, H-2β), 5.12 (1H, d, *J*=4.9 Hz, H-3β), 2.23 (1H, s, H-5), 3.21 (1H, br.s, W1/2=6.0 Hz, H-6), 2.00 (1H, m, H-7α), 1.49 (1H, dd, *J*=2.2, 13.9 Hz, H-7β), 2.40 (1H, d, *J*=9.4 Hz, H-9), 5.40 (1H, d, *J*=9.4 Hz, H-11β), 2.47 (1H, d, *J*=2.8 Hz, H-12), 5.55 (1H, t, *J*=2.4 Hz, H-13β), 2.18, 2.30 (each 1H, dt, *J*=2.0, 18.0 Hz, H_2-15), 4.87, 5.01 (each 1H, br.s, H_2-17), 1.05 (3H, s, H_3-18), 2.41, 3.23 (each 1H, d, *J*=12.5 Hz, H_2-19), 3.68 (1H, s, H-20), 1.30 (1H, m, H-2'''), 1.20 (2H, m, H_2-3'''), 0.57 (3H, t, *J*=7.4 Hz, H_3-4'''), 0.88, (3H, d, *J*=7.4 Hz, H_3-5'''), 7.45 (2H, t, *J*=7.6 Hz, H_2-3", 5"), 7.56 (1H, t, *J*=7.6 Hz, H-4"), 8.11 (2H, dd, *J*=7.6, 1.6 Hz, H_2-2", 6"), 1.87, 1.90, 2.09 (each 3H, s, 3×OAc)

TABLE XXXIII (*continued*)

AVII1a-45 (13-acetyl-14-hydroxy-2-propionylhetisine) (*255*)	1.83 (1H, dd, *J*=4.3, 16.1 Hz, H-1a), 3.14 (1H, d, *J*=16.1 Hz, H-1b), 5.18 (1H, m, H-2), 1.62 (1H, dd, *J*=4.6, 15.2 Hz, H-3a), 1.88 (1H, d, *J*=15.2 Hz), 1.62 (1H, br.s, H-5), 3.19 (1H, br.s, H-6), 1.45 (1H, dd, *J*=2.1, 14.1 Hz, H-7b), 1.83 (1H, dd, *J*=4.9, 14.1 Hz, H-7a), 2.03 (1H, d, *J*=8.8 Hz, H-9), 4.21 (1H, d, *J*=8.8 Hz, H-11), 2.56 (1H, br.s, H-12), 4.91 (1H, br.s, H-13), 2.07 (1H, dd, *J*=1.7, 15.1 Hz, H-15), 4.72, 4.91 (each 1H, br.s, H_2-17), 1.01 (3H, s, H_3-18), 2.54, 2.92 (each 1H, ABq, *J*=12.2 Hz, H_2-19), 3.45 (1H, s, H-20), 2.34, 2.37 (each 1H, m, H_2-22), 1.12 (3H, t, *J*=7.6 Hz, H_3-23), 2.02 (3H, s, OAc)
AVII1a-46 (13-*O*-acetyl-9-deoxyglanduline) (*256*)	3.07 (1H, dd, *J*=2.2, 16.2 Hz, H-1α), 2.27 (1H, dd, *J*=4.4, 16.2 Hz, H-1β), 5.50 (1H, m, W1/2=14.0 Hz, H-2β), 4.98 (1H, d, *J*=4.4 Hz, H-3β), 1.79 (1H, s, H-5), 3.13 (1H, br.s, W1/2=6.4 Hz, H-6), 1.89 (1H, dd, *J*=3.4, 14.0 Hz, H-7α), 1.41(1H, dd, *J*=2.5, 14.0 Hz, H-7β), 2.04 (1H, d, *J*=8.9 Hz, H-9), 4.28 (1H, d, *J*=8.9 Hz, H-11β), 2.64 (1H, d, *J*=2.5 Hz, H-1α), 5.06 (1H, t, *J*=2.2 Hz, H-13β), 2.17 (1H, d, *J*=17.9 Hz, H-15α), 2.02 (1H, m, H-15β), 4.77, 4.97 (each 1H, br.s, H_2-17), 1.02 (3H, s, H_3-18), 2.50, 3.35 (each 1H, d, *J*=12.5 Hz, H_2-19), 3.54 (1H, s, H-20), 2.35 (1H, sept, *J*=7.0 Hz, H-2'), 1.48, 1.69 (each 1H, ddq, *J*=7.0, 7.0, 14.0 Hz, H_2-3'), 0.89 (3H, t, *J*=7.4 Hz, H_3-4'), 1.25 (3H, d, *J*=7.2 Hz, H_3-5'), 2.01 (3H, s, 3α-OAc), 1.99 (3H, s, 13α-OAc)
AVII1a-47 (glanduline) (*256*)	3.04 (1H, br.d, *J*=16.0 Hz, H-1α), 2.15 (1H, dd, *J*=3.7, 16.0 Hz, H-1β), 5.45 (1H, m, W1/2=14.0 Hz, H-2β), 4.90 (1H, d, *J*=4.7 Hz, H-3β), 2.72 (1H, br.s, H-5), 3.34 (1H, br.s, W1/2=6.4 Hz, H-6), 1.80 (1H, d, *J*=18.0 Hz, H-7α), 1.85 (1H, d, *J*=18.0 Hz, H-7β), 4.02 (1H, s, H-11β), 2.51 (1H, d, *J*=18 Hz, H-1α), 4.09 (1H, br.s, H-13β), 2.00, 2.10 (each 1H, d, *J*=16.0 Hz, H_2-15), 4.74, 4.91 (each 1H, s, H_2-17), 1.10 (3H, s, H_3-18), 2.70, 3.59 (each 1H, d, *J*=12.5 Hz, H_2-19), 4.06 (1H, s, H-20), 2.45 (1H, sext, *J*=7.0 Hz, H-2'), 1.49, 1.70 (each 1H, ddq, *J*=7.0, 7.0, 14.0 Hz, H_2-3'), 0.92 (3H, t, *J*=7.4 Hz, H_3-4'), 1.18 (3H, d, *J*=17.0 Hz, H_3-5'), 2.01 (3H, s, 3α-OAc)

TABLE X X XIII (*continued*)

AVII1a-48 (13-*O*-acetylglanduline) (*256*)	3.13 (1H, dd, *J*=2.0, 6.6 Hz, H-1α), 2.09 (1H, dd, *J*=4.7, 16.6 Hz, H-1β), 5.50 (1H, m, H-2β), 4.90 (1H, d, *J*=4.7 Hz, H-3β), 2.59 (1H, s, H-5), 3.10 (1H, br.s, H-6), 1.70 (1H, dd, *J*=3.0, 13.4 Hz, H-7α), 1.75 (1H, dd, *J*=2.2, 13.8 Hz, H-7β), 4.10 (1H, s, H-11β), 2.65 (1H, d, *J*=2.2 Hz, H-12), 4.96 (1H, d, *J*=2.2 Hz, H-13β), 2.04 (1H, d, *J*=18.0 Hz, H-15α), 1.99 (1H, d, *J*=18.0, H-15β), 4.78, 4.97 (each 1H, s, H_2-17), 1.03 (3H, s, H_3-18), 3.38 (1H, d, *J*=12.5 Hz, H-19α), 2.54 (1H, d, *J*=12.5Hz, H-19β), 3.62 (1H, s, H-20), 2.36 (1H, sept, *J*=7.0 Hz, H-2'), 1.86 (1H, ddq, *J*=7.3, 7.3, 14.6 Hz, H-3'A), 1.48 (1H, ddq, *J*=7.3, 7.3, 14.6 Hz, H-3'B), 0.89 (3H, t, *J*=7.4 Hz, H_3-4'), 1.23 (3H, d, *J*=7.0 Hz, H_3-5'), 2.02 (3H, s, 3α-OAc), 1.99 (3H, s, 13α-OAc)
AVII1a-49 (14-*O*-acetylglanduline) (*256*)	3.03 (1H, br.d, *J*=15.5 Hz, H-1α), 2.11 (1H, dd, *J*=5.5, 14.5 Hz, H-1β), 5.46 (1H, m, H-2β), 4.95 (1H, d, *J*=4.6 Hz, H-3β), 1.98 (1H, s, H-5), 3.51 (1H, br.d, H-6), 2.16 (1H, dd, *J*=3.5, 14.0 Hz, H-7α), 1.50 (1H, br.d, *J*=14.0 Hz, H-7β), 2.08 (1H, d, *J*=8.7 Hz, H-9), 4.24 (1H, d, *J*=8.8 Hz, H-11β), 2.56 (1H, s, H-12), 4.14 (1H, s, H-13β), 2.15 (1H, d, *J*=17.7 Hz, H-15α), 2.04 (1H, d, *J*=17.7 Hz, H-15β), 4.73, 4.93 (each 1H, s, H_2-17), 1.12 (3H, s, H_3-18), 3.65 (1H, d, *J*=12.5 Hz, H-19α), 2.73 (1H, d, *J*=12.5 Hz, H-19β), 4.21 (1H, s, H-20), 2.46 (1H, sept, *J*=7.0 Hz, H-2'), 1.70 (1H, ddq, *J*=7.0, 7.0, 14.0 Hz, H-3'A), 1.49 (1H, ddq, *J*=7.0, 7.0, 14.0 Hz, H-3'), 0.94 (3H, t, *J*=7.4 Hz, H_3-4'), 1.21 (3H, d, *J*=7.0 Hz, H_3-5'), 2.00 (3H, s, 3α-OAc), 1.99 (3H, s, 14α-OAc)
AVII1a-50 (11, 13-*O*-diacetyl-9-deoxyglanduline) (*256*)	2.85 (1H, dd, *J*=1.8, 15.3 Hz, H-1α), 1.83 (1H, dd, *J*=4.5, 15.3 Hz, H-1β), 5.47 (1H, m, H-2), 4.92 (1H, d, *J*=4.7 Hz, H-3β), 1.80 (1H, s, H-5), 3.14 (1H, br.s, W1/2=6.2 Hz, H-6), 1.91 (1H, dd, *J*=3.3, 14.0 Hz, H-7α), 1.44 (1H, dd, *J*=2.0, 14.0 Hz, H-7β), 2.23 (1H, d, *J*=9 Hz, H-9), 5.11 (1H, d, *J*=8 Hz, H-11β), 2.68 (1H, d, *J*=2.4 Hz, H-12), 5.02 (1H, br.s, H-13β), 2.20, 2.12 (each 1H, d, *J*=14.0 Hz, H-15α), 4.83, 5.02 (each 1H, br.s, H_2-17), 1.02 (3H, s, H_3-18), 3.34, 2.50 (each 1H, d, *J*=12.5 Hz, H_2-19), 3.57 (1H, s, H-20), 2.38 (1H, sept, *J*=7.4 Hz, H-2'), 1.50 , 1.70 (each 1H, ddq, *J*=7.4, 7.4, 14.8 Hz, H_2-3'), 0.92 (3H, t, *J*=7.4 Hz, H_3-4'), 1.24 (3H, d, *J*=7.0 Hz, H_3-5'), 2.02 (3H, s, 3α-OAc), 2.00 (3H, s, 11α-OAc), 1.99 (3H, s, 13α-OAc)

TABLE XXXIII (*continued*)

AVII1a-51 (davisinol) (*196*)	1.40 (1H, m, H-1β), 1.50 (1H, m, H-1α), 1.40~1.50 (1H, m, H-2β), 1.70 (1H, m, H-2α), 1.48 (2H, m, H_2-3), 1.72 (1H, s, H-5), 1.57 (1H, d, H-7β), 1.65 (1H, d, H-7α), 1.38 (1H, s, H-9), 4.01 (1H, d, *J*=4.8 Hz, H-11), 2.28 (1H, d, *J*=4.8 Hz, H-12), 0.91 (1H, m, H-13β), 1.90 (1H, m, H-13α), 1.78 (1H, m, H-14), 2.10 (2H, m, H_2-15), 4.83, 4.83 (each 1H, d, *J*=1.8 Hz, H_2-17), 3.28, 3.43 (each 1H, ABq, *J*=10.8 Hz, H_2-18), 2.23, 2.55 (each 1H, ABq, *J*=12.5 Hz, H_2-19), 2.40 (1H, s, H-20)
AVII1a-52 (18-benzoyldavisinol) (*196*)	1.51 (1H, m, H-1β), 1.92 (1H, m, H-1α), 1.51 (1H, m, H-2β), 1.79 (1H, m, H-2α), 1.62 (2H, m, H_2-3), 1.88 (1H, m, H-5), 3.27 (1H, br.s, H-6), 1.61 (1H, m, H-7β), 1.76 (1H, m, H-7α), 1.45 (1H, s, H-9), 4.07 (1H, d, *J*=4.8 Hz, H-11), 2.33 (1H, br.s, W1/2=9 Hz, H-12), 1.02 (1H, m, H-13β), 1.95 (1H, m, H-13α), 1.90 (1H, m, H-14), 2.20 (1H, m, H-15β), 2.27 (1H, m, H-15α), 4.89 (2H, br.s, H_2-17), 4.06, 4.24 (each 1H, ABq, *J*=12.8 Hz, H_2-18), 2.44, 2.72 (each 1H, ABq, *J*=17.9 Hz, H_2-19), 2.51 (1H, s, H-20), 8.02 (2H, d, *J*=7.5 Hz, H-2' and H-6'), 7.46 (2H, dd, *J*=7.6 Hz, H-3' and H-5'), 7.58 (1H, dd, *J*=7.4 Hz, H-4')
AVII1a-53 (spirasine IX) (*190*)	1.08 (3H, s, H_3-18), 2.72, 2.87 (each 1H, ABq, *J*=11.5 Hz, H_2-19), 3.72 (1H, br.s, H-6), 4.82, 4.94 (each 1H, br.s, H_2-17)
AVII1a-54 (spirasine X) (*257*)	1.01(3H, s, H_3-18), 1.68, 1.87 (each 1H, dd, H_2-17), 2.04 (1H, d, H-20), 2.26, 2.32 (each 1H, br.d, H_2-15), 2.41 (1H, q, H-14), 2.47, 2.58 (each 1H, ABq, *J*=11.5 Hz, H_2-19), 2.94 (1H, d, H-11), 3.25 (1H, s, H-9), 3.30 (1H, br.s, H-6), 4.24 (1H, q, H-11), 4.85, 5.02 (each 1H, br.s, H_2-17)
AVII1a-55 (11-dehydrokobusine) (*258*)	0.93 (3H, s, H_3-18), 5.07, 5.11 (each 1H, br.s, H_2-17), 4.07 (1H, br.s, H-15)
AVII1a-56 (spirasine IV) (*190*)	1.04 (3H, s, H_3-18), 2.46, 2.72 (each 1H, d, *J*=11.5 Hz, H_2-19), 3.40 (1H, br.s, H-6), 4.84, 4.96 (each 1H, br.s, H_2-17)
AVII1a-57 (2-dehydrohetisine) (*204, 212*)	1.17 (3H, s, H_3-18), 3.29 (2H, br.s, 2×OH), 4.21 (2H, d, *J*=8.6 Hz, H-11β, H-13α), 4.70, 4.88 (each 1H, br.s, H_2-17)
AVII1a-58 (venuluson) (*259*)	2.75 (1H, d, *J*=9 Hz, H-14), 3.10 (1H, s, H-20), 4.05 (1H, br.s, H-15), 4.20 (1H, br.d, *J*=9 Hz, H-13), 4.71, 4.90 (each 1H, br.s, H_2-17)

TABLE XXXIII (*continued*)

AVII1a-59 (fissumine) (*223*)	2.05 (3H, s, H_3-18), 2.52 (1H, d, H-14), 2.75 (1H, H-20), 2.75, 3.04 (each 1H, d, *J*=13.0 Hz, H_2-19), 4.24 (1H, d, *J*=9 Hz, H-13), 4.69, 4.88 (each 1H, br.s, H_2-17)
AVII1a-60 (cardiopetamine) (*204, 260, 261*)	1.13 (3H, s, H_3-18), 3.22 (1H, br.s, W1/2=6.5 Hz, H-6), 3.73 (1H, br.s, W1/2=5 Hz, H-15), 3.90 (1H, br.d, *J*=10.8 Hz, W1/2=6.5 Hz, H-13), 5.18 (2H, br.s, H_2-17), 5.48 (1H, d, *J*=8.5 Hz, H-11), 7.54, 8.08 (3H and 2H, m, Ar-H)
AVII1a-61 (15-acetylcardio-petamine) (*260, 261*)	2.28 (1H, d, *J*=13.3 Hz, H-1β), 3.48 (1H, d, *J*=13.2 Hz, H-1α), 2.02 (1H, s, H-5), 3.37 (1H, br.s, W1/2=8 Hz, H-6), 1.82 (2H, m, H_2-7), 2.71 (1H, d, *J*=9 Hz, H-9), 5.57 (1H, d, *J*=9 Hz, H-11β), 2.58 (1H, d, *J*=2.5 Hz, H-12), 4.18 (1H, br.d, *J*=9.7 Hz, W1/2=6 Hz, H-13), 2.29 (1H, d, *J*=10 Hz, H-14), 5.15 (1H, s, H-15α), 5.26, 5.34 (each 1H, s, H_2-7), 1.10 (3H, s, H_3-18), 2.22 (1H, d, *J*=12 Hz, H-19β), 2.71 (1H, d, *J*=12 Hz, H-19α), 3.11 (1H, s, H-20), 2.10 (3H, s, OAc), 7.42-8.08 (5H, m, Ar-H)
AVII1a-62 (15-acetyl-13-dehydrocardiopetamine) (*261*)	1.12 (3H, s, H_3-18), 1.87, 1.93 (each 1H, dd, *J*=10, 2.2 Hz, H_2-7), 2.08 (1H, s, H-5), 2.17 (3H, s, OAc), 2.21 (1H, d, *J*=13.7 Hz, H-19β), 2.41 (1H, d, *J*=14 Hz, H-1β), 2.56 (1H, d, *J*=1.8 Hz, H-14), 2.71 (1H, d, *J*=13.2 Hz, H-19α), 2.75 (1H, d, *J*=14 Hz, H-1α), 2.80 (1H, s, H-12), 2.91 (1H, dd, *J*=2.1, 8.5 Hz, H-9), 3.16 (1H, s, H-20), 3.40 (1H, br.s, W1/2=7 Hz, H-6), 5.34, 5.52 (each 1H, s, H_2-17), 5.50 (1H, s, H-15), 5.68 (1H, d, *J*=8.4 Hz, H-11), 7.48-7.95 (5H, m, Ar-H)
AVII1a-63 (orientinine, 7, 11, 14-trihydroxy-2, 13-dioxohetisine) (*262*)	1.02 (3H, s, H_3-18), 2.00 (1H, d, *J*=9 Hz, H=9), 2.31 (1H, d, *J*=11 Hz, H-19α), 2.62 (1H, d, *J*=11 Hz, H-11α), 2.90 (1H, br.s, H-12), 3.47 (1H, br.s, H-6), 4.24 (1H, br.d, *J*=9 Hz, H-11β), 4.50 (1H, t, *J*=2 Hz, H-7β), 4.86, 4.98 (each 1H, br.s, H_2-17)
AVII1a-64 (eraconine) (*191*)	0.90 (3H, s, H_3-18), 2.19 (6H, s, $N(CH_3)_2$), 3.10 (1H, br.s), 4.38 (2H, br.s, 5.69 (1H, br.s), 6.68, 6.95 (each 1H, d, *J*=8.5 Hz, Ar-H)

TABLE XXXIII (*continued*)

AVII2a-1 (delatisine) (*264*)	1.70 (1H, dd, *J*=1.0, 13.1 Hz, H-1β), 2.52 (1H, dd, *J*=5.4, 13.1 Hz, H-1α), 4.50 (1H, br.t, *J*=5.4, 5.7 Hz, H-2), 1.57 (1H, dd, *J*=<1.0, 11.2 Hz, H-3β), 1.64 (1H, dd, *J*=5.7, 11.2 Hz, H-3α), 1.74 (1H, s, W1/2=2.7 Hz, H-5), 3.44 (1H, br.s, W1/2=7.6 Hz, H-6), 1.63 (1H, m, H-7), 2.18 (1H, dd, *J*= 2.1, 8.6 Hz, H-9), 4.11 (1H, br.d, *J*=2.1, 2.3, 8.6 Hz, H-11), 2.46 (1H, br.s, W1/2=6.2 Hz, H-12), 4.25 (1H, m, H-13), 1.87 (1H, dd, *J*=2.1, 9.1 Hz, H-14), 2.01, 2.16 (each 1H, ABq, *J*=18.0 Hz, H_2-15), 4.67, 4.88 (each 1H, br.s, H_2-17), 4.67 (1H, s, H-19), 1.15 (3H, s, H_3-18), 4.26 (1H, s, W1/2=4.5 Hz, H-20)
AVII2b-2 (venulol) (*259*)	1.37 (3H, s, H_3-18), 2.30 (1H, d, *J*=4.5 Hz, H-9), 2.50 (1H, br.d, *J*=4.6 Hz, H-12), 2.86, 3.28 (each 1H, ABq, *J*=12.5 Hz, H_2-19), 3.97 (1H, d, *J*=4.5 Hz, H-11), 4.70, 4.77 (each 1H, br.s, H_2-17)
AVII2b-4 (spirasine XIV) (*268*)	1.38 (3H, s, H_3-18), 2.08, 2.30 (each 1H, d, *J*=12.6 Hz, H_2-19), 3.69 (1H, br.d, *J*=10.0 Hz, H-13β), 4.62, 4.77 (each 1H, br.s, H_2-17)
AVII2b-5 (spirasine XV) (*268*)	1.49 (3H, s, 3H-18), 4.85 (2H, br.s, H_2-17)
AVII2b-6 (pseudokobusine) (*141*)	1.60 (1H, m, H-1α), 1.36 (1H, m, H-1β), 1.57 (1H, m, H-2α), 1.39 (1H, m, H-2β), 1.43 (1H, m, H-3α), 1.30 (1H, m, H-3β), 1.44 (1H, s, H-5), 2.30 (1H, m, H-7α), 1.54 (1H, m, H-7β), 1.62 (1H, br.s, H-9), 3.94 (1H, d, *J*=4.8 Hz, H-11), 2.41 (1H, m, *J*=2 Hz, H-12), 1.72 (1H, br.s, W1/2=9.2 Hz, H-13α), 0.85 (1H, d, *J*=9.2 Hz, H-13β), 1.72 (1H, m, H-14), 3.85 (1H, br.s, H-15), 5.05, 5.15 (each 1H, br.s, H_2-17), 1.28 (3H, s, H_3-18), 2.26, 3.00 (each 1H, ABq, *J*=11.9 Hz, H_2-19), 2.41 (1H, s, H-20)
AVII2b-6 (pseudokobusine) (*198, 199*)	1.34 (3H, s, H_3-18), 3.87 (1H, d, *J*=5 Hz, H-15α), 4.01 (1H, d, *J*=5 Hz, H-11α), 5.07, 5.17 (each 1H, br.s, H_2-17)
AVII2b-7 (yesodine) (*270*)	0.96 (3H, t, *J*=7.3 Hz, H_3-4'), 1.16 (3H, d, *J*=6.9 Hz, H_3-5'), 1.34 (3H, s, H_3-18), 4.00 (1H, d, *J*=4.6 Hz, H-11α), 5.23, 5.33 (each 1H, s, H_2-17), 5.59 (1H, s, H-15α)
AVII2b-8 (15-benzoylpseudo-kobusine) (*134*)	1.33 (3H, s, H_3-18), 4.07 (1H, d, *J*=4.6 Hz, H-11α), 5.27, 5.48 (each 1H, s, H_2-17)*, (1H, s), 5.48 (1H, s), 5.82 (1H, s, H-15)*, 7.34-7.63 (3H, m), 7.91-8.03 (2H, m) (OBz)*

TABLE XXXIII (*continued*)

AVII2b-9 (15-veratroylpseudo kobusine) (*134*)	1.35 (3H, s, H_3-18), 3.92, 3.94 (each 3H, s, 2×OCH_3), 5.27 (1H, s), 5.45 (1H, s), 5.86 (1H, s), 6.82 (1H, d, *J*=8.3 Hz), 7.53 (1H, d, *J*=2.0 Hz), 7.62 (1H, dd, *J*=2.0, 8.3 Hz)
AVII2b-10 (tatsirine) (*129*)	1.55 (3H, s, H_3-18), 4.72, 4.85 (each 1H, br.s, H_2-17)
AVII2b-11 (acorientine, 6, 13, 15-trihydroxyhetisine) (*262*)	1.42 (3H, s, H_3-18), 2.45 (1H, br.s, H-14), 3.86 (1H, s, H-20), 3.98 (1H, d, *J*=5.0 Hz, H-13), 4.02 (1H, s, H-15α), 5.16, 5.27 (each 1H, br.s, H_2-17)
AVII2b-12 (cardionine) (*272*)	1.22 (6H, d, *J*=7 Hz, H_3-3' and H_3-4'), 1.39 (3H, s, H_3-18), 1.62 (1H, s, H-5), 1.66 (1H, d, *H*=1.7 Hz, H-9), 2.36 (1H, br.d, *J*=10.7 Hz, W1/2=7.5 Hz, H-14), 2.51 (1H, d, *J*=11.8 Hz, H-19α), 2.63 (1H, sept, *J*=7 Hz, H-2'), 2.73 (1H, s, H-20), 3.18 (1H, d, *J*=11.8 Hz, H-19β), 3.86 (1H, s, H-11α), 5.07, 5.36 (each 1H, d, *J*=2 Hz, H_2-17), 5.73 (1H, t, *J*=2 Hz, H-15β)
AVII2b-13 (11-acetylcardionine) (*272*)	1.20 (6H, d, *J*=7 Hz, H_3-3' and H_3-4'), 1.33 (3H, s, H_3-18), 1.56 (1H, s, H-5), 1.65 (1H, d, *J*=2 Hz, H-9), 2.04 (3H, s, OAc), 2.32 (1H, br.d, *J*=10.8 Hz, W1/2=7.5 Hz, H-14), 2.37 (1H, d, *J*=12.2 Hz, H-19α), 2.59 (1H, s, H-20), 2.63 (1H, sept, *J*=7 Hz, H-22), 3.08 (1H, d, *J*=12.2 Hz, H-19β), 4.99 (1H, s, H-11α), 5.01, 5.34 (each 1H, d, *J*=2.5 Hz, H_2-17), 5.68 (1H, t, *J*=2.2 Hz, H-15β)
AVII2b-14 (geyerinine) (*273*)	0.95 (3H, t, *J*=7.0 Hz, H_3-4")*, 1.21 (3H, d, *J*=7 Hz, H_3-5")*, 1.32 (1H, s)*, 1.40 (3H, s, H_3-18), 1.48-1.60 (2H, m)*, 1.73 (1H, m)*, 1.82-2.10 (6H, m)*, 2.15 (3H, s, OAc)*, 2.20-2.50 (4H, m)*, 2.64 (1H, m)*, 3.02, 3.48 (each 1H, ABq, *J*=12 Hz, H_2-19), 3.12 (1H, dd, *J*=15, 21 Hz, H-1α), 3.76 (1H, s, H-20), 4.13 (1H, m, W1/2=12 Hz, H-2β), 4.32 (1H, br.d, *J*=1, 9 Hz H-13), 4.78, 4.94 (each 1H, br.s, H_2-17), 4.86 (1H, d, *J*=4 Hz, H-3), 5.13 (1H, dd, *J*=3, 9 Hz, H-11)
AVII2b-16 (geyeridine) (*273*)	1.48 (3H, s, H_3-18), 1.79 (1H, d, *J*=13 Hz), 2.00 (1H, s), 2.04 (3H, s, OAc), 2.09 (1H, br.s), 2.17-2.28 (6H, m), 2.35-2.43 (5H, m), 2.98 (1H, s, H-20), 3.20 (1H, d, *J*=12 Hz, H-3α), 3.34 (1H, dd, *J*=2, 13 Hz, H-1α), 4.17 (1H, ddd, *J*=1, 3, 9 Hz, H-11), 4.79, 4.94 (each 1H, br.s, H_2-17), 5.14 (1H, br.d, *J*=1, 9 Hz, J<1Hz, H-13)

TABLE XXXIII (*continued*)

AVII2b-17 (geyerine) (*273*)	0.96 (3H, dd, *J*=7.7 Hz, H_3-4'), 1.20 (3H, dd, *J*=7 Hz, H_3-5'), 1.49-1.53 (2H, m, H_2-3'), 1.55 (3H, s, H_3-18), 1.70 (1H, m), 1.96-2.14 (6H, m), 2.23-2.34 (4H, m), 2.43-2.48 (2H, m), 2.50 (1H, dd, *J*=1, 3 Hz, H-12), 2.58 (1H, m, *J*=7 Hz, H-2'), 2.65 (1H, d, *J*=14 Hz, H-1β), 2.88 (1H, s, H-20), 3.36 (1H, br.d, *J*=12 Hz, H-3α), 3.54 (1H, dd, *J*=2, 15 Hz, H-1α), 4.36 (1H, ddd, *J*=1, 1, 9 Hz, H-13), 4.80, 4.98 (each 1H, br.s, H_2-17), 5.14 (1H, ddd, *J*=1, 3, 10 Hz, H-11)
AVII2b-18 (spiradine A) (*265*)	1.33 (3H, s, H_3-18), 4.73, 4.87 (each 1H, s, H_2-17)
AVII2b-19 (panicudine) (*274*)	1.29 (3H, s, H_3-18), 2.20 (1H, s, W1/2=5 Hz, H-14), 2.22, 2.52 (each, 1H, dt, *J*=1.5, 18 Hz, H_2-15), 2.74 (1H, br.d, *J*=4 Hz, H-12), 2.95, 3.12 (each 1H, d, *J*=11.5 Hz, H_2-19), 3.49 (1H, s, H-20), 4.02 (1H, m, W1/2=10 Hz, H-2β), 4.76, 4.87 (each 1H, s, W1/2=4 Hz, H_2-17)
AVII2b-20 (spirasine XII) (*268*)	1.32 (3H, s, H_3-18), 1.89 (2H, d, *J*=1.5 Hz)*, 2.02 (1H, d, *J*=2.0 Hz)*, 2.28 (1H, d, *J*=2.0 Hz)*, 2.40 (1H, d, *J*=10, 2 Hz)*, 2.42, 3.08 (each 1H, ABq, *J*=11.5 Hz, H_2-19)*, 2.83 (1H, d, *J*=3.5 Hz)*, 4.12 (1H, dd, *J*=3.5, 10 Hz, H-13)*, 4.86, 4.96 (each 1H, br.s, H_2-17)
AVII2b-21 (spirasine XIII) (*268*)	1.38 (3H, s, H_3-18), 2.39, 3.11 (each 1H, d, *J*=12.0 Hz), 2.94 (1H, s), 3.05 (1H, d, *J*=4.0 Hz), 3.65 (1H, d, *J*=4.0 Hz), 4. 97, 5.02 (each 1H, br.s, H_2-17), 4.57 (1H, s, OH)
AVII2b-22 (paniculadine) (*275*)	1.50 (3H, s, H_3-18), 1.59 (2H, m), 1.88 (2H, s), 1.97 (1H, s), 2.00 (2H, s), 2.05 (1H, s), 2.17 (2H, s), 2.20 (3H, s), 2.25-2.45 (3H, m), 2.63 (1H, s), 2.85 (1H, t, *J*=7 Hz, H-1α), 3.32 (1H, d, *J*=12 Hz, H-19α), 4.62, 4.79 (each 1H, s, H_2-17)
AVII2b-23 (delnuttidine) (*224*)	1.49 (1H, dd, *J*=8.7, 14.5 Hz, H-11β), 1.65 (3H, s, H_3-18), 1.91 (1H, d, *J*=8.7 Hz, H-9), 1.95 (1H, d, *J*=17.4 Hz, H-15β), 2.12 (1H, d, *J*=14.5 Hz, H-11α), 2.17 (1H, d, *J*=17.4 Hz, H-15α), 2.25 (1H, s, H-5), 2.27 (1H, d, *J*=13.7 Hz, H-7β), 2.35 (1H, d, *J*=13.7 Hz, H-1β), 2.40, 2.52 (each 1H, d, *J*=14.5 Hz, H_2-3), 2.74 (1H, d, *J*=13.7 Hz, H-7α), 2.83 (1H, d, *J*=12.1 Hz, H-19β), 3.29 (1H, d, *J*=13.7 Hz, H-1α), 3.37 (1H, d, *J*=9.3 Hz, H-14), 3.85 (1H, d, *J*=12.1 Hz, H-19α), 3.90 (1H, s, H-20), 4.24 (1H, d, *J*=9.3 Hz, H-13α), 4.61, 4.80 (each 1H, br.s, H_2-17)

TABLE XXXIII (*continued*)

AVII2b-24 (delnuttaline) (*224*) (pyridine-d_5)	1.68 (3H, s, H_3-18), 1.79 (1H, d, *J*=14.5 Hz, H-11β), 1.90 (1H, d, *J*=12.7 Hz, H-7β), 1.92 (1H, d, *J*=17.8 Hz, H-15β), 2.27 (3H, s, OAc), 2.34 (1H, d, *J*=13.9 Hz, H-3α), 2.38 (1H, d, *J*=2.2 Hz, H-19β), 2.41 (1H, br.s H-12), 2.58 (1H, d, *J*=13.9 Hz, H-3β), 2.60 (1H, d, *J*=14.2 Hz, H-11α), 2.62 (1H, d, *J*=9.6 Hz, H-14), 2.68 (1H, d, *J*=13.0 Hz, H-1β), 2.77 (1H, d, *J*=12.7 Hz, H-7α), 2.87 (1H, d, *J*=13 Hz, H-1α), 3.08 (1H, s, H-5), 3.55 (1H, d, *J*=12.2 Hz, H-19α), 4.70, 4.91 (each 1H, br.s, H_2-17), 5.09 (1H, br.d, *J*=9.6 Hz, H-13α)
AVII2c-1 (acsinatine) (*277*)	1.01 (3H, s, H_3-18), 1.98 (3H, s OAc), 2.72 (1H, br.s), 3.45 (1H, br.s), 4.51 (2H, br.s, H-17 and H-19), 4.67 (1H, br.s, H-17), 5.17 (1H, br.s, H-2β)
AVII2c-2 (andersobine) (*279*) [$(CD_3)_2SO$]	1.31 (1H, dd, *J*=4.0, 13.0 Hz, H-1β), 1.83 (1H, m, *J*=13.0 Hz, H-1α), 1.42 (1H, m, H-2α), 1.68 (1H, m, H-2β), 3.30 (1H, m, H-3β), 1.38 (1H, s, H-5), 3.34 (1H, br.s, H-6), 1.40 (1H, m, H-7α), 1.62 (1H, dd, *J*=2.5, 13.0 Hz, H-7β), 1.68 (1H, m, H-9), 1.47 (1H, td, *J*=2.0, 2.0, 13.0 Hz, H-11β), 1.87 (1H, dd, *J*=4.0, 13.0 Hz, H-11α), 2.17 (1H, m, H-12), 1.15 (1H, td, *J*=2.0, 2.0, 13.0 Hz, H-13α), 1.68 (1H, m, H-13β), 1.80 (1H, d, *J*=11.6 Hz, H-14), 5.29 (1H, br.s, *J*<10 Hz, H-15α), 4.83, 4.92 (each 1H, t, *J*=1.6 Hz, H_2-17), 0.95 (3H, s, H_3-18), 4.07 (1H, s, H-19), 2.52 (1H, br.s, H-20), 2.02 (3H, s, OAc), 4.40 (1H, d, *J*=4.6 Hz, 3-OH), 5.12 (1H, s, 19-OH)
(pyridine-d_5)	1.42 (1H, m, H-1β), 1.82 (1H, m, H-1α), 1.84 (1H, m, H-2α), 2.08 (1H, m, H-2β), 3.83 (1H, dd, *J*=5.5, 11.4 Hz, H-3), 1.50 (1H, s, H-5), 3.86 (1H, s, H-6), 1.78 (2H, m, H_2-7), 1.82 (1H, m, H-9), 1.68 (1H, m, H-11β), 1.91 (1H, m, H-11α), 2.14 (1H, m, H-12), 1.08 (1H, td, *J*=3.0, 3.0, 13.0 Hz, H-13α), 1.71 (1H, m, H-13β), 2.08 (1H, td, *J*=2.0, 10.3 Hz, H-14), 5.67 (1H, t, *J*<10 Hz, H-15α), 5.18 (1H, t, *J*=1.6 Hz, H-17a), 5.00 (1H, t, *J*=1.6 Hz, H-17b), 1.64 (3H, s, H_3-18), 4.89 (1H, s, H-19), 2.72 (1H, s, H-20), 2.16 (3H, s, OAc), 6.08 (1H, d, *J*=4.5 Hz, 3-OH), 4.94 (1H, s, 19-OH)

TABLE XXXIII (*continued*)

AVII2c-3 (vakhmatine) (*148*)	1.04 (3H, s, H_3-18), 1.55 (1H, dt, *J*=4.8, 15.2 Hz, H-3β), 1.91 (1H, dd, *J*=2.1, 9.0 Hz, H-9), 1.99, 2.25 (each 1H, br.d, *J*=17.7 Hz, H_2-15), 2.12 (1H, dd, *J*=1.8, 9.3 Hz, H-14), 2.35 (1H, d, *J*=2.6 Hz, H-12), 3.00 (1H, br.d, *J*=15.3 Hz, H-1α), 3.38 (1H, br.s, H-6), 4.02 (1H, br.m, H-2β), 4.11 (1H, dt, *J*=2.3, 9.3 Hz, H-13β), 4.18 (1H, s, H-19), 4.22 (1H, d, *J*=9.1 Hz, H-11β), 4.67, 4.84 (each 1H, br.s, H_2-17)
AVII2c-4 (13-*O*-acetyl vakhmatine) (*280*)	1.82 (1H, dd, *J*=4.0, 15.0 Hz, H-1β), 2.66 (1H, br.d, *J*=15.0 Hz, H-1α), 4.18 (1H, br.s, W1/2=8.0 Hz, H-2β), 1.55 (1H, dd, *J*=2.1, 7.8 Hz, H-3β), 1.98 (1H, br.d, *J*=7.8 Hz, H-3α), 1.45 (1H, s, H-5), 3.55 (1H, m, H-6), 1.56 (1H, m, H-7β), 1.71 (1H, dd, *J*=2.7, 14.0 Hz, H-7α), 1.91 (1H, d, *J*=9.0 Hz, H-9), 4.23 (1H, d, *J*=9.0 Hz, H-11β), 2.42 (1H, dd, *J*=2.5, <1 Hz, H-12), 5.00 (1H, br.d, *J*=9.0 Hz, H-13), 2.38 (1H, d, *J*=9.0 Hz, H-14), 2.03 (1H, ABq, *J*=18.0 Hz, H-15α), 2.18 (1H, ABq, *J*=18.0 Hz, H-15β), 4.70, 4.86 (each 1H, s, H_2-17), 1.00 (3H, s, H_3-18), 4.71 (1H, s, H-19), 3.28 (1H, s, H-20), 2.20 (3H, s, OAc)
AVII2c-5 (septenine) (*281*)	1.00 (3H, s, H_3-18), 1.99 (3H, s, OAc), 3.55 (1H, br.s), 4.47 (1H, s, H-19), 4.54, 4.68 (each 1H, br.s, H_2-17), 4.95 (1H, br.s, H-2β)
AVII2c-6 (septentriosine) (*282*)	1.02 (3H, s, H_3-18), 3.30 (1H, br.s, H-6), 3.60 (1H, br.s, H-20), 4.08 (1H, s, H-19), 4.48, 4.65 (each 1H, s, H_2-17)
AVII2c-7 (2-acetylsepten-triosine) (*283*)	1.08 (3H, s, H_3-18), 2.07 (3H, s, OAc), 2.76 (1H, br.s, H-20), 3.60 (1H, br.s, H-6), 4.18 (1H, s, H-19), 4.52 (1H, s, H-1), 4.59, 4.74 (each 1H, d, *J*=1.5 Hz, H_2-17), 5.00 (1H, t, *J*=1.5 Hz, H-2)
AVII2c-8 (delgramine) (*284*)	3.96 (1H, s, H-1), 5.28 (1H, br.m, W1/2=10 Hz, H-2), 3.30 (1H, s, H-6), 4.29 (1H, d, *J*=9.7 Hz, H-1), 2.33 (1H, d, *J*=2.5 Hz, H-12), 4.05 (1H, dd, *J*=3.0, 9.3 Hz, H-13α), 4.67, 4.96 (each 1H, s, H_2-17), 1.03 (3H, s, H_3-18), 4.82 (1H, s, H-19), 3.60 (1H, s, H-20), 7.50 (2H, t, *J*=7.6 Hz); 7.60 (1H, t, *J*=7.4 Hz); 8.05 (2H, d, *J*=7.1 Hz) (Ar-H)
AVII2c-10 (ternatine) (*395*)	0.99 (3H, s, H_3-18), 1.21, 1.23 (each 3H, d, *J*=7 Hz, HC(CH_3)$_2$), 2.12 (1H, d, J=8.8 Hz, H-9), 2.20 (1H, t, W1/2=6 Hz, H-12), 2.69 (1H, m, *H*C(CH_3)$_2$), 2.77 (1H, s, H-20), 3.52 (1H, m, H-19), 4.21 (1H, s, H-15), 4.46 (1H, dd, *J*=8.4 Hz, H-11β) , 5.05 (2H, s, H_2-17), 5.16 (1H, d, *J*=2.9 Hz, H-7)

TABLE XXXIII (*continued*)

AVII2d-1 (orgetine) (*285*)	1.28 (3H, s, H_3-18), 3.00 (1H, d, *J*=12 Hz), 3.82 (1H, s, H-15), 3.97 (1H, d, *J*=5 Hz, H-11α), 5.05, 5.15 (each 1H, br.s, H_2-17)
AVII3-1 (guan-fu base Z *N*-oxide) (*286*)	1.15 (3H, s, H_3-18), 1.16 (6H, d, *J*=6 Hz, H_3-3', H_3-4'), 2.91 (1H, d, *J*=12 Hz, H-19β), 3.73 (2H, m, H-6, H-13), 3.93 (1H, br.s, H-20), 4.02 (1H, d, *J*=12 Hz, H-19α), 4.14 (1H, br.d *J*=9 Hz, H-11), 4.65, 4.75 (each 1h, br.s, H_2-17), 5.10 (1H, m, H-2)
AVII3-2 (guan-fu base F *N*-oxide) (*287*)	1.20 (3H, s, H_3-18), 1.15, 1.24 (each 3H, d, *J*=4 Hz, $HC(CH_3)_2$), 2.04 (3H, s, OAc), 4.90, 4.99 (each 1H, br.s, H_2-17)
AVII3-3 (zeaconine *N*-oxide) (*288*)	0.93 (3H, s, H_3-18), 3.14 (6H, s, 2×NCH_3), 4.42 (2H, br.s), 5.72 (1H, br.s), 6.73, 7.03 (each 2H, d, *J*=7.5 Hz, *O*-Ar-H)
AVII3-4 (eraconine *N*-oxide) (*288*)	0.93 (3H, s, H_3-18), 3.14 (6H, s, 2×NCH_3), 3.44 (2H, br.s), 4.42 (1H, br.s), 5.72 (1H, br.s), 6.73, 7.03 (each 2H, d, *J*=8.5 Hz, O-Ar-H)

TABLE XXXIV

^{1}H NMR DATA OF VAKOGNAVINE TYPE DITERPENOID ALKALOIDS (AVIII)

code (name) (*ref*)	δ_H
AVIII1-1 (15-deacetyl-vakognavine) (*215*)	1.07 (3H, s, H_3-18), 2.02 (6H, s, 2×OAc), 2.28 (3H, s, NCH_3), 3.16 (1H, br.s, H-6), 3.85 (1H, s, H-20), 5.41 (1H, d, *J*=3.7 Hz, H-1α), 5.65 (1H, dd, *J*=1.3, 7.9 Hz, H-11β), 5.72 (1H, br.m, W1/2=9.0 Hz, H-2β), 7.53 (3H, m); 7.93 (2H, m) (Ar-H)
AVIII1-2 (vakognavine) (*215*)	1.05 (3H, s, H_3-18), 2.01, 2.03, 2.13 (each 3H, s, 3×OAc), 2.27 (3H, d, NCH_3), 3.13 (1H, br.s, H-6), 3.84 (1H, s, H-20), 5.24, 5.37 (each 1H, br.s, H_2-17), 5.40 (1H, d, *J*=3.2 Hz, H-1α), 5.46 (1H, s, H-15α), 5.56 (1H, d, *J*=8.8 Hz, H-11β), 5.69 (1H, br.m, W1/2=12.0 Hz, H-2β), 7.43 (2H, t, *J*=7.5 Hz); 7.55 (1H, t, *J*=7.3 Hz); 7.90 (2, d, *J*=7.8 Hz) (Ar-H), 9.27 (1H, s, H-19)

TABLE X X X IV
(*continued*)

AⅧ1-3 (barbisine) (*293*)	1.11 (3H, s, H_3-18), 2.10, 2.14 (each 3H, s, 2×OAc), 2.45 (3H, s, NCH_3), 3.10 (1H, d, *J*=4.5 Hz, H-9), 3.62 (1H, s, H-20), 3.78 (1H, d, *J*=4.5 Hz, H-11α), 4.23 (1H, s, H-19), 4.95, 5.03 (each 1H, d, *J*=2.1 Hz, H_2-17), 5.05 (1H, s, H-7β), 5.17 (1H, d, *J*=3.1 Hz, H-1α), 5.30 (1H, q, *J*=3.1 Hz, H-2β), 7.43, 7.56, 7.85 (5H, m, Ar-H)
AⅧ1-4 (delgrandine) (*294*)	1.88, 2.02, 2.11 (each, 3H, s, 3×OAc), 6.00 (1H, d, *J*=3.5 Hz, H-1), 6.5 (1H, dd, *J*=3.5, 3.5 Hz, H-2), 5.15 (1H, d, *J*=3.5 Hz, H-3), 2.05 (1H, s, H-5), 3.28 (1H, br.s, H-6), 3.82 (1H, br.s, W1/2=10.0 Hz, H-7), 2.40 (1H, d, *J*=9.3 Hz, H-9), 5.23 (1H, d, *J*=9.3 Hz, H-11), 2.58 (1H, br.s, W1/2=10.0 Hz, H-12), 5.35 (1H, d, *J*=9.3 Hz, H-13), 3.35 (1H, d, *J*=9.3 Hz, H-14), 2.20, 2.80 (each 1H, d, *J*=19.0 Hz, H-15), 4.90, 5.05 (each 1H, br.s, H_2-17), 1.11 (3H, s, H_3-18), 9.00 (1H, br.s, H-19), 3.92 (1H, s, H-20), 3.50 (1H, br.s, OH), 7.04 (2H, t, *J*=8.0 Hz); 7.33 (3H, m) (Ar-H); 7.54 (3H, m); 7.69 (2H, d, *J*=8.0 Hz) (Ar-H), 3.50 1H, br.s)
AⅧ1-5 (acetyldelgrandine) (*294*)	6.00 (1H, d, *J*=3.9 Hz, H-1), 6.08 (1H, t, *J*=3.6, 3.9 Hz, H-2), 5.18 (1H, t, *J*=3.6 Hz, H-3), 2.15 (1H, s, H-5), 3.10 (1H, br.s, H-6), 4.90 (1H, br.s, W1/2=10.5 Hz, H-7), 2.47 (1H, d, *J*=9.6 Hz, H-9), 5.49 (1H, d, *J*=9.6 Hz, H-11), 2.58 (1H, d, *J*=3.0 Hz, H-12), 5.30 (1H, d, *J*=9.0 Hz, H-13), 3.24 (1H, d, *J*=9.0 Hz, H-14), 2.20, 2.43 (each 1H, d, *J*=20.0 Hz, H-15), 4.90, 5.07 (each 1H, br.s, H_2-17), 1.12 (3H, s, H_3-18), 9.48 (1H, br.s, H-19), 3.90 (1H, s, H-20), 2.51 (3H, s, NCH_3), 1.88, 2.04, 2.13, 2.15 (each 3H, s, 4×OAc); 7.06 (2H, t, *J*=8.0 Hz); 7.32 (3H, m); 7.52 (3H, m); 7.71 (2H, d, *J*=8.0 Hz) (2×Ar-H)
AⅧ1-6 (barbaline) (*295*)	5.55 (1H, d, *J*=4.2 Hz, H-1), 6.09 (1H, t, *J*=4.2 Hz, H-2), 5.22 (1H, d, *J*=3.9 Hz, H-3β), 2.52 (1H, s, H-5), 3.03 (1H, br.d, *J*=4.0 Hz, H-6), 3.94 (1H, d, *J*=4.0 Hz, H-7α), 2.96 (1H, dd, *J*=4.5, 9.5 Hz, H-9), 5.43 (1H, dd, *J*=2.0, 9.5 Hz, H-11β), 2.84 (1H, d, *J*=2.0 Hz, H-12), 2.80 (1H, br.d, *J*=4.0 Hz, H-14), 2.77 (1H, d, *J*=18.0 Hz, H-15), 2.93 (1H, dt, *J*=1.5, 18.0 Hz, H-15), 4.96, 5.06, (each 1H, br.s, *J*=1.5 Hz, H_2-17), 1.16 (3H, s, H_3-18), 9.69 (1H, br.s, H-19), 3.81 (1H, s, H-20), 2.43 (3H, s, NCH_3), 1.96, 2.03, 2.10 (each 3H, s, 3×OAc), 7.48-7.66, 7.98 (5H, m, Ar-H)

TABLE X X X V

^{1}H NMR DATA OF VEATCHINE TYPE DITERPENOID ALKALOIDS (B Ⅰ)

code (name) (*ref*)	δ_H
B Ⅰ 1a-3 (ovatine) (*305*)	0.72 (0.80) (3H, s, H_3-18), 2.15 (3H, s, OAc), 2.60 (2H, br.s, NCH_2), 4.88, 5.14 (each 1H, br.s, H_2-17), 3.95 (4.25) (1H, br.s, H-20)
B Ⅰ 1a-4 (cuauchichicine) (*306*)	0.81 (3H, s, H_3-18), 1.11 (3H, d, H_3-17), 2.65 (1H, br.s, H-19), 4.29 (1H, br.s, H-20)
B Ⅰ 1a-6 (isogarryfoline) (*306*)	1.05 (3H, s, H_3-18), 2.66 (2H, br.s, H_2-20), 3.78 (2H, m, H_2-22), 3.98 (1H, br.s, H-19), 5.00, 5.18 (each 1H, br.s, H_2-17)
B Ⅰ 1a-7 (isocuauchichicine) (*307*)	1.07 (3H, s, H_3-18), 1.11 (3H, d, H_3-17), 3.95 (1H, s, H-19)
B Ⅰ 1b-1 (lindheimerine) (*305*)	0.82 (3H, s, H_3-18), 2.18 (3H, s, OAc), 3.42 (2H, s, H_2-19), 8.00 (1H, br.s, H-20)

TABLE X X X Ⅵ

^{1}H NMR OF NAPELLINE TYPE DITERPENOID ALKALOIDS (B Ⅱ)

code (name) (*ref*)	δ_H
B Ⅱ 1-1 (liangshanine) (*315*)	1.04 (3H, t, *J*=6.8 Hz, H_3-22), 0.73 (3H, s, H_3-18), 5.09, 5.31 (each 1H, d, *J*=0.8 Hz, H_2-17), 4.16 (1H, dd, *J*=4.4, 9.1 Hz, H-12), 4.18 (1H, br.s, H-15)
B Ⅱ 1-2 (12-epiluciduscline) (*315*)	0.98 (3H, t, *J*=7.2 Hz, H_3-22), 0.69 (3H, s, H_3-18), 3.24 (1H, s, H-20), 3.84 (1H, dd, *J*=6.0, 7.8 Hz, H-1), 5.08, 5.15 (each 1H, d, *J*=2.2 Hz, H_2-17), 2.05 (3H, s, OAc), 5.50 (1H, d, *J*=2.2 Hz, H-15)

TABLE XXXVI (*continued*)

B II 1-3 (napelline, luciculine) (*316*)	4.05 (1H, dd, *J*=7.0, 10.9 Hz, H-1), 2.72 (1H, m, H-2α), 2.14 (1H, m, H-2β), 1.23 (1H, m, H-3α), 1.53 (1H, m, H-3β), 1.59 (1H, d, *J*=7.3 Hz, H-5), 1.49 (1H, dd, *J*=4.7, 12.8 Hz, H-6α), 3.34 (1H, dd, *J*=7.9, 12.8 Hz, H-6β), 2.38 (1H, d, *J*=5.9 Hz, H-7), 2.23 (1H, dd, *J*=6.2, 13.2 Hz, H-9), 2.72 (1H, m, H-11α), 2.40 (1H, m, H-11β), 3.99 (1H, dd, *J*=6.4, 10.2 Hz, H-12), 2.86 (1H, d, *J*=3.5 Hz, H-13), 2.18 (1H, d, *J*=12.0 Hz, H-14α), 1.16 (1H, d, *J*=4.2, 12.0 Hz, H-14β), 4.53 (1H, br.s, H-15), 5.29, 5.48 (each 1H, br.s, H_2-17), 0.76 (3H, s, H_3-18), 2.68, 3.15 (each 1H, ABq, *J*=12.2 Hz, H_2-19), 4.11 (1H, s, H-20), 3.02, 3.12 (each 1H, m, N*C*H_2), 1.42 (3H, t, *J*=6.8 Hz, NCH$_2$*C*H_3)
B II 1-4 (12-epinapelline) (*316, 330*)	4.02 (1H, dd, *J*=6.5, 9.9 Hz, H-1), 2.68 (1H, m, H-2α), 1.96 (1H, m, H-2β), 1.24 (1H, m, H-3α), 1.53 (1H, m, H-3β), 1.41 (1H, d, *J*=7.7 Hz, H-5), 1.34 (1H, dd, *J*=5.3, 12.9 Hz, H-6α), 2.94 (1H, dd, *J*=7.1, 12.0 Hz, H-6β), 2.13 (1H, d, *J*=5.6 Hz, H-7), 2.50 (1H, m, H-9), 2.91 (1H, m, H-11α), 2.11 (1H, m, H-11β), 4.44 (1H, br.t, *J*=7.3 Hz, H-12), 2.88 (1H, dd, *J*=4.2, 7.9 Hz, H-13), 1.88 (1H, d, *J*=11.9 Hz, H-14α), 1.15 (1H, dd, *J*=4.2, 12.0 Hz, H-14β), 4.55 (1H, br.s, H-15), 5.34, 5.62 (each 1H, br.s, H_2-17), 0.68 (3H, s, H_3-18), 2.18, 2.49 (each 1H, ABq, *J*=11.0 Hz, H_2-19), 3.67 (1H, s, H-20), 2.37, 2.48 (each 1H, m, N*C*H_2), 1.42 (3H, t, *J*=6.8 Hz, NCH$_2$*C*H_3)
B II 1-5 (1-epi-napelline) (*316*)	0.80 (3H, s, H_3-18), 1.13 (3H, t, *J*=7.1 Hz, NCH$_2$*C*H_3), 1.00 (1H, dd, *J*=4.0, 12.0 Hz, H-14e), 1.98 (1H, d, *J*=12.0 Hz, H-14a), 2.38 (1H, d, *J*=3.7 Hz, H-13), 3.45 (1H, br.s, H-20), 3.89 (1H, dd, *J*=6.3, 9.9 Hz, H-11), 3.52 (1H, dd, *J*=7.0, 9.5 Hz, H-12), 4.15 (1H, br.s, H-15), 5.12, 5.15 (each 1H, H_2-17), 2.09, 2.37 (each 1H, ABq, *J*=11.2 Hz, H_2-19)
B II 1-6 (12-acetylnapelline) (*333*)	0.70 (3H, s, H_3-18), 1.05 (3H, t, *J*=7 Hz, NCH$_2$*C*H_3), 1.91 (3H, s, OAc), 4.93, 5.10 (each 1H, d, *J*=1.5 Hz, H_2-17)
B II 1-7 (lucidusculine) (*316*)	4.03 (1H, dd, *J*=7.3, 11.2 Hz, H-1), 2.93 (1H, m, H-2α), 2.20 (1H, m, H-2β), 1.22 (1H, m, H-3α), 1.47 (1H, m, H-3β), 1.48 (1H, m, H-5), 1.52 (1H, m, H-6), 1.97 (1H, dd, *J*=8.2, 14.2 Hz, H-6β), 2.33 (1H, dd, *J*=4.4 Hz, H-7), 2.10 (1H, dd, *J*=6.1, 13.4 Hz, H-9), 2.80 (1H, m, H-11α), 2.43 (1H, m, H-11β), 3.99 (1H, dd, *J*=6.3, 10.5 Hz, H-12), 2.34 (1H, d, *J*=3.9 Hz, H-13), 2.14

TABLE XXXVI (*continued*)

	(1H, d, *J*=12.4 Hz, H-14α), 1.16 (1H, dd, *J*=4.1, 12.0 Hz, H-14β), 5.85 (1H, br.s, H-15), 5.19 (2H, br.s, H_2-17), 0.76 (3H, s, H_3-18), 2.67, 3.26 (each 1H, ABq, *J*=13.2 Hz, H_2-19), 4.15 (1H, s, H-20), 3.00, 3.18 (each 1H, m, N*C*H_2), 1.48 (3H, t, *J*=6.8 Hz, NCH$_2$*C*H_3), 2.24 (3H, s, OAc)
B II 1-8 (12-acetyl lucidusculine) (*134, 316*)	0.74 (3H, s, H_3-18), 1.04 (3H, t, *J*=6.8 Hz, NCH$_2$*C*H_3), 1.17 (1H, dd, *J*=3.8, 12.4 Hz, H-14e), 1.98 (1H, d, *J*=12.8 Hz, H-14a), 2.47 (1H, d, *J*=3.4 Hz, H-13), 3.37 (1H, br.s, H-20), 3.89 (1H, br.t, *J*=7.1 Hz, H-1), 4.85 (1H, t, *J*=8.7 Hz, H-12), 5.49 (1H, br.s, H-15), 4.97, 5.23 (each 1H, br.s, H_2-17), 2.20, 2.43 (each 1H, ABq, *J*=11.3 Hz, H_2-19), 2.01 (3H, s, 12-OAc), 2.09 (3H, s, 15-OAc)
B II 1-9 (turpelline) (*340*)	2.01, 2.09 (each 1H, m, H_2-2), 1.16, 1.36 (each 1H, m, H_2-3), 1.56 (1H, br.d, *J*=7.9 Hz, H-5), 1.34 (1H, dd, *J*=4.5, 13.5 Hz, H-6β), 3.23 (1H, dd, *J*=8.3, 13.5 Hz, H-6α), 2.23 (1H, d, *J*=5.0 Hz, H-7), 2.31 (1H, d, *J*=10.3 Hz, H-9), 4.82 (1H, dd, *J*=7.8, 10.3 Hz, H-11), 3.90 (1H, br.d, *J*=7.5 Hz, H-12), 2.81 (1H, br.d, *J*=4.4 Hz, H-13), 1.05 (1H, dd, *J*=4.4, 12.1 Hz, H-14α), 2.09 (1H, d, *J*=12.1 Hz, H-14β), 4.45 (2H, t, *J*=2.4 Hz, H_2-15), 5.16 (1H, d, *J*=2.0 Hz, H-17b), 5.32 (1H, br.s, H-17a), 0.62 (3H, s, H_3-18), 2.45 (1H, brd, *J*=13.5 Hz, H-19a), 2.90 (1H, m, H-19b), 2.86 (2H, m, N*C*H_2), 1.37 (3H, t, *J*=7.4 Hz, NCH$_2$*C*H_3)
B II 1-11 (songorine) (261, *343*)	2.73 (1H, m, H-2α), 1.97 (1H, m, H-2β), 1.24 (1H, m, H-3α), 1.52 (1H, m, H-3β), 1.42 (1H, d, *J*=8.0 Hz, H-5), 1.39 (1H, dd, *J*=5.2, 13.6 Hz, H-6α), 3.23 (1H, dd, *J*=8.0, 12.9 Hz, H-6β), 2.27 (1H, d, *J*=5.1 Hz, H-7), 2.34 (1H, dd, *J*=7.3, 11.0 Hz, H-9), 4.13 (1H, dd, *J*=11.1, 17.2 Hz, H-11α), 2.66 (1H, dd, *J*=7.2, 17.3 Hz, H-11β), 3.23 (1H, d, *J*=3.9 Hz, H-13), 2.21 (1H, d, *J*=8.9 Hz, H-14α), 1.45 (1H, dd, *J*=4.0, 8.9 Hz, H-14β), 4.68 (1H, br.s, H-15), 5.49, 5.54 (each 1H, br.s, H_2-17), 0.70 (3H, s, H_3-18), 3.08 (1H, s, H-19), 3.76 (1H, s, H-20), 2.41 (3H, s, NH*CH*), 2.52 (1H, m, N*H*CH), 6.90 (1H, br.d, *J*=6.8 Hz, OH)
B II 1-12 (15-acetylsongorine) (*345*)	0.74 (3H, s, H_3-18), 1.03 (3H, t, *J*=7 Hz, NCH$_2$*C*H_3), 2.03 (3H, s, OAc), 4.85, 5.18 (each 1H, br.s, H_2-17), 5.55 (1H, br.s, H-115)
B II 1-13 (liongshanone) (*315*)	1.06 (3H, t, *J*=6.9 Hz, H_3-22), 0.75 (3H, s, H_3-18), 5.29 (1H, dd, *J*=1.2, 2.6 Hz, H-17), 5.20 (1H, s, H-17), 4.34 (1H, br.s, H-15), 3.28 (3H, s, OCH_3), 3.30 (1H, dd, *J*=6.6, 10.5 Hz, H-1β)
B II 1-15 (dihydrosongorine) (*346*)	0.68 (3H, s, H_3-18), 0.74 (3H, d, *J*=7 Hz, 3H-17), 1.00 (3H, t, *J*=7 Hz, NCH$_2$*C*H_3)

TABLE XXXVI (*continued*)

B II 1-16 (karakomine) (*347*)	3.89 (1H, d, *J*=5.9, 6.6 Hz, H-1), 1.84, 1.95 (each 1H, m, H_2-2), 1.36, 1.63 (each 1H, m, H_2-3), 1.33 (1H, d, *J*=8.1 Hz, H-5), 1.47 (1H, dd, *J*=4.4, 14.7 Hz, H-6), 2.79 (1H, dd, *J*=8.1, 14.7 Hz, H-6), 2.22 (1H, br.d, *J*=4.4 Hz, H-7), 1.69 (1H, m, H-9), 1.68, 2.40 (each 1H, m, H_2-11), 4.43 (1H, dd, *J*=7.5, 8.1 Hz, H_2-12), 2.17 (1H, dd, *J*=4.4, 8.1 Hz, H-13), 1.48 (1H, dd, *J*=4.4, 12.5 Hz, H-14), 1.79 (1H, dd, *J*=2.2, 12.5 Hz, H-14), 2.89 (1H, dq, *J*=2.2, 7.3 Hz, H-16), 1.07 (3H, d, *J*=7.3 Hz, 3H-17), 0.78 (3H, s, H_3-18), 2.24, 2.40 (each 1H, ABq, *J*=10.3 Hz, H_2-19), 3.23 (1H, br.s, H-20), 2.43, 2.54 (each 1H, m, NCH_2), 1.07 (3H, t, *J*=7.3 Hz, NCH_2CH_3)
B II 1-17 (chuanfunine) (*348*)	4.72 (1H, dd, *J*=7, 11 Hz, H-1β), 2.15, 2.94 (each 1H, m, H_2-2), 1.26, 1.48 (each 1H, m, H_2-3), 2.69 (1H, d, *J*=9 Hz, H-15), 5.28 (1H, d, *J*=9 Hz, H-16β), 2.26 (1H, br.s, H-7), 1.65 (1H, d, *J*=8 Hz, H-9), 1.61, 3.76 (each 1H, m, H_2-11), 1.51, 2.41 (each 1H, m, H_2-12), 2.47 (1H, d, *J*=5 hz, H-13), 1.30, 1.90 (each 1H, m, H_2-14), 4.52 (1H, s, H-15), 4.62, 4.79 (each 1H, d, *J*=1.2 Hz, H_2-17), 0.73 (3H, s, H_3-18), 2.80, 3.42 (each 1H, d, *J*=13 Hz, H_2-19), 4.61 (1H, br.s, H-20), 3.16, 3.40 (each 1H, m, H_2-21), 1.56 (3H, t, *J*=7 Hz, NCH_2CH_3)
B II 1-18 (acofine) (*349*)	0.66 (3H, s, H_3-18), 0.99 (3H, t, *J*=7 Hz, NCH_2CH_3), 1.35, 1.39, 1.44 (each 3H, s, 3×OAc), 3.23 (1H, br.s), 4.17 (1H, dd, *J*=7, 10 Hz, H-1β)
B II 2a-1 (dehydronapelline) (*142, 316*)	4.30 (1H, d, *J*=5.2 Hz, H-1), 1.76 (1H, m, H-2α), 1.39 (1H, m, H-2β), 1.17 (1H, m, H-3α), 1.56 (1H, m, H-3β), 1.51 (1H, br.d, *J*=7.7 Hz, H-5), 1.83 (1H, m, H-6α), 2.86 (1H, dd, *J*=3.5, 13.4 Hz, H-6β), 1.96 (1H, d, *J*=5.6 Hz, H-7), 2.02 (1H, m, H-9), 1.95 (1H, m, H-11α), 1.70 (1H, m, H-11β), 4.08 (1H, br.t, *J*=7.5 Hz, H-12), 2.91 (1H, d, *J*=4.2 Hz, H-13), 2.18 (1H, d, *J*=12.0 Hz, H-14α), 1.25 (1H, dd, *J*=4.6, 12.0 Hz, H-14β), 4.60 (1H, br.d, *J*=7.0 Hz, H-15), 5.25, 5.56 (each 1H, br.s, H_2-17), 0.84 (3H, s, H_3-18), 3.80 (1H, s, H-19), 3.00 (1H, s, H-20), 2.70, 2.83 (each 1H, m, NCH_2), 1.03 (3H, t, *J*=7.1 Hz, NCH_2CH_3), 6.44 (1H, br.d, *J*=7.3 Hz, 15-OH), 1.16 (3H, t, *J*=6.8 Hz, NCH_2CH_3)
B II 2a-2 (12-epi-19-dehydro-napelline) (*331*)	0.81 (3H, s, H_3-18), 1.00 (3H, t, *J*=7.0 Hz, NCH_2-CH_3), 2.66, 2.67 (each 1H, dq, *J*=7.1 Hz, NCH_2CH_3), 2.73 (1H, d, *J*=1.7 Hz, H-20), 2.80 (1H, dd, *J*=4.5, 8.7 Hz, H_2-13), 4.12 (1H, dd, *J*=4.0, 8.5 Hz, H-12α), 4.27 (1H, br.s, H-15α), 5.20, 5.39 (each 1H, br.s, H_2-17)

TABLE XXXVI (*continued*)

B II 2a-3 (dehydrolucidasculine) (*331a*)	0.81 (3H, s, H_3-18), 1.01 (3H, t, *J*=7.0 Hz, NCH_2CH_3), 2.13 (3H, s, OAc), 5.49 (1H, br.s, H-15), 4.92, 5.12 (each 1H, s, H_2-17)
B II 2a-4 (12-epi-acetyl dehydronapelline) (*331*)	0.82 (3H, s, H_3-18), 1.01 (3H, t, *J*=7.0 Hz, NCH_2CH_3), 1.99 (3H, s, OAc), 2.67, 2.68 (each 1H, dq, *J*=7.2 Hz, NCH_2CH_3), 2.73 (1H, br.s, H-20), 3.02 (1H, dd, *J*=5.5, 8.6 Hz, H-13), 3.68 (1H, s, H-19), 4.01 (1H, d, *J*=4.9 Hz, H-1β), 4.24 (1H, br.s, H-15α), 4.95, 5.22 (each 1H, br.s, H_2-17), 5.11 (1H, dd, *J*=6.1, 8.5 Hz, H-12α)
B II 2a-5 (12-acetyldehydro-lucidusciline) (*134*)	0.81 (3H, s, H_3-18), 1.01 (3H, t, *J*=7.0 Hz, NCH_2CH_3), 2.06, 2.14 (each 3H, s, 2×OAc), 4.59 (1H, m, H-12β), 5.48 (1H, br.s, H-15α), 4.98, 5.29 (each 1H, s, H_2-17), 3.68 (1H, s,), 4.20 (1H, d, *J*=5.0 Hz)
B II 2a-6 (12-epi-acetyldehydro-lucidusculine) (*350*)	2.95 (1H, dd, *J*=4.0, 8.8 Hz, H-13), 4.85, 4.95 (each 1H, d, *J*=2.0 Hz, H_2-17), 5.10 (1H, dd, *J*=4.0, 8.8 Hz, H-12α), 5.45 (1H, d, *J*=2.0 Hz, H-15α)
B II 2a-7 (subdesculine) (*351*)	0.81 (3H, s, H_3-18), 1.02 (3H, t, *J*=7.1 Hz, H_3-22), 2.04 (3H, s, OAc), 3.69 (1H, s, H-19), 4.04 (1H, d, *J*=4.9 Hz, H-1β), 4.24 (1H, br.s, H-15α), 4.59 (1H, dd, *J*=6.0, 8.0 Hz, H-12β), 5.23, 5.34 (each, 1H, s, H_2-17)
B II 2a-8 (*N*-deethyldehydro lucidusculine) (*331a*)	0.86 (3H, s, H_3-18), 2.14 (3H, s, OAc), 3.87 (1H, s, H-19), 4.15 (1H, d, *J*=4.8 Hz, H-1β), 4.93, 5.16 (each 1H, s, H_2-17), 5.50 (1H, s, H-15)
B II 2a-9 (songoramine) (*261*)	0.85 (3H, s, H_3-18), 1.03 (3H, t, *J*=7.2 Hz, NCH_2CH_3), 2.68, 2.71 (each 1H, q, *J*=7.2 Hz, H_2-21), 2.94 (1H, s, H-20), 3.15 (1H, d, *J*=4.1 Hz, H-13), 3.71 (1H, s, H-19), 3.98 (1H, d, *J*=5.2 Hz, H-1), 4.40 (1H, t, *J*=2.1 Hz, H-15), 5.20, 5.31 (each 1H, s, H_2-17)
B II 2a-10 (15-acetylsongo-ramine) (*352*)	0.78 (3H, s, H_3-18), 0.97 (3H, t, *J*=7.2 Hz, NCH_2CH_3), 2.10 (3H, s, OAc), 5.16, 5.22 (each 1H, s, H_2-17)
B II 2a-11 (norsongoramine) (*353*)	1.12 (3H, s, H_3-18), 4.63, 4.85 (each 1H, br.s, H_2-17)

TABLE XXXVI (*continued*)

B II 3-1 (flavamine) (*142*)	4.15 (1H, d, *J*=6.4 Hz, H-1), 2.74 (1H, m, H-2α), 1.99 (1H, m, H-2β), 1.23 (1H, m, H-3α), 1.25 (1H, m, H-3β), 1.63 (1H, d, *J*=7.5 Hz, H-5), 1.43 (1H, dd, *J*=4.9, 13.6 Hz, H-6α), 3.40 (1H, dd, *J*=8.0, 13.6 Hz, H-6β), 2.12 (1H, d, *J*=5.0 Hz, H-7), 2.25 (1H, m, H-9), 1.57 (1H, m, H-11α), 1.47 (1H, m, H-11β), 4.07 (1H, dd, *J*=6.6, 10.2 Hz, H-12), 2.91 (1H, d, *J*=3.9 Hz, H-13), 2.18 (1H, d, *J*=11.9 Hz, H-14α), 1.19 (1H, dd, *J*=4.5, 12.0 Hz, H-14β), 4.55 (1H, br.d, *J*=7.9 Hz, H-15), 5.27, 5.51 (each 1H, br.s, H_2-17), 0.69 (3H, s, H_3-18), 3.20, 3.29 (each 1H, ABq, *J*=13.2 Hz, H_2-19), 4.11 (1H, s, H-20), 3.11, 3.24 (each 1H, m, N*C*H_2), 1.40 (3H, t, *J*=7.0 Hz, NCH_2*C*H_3), 6.61 (1H, d, *J*=7.9 Hz, 15-OH)
B II 3-2 (12-epi-napelline *N*-oxide) (*355*)	0.82 (3H, s, H_3-18), 1.13 (1H, dd, *J*=4.1, 12.0 Hz, H-14α), 1.30 (2H, m, H-3α, H-6α), 1.39 (3H, t, *J*=7.1Hz, NCH_2*C*H_3), 1.50 (1H, br.d, *J*=7.9 Hz, H-15), 1.70 (1H, dd, *J*=6.5, 15.0 Hz, H-11), 1.72 (1H, d, *J*=12.0 Hz, H-14e), 1.95 (2H, m, H-2a, H-3e), 2.02 (1H, d, *J*=5.3 Hz, H-7), 2.08 (1H, dd, *J*=6.5, 13.0 Hz, H-9), 2.25 (1H, ddd, *J*=6.0, 12.9, 15.0 Hz, H-11e), 2.45 (1H, m, H-2e), 2.71 (1H, dd, *J*=7.9, 14.0 Hz, H-6e), 2.80 (1H, dd, *J*=4.1, 8.7 Hz, H-13), 3.10 (2H, d, *J*=13.8 Hz, H-19β, m, N*C*H_2CH_3), 3.24 (1H, m, N*H*CHCH_3), 3.28 (1H, d, *J*=13.8 Hz, H-19a), 3.75 (1H, br.s, H-20), 3.86 (1H, t, *J*=7.1 Hz, H-1), 4.18 (1H, dd, *J*=6.0, 8.7 Hz, H-12α)
B II 3-3 (12-acetylnapelline *N*-oxide) (*356*)	0.80 (3H, s, H_3-18), 1.37 (3H, t, *J*=7 Hz, *N*CH_2*C*H_3), 1.91 (3H, s, OAc), 4.86, 5.11 (each 1H, s, H_2-17)
B II 3-4 (flavadine) (*142*)	4.07 (1H, d, *J*=6.8 Hz, H-1), 2.85 (1H, m, H-2α), 2.06 (1H, m, H-2β), 1.25 (1H, m, H-3α), 2.05 (1H, m, H-3), 1.53 (1H, d, *J*=7.6 Hz, H-5), 1.43 (1H, dd, *J*=5.1, 14.1 Hz, H-6α), 1.92 (1H, dd, *J*=6.9, 14.1 Hz, H-6β), 2.04 (1H, d, *J*=5.1 Hz, H-7), 2.06 (1H, m, H-9), 2.55 (1H, m, H-11α), 2.4 (1H, m, H-11β), 4.02 (1H, dd, *J*=6.9, 9.6 Hz, H-12), 2.85 (1H, d, *J*=4.0 Hz, H-13), 2.20 (1H, d, *J*=11.9 Hz, H-14α), 1.21 (1H, dd, *J*=4.1, 11.8 Hz, H-14β), 5.82 (1H, t, *J*=2.2 Hz, H-15), 5.15 (2H, m, H_2-17), 0.71 (3H, s, H_3-18), 3.22, 3.38 (each 1H, ABq, *J*=13.6 Hz, H_2-19), 4.05 (1H, s, H-20), 3.12, 3.31 (each 1H, m, N*C*H_2), 1.40 (3H, t, *J*=7.0 Hz, NCH_2*C*H_3), 2.24 (3H, s, OAc)
B II 3-5 (songorine *N*-oxide) (*357*)	0.84 (3H, s, H_3-18), 1.36 (3H, t, *J*=7 Hz, NCH_2*C*H_3)

TABLE X X X VII

^{1}H NMR OF ANOPTERINE TYPE DITERPENOID ALKALOIDS (BIII)

code (name) (*ref*)	δ_H
BIII1-1 (anopterine) (*360, 361*)	1.47 (3H, br.d, *J*=7 Hz, NCH_2CH_3), 1.56 (3H, s, H_3-18), 1.71 (3H, br.d, *J*=7 Hz, CH_2CH_3), 1.74 (3H, br.s, CCH_3), 2.00 (3H, br.s, C-CH_3), 2.32 (3H, s, CCH_3), 4.16 1H, m, H-6), 4.21 (1H, d, *J*=11 Hz, H-19), 4.36 (1H, s, H-20), 4.41 (1H, m, H-2), 4.77, 5.05 (each 1H, m, H_2-17), 5.60 (1H, dd, *J*=3, 6 Hz, H-12), 5.85 (1H, dd, *J*=6.4 Hz, H-11), 6.90 (1H, bq, *J*=7 Hz, $CHCH_3$), 7.64 (1H, bq, *J*=7 Hz, CH-CH_3), 10.00 (1H, d, *J*=11 Hz, 6-OH)
BIII1-2 (dihydroxyanopterine) (*359, 360*)	1.58 (3H, s, H_3-18), 1.74 (3H, br.d, *J*=7 Hz, CH=C-CH_3), 1.84 (3H, br.s, C-CH_3) (tiglate or hydroxytiglate), 2.05 (3H, br.s, CCH_3, tiglate or hydroxytiglate), 2.36 (3H, s, NCH_3), 4.83, 5.10 (each 1H, br.s, H_2-17), 5.70 (1H, dd, *J*=3, 6 Hz, H-12), 5.97 (1H, dd, *J*=4.6 Hz, H-11), 7.29 (1H, d, *J*=7 Hz, -CH=C, hydroxytiglate), 7.64 (1H, d, *J*=7 Hz, -CH=C, tiglate)
BIII1-3 (hydroxyanopterine) (*360*)	1.21 (3H, s, H_3-18), 1.42 (3-3e), 1.75 (3H, s, -(CH_3) C=, 11-tiglate), 1.76 (3H, d, C=CH-CH_3 , 11-tiglate), 1.84 (3H, CH-CH_3, 12-tiglate), 3.92 (1H, H-7e), 1.92 (-CH=C, 12-tiglate), 1.97 (1H, H-3a), 2.13 (1H, H-1α), 2.29 (1H, H-15), 2.78 (1H, H-9), 2.31 (1H, s, NCH_3), 2.43 (1H, H-14e), 2.47 (1H, H-1e), 2.66 (1H, H-19e), 3.03 (1H, H-15), 2.98 (1H, H-13e), 3.62 (1H, H-6e), 3.75 (1H, H-9a), 4.11 (1H, H-20), 4.15 (1H, H-2e), 4.91, 5.09 (each 1H, s, H_2-17), 5.20 (1H, H-12e), 5.49 (1H, H-1a), 6.76 (1H, CH, 11-tiglate), 7.09 (1H, CH, 12-tiglate)
BIII2-1 (anopterimine) (*358*)	1.03 (3H, s, H_3-18), 1.74 (3H, br.d, *J*=7 Hz, CH-CH_3, tiglate), 1.82 (3H, br.s, CCH_3, tiglate), 3.17 (1H, m, H-13), 4.37 (1H, dd, *J*=4.6 Hz, H-11), 4.61 (1H, br.s, H-20), 4.77, 5.02 (each 1H, br.s, H_2-17), 5.11 (1H, dd, *J*=3.6 Hz, H-12), 6.87 (1H, bq, -CH=, tiglate), 7.42 (1H, br.s, H-19)
BIII3-1 (anopterimine *N*-oxide) (*358*)	1.08 (3H, s, H_3-18), 1.80 (3H, br.d, *J*=7 Hz, CH-CH_3, tiglate), 1.85 (3H, br.s, CCH_3, tiglate), 3.17 (1H, m, H-13), 4.38 (1H, dd, *J*=4, 6 Hz, H-11), 4.79, 5.03 (each 1H, br.s, H_2-17), 4.94 (1H, br.s, H-20), 5.13 (1H, dd, *J*=3, 6 Hz, H-12), 6.89 (2H, m, H-19 and =CH-, tiglate)

TABLE XXXVIII
^{1}H NMR OF DELNUDINE TYPE DITERPENOID ALKALOIDS (C I)

code (name) (*ref*)	δ_H
C I 1-1 (delnudine) (*364*)	1.63 (3H, s, H_3-18), 4.72, 4.96 (each 1H, br.s, H_2-17)

TABLE XXXIX
^{1}H NMR OF KUSNESOLINE TYPE DITERPENOID ALKALOIDS (C II)

code (name) (*ref*)	δ_H
C II 1-1 (kusnesoline, no name) (*366*)	1.57 (1H, m, H-1β), 2.34 (1H, br.d, *J*=16.0 Hz, W1/2=5.5 Hz, H-1α), 4.20 (1H, dt, *J*=2.4, 16.0 Hz, H-2), 1.49 (1H, m, H-3β), 1.84 (1H, dt, *J*=2.0, 16.0 Hz, H-3α), 1.59 (1H, m, H-5), 3.29 (1H, m, H-6), 1.51 (1H, m, H-7β), 1.66 (1H, m, H-7α), 1.57 (1H, m, H-9), 5.01 (1H, d, *J*=3.6 Hz, H-11β)1.47 (1H, m, H-12α), 2.06 (1H, dt, *J*=4.0, 13.2 Hz, H-12β), 4.08 (1H, br.s, W1/2=8.2 Hz, H-13), 1.88 (1H, t, *J*=2.4 Hz, H-14), 1.47 (1H, m, H-15β), 1.68 (1H, m, H-15α), 1.18 (1H, s, H-17), 1.00 (3H, s, H_3-18), 2.49, 3.27 (each 1H, ABq, *J*=12.0 Hz, H_2-19), 3.64 (1H,.s, H-20)
C II 1-2 (guan-fu base K) (*368*)	1.02 (3H, s, H_3-18), 1.16 (3H, s, 3H-17), 3.86 (1H, dd, *J*=1.8, 3 Hz, H-13), 4.25 (1H, m, H-2β), 4.98 (1H, d, *J*=3 Hz, H-11)

TABLE XL

^{1}H NMR OF ACTALINE TYPE DITERPENOID ALKALOIDS (CIII)

code (name) (*ref*)	δ_H
CIII1-1 (actaline) (*369*)	0.80 (3H, s, H_3-18), 1.03 (3H, t, NCH_2CH_3), 3.20 (1H, s), 4.51, 4.53 (each 1H, br.s, H_2-17),
CIII1-2 (ajabicine) (*370*)	3.96 (1H, dd, *J*=2.9, 4.2 Hz, H-1), 1.74, 1.87 (each 1H, m, H_2-2), 1.44, 1.78 (each 1H, m, H_2-3), 1.55 (1H, d, *J*=7.7 Hz, H-5), 1.66 (1H, dd, *J*=8.0, 14.5 Hz, H-6β), 2.22 (1H, dd, *J*=7.7, 14.5 Hz, H-6α), 2.33 (1H, d, *J*=8.0 Hz, H-7), 2.63 (1H, d, *J*=7.3 Hz, H-9), 2.00 (1H, m, $J_{10,12b}$=7.5 Hz, $J_{10,q}$=7.3 Hz, H-10), 2.17 (2H, m, H_2-12), 2.51 (1H, m, H-13), 1.60, 2.16 (each 1H, m, H_2-15), 1.84, 1.96 (each 1H, m, H_2-16), 4.89, 5.00 (each 1H, d, *J*=1.9 Hz, H_2-17), 0.80 (3H, s, H_3-18), 1.98, 2.20 (each 1H, ABq, *J*=11.0 Hz, H_2-19), 3.38 (1H, s, H-20), 2.32, 2.46 (each 1H, dq, *J*=7.0, 12.2 Hz, NCH_2), 1.03 (3H, t, *J*=7.0 Hz, NCH_2CH_3)

TABLE XLI

^{1}H NMR OF RACEMULOSINE DITERPENOID ALKALOIDS (CIV)

code (name) (*ref*)	δ_H
CIV1-1 (racemulosine) (*371*) ($CDCl_3$-CD_3OD)	3.86 (1H, d, *J*=8.8 Hz, H-1β), 1.63 (1H, m, H-2a), 2.24 (1H, dd, *J*=9.6, 14.4 Hz, H-2e), 5.63 (1H, dd, *J*=11.2, 17.6 Hz, H-3), 1.93 (1H, t, *J*=7.8 Hz, H-5), 1.50 (1H, m, H-6a), 2.00 (1H, m, H-6e), 2.10 (1H, m, H-7), 2.08 (1H, m, H-9), 1.30 (1H, m, H-11a), 2.15 (1H, m, H-11e), 2.54 (1H, m, H-12), 1.70 (1H, m, H-13a), 2.10 (1H, m, H-13e), 1.72 (2H, m, H_2-14), 2.38 (1H, m, H-15), 2.66 (1H, t, *J*=4.0 Hz, H-16), 4.90 (1H, dd, *J*=1.2, 17.2 Hz, H-18a), 4.95 (1H, dd, *J*=1.2, 11.0 Hz, H-18b), 2.37, 2.61 (each 1H, ABq, *J*=10.8 Hz, H_2-19), 3.00 (1H, s, H-20), 2.58 (2H, q, *J*=7.0 Hz, NCH_2), 1.11 (3H, t, *J*=7.0 Hz, NCH_2CH_3)

TABLE XL II

^{1}H NMR OF ATISINE-HETIDINE TYPE BISDITERPENOID ALKALOIDS (D Ⅰ)

code (name) (*ref*)	δ_H
D Ⅰ 1-1 (staphisagrine) (*372*)	0.82, 0.93 (each 3H, s, H_3-18 and H_3-18'), 2.21 (3H, s, NCH_3), 4.06 (NCH_2), 5.93 (1H, H-11')
D Ⅰ 1-2 (staphisagnine) (*372*)	0.82, 0.93 (each 3H, s, H_3-18 and H_3-18'), 2.27 (3H, s, NCH_3), 3.30 (3H, s, OCH_2), 4.06 (NCH_2), 5.93 (1H, H-11')

TABLE XLIII

^{1}H NMR OF REARRANGED ATISINE-HETIDINE TYPE BISDITERPENOID ALKALOIDS (D Ⅱ)

code (name) (*ref*)	δ_H
D Ⅱ 1-1 (staphidine) (*373, 374*)	0.91 (3H, s, H_3-18), 0.91 (3H, s, H_3-18'), 2.13 (3H, s, NCH_3'), 2.21 (3H, s, NCH_3), 5.85 (1H, H-11')
D Ⅱ 1-2 (staphisine) (*373, 375*)	0.91 (3H, s, H_3-18), 0.91 (3H, s, H_3-18'), 2.13 (3H, s, NCH_3'), 2.27 (3H, s, NCH_3), 3.30 (3H, s, OCH_3), 5.85 (1H, H-11' or H-12'), 0.18 (1H, s, H-13'), 0.72 (1H, m, H-12' or H-11'), 0.85 (3H, s, angular-CH_3), 2.03 (6H, s, NCH_3), 2.22 (3H, s, OMe), 3.18 (2H, m, H-13 and H-15), 6.18 (1H, d)
D Ⅱ 1-3 (staphirine) (*374, 376*)	0.94 (3H, s, H_3-18'), 1.12 (3H, s, H_3-18), 2.13 (3H, s, NCH_3'), 2.92 (3H, s, NCH_3), 5.85 (1H, H-11')
D Ⅱ 1-4 (staphigine) (*374, 376*)	0.94 (3H, s, H_3-18'), 1.12 (3H, s, H_3-18), 2.13 (3H, s, NCH_3'), 2.98 (3H, s, NCH_3), 3.30 (1H, s, OCH_3), 5.85 (1H, H-11')
D Ⅱ 1-5 (staphimine) (*373, 374*)	0.94 (3H, s, H_3-18'), 1.10 (3H, s, H_3-18), 2.13 (3H, s, NCH_3'), 5.85 (3H, H-11'), 7.30 (1H, s, H-19)
D Ⅱ 1-6 (staphinine) (*373, 374*)	0.94 (3H, s, H_3-18'), 1.00 (3H, s, H_3-18), 2.13 (3H, s, NCH_3'), 3.30 (3H, s, OCH_3), 5.85 (1H, H-11'), 7.30 (1H, s, H-19)

TABLE XLIV

^{1}H NMR OF DENUDATINE-DENUDATINE TYPE BISDITERPENOID ALKALOIDS (DIII)

code (name) (*ref*)	δ_H
DIII1-1 (pukeensine) (*377*)	0.75, 0.96 (each 3H, s, H_3-18 and H_3-18'), 4.78 (2H, br.s, H_2-15), 5.02, 5.07 (each 1H, t, *J*=1.5 Hz, H_2-17')

TABLE XLV

^{1}H NMR OF HETERATISINE-HETIDINE-TYPE BISDITERPENOID ALKALOIDS (DIV)

code (name) (*ref*)	δ_H
DIV1-1 (tungirine) (*378*)	1.42 (2H, m, H_2-1), 1.07, 1.32 (each 1H, H_2-2), 1.22 (1H, m, H-3), 1.18 (1H, br.s, H-5), 1.48 (1H, m, H-6), 1.36 (1H, m, H-7a), 1.48 (1H, m, H-7b), 0.87 (1H, m, H-9), 1.43, 1.50 (each 1H, m, H_2-11), 2.00 (1H, m, H-12), 1.05 (1H, m, H-13a), 1.52 (1H, m, H-13b), 4.98 (1H, br.s, H-15), 3.82 (2H, ABq, *J*=12.0 Hz, H_2-17), 1.00 (3H, m, H_3-18), 7.32 (1H, s, *J*=2.5 Hz, H-19), 3.30 (1H, br.s, H-20); 3.18 (1H, m, H-1'), 2.13 (1H, m, H-2'), 1.22 (1H, m, H-3'a), 1.59 (1H, m, H-3'b), 1.58 (1H, br.s, H-5'), 5.46 (1H, d, *J*=7.2 Hz, H-6'), 2.95 (1H, d, *J*=7.2 Hz, H-7'), 4.19 (1H, d, *J*=8.0 Hz, H-9'), 2.45 (1H, m, H-10'), 2.13, 3.15 (each 1H, m, H_2-12'), 4.73 (1H, dd, *J*=5.5 Hz, H-13'), 1.82 (1H, m, H-15'a), 2.04 (1H, m, H-15'b), 1.83 (1H, m, H-16'a), 2.40 (1H, m, H-16'b), 3.60 (1H, br.s, H-17'), 0.86 (3H, s, H_3-18'), 2.19 (1H, ABq, *J*=12.0 Hz, H-19'a), 2.65 (1H, ABq, *J*=12.0 Hz, H-19'b), 2.52 (2H, *J*=7.2 Hz, N*CH*$_2$), 1.08 (3H, t, *J*=7.2 Hz, NCH$_2$*CH*$_3$), [8.05 (2H, dd, *J*=1.4, 7.0 Hz); 7.43 (2H, t, *J*=7.1 Hz); 7.53 (1H, t, *J*=7.1 Hz), 6'-OBz], 3.29 (3H, s, OCH_3-1'α)

D. ^{13}C NMR SPECTROSCOPY

^{13}C NMR spectroscopy is one of the most powerful and general approaches to organic structural elucidation. In 1982, Wang (*21*) provided an initial summary of the ^{13}C NMR data of the 186 known diterpenoid alkaloids. This was followed by reviews from Wang (*29*) and Ding (*31*). In recent years, Atta-ur-Rahman (*40*) has published the spectral data, including the ^{13}C NMR spectra, for the diterpenoid alkaloids. But, there is still a need for a timely and systematic summation of the ^{13}C NMR spectra of the about 247 entries now available. Here we have tried to delineate the characteristic features of the ^{13}C NMR spectra for the skeleta, the special structural units, and the common substituent groups in the C_{20}-diterpenoid alkaloids, arranged in the order of our proposed classification.

1. Quaternary Carbons. Assignment of the key quaternary carbons in the structural elucidation of C_{20}-diterpenoid alkaloids is very important. The feature of these carbons having sizable signal intensties are easily assignable chemical shifts, the so-called "finger-prints of diterpenoid alkaloids" (*421*). Significant changes occur only with large changes of the skeleta or structures. Thus, the δ values of quaternary carbons in the ^{13}C NMR spectra of C_{20}-diterpenoid alkaloids are very useful for establishing the skeleta and the location of substituent groups. There are frequently four, non-oxygenated, quaternary carbons, e. g., C-4, C-8, C-10 and, in most cases, the olefinic bond C-16. These are often accompanied by four oxygenated quaternary carbons, such as C-5, C-9, C-12, and C-16. The close relationship between the δ values, the "finger-print" characteristics, and their skeletal types, as well as the substitution patterns are presented in Tables XLVI and XLVII.

TABLE XLVI

RELATIONSHIP BETWEEN THE STRUCTURAL TYPES AND THE δ VALUES OF NON-OXYGENATED QUATERNARY CARBONS IN THE ^{13}C NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS

type	C-4	C-8	C-10	C-16
atisines (A I)	32-34 33-34[normal-type, N=C-20] ~35-36[iso-type, C-7-O-C-20-*N*, $\overset{+}{N}$=C-20] 38-40[iso-type, *N*-C-20-O-C-2] 41~44 (normal-type/19-CO) 36-37 (19-OH)	36-43 40-42 [*N*-C-20-O-C-7][a] ~44 (15-CO) 51-55 (7 or 14 or 20-CO)	37-38 34-36 [iso-type, *N*-C-20-O-C-7] 40-42 (normal-type) 42-44 [*N*=C-20, *N*-C-20-O-C-2] ~48 [$\overset{+}{N}$=C-20][b]	150-17 [15-OH (OAc)/H] 146-148 (14 or 15-CO)
deundatines (A II)	~34-35 ~38[*N*-C-19-O-C-1]	42-47	48-50 44-46 (15,16,17-OH or 15β-OH) ~54 (1α-OH/ N→O)[c]	153-155 ~148 [15β-OAc, 11β-OH, e.g., kirinine A (*122*)]
hetidines (AIV)	37-39 (including 6-CO) 34-37 (normal-type/iso-type)	42-45 ~47-50 (15-OH/OAc, 9-OH, 7-OH, 7, 15-OH/no 6-CO	43-~48	140-~144 146-151 (9-OH, 12-OH, 13-OH/OAc, 15-OCOR)[e]

TABLE XLVI (*continued*)

type	C (4)	C (8)	C (10)	C (16)
	~34 (non-6-CO) 40-41 (3-OH/OAc/OBz 2-CO/no 6-CO) 42-45[*N*=C-19, bisditerpenoids] ~47[11 or 19-CO or N=C-19 + 5-OH][d]		~50 (2-CO)	
hetisines (AVII)	36-38 40-44 (2, 3-OH/OAc/OBz, 2-OCOR, 2-CO, 2-CO and 6-OH, 4-CHO	42-45 ~45-52 (7/9/14-OH, 15-OH/OCOR) ~41 [11β-OH, 13, 15-OH, e.g., acorientine (*262*)] ~56 (15-CO)	50-52 ~46-47 (2,3-OH/OCOR, 2α-OH/OCOR, 11α-OH) 48-49 (19-OH, 2-CO and 11α-OH)	144-148 134-137 (4-CHO) ~138-143 (11-CO/13-CO/15-CO)
	~50[N-C-19-O-C-1, 19-OH and 3-OH]		~53-58 [1,9-OH, 1-OH/OAc, N-C-19-O-C-1, 2-CO, 6-OH and 11α-OH]	~150-152 (9-OH, 13β, 15β-OH, 15β-OAc, 11α-OAc and 15β-OH, 11, 15β-OH)
	~53 (19-OH and 6-OH)[f]		56-57 (4-CHO)	155-157 (15β-OH)

TABLE XLVI (*continued*)

type	C (4)	C (8)	C (10)	C (16)
vakognavines (AⅧ)	~44	~47	54-56	133-137 (13-CO, 15β-OAc, non-15-substitution)
	~49 (3β-OAc)	48-50 (15β-OH, 7 β- OH/ OAc)		140-142 (13β-OBz, 15β-OH)
veatchines (B Ⅰ)	~34	45-49	40-42 (normal-type)	158-160
	32-34 (normal-type) ~40 (iso-type)	50-52 (15-CO)	~36 (iso-type) 45-46 [*N*=C-20]	151 (15-CO) 154-156 (15-OAc)
napellines (B Ⅱ)	34-36 ~38[N-C-19-O-C-1]	49-51 ~43 (6-OH, 15β-OH)	50-~55	150-160 ~148 (12β-OAc)
anopterines (BⅢ)	36-37 40-41 [*N*=C-19]	51-57	47-48 50-51 [*N*=C-19]	148-150

a. 36.3 [e.g., spiramine Y (*85*)]; b. ~47 [21-CHO, e.g., chellespontine (*64*); ~44 [*N*-CH=CH-OH-containing, e.g., uncinatine (*72*)]; c. 53.6 (11α-OH, e g., lepenine *N*-oxide (*137*); d. except for example, 6, 7-diketo-containing, e.g., vilmorrianone (*163*), C-4: 54.1, C-8: 44.5, C-10: 40.0; e. except for example, e.g., spirafine Ⅱ (*145*), sczukidine (*144*); f. except for example, 51.5 [6-OH, 3α-OAc, 2α-OH, e.g., geyerinine (*273*); g. except for example, e. g.; orientinine [48.2 (2-CO, 1α-OH)].

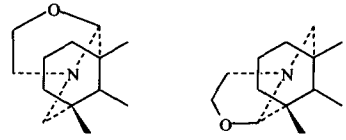
TABLE XLVII
RELATIONSHIP BETWEEN THE STRUCTURAL TYPES AND THE δ VALUES OF OXYGENATED QUATERNARY CARBONS IN THE ^{13}C NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS

type	C-5	C-9	C-12	C-16
atisines (A I)				74-76 (15, 16-OH)
denudatines (A II)				64-65 (16, 17-epoxy) 80-81 (15, 16-OH, 17-OH/OBz)
hetidines (AIV)		84-85 (11-CO) 77-82 (OH)	73 (OH)	69-70 (16-OH) 72-74 (bisditer-penoids)
hetisines (AVII)	79-80 (OH)	73-75 (OH)		
napellines (B II)				80 (16, 17-OH) 88 (15, 16- ketal, 17-OH)
anopterines (BIII)	77-80 (OH) 66 (5, 6-epoxy)			

2. The Special Structural Units

a. The *N*, *O*-mixed acetal/ketal-containing alkaloids

(a) Oxazolidine ring system There are generally two types: normal-



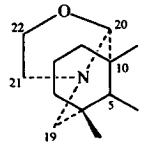
A B

Fig. 7 Classification of oxazolidine ring systems in C_{20}-diterpenoid alkaloids

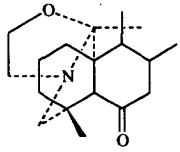
type (**A**) and iso-type (**B**) (Fig. 7) (*2*). The former are atisines (A I 2a, A I 2d), veatchines (B I 1a), and hetidines (A II 2a), and the latter atisines (A I 2a,), hetidines (A II 2a), and veatchines (B I 1a). A tabulation of the characteristic δ value ranges of the carbons influencing these special moieties is given in Table XLVIII. It is important to note that the epimers at C-19 in these alkaloids, such as A I 2a (iso-type), B I 1a (iso-type), AIV2a, and A I 2c, could be differentiated by their NMR spectra (Tables X X VI and XLVIII).

TABLE XLVIII

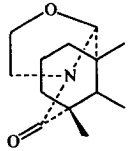
CHARACTERISTIC CARBON-13 SIGNALS AND THEIR δ VALUE RANGE IN THE ^{13}C NMR SPECTRA OF THE OXAZOLIDINE RING-CONTAINING C_{20}-DITERPENOID ALKALOIDS



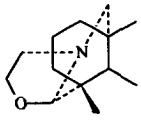
A I 2a (normal-type)
B I 1a (normal-type)



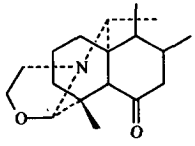
AIV2a (normal-type)



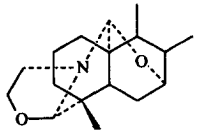
A I 2d



A I 2a (iso-type)
B I 1a (iso-type)



AIV2a (iso-type)



A I 2c

group	C-4	C-5	C-10	C-19	C-20	C-21	C-22
A I 2a (normal-type)	33-35	52-53	~40	~57	~94	~51	~94
B I 1a (normal-type)	33-35	52-53	~41	~57	~93 (20*S*) ~95 (20*R*)	~50 (20*S*) ~51 (20*R*)	~93 (20*S*) ~95 (20*R*)
AIV2a	33-35	~53 ~47 (7α-OH)	~47	~57	104-106	~51	~61

TABLE XLVIII (*continued*)

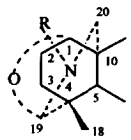
A I 2d	41-43	~50	39-41	171-173	~88	40-43	~65
A I 2a (iso-type)	35-38	~48	35-38	~98 (*S*) ~95 (*R*)	~50 (19*S*) ~55 (19*R*)	~55 (19*S*) ~59 (19*R*)	~59 (19*S*) ~65 (19*R*)
B I 1a (iso-type)	~40	~49-51	~36	~98 (*S*) ~97 (*R*)	~49-51	~55-57	~59 (19*S*) ~65 (19*R*)
AIV2a (iso-type)	35-37	~50 ~56	45-48	~98 (*S*) ~94 (*R*)	70-73	51-53	~65 (19*S*) ~63 (19*R*)
A I 2c (R=H)	~36	45-48	~34	~95 (*S*) ~92 (*R*)	~86 ~83	46-52	63-65
A I 2c (R=H, OAc)	~36 ~36	52-60	35-37	94-96 (*S*) ~92 (*R*)	82~86 ~82	45-52	63-65

(b). The C_{20}-diterpenoid alkaloids having *N*-C-19-O-C-1, *N*-C-19-O-C-2, *N*-C-6-OH, *N*-C-19-OR and *N*-C-20-O-C-7 units

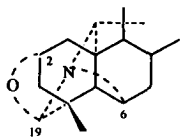
The presence of these special structural units leads to characteristic δ value ranges of the related carbons, as a diagnostic criterion, as seen in Table XLIX.

TABLE XLIX

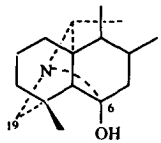
CHARACTERISTIC CARBON-13 SIGNALS AND THEIR δ VALUE RANGE IN THE ^{13}C NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS HAVING *N*, *O*-MIXED ACETAL/KETAL UNITS



A II 2
B II 2

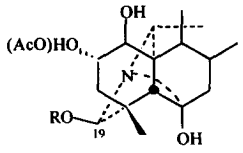


A V II 2a

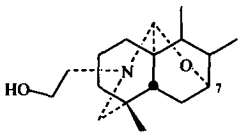


A VII2b

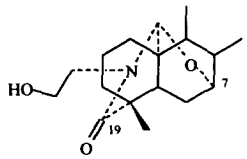
TABLE XLIX (*continued*)



AVII2c



A I 2b



A I 2c

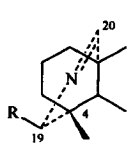
group	C-1	C-2	C-4	C-5	C-6	C-7	C-18	C-19	C-20
A II 2	~68		~37					92-93	~76
B II 2	~68		~37					92-93	~66
(-NH-)	~68		~37					~88	~58
AVII2a		~80	~50					~100	~64
AVII2b	35~43			58-63	98-102			57-62	67-73
2α-OH/3α-OAc	~51			~63	~96			~77	~68
2-CO	~42			~60	98-102			60-63	68-72
2-CO/9-OH	~46			~56	98-102			60-63	68-72
2α-OH	~38			~63	~100			~62	~70
AVII2c			39-44	50-62			21-24 (19*S*) ~29 (19*R*)	~92 (*S*) ~95 (*R*)	63-68 (19*S*)~61 (19*R*)
3α-OH			~49	~63			~19	~88 (*R*)	~70
A I 2b						~75		51-53	~88
A I 2e			~44			~70		~175	85-87

b. Structual units having imine or lactam groups

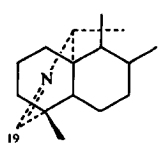
The C_{20}-diterpenoid alkaloids having these structural units are the A I 2f and A I 3 groups in atisines, the AIV3 and AIV2b in hetidines, as well as the B I 1b and BIII2 groups in veatchines (Table XLX) with characteristic carbon signals such as C-4, C-18, C-19, and C-20. The close relationship between the δ values for these carbons and their structural units is presented in Table XLX.

TABLE XLX

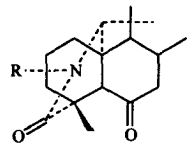
CHARACTERISTIC CARBON-13 SIGNALS AND THEIR δ VALUES IN THE ^{13}C NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS HAVING IMINE OR LACTAM GROUPS



A I 2f
A I 3
B I 1b



AIV3
BIII2



AIV2b

group	C-4	C-18	C-19	C-20
A I 2f (R=H)	~33		~60	~166
R=CH_2COCH_3	~35		~63 (*R/S*)	~164
R=OH	~37		~89 (*R*)	~164
R=OCH_3	~37		~97 (*R*)	163~165
R=OEt	~37		~95 (*R*)	136~165
AIV3	~42	~19	~173	73~76
5-OH	~47	~24	~169	~81
BIII2	~40	24~26	~177	~63
AIV2b (6-CO)	~47	24~26	~177	~54
	~47	24~26	~177	

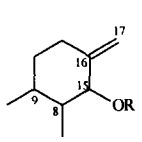
Table XLX shows that the configuration at C-19 in the A I 2f group, except for R=CH_2COCH_3, was easily confirmed by the δ values of C-19.

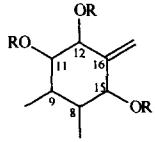
c. Allylic secondary alcohol system

Most of the C_{20}-diterpenoid alkaloids have this structural unit. They may be divided into two groups: those bases containing the 15-OR (R=H, Ac) and those with the 11/12, 15-OR (R=H, Ac) groups. The presence of the close relationship between the skeletal types and the δ values of C-8, C-15, and C-16 is shown in Table XLXI.

TABLE XLXI

RELATIONSHIP BETWEEN THE SKELETAL TYPES AND THE CHARACTERISTIC CARBON-13 SIGNALS IN THE ^{13}C NMR SPECTRA OF C_{20}-DITERPENOID ALKALOIDS HAVING AN ALLYLIC SECONDARY ALCOHOL SYSTEM





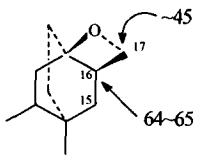
type	C-8	C-15	C-16
atisines	37	74-77	150-157
	42[*N*-C-20-O-C-7]	69-72 [*N*-C-20-O-C-7]	
hetisines	44 (9-OH)	72-74	155-156
veatchines	45-47	80-84	154-160

d. C_{20}-diterpenoid alkaloids having epoxy or 15, 16, 17-OH groups

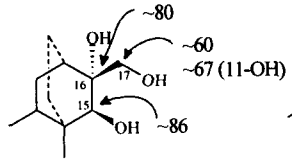
There are a few alkaloids possessing 15, 16, 17-trihydroxy groups or a 16, 17-epoxy group [e.g., dehydrodictysine (*125, 126*), gomandonine (*132, 133*), goman-donine 13-*O*-acetate (*133*), dictyzine (*124~130*), macrocentrine (*127*), paniculamine (*139*), and chuanfumine (*348*)].

The characteristic carbon signals in the ^{13}C NMR spectra of these alkaloids having these special units are very diagnostic and valuable (Table XLXII).

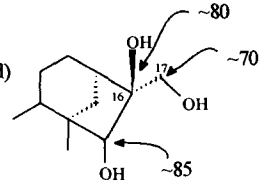
TABLE XLXII



AII



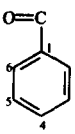
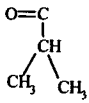
AII2



B

3. The Chemical Shift Ranges of Common Substituent Groups (Table XLXIII)

TABLE XLXIII

group	δ_C	group	δ_C
	41-47		48-52; 67~68 ()
	36 [C-12-O-C-20-*N*]		12~14; ~7 ()
	33~35 [N-C-19-OH]		
	~58, ~50 (19-CO)		168~172
	~61		20~22
	165~167		~166
1,	129~132		~118
2, 6,	128~130		~145
3, 5,	128~130		
4,	133~135	1,	~135
	~176	2, 6,	~129
	~34	3, 5,	~128
	~19	4	~130

4. Tables XLXIV~XLXXV are comprehensive. In order to make full use of the data for structural determination, the arrangement according to our classification of the known naturally-occurring C_{20}-diterpenoid alkaloids with the references cited should be consulted. In addition, some apparent assignment errors for some alkaloids, e. g., spiramine Q (*93, 94*) and spiramine T (*90, 94*), were revised in the editorial process. The ^{13}C NMR data of diterpenes from *Spiraea* spp. plants (Table XLXXVI) are also presented.

Table XLXIV

^{13}C NMR OF ATISINE TYPE DITERPENOID ALKALOIDS (A I)

carbon	A I 1-1 (*59*) (dehydroatisine)	A I 1-2 (*62, 63*) (dihydroajaconine)	A I 1-3 (*64*) (chellespontine)	A I 1-4 (*419*) (spiratine A)	A I 1-5 (*59*) (atidine)	A I 1-6 (*68, 69*) (spiramine G)	A I 1-7 (*70*) (spiramine H)
1	40.2	39.8	25.9	35.2	40.7	39.5	39.9
2	23.2	23.1	19.8	20.0	22.6	22.8	22.9
3	41.4	41.1	41.0	41.6	39.1	41.1	41.4
4	33.6	33.5	33.4	34.2	33.5	33.5	33.6
5	49.6	47.9	44.9	43.9	47.9	48.4	45.1
6	17.4	20.6	19.4	28.7	36.2	28.1	17.6
7	31.5	70.4	35.0	77.2	215.8	76.2	27.3
8	37.4	42.6	38.1	41.9	53.0	51.8	53.2
9	39.5	39.5	40.1	45.8	41.6	49.4	49.3
10	38.0	38.0	46.4	47.0	37.2	38.2	38.1
11	28.0	28.1	31.0	28.2	28.0	27.3	27.6
12	36.4	36.1	36.3	36.5	36.0	38.6	36.9
13	27.7	26.4	25.9	26.1	26.6	45.6	44.6
14	26.4	25.4	28.1	14.8	25.3	219.8	213.8
15	76.8	71.9	75.0	80.1	72.8	38.2	79.4
16	156.3	156.0	156.4	154.8	151.5	146.3	151.9
17	109.6	110.1	109.5	110.2	109.5	107.7	111.6
18	26.4	26.5	24.7	24.8	25.8	26.3	26.4
19	60.2	60.2	59.5	60.5	58.9	59.6	59.6
20	54.0	53.9	58.3	58.6	53.5	52.4	52.4
21	58.0	85.0	64.5	65.0	58.0	58.0	57.8
22	60.7	60.7	183.5	182.9	60.5	60.3	60.2

Table XLXIV (*continued*)

carbon	A I 1-8 (*70*) (spiramine I)	A I 1-9 (*71*) (beiwusine A)	A I 1-10 (*71*) (beiwusine B)	A I 1-11 (*72*) (uncinatine)	A I 2a-1 (*59, 73*) (atisine)	A I 2a-2 (*63, 73, 76*) (isoatisine)
1	39.2	80.6	70.1	35.4	42.0* (42.0*)	40.6*
2	22.9	33.2	31.8	19.5	22.4 (21.7)	22.1
3	41.2	38.9	35.9	41.6	41.0* (40.9*)	40.0*
4	33.6	33.0	33.6	34.1	33.8 (28.2)	38.1
5	45.6	45.2	37.0	44.2	51.6 (48.9)	48.6
6	17.6	17.5	17.1	20.0	17.8 (18.5)	19.1
7	27.3	27.6	26.9	68.8	34.6 (32.0)	31.9
8	52.2	53.4	52.0	46.9	37.5 (37.5)	37.5
9	49.3	46.8	40.8	40.4	40.0 (39.6)	39.6
10	38.3	42.2	41.8	43.5	40.4 (40.4)	35.9
11	27.4	30.1	26.2	28.9	28.2 (28.2)	28.1
12	37.2	36.8	36.7	36.7	36.6 (36.6)	36.4
13	44.4	44.5	44.5	28.5	27.7 (27.7)	27.6
14	212.2	214.7	215.0	24.8	25.5 (25.5)	26.4
15	78.5	79.2	79.3	70.8	77.0 (77.0)	76.8
16	147.7	151.8	151.5	155.8	157.5 (157.5)	156.2
17	113.2	111.4	111.6	110.5	108.9 (108.4)	109.2
18	26.3	26.2	26.0	25.8	26.7 (26.1)	24.3
19	59.6	60.0	58.8	60.3	56.4 (53.3)	98.4
20	52.2	47.3	50.3	64.9	93.9 (94.2)	49.8
21	58.1	59.6	60.0	132.4	50.3 (50.3)	54.9
22	60.4	58.1	57.9	116.7	64.1 (59.2)	58.6
OAc	170.6, 20.9					

Table XLXIV (*continued*)

carbon	A I 2a-3 (*75*) (spiramidines A (B))	A I 2b-1 (*63*) (ajaconine)	A I 2b-2 (*75*) (deacetylspiramine F)	A I 2b-3 (*68*) (spiramine F)	A I 2b-4 (*85*) (spiramine Y)	A I 2b-5 (*68*) (spiramine E)
1	40.0 (40.0)	41.2[a] (42.4[b])	41.7	41.2	28.8	41.2
2	21.6 (21.5)	21.1 (22.0)	21.5	21.2	25.3	21.2
3	29.8 (29.8)	26.6 (41.4)	30.4	30.1	19.8	30.1
4	35.4 (35.9)	33.5 (34.5)	34.9	34.8	43.8	34.6
5	48.5 (46.9)	44.3 (45.4)	44.8	44.5	55.1	44.8
6	27.7 (27.7)	25.3 (27.4)	25.7	25.1	71.6	25.2
7	76.5 (76.5)	75.4 (76.3)	74.5	74.5	70.7	74.6
8	51.9 (51.9)	41.6 (42.9)	41.7	40.8	36.0	41.0
9	49.6 (49.5)	36.9 (38.3)	44.8	44.9	46.2	44.6
10	39.3 (39.3)	35.4 (36.5)	34.9	33.6	34.3	34.6
11	27.7 (27.3)	30.1 (31.2)	24.1	23.8	39.2	23.8
12	38.5 (38.4)	40.2 (27.9)	37.9	36.9	36.4	36.9
13	45.5 (44.8)	27.0 (27.9)	25.4	25.1	26.6	25.2
14	219.4 (219.4)	26.4 (26.4)	21.2	21.2	26.7	20.7
15	38.2 (38.1)	72.2 (73.5)	70.2	70.0	39.6	69.7
16	147.1 (146.3)	157.2 (157.2)	156.5	150.2	149.8	150.3
17	107.5 (107.0)	108.0 (108.0)	111.6	114.2	108.4	114.1
18	24.0 (24.0)	25.1 (25.5)	26.8	26.0	20.6	26.1
19	97.7 (95.5)	51.7 (50.4)	53.9	51.9	175.3	53.0
20	54.7 (54.7)	87.8 (89.7)	88.0	87.4	86.1	87.3
21	58.7 (58.6)	57.4 (58.3)	58.4	57.7	51.7	53.4
22	64.5 (63.0)	58.0 (60.0)	59.9	57.9	61.9	62.1
OAc				171.1, 21.0	169.4, 21.1	171.1, 170.9 21.0, 21.2

A I 2b-1: a: $CDCl_3$; b: CD_3OD

Table XLXIV (*continued*)

ccrbon	A I 2c-1 (*86*) (spiramine C)	A I 2c-2 (*86~88*) (spiramine A)	A I 2c-5 (*86*) (spiramine D)	A I 2c-6 (*86, 87*) (spiramine B)	A I 2c-7 (*94*) (spiramine P)	A I 2c-8 (*94*) (spiramine U)
1	40.8	41.0[a] (40.9[b])	34.2	33.9	29.6	29.2
2	23.0	22.9 (23.3)	23.0	22.9	20.9	20.2
3	20.9	29.8 (29.9)	30.0	29.8	41.3	40.6
4	35.4	35.4* (35.6*)	35.6	35.4	35.8	35.4
5	45.5	45.2 (45.2)	47.3	47.4	56.8	52.8
6	25.2	25.2 (25.2)	25.5	25.3	69.1	70.8
7	74.3	74.2 (69.3)	74.5	74.3	75.2	70.8
8	41.5	40.8 (40.9)	41.9	41.0	37.5	36.4
9	43.1	43.0 (42.7)	44.3	43.9	43.5	43.2
10	34.1	34.2* (34.3*)	34.2	34.9	36.0	35.2
11	23.5	23.5 (23.6)	23.1	23.1	23.3	22.7
12	37.0	36.7 (37.2)	37.6	36.4	40.0	39.0
13	19.9	21.1[Δ] (21.1[Δ])	21.3	21.2	22.3	21.2
14	20.4	20.9[Δ] (20.9[Δ])	20.4	20.8	27.8	26.3
15	69.0	69.2 (74.2)	69.6	69.7	48.9	47.4
16	155.3	150.1 (151.0)	156.2	150.1	71.7	72.4
17	112.0	114.2 (114.1)	111.6	114.3	32.0	31.3
18	26.4	26.0 (26.3)	26.9	25.9	23.3	22.5
19	95.3	95.2 (95.3)	91.5	91.3	95.4	94.6
20	85.9	85.8 (85.9)	83.6	83.5	85.5	85.4
21	51.0	51.0 (51.3)	45.7	45.7	51.5	51.0
22	63.1	63.1 (63.4)	64.9	64.9	63.4	63.3
OAc		170.5, 20.7		171.1, 20.8	—	169.4, 21.2

A I 2c-2: a: $CDCl_3$; b: C_6D_6

Table XLXIV (*continued*)

carbon	A I 2c-9 (*91, 92*) (thalicsiline)	A I 2c-10 (*93, 94*) (spiramine Q)	A I 2c-11 (*90, 94*) (spiramine T)	A I 2c-12 (*95*) (spiramine W)	A I 2d-1 (*96*) (spiramine S)	A I 2d-2 (*96*) (spiramine V)
1	40.5	29.1*	29.0*	29.6	40.1	40.1
2	22.7	20.3*	20.3*	21.3	20.6	20.6
3	47.2	40.9*	33.8*	34.6	41.3	41.3
4	35.2	35.2	36.2	35.2	42.3	42.4
5	52.2	55.9*	56.3*	60.6	49.0	49.1
6	70.8	69.4*	70.0*	69.1	16.4	16.4
7	70.9	73.9*	70.8*	75.0	80.6	79.8
8	36.3	36.3	34.7	37.4	41.3	41.8
9	42.5	42.2*	38.3	42.3	46.0	46.5
10	35.3	35.6	36.1	36.9	39.7	39.5
11	29.0	23.5*	23.5*	23.3	26.2	26.2
12	38.3	40.8*	41.2*	40.0	35.6	35.3
13	26.7	22.7*	22.7*	22.3	28.6	28.6
14	23.5	27.3*	26.5*	27.8	28.0	27.9
15	20.2	47.3*	45.4*	48.9	75.2	76.5
16	73.8	73.9	73.7	71.7	150.3	154.9
17	30.2	30.1	30.1	32.0	110.7	109.4
18	22.6	22.7	22.5	23.1	22.0	22.0
19	94.6	95.1	91.4	92.3	171.0	171.0
20	85.6	85.5	83.1	82.9	88.8	88.2
21	51.0	51.0	47.3	45.9	42.5	42.5
22	63.3	63.1	64.9	65.0	64.6	64.6
OAc	169.7, 21.4	—	169.6, 21.3	—	170.8, 21.5	172.9, 21.3

*Reassignments by us according to ref. [73]

Table XLXIV (*continued*)

carbon	A I 2d-3 (*75*) (deacetylspiram-ine S)	A I 2d-4 (*420*) (spiramide)	A I 2e-1 (*93*) (spiramine R)	A I 2e-2 (*85*) (spiramine X)	A I 2f-1(*75*) (19-*O*- deethyl-spiramine N)	A I 2f-2 (*419*) spiratine B	A I 2f-3 (*98*) (spiramine N)
1	33.6	34.3	39.4	28.9	35.4	34.4	35.1
2	20.4	20.8	20.6	25.4	20.1	19.4	19.5
3	40.0	42.5	29.4	19.9	34.3	35.9	34.1
4	41.2	43.0	44.4	43.7	36.8	36.9	36.3
5	49.7	53.1	45.2	55.1	49.8	51.8	48.3
6	15.3	69.4	25.3	71.8	14.6	69.1	13.6
7	77.3	79.9	69.4	70.3	77.6	79.5	79.9
8	41.1	38.3	40.7	36.1	41.6	38.0	42.9
9	45.7	47.4	45.2	46.3	44.8	45.7	44.3
10	39.5	41.5	33.2	34.3	43.2	43.8	42.9
11	26.0	28.8	25.6	39.3	28.6	27.8	27.7
12	35.5	36.0	36.5	36.5	36.3	35.7	35.2
13	27.2	26.2	25.6	26.7	27.5	25.7	27.2
14	27.6	24.1	19.8	26.6	26.3	21.6	25.9
15	80.7	45.5	74.0	39.4	80.1	41.4	77.1
16	147.1	149.3	149.3	150.1	156.0	149.4	155.2
17	109.0	106.6	114.7	108.4	108.7	105.9	109.0
18	21.8	24.6	21.1	20.7	25.7	26.6	24.9
19	173.2	172.7	175.5	174.6	88.9	87.8	94.8
20	88.7	87.9	86.7	85.7	163.2	163.4	165.4
21	42.2	41.5	51.6	45.4	—		—
22	64.4	64.7	61.8	62.4	—		—
OAc	—	170.4, 20.6	171.0, 21.1	170.6, 20.8	—	170.3, 20.3	—
	—		—	169.3, 21.1	—	170.5, 21.4	—
OEt	—	169.8, 21.3	—	—	—	—	64.5, 15.3

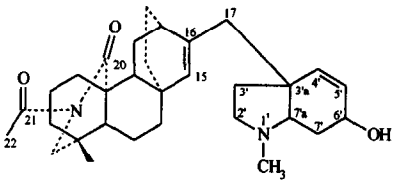
Table XLXIV (*continued*)

carbon	A I 2f-4 (*99*) (brunonine)	A I 2f-5 (*70*) (spiramine O)	A I 2f-6 (*85*) (spiramine Z)	A I 2f-7 (*100*) (spiramine J)	A I 2f-8 (*100*) (spiramine L)	A I 2f-9 (*100*) (spiramine M)
1	35.1	35.1	34.2	34.3	34.5	34.4
2	19.5	19.4	36.1	19.3	19.2	19.2
3	34.0	34.0	19.4	48.2	48.2	48.2
4	36.2	36.4	36.7	34.9	34.9	34.9
5	48.5	48.2	51.9	45.6	45.4	45.5
6	19.5	13.5	69.2	13.4	14.3	14.3
7	69.5	80.1	79.4	79.7	79.6	78.2
8	42.9	43.0	37.7	40.9	41.2	40.8
9	38.2	44.2	45.5	44.2	44.5	44.5
10	42.6	43.0	43.6	44.2	44.2	44.1
11	28.2	27.7	27.8	27.3	27.6	27.6
12	35.9	35.1	35.6	35.5	33.5	34.9
13	28.0	27.1	25.7	30.6	29.7	27.0
14	25.5	25.9	21.4	25.9	25.9	25.6
15	70.6	77.4	41.3	77.5	75.8	77.3
16	115.7	155.8	149.3	154.9	150.5	155.2
17	109.1	109.5	105.9	109.1	110.9	108.9
18	24.9	25.0	26.4	24.5	24.4	25.6
19	94.7	97.1	94.1	63.0	63.3	63.1
20	165.5	165.2	163.2	164.2	163.5	163.6
OAc	—	—	170.4, 20.6		171.0, 21.1	171.1, 21.0
OMe						
OEt	64.6, 15.2		64.2, 15.1		—	—

CH_2COCH_3: A I 2f-6 (42.3, 207.6, 30.6); A I 2f-7 (42.5, 207.5, 30.6); A I 2f-6 (42.2, 207.2, 30.3).

Table XLXIV (*continued*)

carbon	A I 2f-10 (*100*) (spiramine K)	A I 3-1 (*59, 64*) (azitime)	A I 4-1 (*103*) (coryphidine)
1	37.2	25.9 (26.1)	46.3
2	19.7	19.5 (19.6)	22.4
3	34.1	34.2 (34.1)	40.5
4	34.6	32.9 (32.8)	38.9
5	47.5	46.9 (46.9)	55.3
6	13.4	20.1 (20.0)	20.2
7	80.0	42.3 (42.4)	37.4
8	41.1	37.3 (37.4)	40.6
9	44.3	38.1 (38.1)	52.8
10	44.1	42.5 (42.5)	55.3
11	27.6	30.9 (31.0)	28.7
12	35.5	35.9 (36.0)	36.6
13	27.0	25.1 (25.5)	32.9
14	25.9	28.1 (28.1)	31.5
15	77.1	75.8 (75.2)	135.7
16	155.3	156.6 (156.2)	147.8
17	109.0	109.2 (108.9)	36.5
18	25.9	25.9 (25.8)	27.6
19	62.6	60.4 (60.2)	55.4
20	163.9	166.2 (166.4)	171.4
21	42.4		171.5
22	208.4		23.2



A I 4-1

C-2'	54.8
C-3'	38.0
C-3'a	43.1
C-4'	131.2
C-5'	130.7
C-6'	63.9
C-7'	35.1
C-7'a	70.5

CH_2COCH_3: A I 2f-9 (42.4, 208.4, 30.9)

TABLE XLXV

^{13}C NMR OF DENUDATINE TYPE DITERPENOID ALKALOIDS (A II)

carbon	A II 1-1 (*107*) (gymnandine)	A II 1-2 (*115*) (denudatine)	A II 1-4 (*115*) (lepenine)	A II 1-5 (*116*) (11α-hydroxy-lepenine)	A I 1-6 (*119*) (kirinine C)	A II 1-7 (*120*) (11-acetyllepenine)
1	40.5*	26.1	70.7	71.8	72.6	70.2
2	23.2	20.3	31.1	32.3	27.1	30.9
3	28.7	40.0	38.6	40.3	33.5	38.5
4	34.6	33.5	33.7	35.2	44.6	33.6
5	52.6	51.9	52.3	54.2	49.1	49.0
6	21.0	22.5	23.1	24.8	24.5	23.5
7	43.4	41.9	42.2	43.7	47.9	43.2
8	45.4	43.2	43.6	45.5	47.9	43.5
9	44.3	53.0	53.8	55.0	56.3	51.9
10	44.0	45.0	50.9	52.6	48.1	50.9
11	28.1	71.4	72.9	74.5	73.8	76.1
12	37.2	46.8	46.2	49.5	46.7	42.0
13	26.8	24.2	24.5	26.0	25.1	23.9
14	26.8	27.6	27.4	29.0	26.7	37.1
15	78.6	77.0	77.9	79.0	77.3	77.6
16	155.3	153.8	154.3	154.7	154.3	153.7
17	107.1	108.9	109.3	110.1	109.7	109.5
18	27.3	26.3	26.0	26.9	21.0	25.9
19	57.7	57.1	57.0	58.6	169.3	56.5
20	72.2	71.7	67.8	69.4	68.8	67.5
21	51.4	50.3	50.8	52.4		50.7
22	13.7	13.3	13.6	14.2		13.5
OAc	—	—	—	—	170.7, 21.6	171.0, 21.5

TABLE XLXV (*continued*)

carbon	A II 1-8 (*122, 121*) (kirinine A)	A II 1-11 (*127, 128, 130*) (dictyzine)	A II 1-13 (*127*) (macrocentrine)	A II 1-14 (*131*) (lassiocarpine)	A II 1-16 (*132, 133*) (gomandonine)	A II 1-17 (*133*) (gomandonine 13-*O*-acetate)
1	70.4	40.2[a] (27.6[b])	31.9[c] (33.0[d])	70.4	70.6	70.6
2	31.2	20.8 (21.8)	69.0 (70.1)	32.0	32.1	31.4
3	38.5	27.7 (41.2)	67.5 (68.5)	39.4	40.1	36.1
4	33.4	34.4 (35.3)	38.7 (39.3)	33.9	33.8	33.7
5	52.4	44.2 (54.0)	39.6 (41.0)	53.6	52.7	51.8
6	22.7	26.6 (24.0)	27.5 (28.7)	24.1	24.1	23.5
7	46.3	36.2 (44.0)	35.7 (36.1)	43.2	42.6	38.8
8	43.4	42.0 (43.0)	41.9 (42.4)	44.1	44.6	43.6
9	55.0	52.8 (42.5)	51.5 (52.5)	51.9	43.9	43.9
10	50.5	45.6 (46.9)	45.4 (46.0)	51.9	51.4	50.9
11	72.5	21.9 (24.7)	21.5 (22.8*)	71.6	25.6	23.9
12	41.5	42.8 (36.5)	42.7 (43.6)	45.5	41.6	40.7
13	24.0	23.1 (23.0)	23.3 (24.4)	22.0	69.1	71.5
14	27.1	26.6 (29.0)	22.2 (22.6*)	28.7	39.2	38.2
15	77.6	86.7 (87.1)	86.0 (86.4)	86.2	76.5	76.6
16	147.6	79.8 (81.1)	79.2 (80.4)	79.1	65.5	45.5
17	109.2	59.8 (67.9)	67.3 (67.3)	72.3	45.0	25.8
18	25.9	23.6 (27.0)	21.7 (22.8)	26.5	26.3	59.1
19	56.8	67.8 (60.8)	48.7 (50.1)	57.5	59.6	68.5
20	67.1	73.5 (74.7)	75.9 (76.8)	68.3	68.9	
21	50.5	—	—	51.1	43.9	41.7
22	13.6	—	—	14.0	—	—
OAc	170.9, 21.4	170.6, 20.9			—	170.7, 21.4

a: $CDCl_3$; b: CD_3OD; A II 1-11: c: CD_3OD; d: Py-d_5; OBz (A II 1-12) 167.3 (s), 132.1 (s), 130.0 (d), 128.5 (d), 132.6 (d)

TABLE XLXV (*continued*)

carbon	A II 1-18 (*133, 134*) (yesoxine)	A II 2-1 (*137*) (lepenine *N*-oxide)	A II 3a-1 (*119*) (kirinine B)	A II 3a-2 (*138*) (11-acetyl-1, 19-epoxydenudatine)	A II 3a-3 (*140*) (vilmorinianine)
1	74.0	67.4	68.7	68.3	69.0
2	26.4	30.6	24.6	24.1	24.3
3	36.0	36.5	30.0	29.7	29.8
4	33.5	35.4	37.6	37.5	37.6
5	52.4	50.7	50.2	49.6	49.7
6	23.4	28.7	24.6	24.4	24.8
7	38.5	48.0	47.5	47.4	47.5
8	43.3	44.1	45.9	45.5	45.5
9	43.8	55.3	51.8	46.5	48.5
10	48.2	53.6	49.8	49.4	49.6
11	22.9	73.1	72.7	74.2	81.9
12	41.4	45.6	47.2	43.3	40.6
13	71.4	23.0	24.7	24.3	24.4
14	37.9	25.2	27.2	26.9	27.2
15	76.3	77.8	77.3	77.1	77.5
16	64.0	153.6	154.3	153.7	155.1
17	45.5	110.7	110.4	110.7	110.4
18	25.6	26.4	18.7	18.6	18.7
19	59.1	67.8	93.1	92.9	93.2
20	69.0	83.9	70.1	69.8	69.6
21	41.0	74.6	48.5	48.4	48.5
22	—	8.0	14.1	14.1	14.2
OAc	170.6, 170.7;	—	—	170.4, 21.1	—
OMe		—	—	—	56.2

TABLE XLXVI

^{13}C NMR OF HETIDINE TYPE DITERPENOID ALKALOIDS (AIV)

carbon	AIV1a-1 (*141*) (trabzonine)	AIV1a-2 (*142*) (yesonine)	AIV1a-3 (*143*) (yesoline)	AIV1a-4 (*144*) (sczukitine)	AIV1a-5 (*145*) (spirafine III)	AIV1a-6 (*145*) (spirafine II)
1	32.0			35.3	35.4	36.4
2	20.6			68.9	18.8	18.8
3	41.6			42.9	40.4	40.6
4	34.0	37.9	38.1	36.6	37.5	37.4
5	44.9			59.3	60.4	60.6
6	33.0	191.2	203.1	209.6	206.0	206.0
7	69.6			48.5	52.6	51.0
8	49.9			44.6	40.3	44.0
9	44.3			47.9	50.1	52.0
10	44.6			45.8	46.9	46.2
11	29.2	67.5	67.6	22.1	29.6	29.0
12	34.5			58.7	34.0	34.5
13	35.9			212.7	31.9	33.1
14	44.3			52.6	45.8	47.6
15	68.1	69.1	70.9	71.9	35.3	125.7
16	157.1	149.1	144.5	144.5	151.4	146.3
17	104.3	113.9	117.1	114.0	103.0	19.5
18	28.2	30.8	30.7	31.2	30.7	30.8
19	56.9		61.0	61.8	56.8	56.9
20	76.4		78.1	71.6	77.5	75.7
21	58.4	41.3	42.8	43.2	55.8	56.0
22	58.9	—	—	—	59.6	59.5

AIV1a-2: 77.6d, 61.9t, 60.4d, 55.1d, 45.3 (2s and 1t), 41.2d, 40.8d, 39.3s, 31.2t, 31.1t, 18.7t; R=COC_6H_3-$(OCH_3)_2$ (3", 4") (AIV1a-3): 165.8 (COO), 122.1 (1'), 112.1 (2'), 148.7 (3'), 153.2 (4'), 110.2 (5'), 123.4 (6'), 55.9, 56.7 ($2\times OCH_3$); R=$COCH(CH_3)CH_2CH_3$ (AIV 1a-4): 176.2 (176.9), 41.3/16.8 (41.3/16.2), 26.8 (26.2), 11.8 (11.6); OAc (AIV1a-4): 169.4, 21.4

TABLE XLXVI (*continued*)

carbon	AIV1a-7 (*146*) (racemulodine)	AIV1a-8 (*147*) (delcarduchol)	AIV1a-9 (*148*) (vakhmadine) (D_2O)	AIV1a-10 (*150*) (panicutine)	AIV1a-11 (*153*) (deacetylheterophylloidine)
1	41.1	48.2	30.0		40.7[a] (40.6)[b]
2	66.7	213.0	69.3		64.5 (64.8
3	76.9	52.0	73.5		48.3 (48.5)
4	41.8	41.0	40.6		37.1 (36.9)
5	58.1	59.9	58.9	20.38	59.9 (59.7)
6	208.6	29.3	105.0		208.7 (206.6)
7	51.8	36.2	40.1		52.3 (51.9)
8	44.4	40.6	41.5		40.9 (40.6)
9	47.6	46.6	45.3		46.4 (46.9)
10	45.0	50.4	45.2		45.0 (45.9)
11	23.3	23.4	21.4	211.5	23.4 (23.4)
12	53.2	53.4	41.5		53.5 (53.8)
13	208.6	210.5	67.8		210.5 (209.4)
14	51.8	56.6	48.1		56.6 (57.7)
15	130.9	75.0	31.8		36.2 (35.9)
16	140.3	155.1	148.1	142.3	142.7 (144.0)
17	19.4	110.0	107.2	110.5	109.9 (108.9)
18	22.5	27.3	25.3	31.2	27.2 (28.4)
19	51.6	57.9	66.7		57.5 (58.0)
20	66.8	67.3	73.2		67.1 (68.2)
21	41.6	41.8	36.3	43.3	41.9 (42.0)
22	—	—	—	169.8, 21.6	—

AIV1a-10: 70.9d, 68.5d, 63.2d, 60.4t, 59.2d, 52.8d, 50.4t, 50.0d, 44.5s, 43.9t, 41.8s, 36.8s, 35.9t, 34.8t, 22.7t.

TABLE XLXVI (*continued*)

carbon	AIV1a-12 (*152~154*) (heterophylloidine)	AIV1a-13 (*152*) (hetidine)	AIV1a-14 (*157, 158*) (episcopalidine)	AIV1a-15 (*161*) (contorine)	AIV1a-16 (*161*) (contorsine)	AIV1a-17 (*161*) (contortine)
1	35.9	39.0[c] (38.9)[d]	34.6	34.5	34.4	34.3
2	70.9	66.7 (67.2)	67.4	67.6	67.2	67.3
3	43.9	76.9 (77.6)	76.1	75.8	75.3	75.3
4	36.8	41.8 (41.9)	41.7	41.8	41.5	41.5
5	63.2	58.2 (57.9)	63.0	58.2	58.1	58.2
6	203.8	208.4 (208.9)	200.6	*	*	*
7	50.4	52.1 (52.3)	50.2	50.3	49.7	49.3
8	41.8	41.2 (40.7)	41.8	44.3	44.3	44.4
9	50.0	46.3 (46.1)	49.6	49.7	49.6	49.6
10	44.5	44.6 (44.4)	44.3	41.9	41.9	41.9
11	22.7	23.4 (23.5)	22.8	22.9	22.8	22.8
12	52.8	53.4 (53.7)	52.7	52.7	52.7	52.6
13	211.5	210.2 (208.9)	211.4	211.5	211.2	211.0
14	59.2	56.5 (56.6)	58.1	63.1	62.8	62.5
15	34.8	36.1 (36.0)	34.5	34.7	34.6	34.5
16	142.3	142.3 (143.8)	141.8	141.9	141.8	141.6
17	110.5	110.3 (109.1)	110.9	110.9	111.0	111.1
18	31.2	22.7 (23.4)	25.6	25.7	25.4	25.4
19	60.4	51.7 (51.9)	56.3	56.3	56.5	56.9
20	68.5	67.2 (67.5)	70.6	70.6	70.6	70.8
21	43.3	42.3	43.2	43.3	43.1	42.9
OAc	169.8, 21.6	169.7, 21.5	169.3, 21.2	169.3, 21.2	—	—

a: $CDCl_3$; b: C_6D_6; c: $CDCl_3$+Py-d_6; d: $CDCl_3$+C_6D_5; OBz (AIV1a-14): 165.5 (COO), 129.7 (1'), 128.5 (2', 6'), 132.9 (3', 5'), 133.3 (4'); OAs (AIV1a-15): 165.2 (COO), 113.6 (1'), 122.1 (2',6'), 131.6 (3', 5'), 163.7 (4'), 55.5 (4'-OCH_3); R=COCH $(CH_3)_2$ (AIV1a-16): 175.9 (1'), 18.8 (2'), 34.1 (3'), 18.9 (4'); * not be detected

TABLE XLXVI (*continued*)

carbon	AIV1a-18 (*144*, *162*) (sczukidine)	AIV1a-19 (*144*, *162*) (sczukinine)	AIV1a-21 (*163*) (vilmorrianone)	AIV2a-1 (*171*) (septatisine)	AIV2a-2 (*174*) (coriphine)	AIV2a-3 (*88*) (spiradine D)
1	39.7	35.9	35.1	30.2	44.4	49.2
2	65.2	68.5	67.9	19.6	23.1	18.7 (20.8)
3	47.8	43.8	42.6	41.3	41.5	31.7 (32.6)
4	37.3	37.1	54.1	34.4	35.0	36.7
5	59.9	59.4	64.1	46.6	53.3	50.7
6	205.1	203.6	187.0	32.3	19.9	*
7	49.0	48.8	192.9	70.0	34.4	52.3 (52.4)
8	44.7	44.3	44.5	50.0	43.8	40.5 (42.1)
9	48.0	47.6	47.4	44.0	48.3	46.0
10	47.0	46.9	40.0	47.1	47.1	45.6 (46.6)
11	22.4	21.9	22.4	29.2	27.9	36.0 (37.2)
12	57.4	58.2	52.0	34.5	35.6	34.2
13	211.0	210.9	208.3	27.4	31.4	36.3
14	53.3	52.0	58.8	49.6	54.4	49.3
15	71.5	71.5	27.8	68.7	136.3	27.3 (27.4)
16	150.0	147.6	140.1	157.9	146.5	151.6 (151.7)
17	112.3	113.4	112.7	103.8	34.7	103.0 (103.3)
18	30.6	31.2	31.0	28.6	28.5	23.3 (30.4)
19	59.9	60.4	60.7	57.3	57.8	93.6 (98.0)
20	70.1	70.7	69.0	104.6	105.7	73.0 (73.6)
21	42.6	43.1	41.9	51.5	51.7	52.9
22	—	—	—	61.7	61.4	62.8 (65.0)
OAc	—	169.9, 21.6	169.6, 21.5	—		

R= $COCH(CH_3)CH_2CH_3$ (AIV1a-18): 175.4 (1'), 41.2 (2'), 26.5 (3'), 11.5 (4'), 16.4 (5'); AIV2a-2: 54.6 (2'). 36.0 (3'), 47.4 (3'a), 156.1 (4'), 125.9 (5'), 197.6 (6'), 37.3 (7'), 70.1 (7'a), 40.0 (NCH'_3); * not be detected

TABLE XLXVI (*continued*)

carbon	AIV2a-4 (*176*) (spirasine II)	AIV2a-5 (*176*) (spirasine I)	AIV2a-6 (*177*) (spirasine V)*	AIV2a-7 (*177*) (spirasine VI)*	AIV2a-8 (*176*) (spirasine VII)
1	48.7 (48.4)	49.4 (49.0)	40.4	41.4	49.1 (48.6)
2	20.5 (18.4)	20.7 (18.6)	17.3	17.8	20.6 (18.2)
3	32.6 (32.3)	31.6 (30.1)	33.8	34.5	32.8 (31.7)
4	35.7 (35.7)	36.5 (35.9)	38.9	40.9	35.9 (35.9)
5	55.9 (55.4)	56.1 (55.6)	59.8	60.4	56.0 (55.5)
6	209.0 (204.0)	206.2 (206.2)	104.8	105.6	210.0 (205.0)
7	48.1 (47.9)	47.9 (47.9)	26.3	27.0	47.1 (47.1)
8	42.6 (42.2)	41.0 (41.0)	39.9	40.9	42.5 (42.5)
9	78.0 (77.8)	82.1 (82.1)	34.4	35.3	76.8 (76.8)
10	47.1 (47.1)	47.2 (46.5)	47.8	48.5	48.1 (47.5)
11	36.8 (36.8)	37.1 (36.2)	22.8	27.6	37.0 (37.0)
12	38.1 (38.1)	40.0 (40.0)	47.6	48.0	38.0 (38.0)
13	35.1 (34.8)	40.6 (40.6)	24.4	20.8	29.1 (28.0)
14	43.0 (43.0)	44.4 (44.4)	39.3	39.9	41.9 (41.9)
15	29.0 (28.2)	125.0 (124.0)	40.1	41.4	42.0 (39.0)
16	150.9 (150.7)	147.0 (147.0)	68.5	69.4	69.1 (69.1)
17	102.8 (102.6)	19.6 (19.6)	27.2	28.8	30.4 (30.4)
18	29.3 (23.4)	30.5 (23.4)	21.3	22.1	23.7 (23.7)
19	97.2 (93.2)	97.8 (93.9)	104.8	105.2	97.2 (93.2)
20	70.6 (70.6)	69.9 (69.8)	73.3	73.7	70.6 (70.6)
21	51.8 (51.8)	52.1 (52.1)	43.3	44.2	51.9 (51.9)
22	64.2 (62.1)	64.7 (62.6)	68.5	69.1	64.1 (62.1)

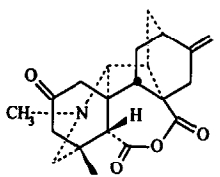
*The data repoted here should be for their salts based on the δ values (~104 ppm) at C-6

TABLE XLXVI (*continued*)

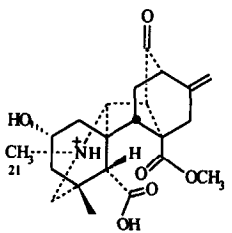
carbon	AIV2a-9 (*176*) (spirasine VIII)	AIV2a-10 (*178*) (spiredine)	AIV2a-12 (*178*) (spirasine III)	AIV2b-1 (*92, 182*) (thalicsessine)	AIV2b-2 (*147*) (carduchoron)	AIV3-1 (*183*) (tongolinine)
1	50.3 (49.8)	49.8 (48.9)	48.6 (48.6)	39.8	38.1	29.2
2	21.6 (19.4)	20.3 (18.3)	20.4 (18.2)	20.6	23.0	21.9
3	30.5 (30.1)	33.9 (32.7)	32.1 (31.9)	34.2	35.2	31.7
4	36.9 (35.9)	36.8 (36.7)	36.6 (36.2)	46.5	46.9	46.7
5	57.2 (56.7)	61.5 (61.5)	55.5 (55.5)	60.0	58.9	43.4
6	211.5 (208.0)	206.6 (206.6)	206.9 (206.9)	207.6	207.6	30.3
7	49.3 (48.0)	50.9 (50.3)	45.3 (45.1)	51.5	50.9	27.3
8	41.7 (41.7)	43.3 (42.1)	47.3 (46.8)	43.9	44.5	46.5
9	78.1 (78.1)	64.7 (64.7)	85.5 (85.5)	75.6	74.1	46.3
10	48.6 (48.6)	47.6 (46.7)	49.0 (48.1)	42.9	43.5	46.8
11	37.9 (36.5)	210.1 (210.1)	214.3 (214.3)	208.9	209.0	38.5
12	39.0 (39.0)	53.4 (53.3)	53.2 (53.0)	63.7	61.1	36.4
13	29.8 (29.2)	39.7 (39.7)	39.5 (39.5)	33.3	29.7	32.2
14	43.1 (43.1)	45.2 (45.2)	54.9 (54.9)	47.0	47.4	29.9
15	42.8 (44.8)	30.0 (29.6)	29.8 (29.5)	35.1	48.5	73.0
16	70.2 (70.2)	143.4 (143.2)	143.6 (143.5)	141.9	144.5	158.0
17	31.3 (31.3)	110.3 (110.2)	111.1 (110.9)	111.1	110.1	104.5
18	24.4 (24.4)	30.2 (23.1)	30.6 (23.3)	25.5	23.8	19.2
19	98.5 (94.3)	97.6 (93.3)	98.0 (93.8)	177.1	177.5	173.4
20	71.0 (71.0)	73.1 (72.5)	70.4 (70.4)	53.9	53.2	80.6
21	52.6 (52.6)	52.2 (52.2)	51.8 (51.8)	49.7	42.6	—
22	65.2 (63.1)	64.8 (62.8)	64.8 (62.8)	60.9	—	—

TABLE XLXVII

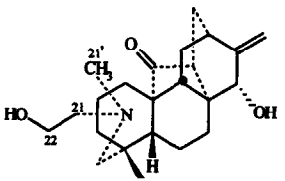
^{13}C NMR OF CARDIONIDINE AND ALBIVIONITINE TYPE DITERPENOID ALKALOIDS (AV AND AVI)



AV1-1
(cardionidine)



AV1-2
(vilmoridine)



AVI1-1
(albovionitine)

AV1-1 (*187*): 22.7 (C-18), 29.3, 29.6, 33.4, 36.5, 40.9, 41.8 (NCH_3), 45.6, 45.8, 56.3, 51.6, 62.3, 64.2, 67.9, 69.2 (C-13), 107.3 (C-17), 146.1(C-16), 167.6 (C- 6), 170.9 (C-7), 210.1 (C-2)

carbon	AV1-2 (*188*)	AVI1-1 (*189*)	Carbon	AV1-2 (*188*)	AVI1-1 (*189*)
1	35.4	29.6	13	not detected	32.6
2	66.6	18.3	14	55.7	51.4
3	44.3	30.2	15	46.2	71.3
4	33.9	41.2	16	140.0	155.9
5	62.7	50.6	17	111.4	106.9
6	175.3	21.6	18	29.6	73.9
7	174.9	31.6	19	62.4	57.4
8	53.5	43.4	20	70.3	227.4
9	45.5	47.2	21	40.0	62.6
10	47.3	53.4	21'	—	45.2
11	23.5	28.2	22	—	59.9
12	53.1	34.6	OCH_3	52.9	—

TABLE XLXVIII

^{13}C NMR OF HETISINE TYPE DITERPENOID ALKALOIDS (AVII)

carbon	AVII1a-1 (*190*) (spirasine XI)	AVII1a-2 (*193*) (nominine)	AVII1a-3 (*191*) (zeraconine)	AVII1a-4 (*195, 196*) (cossonidine)	AVII1a-6 (*196*) (kobusine)	AVII1a-7 (*148, 200, 202*) (hetisine)
1	34.6	33.1	27.7	66.3	26.5	34.5[a] (35.1[b])
2	19.1	19.7	29.8	27.2	18.9	67.0 (67.8
3	33.6	34.1	33.2	27.9	28.4	39.4 (39.9)
4	37.1	37.8	37.4	37.2	43.5	36.7 (37.7)
5	58.1	60.9	48.6	56.6	56.0	61.7 (62.6)
6	65.7	65.4	65.5	65.8	64.8	64.5 (65.5)
7	33.3	26.8	—	32.6	35.8	36.6 (37.3)
8	42.2	45.6	50.0	45.8	40.5	43.6 (44.6)
9	49.1	43.5	31.2	41.4	59.5	55.8 (56.7)
10	50.1	49.7	44.9	55.1	49.6	51.2 (52.0)
11	21.8	27.0	—	26.8	67.4	76.7 (77.0)
12	49.8	33.8	61.9	33.7	41.9	50.8 (52.3)
13	67.7	32.7	33.5	33.1	29.6	72.4 (73.2)
14	41.9	43.9	50.1	43.6	44.0	52.9 (53.4)
15	24.0	74.7	114.8	71.6	33.6	34.5 (34.6)
16	147.2	156.8	132.5	156.4	145.8	146.4 (148.3)
17	107.0	108.5	69.0	108.9	110.1	107.7 (107.6)
18	28.5	28.8	28.9	28.5	69.2	30.3 (30.2)
19	59.8	62.6	63.1	63.0	58.2	63.7 (64.1)
20	69.1	71.7	74.2	75.8	75.7	68.4 (69.1)

AVII1a-3: 157.4 (1'), 129.4 (2', 6'), 128.7 (3', 5'), 144.2 (4'), 19.6 (1''), 61.8 (2''); AVII1a-7: a: $CDCl_3$; b: CD_3OD

TABLE XLXVIII (*continued*)

carbon	AVIII1a-8 (*215*) (13-acetylhetisine)	AVIII1a-9 (*215*) (palmasine)	AVIII1a-10 (*215*) (palmadine)	AVIII1a-11 (*216*) (hanamisine)	AVIII1a-13 (*132*) (torokonine)	AVIII1a-14 (*219*) (souline F)
1	33.5*	33.4*	32.0*	69.8	28.9	34.2
2	66.7	66.5	67.2	69.9	70.2	65.4
3	40.3	33.9	40.3	33.7	39.2	39.2
4	36.6	36.4	33.6	36.4	35.4	36.5
5	61.3	61.2	61.1	56.9	51.5	51.9
6	64.3	64.3	64.3	65.1	69.7	68.4
7	36.0	35.8	35.9	32.7	64.3	71.3
8	43.6	43.7	43.9	44.7	48.9	52.0
9	55.2	55.2	53.2	42.4	79.6	55.3
10	50.6	50.8	50.6	52.1	49.8	51.0
11	75.6	75.2	75.9	26.8	36.9	74.4
12	48.5	46.9	45.0	33.4	34.6	36.0
13	74.5	74.4	73.4	33.2	32.7	33.4
14	50.4	50.0	50.1	43.9	36.0	43.3
15	33.8*	33.7*	33.9*	71.4	66.6	34.1
16	144.8	144.9	143.6	156.1	153.6	146.9
17	108.7	108.9	109.9	108.8	110.5	107.5
18	29.7	29.5	29.7	29.0	29.3	29.2
19	63.2	62.9	63.4	63.5	62.2	59.7
20	68.6	68.4	68.5	73.8	73.3	58.4
OAc	170.3, 21.2	—	170.6, 21.5	169.8, 20.9	—	—

AVIII1a-9: 166.5 (COO), 118.3 (Cα), 145.1 (Cβ), 134.6 (1'), 128.7 (2', 6'), 128.0 (3', 5'), 130.1 (4'); AVIII1a-10: 166.1 (COO), 118.7

* exchangeable

TABLE XLXVIII (*continued*)

carbon	AVII1a-17 (*221*) (ryosenamine)	AVII1a-18 (*223*) (delfissinol)	AVII1a-19 (*224*) (delnuttine)	AVII1a-20 (*216*) (deacetylhanamisine)	AVII1a-21 (*226*) (venudelphine)	AVII1a-22 (*227*) (tangutisine)
1	29.2	34.4	27.9	66.7	73.1	33.2
2	70.8	19.2	19.6	75.3	71.1	66.7
3	38.8	32.3	33.0	33.9	36.7	38.1
4	35.9	38.7	37.5	36.2	37.4	36.4
5	54.3	56.7	59.0	57.2	54.7	57.4
6	64.1	65.6	70.3	65.6	67.1	66.0
7	29.1	70.1	66.8	33.7	35.7	30.3
8	44.1	44.3	50.8	45.2	43.9	44.9
9	79.3	50.5	46.4	43.4	63.2	53.7
10	50.5	51.5	53.0	54.0	52.8	46.9
11	37.2	75.8	75.6	27.6	29.2	74.6
12	35.0	50.8	40.0	34.8	49.4	51.7
13	33.6	73.2	28.9	34.1	74.9	81.8
14	42.0	52.0	37.6	44.8	51.6	81.4
15	72.5	35.4	65.4	71.2	34.1	30.4
16	155.2	145.2	152.0	157.7	142.1	145.2
17	109.6	108.2	111.5	108.0	110.6	109.6
18	29.5	29.9	28.7	29.1	29.2	29.2
19	63.7	62.0	61.9	64.3	64.1	60.6
20	74.2	70.1	73.4	74.1	60.3	70.3

AVII1a-17: (COO), (1'), (2', 6'), (3', 5'), (4'); AVII1a-19: 170.7, 21.2 (OAc); AVII1a-20: 165.9 (COO), 130.9 (1'), 129.8 (2', 6'), 129.0 (3', 5''), 133.4 (4'); AVII1a-21:170.8, 21.0; 169.7, 21.5; 169.9, 21.3 (3×OAc)

TABLE XLXVⅢ (*continued*)

carbon	AⅦ1a-23 (*229, 228*) (guan-fu base Y)	AⅦ1a-24 (*230, 228*) (guan-fu base Z)	AⅦ1a-25 (*231*) (acoridine)	AⅦ1a-27 (*235*) (guan-fu base O)	AⅦ1a-32 (*221*) (hypognavine)	AⅦ1a-33 (*244, 245*) (paniculatine)
1	31.2	31.4	31.2	32.9	68.1	71.6
2	70.1	69.6	69.9	75.8	73.2	70.9
3	36.6	36.7	36.8	38.5	33.0	34.1
4	37.5	37.6	37.7	39.0	35.8	36.9
5	60.1	59.9	60.1	62.2	50.6	51.7
6	63.1	63.0	63.1	65.4	64.1	65.6
7	32.0	32.0	32.1	33.6	29.0	33.1
8	44.2	44.3	44.4	46.8	44.3	44.0
9	53.6	53.5	53.6	55.7	80.3	64.2
10	46.4	46.3	46.5	48.3	54.9	54.6
11	76.2	76.0	76.0	75.8	39.2	68.7
12	52.7	52.7	52.7	51.2	34.8	51.8
13	80.0	80.0	79.9	84.0	33.5	75.3
14	80.3	80.2	80.4	81.0	42.4	50.0
15	31.2	31.1	31.2	32.5	72.4	36.3
16	144.8	144.7	144.9	147.2	154.6	144.3
17	108.2	108.2	108.2	109.6	110.0	109.0
18	29.7	29.7	29.7	30.6	29.3	29.4
19	63.1	63.0	63.1	64.2	63.5	64.0
20	69.2	69.1	69.2	71.8	71.8	58.1

AⅦ1a-23: 171.2, 21.6 (OAc); AⅦ1a-24: 176.5 (COO), 34.4 (2'), 19.1 (3'); AⅦ1a-25: 174.0 (COO), 28.3 (2'), 9.2 (3'); AⅦ1a-27: 172.7, 22.2 (OAc), 175.8 (COO), 29.9 (2'), 10.1 (3'); AⅦ1a-32: (COO), (1'), (2', 6'), (3', 5"), (4'); AⅦ1a-33: 170.1, 21.3; 171.4, 21.8 (2×OAc), 165.5 (COO), 130.3 (1'), 129.9 (2', 6'), 128.6 (3', 5'), 133.0 (4')

TABLE XLXⅧ (*continued*)

carbon	AⅦ1a-34 (*216*) (1-*O*-acetylhypog-navine)	AⅦ1a-35 (*216*) (1, 15-di-*O*-acetylhypog-navine)	AⅦ1a-36 (*246*) (tadzhaconine)	AⅦ1a-37 (*247*) (3-epi-ignavinol)	AⅦ1a-39 (*253*) (cossonine)	AⅦ1a-40 (*254*) (cardiopimine)
1	70.2	69.5	71.6	31.6	31.9	74.2
2	70.3	70.2	68.8	70.5	72.3	67.0
3	33.5	33.4	36.6	75.3	77.2	73.3
4	35.7	35.6	36.1	43.0	43.6	41.8
5	51.5	51.3	57.9	56.7	62.2	59.6
6	64.7	64.3	64.3	64.9	64.1	63.7
7	28.9	28.3	34.0	30.1	35.8	35.7
8	44.7	44.4	43.9	45.1	44.0	43.6
9	79.8	79.1	51.9	80.5	54.3	51.6
10	54.4	54.4	54.6	51.9	51.9	53.9
11	39.3	39.7	76.1	39.9	74.8	75.2
12	34.8	34.9	49.3	36.6	48.3	46.0
13	33.1	32.5	70.3	34.1	73.6	73.7
14	42.2	42.4	51.4	43.2	49.9	50.2
15	72.6	73.1	33.1	73.8	33.6	33.7
16	154.5	149.4	144.6	156.1	144.2	142.7
17	109.9	111.7	108.9	110.1	109.3	110.4
18	29.2	29.1	29.3	26.8	24.9	25.5
19	63.5	63.1	63.6	60.7	61.2	60.0
20	73.8	71.8	65.6	73.2	69.2	66.1

AⅦ1a-34: 169.6, 21.2 (OAc), 165.1 (COO), 129.8 (1'), 129.6 (2', 6'), 128.6 (3', 5'), 133.2 (4'); AⅦ1a-35: 169.6, 21.1; 170.3, 21.0 (2×OAc), 164.9 (COO), 129.5 (1'), 129.4 (2', 6'), 128.7 (3', 5'), 133.3 (4'); AⅦ1a-36: 172.0, 21.5; 170.5, 21.3 (2×OAc), 165.9 (COO), 130.3 (1'), 129.9 (2', 6'), 128.7 (3', 5'), 133.2 (4'); AⅦ1a-39: 170.8, 20.8; 170.8, 21.1 (2×OAc), 165.8 (COO), 129.6 (1'), 129.6 (2', 6'), 128.4 (3', 5'), 130.0 (4'); AⅦ1a-40: 170.4, 21.3; 171.0, 21.4 (2×OAc), 165.8 (s), 130.1 (s), 129.9 (d), 128.5 (d), 133.2 (d) (OBz); 176.3(s), 34.1 (d), 18.8 (q), 19.2 (q) ($COCH(CH_3)_2$)

TABLE XLXVIII (*continued*)

carbon	AVIII1a-41 (*254*) (cardiopidine)	AVIII1a-42 (*254*) (cardiopinine)	AVIII1a-43 (*254*) (cardiopine)	AVIII1a-44 (*254*) (cardiodine)	AVIII1a-45 (*255*) (13-acetyl-14-hydoxy-2-propionyl-hetisine)	AVIII1a-46 (*256*) (13-*O*-acetyl-9-deoxy-glanduline)
1	74.1	73.1	73.2	72.4	32.9	29.7
2	67.1	68.9	68.9	65.8	72.5	68.0
3	73.3	70.6	70.8	70.9	38.5	74.1
4	41.8	42.7	42.7	42.5	39.0	42.2
5	59.5	59.3	59.5	58.0	62.2	61.6
6	63.6	63.8	63.9	62.5	62.5	62.6
7	35.7	35.7	35.9	31.3	33.6	31.6
8	43.6	44.1	44.2	44.9	46.8	44.7
9	51.5	51.7	51.7	49.7	55.8	53.2
10	53.7	53.9	53.9	49.5	48.4	45.9
11	75.2	75.3	75.4	74.9	75.8	74.7
12	46.0	46.2	46.6	47.9	51.3	49.7
13	73.9	73.7	73.8	80.4	84.0	81.1
14	50.2	50.4	50.4	78.6	81.0	78.8
15	33.7	33.7	33.9	30.7	32.6	30.7
16	142.7	142.8	142.7	141.5	147.3	143.3
17	110.4	110.3	110.3	110.6	109.7	109.5
18	25.6	25.7	25.7	25.3	30.7	25.4
19	60.0	59.3	59.5	59.1	64.6	59.6
20	66.1	66.1	66.2	67.0	71.9	69.5

AVIII1a-41: 17.4, 21.3; 171.0, 21.4 (2×OAc), 165.7 (s,), 130.1 (s), 130.0 (d), 128.5 (d), 133.2 (d) (OBz); 175.7 (COO), 41.2 (2'), 26.6 (3'), 11.6 4'), 16.7 (5'); AVIII1a-42: 170.2, 21.2; 171.0, 21.4 (2×OAc), 165.8 (s), 130.0 (s), 129.8 (d), 128.7 (d), 133.4 (d) (OBz); 177.4 (COO), 33.1 (2'), 17.9 (3'), 19.3 (4'); AVIII1a-43: 171.0, 21.2; 171.5, 21.5 (2×OAc), 165.9 (s), 130.1 (s), 129.8 (d), 128.7 (d), 133.4 (d) (OBz); 177.2 (COO), 39.6 (2'), 25.0 (3'), 10.8 (4'), 15.7 (5'); AVIII1a-44: 170.0, 21.2; 171.0, 21.4; 169.9, 20.6 (3×OAc), 165.6 (s), 130.0 (s), 129.6 (d), 128.7 (d), 133.5 (d) (OBz); 174.5 (1'), 39.6 (2'), 24.9 (3'), 10.7 (4'), 15.8 (5'); AVIII1a-45: 175.9 (1'), 29.9 (2'), 10.2 (3'), 172.8, 22.2 (OAc); AVIII1a-46: 170.3, 20.7; 169.6, 21.4 (2×OAc), 175.7 (1'), 41.4 (2'), 26.1 (3'), 11.6 (4'), 17.2 (5')

TABLE XLXVIII (*continued*)

carbon	AVII1a-47 (*256*) (glanduline)	AVII1a-48 (*256*) (13-*O*-acetylglanduline)	AVII1a-49 (*256*) (14-*O*-acetyl-9-deoxyglanduline)	AVII1a-50 (*256*) (11, 13-*O*-diacetyl-9-deoxyglanduline)	AVII1a-51 (*196*) (davisinol)	AVII1a-52 (*196*) (18-benzoyl-davisinol)
1	29.7	28.8	31.1	29.9	26.5	26.4
2	67.9	68.1	67.2	67.9	18.9	18.8
3	73.5	74.2	73.1	73.9	28.4	28.9
4	41.2	41.8	41.1	42.2	43.5	42.3
5	55.0	55.7	60.4	61.1	56.0	56.3
6	62.6	61.8	63.2	62.5	64.8	65.2
7	26.1	26.4	31.3	31.3	35.8	35.8
8	50.7	50.6	44.0	44.9	40.5	40.5
9	81.0	80.9	53.3	51.3	59.5	59.6
10	46.7	47.3	46.1	45.6	49.6	49.5
11	85.3	84.0	75.6	75.1	67.4	67.5
12	51.0	48.4	51.6	46.1	41.9	41.9
13	79.7	80.4	80.8	80.5	29.6	29.5
14	78.5	77.3	80.2	78.6	44.0	44.3
15	28.0	27.9	30.5	30.6	33.6	33.6
16	143.6	143.1	143.0	141.8	145.8	145.6
17	108.8	109.5	108.7	110.6	110.1	110.7
18	25.8	25.7	22.5	25.4	69.2	70.8
19	59.4	59.9	58.6	59.6	58.2	58.4
20	67.7	68.0	69.2	69.3	75.7	75.9

AVII1a-47: 170.2, 20.7 (OAc), 175.9 (1'), 41.6 (2'), 26.6 (3'), 11.6 (4'), 17.0 (5'); AVII1a-48: 170.6, 20.7; 169.8, 21.4 (2×OAc), 175.9 ('1), 41.3 (2'), 26.1 (3'), 11.5 (4'), 17.1 (5'); AVII1a-49: 170.0, 20.7; 177.6, 20.6 (2×OAc), 175.6 (1'), 41.5 (2'), 26.6 (3'), 11.5 (4'), 17.0 (5'); AVII1a-50: 170.2, 20.7, 170.4, 21.2; 169.3, 21.4 (3×OAc), 175.7 (1'), 41.4 (2'), 26.6 (3'), 11.6 (4'), 17.1 (5'); AVII1a-51: 170.2, 20.7; 170.4, 21.2; 169.3, 21.4 (3×OAc), 175.7 (1'), 41.4 (2'), 26.6 (3'), 11.6 (4'), 17.1 (5'); AVII1a-52: 166.1 (COO), 130.1 (1'), 129.6 (2', 6'), 128.5 (3', 5'), 133.1 (4')

TABLE XLXVIII (*continued*)

carbon	AVII1a-53 (*190*) (spirasine IX)	AVII1a-54 (*257*) (spirasine X)	AVII1a-56 (*190*) (spirasine IV)	AVII1a-57 (*204, 80*) (hetisinone)	AVII1a-58 (*259*) (venuluson)	AVII1a-59 (*223*) (fissumine)
1	35.2	33.5	34.9	45.3	31.5	44.4
2	19.3	19.2	19.3	213.0	212.5	210.6
3	33.9	25.7	33.7	49.7	41.5	48.9
4	38.0	37.9	38.0	42.3	42.7	41.2
5	61.0	60.1	61.2	60.4	59.9	58.3
6	65.6	65.1	65.4	65.2	63.7	64.7
7	35.2	34.8	33.9	36.1	35.7	28.3
8	44.2	44.9	43.0	44.3	44.2	43.7
9	65.3	67.2	48.9	54.9	45.1	75.1
10	51.0	50.3	49.8	55.4	60.7	54.4
11	211.2	211.0	22.7	75.8	27.8	28.3
12	53.4	62.5	53.3	50.7	42.1	50.3
13	28.3	67.7	213.0	71.6	70.1	70.8
14	45.0	51.6	60.9	52.4	49.6	55.1
15	28.4	33.7	26.0	33.8	75.4	34.5
16	144.1	140.5	142.7	145.2	155.3	143.8
17	110.1	112.4	110.4	108.2	109.3	108.5
18	28.8	28.8	28.8	28.8	28.7	29.4
19	63.1	62.5	62.7	64.3	60.7	61.6
20	75.7	65.1	70.0	70.4	70.2	69.3
OAc		—	—	—	—	176.9, 22.6

TABLE XLXVIII (*continued*)

carbon	AVIII1a-60 (*204*) (cardiopetamine)	AVIII1a-61 (*204*) (15-acetylcardiopetamine)	AVIII1a-62 (*204*) (15-acetyl-13-dehydrocardiopetamine)	AVIII1a-63 (*262*) (orientinine)	AVIII1a-64 (*191*) (eraconine)	AVII2a-1 (*264*) (delatisine)
1	44.0	44.1	45.7	46.0	27.7	34.3
2	212.1	212.0	209.6	214.1	29.8	79.6
3	49.6	50.0	49.7	51.5	33.2	41.6
4	42.1	42.6	42.6	40.3	37.4	50.5
5	59.7	60.2	60.0	60.0	48.6	62.0
6	64.9	65.2	65.5	65.3	65.5	66.3
7	33.1	32.9	31.6	69.8	*	37.3
8	49.3	48.1	48.2	44.2	50.0	45.7
9	48.7	49.4	49.8	54.9	31.2	55.4
10	54.5	55.0	54.5	48.2	44.9	52.7
11	75.1	75.1	71.9	70.0	*	75.7
12	47.7	47.8	57.7	49.5	61.9	50.2
13	69.0	69.6	204.9	211.4	33.5	72.2
14	48.9	49.6	58.8	79.1	50.1	50.0
15	69.8	72.0	71.7	37.0	114.8	33.9
16	150.5	144.7	138.7	146.0	132.5	145.7
17	112.1	116.5	121.3	108.2	69.0	108.2
18	28.3	28.6	28.7	24.2	28.9	21.9
19	65.0	64.6	64.2	62.7	63.1	100.2
20	69.8	70.1	71.9	68.6	74.2	64.4

AVIII1a-60: 165. 8 (COO), 130.1 ('1), 129.6 (2', 6'), 128.9 (3', 5'), 133.5 (4'); AVIII1a-61: 171.0, 21.3 (OAc), 166.6 (COO), 129.8 (1'), 129.6 (2', 6'), 128.7 (3', 5'), 133.3 (4'); AVIII1a-62: 170.8, 21.3 (OAc), 166.2 (COO), 128.9 (1'), 128.9 (2', 6'), 128.9 (3', 5'), 133.9 (4') ; AVIII1a-64: 157.4 (1'), 129.4 (2'), 128.7 (3'), 144.2 (4'), 128.7 (5'), 129.4 (6'), 19.6 (1''), 61.8 (2''); * not be reported

TABLE XLXVIII (*continued*)

carbon	AVII2b-2 (*259*) (venulol)	AVII2b-4 (*268*) (spirasineXIV)	AVII2b-5 (*268*) (spirasineXV)	AVII2b-6 (*141*) (pseudokobusine)	AVII2b-10 (*129*) (tatsirine)	AVII2b-11 (*262*) (acorientine)
1	30.2	35.4	35.1	27.4		39.3
2	19.6	18.6	18.3	19.2		18.9
3	38.6	24.2	26.1	35.5		35.1
4	42.3	37.2	37.3	37.6	36.8	35.9
5	59.4	59.1	58.2	61.2		59.3
6	102.2	99.5	101.5	97.8	97.9	100.9
7	35.9	42.5	41.2	40.2		46.7
8	43.2	43.1	41.2	46.8	44.8	40.9
9	42.9	48.8	47.5	54.1		54.1
10	57.9	49.4	49.4	49.8	49.4	49.6
11	72.6	21.6	23.3	67.5		37.6
12	42.8	48.2	53.7	34.5		39.5
13	27.3	65.9	69.3	29.1		72.0
14	47.7	41.6	41.1	40.7		40.7
15	36.1	33.0	32.3	70.3		73.6
16	146.3	147.1	143.1	149.3	149.1	150.3
17	109.8	106.6	109.4	114.9	106.6	116.1
18	29.2	29.6	29.4	30.3		29.9
19	59.8	58.0	56.7	60.0		57.3
20	68.1	69.0	71.0	73.4		67.2

AVII2b-7 (*270*): 100.0 (6), 44.8 (8), 49.9 (10), 67.3 (11), 70.3 (15), 144.2 (16), 118.7 (17), 58.4 (19), 72.3 (20), 60.0, 41.3, 40.4, 39.5, 37.7, 35.3, 30.0, 28.0, 27.1, 26.8, 19.1, 16.6, 11.6; AVII2b-10: 70.6, 67.4, 66.7, 60.9, 60.9, 51.8, 48.5, 42.9, 42.3, 41.6, 33.9, 32.4, 31.2, 22.4

TABLE XLXVIII (*continued*)

carbon	AVII2b-12 (*272*) (cardionine)	AVII2b-13 (*272*) (11-acetylcardionine)	AVII2b-14 (*273*) (geyerinine)	AVII2b-15 (*212*) (delbidine)	AVII2b-16 (*273*) (geyeridine)	AVII2b-17 (*273*) (geyerine)
1	35.7	35.6	31.6	44.2	43.2	44.4
2	19.6	19.4	67.4	212.9	209.9	211.2
3	27.7	27.7	77.4	51.5	51.4	51.6
4	38.3	38.2	51.5	42.3	45.9	45.8
5	60.9	61.3(1.56)	63.4	60.9	59.2	60.3
6	99.0	99.0	96.9	97.9	100.3	99.2
7	38.8	39.6	33.6	33.3	32.9	33.1
8	45.8	45.8	44.9	45.2	42.8	42.9
9	58.2	56.3(1.65)	54.3	51.3	52.2	53.7
10	-	50.4	57.8	55.6	55.7	56.1
11	71.9	76.3(4.09)	75.1	69.9	69.8	74.0
12	74.6	73.1	48.7	53.7	48.6	48.1
13	35.8	36.2	73.6	73.3	75.3	72.1
14	41.1	40.9(2.32)	49.4	51.1	49.7	48.4
15	71.1	71.1(5.68)	44.7	44.0	42.9	43.8
16	148.6	148.0	144.3	148.1	143.2	143.6
17	110.3	109.4(5.01,5.04)	109.2	106.1	109.9	109.8
18	30.4	30.6(1.33)	26.8	30.2	30.1	30.3
19	59.5	60.3(2.37,3.08)	77.4	62.7	59.9	61.2
20	72.8	73.4(2.54)	67.7	68.9	68.4	69.2

AVII2b-12: 177.9 (1'), 34.7 (2'), 19.5 (3'), 19.5 (4'); AVII2b-13: 172.2, 21.4 (OAc), 177.1 (1'), 34.3 (2'), 19.2 (3'), 19.3 (4'); AVII2b-14: 170.2, 21.1 (OAc), 175.9 (1'), 41.4 (2'), 26.5 (3'), 11.6 (4'), 16.8 (5'); AVII2b-16: 170.6, 21.3 (OAc); AVII2b-17: 176.0 (1'), 40.9 (2'), 26.5 (3'), 11.7 (4'), 16.8 (5')

TABLE XLXVII (*continued*)

carbon	AVII2b-19 (*274*) (panicudine)	AVII2b-20 (*268*) (spirasine XII)	AVII2b-21 (*268*) (spirasine X III)	AVII2b-22 (*275*) (paniculadine)	AVII2b-23 (*224*) (delnuttidine)	AVII2b-24 (*224*) (delnuttaline)
1	34.9	36.4	35.3	43.7	41.7	41.6
2	66.1	19.8	19.0	210.1	209.5	212.2
3	43.3	27.3	28.6	52.4	51.8	52.8
4	37.7	38.4	37.6	43.9	42.8	43.5
5	62.5	62.3	60.7	61.0	58.0	56.0
6	99.7	98.5	98.9	99.0	101.9	99.1
7	44.4	44.3	43.3	44.1	42.5	40.7
8	44.2	46.6	45.1	44.7	43.8	46.2
9	49.7	65.7	73.9	48.6	49.1	78.4
10	49.7	51.2	52.3	54.8	53.1	57.5
11	23.4	210.8	209.2	23.2	22.6	34.4
12	54.0	64.3	61.9	53.2	42.9	41.6
13	210.8	67.3	61.4	210.0	69.1	73.2
14	61.9	51.7	56.0	61.1	49.5	48.5
15	34.0	33.9	32.8	33.2	33.0	30.9
16	144.9	140.8	137.6	143.7	148.1	147.9
17	110.3	111.3	114.9	110.6	107.3	108.1
18	32.0	31.2	30.5	30.4	29.7	30.8
19	61.9	61.9	61.1	63.2	59.1	63.9
20	70.2	68.9	72.0	71.8	68.9	67.5
OAc	—	—	—	—	—	170.2, 20.9

TABLE XLXVIII (*continued*)

carbon	AVII2c-1 (*227, 278*) (acsinatine)	AVII2c-2 (*279*) (andersobine)	AVII2c-3 (*148*) (vakhmatine)	AVII2c-4 (*280*) (13-*O*-acetyl-vakhmatine)	AVII2c-5 (*281*) (septenine)	AVII2c-6 (*282*) (septentriosine)
1	31.8	25.6	35.1	32.8	67.9	69.0
2	70.7	31.8	62.9	66.1	73.1	70.4
3	37.8	73.0	38.5	40.7	33.0	39.1
4	42.2	48.5	42.4	42.0	42.2	39.7
5	55.1	61.7	60.6	61.6	50.8	58.8
6	60.8	60.6	61.6	60.2	60.7	60.5
7	29.6	28.0	36.8	35.6	30.8	31.1
8	42.1	44.0	45.3	44.2	41.7	42.1
9	78.8	43.5	56.8	55.1	79.6	79.8
10	50.4	48.5	51.5	50.2	53.7	53.0
11	39.0	26.2	76.9	75.8	39.2	33.5
12	36.9	33.0	52.4	48.5	36.2	36.2
13	34.3	32.5	73.0	76.6	33.9	33.1
14	43.9	42.9	53.2	49.9	43.9	43.3
15	31.7	71.8	34.5	33.7	31.1	30.7
16	152.1	151.7	148.2	144.8	150.6	150.3
17	114.3	109.9	107.6	108.7	104.7	104.8
18	23.0	19.1	27.5	22.7	22.2	28.4
19	92.0	87.6	95.5	90.9	91.2	95.2
20	70.1	69.9	66.1	65.0	67.9	60.5
OAc	169.6, 21.7	171.2, 21.2	—	172.8, 21.1	170.2, 21.6	—

TABLE XLXVIII (*continued*)

carbon	AVII2c-7 (*283*) (2-acetylseptentriosine)	AVII2c-8 (*284*) (delgramine)	AVII2c-10 (*395*) (ternatine)	AVII2d-1 (*285*) (orgetine)	AVII3-1 (*286*) (guan-fu base Z *N*-oxide)
1	67.9	66.9	30.1	30.6	30.2[a](31.1)[b]
2	73.2	75.0	29.1	19.6	68.2 (69.7)
3	39.2	34.7	20.6	35.9	36.6 (37.3)
4	42.1	43.5	53.2	37.9	—
5	50.7	58.8	61.5	61.9	55.0 (56.0)
6	60.5	61.9	66.6	67.8	75.2 (75.5)
7	30.9	34.7	65.2	29.5	28.5 (29.3)
8	42.1	44.7	43.8	47.2	44.5 (45.6)
9	79.6	54.3	50.0	54.5	52.9 (53.9)
10	53.7	57.0	52.0	50.2	—
11	33.8	75.0	74.0	70.6	71.4 (73.0)
12	36.1	52.7	40.2	41.2	51.5 (53.3)
13	32.9	71.6	34.5	41.4	73.4 (74.8)
14	43.7	53.0	44.4	40.7	83.5 (84.8)
15	30.7	36.7	70.2	73.2	31.9 (32.5)
16	150.4	148.3	153.6	149.8	143.6 (146.6)
17	104.7	106.9	100.2	114.8	108.9 (108.5)
18	21.5	23.5	23.5	27.7	29.5 (29.5)
19	91.7	92.2	91.9	60.5	76.2 (77.4)
20	67.9	63.2	70.1	97.4	82.2 (83.1)

a: $CDCl_3$; b: CD_3OD

TABLE XLXIX

^{13}C NMR OF VAKOGNAVINE TYPE DITERPENOID ALKALOIDS (AVIII)

carbon	AVIII-1 (*215*) (15-deacetylvakognavine)	AVIII-2 (*215*) (vakognavine)	AVIII-3 (*293*) (barbisine)	AVIII-4 (*294*) (delgrandine)	AVIII-5 (*294*) (acetyldelgrandine)	AVIII-6 (*295*) (barbaline)
1	70.5	70.5	68.8	72.0	71.7	72.4
2	67.2	67.2	68.4	66.2	65.9	66.6
3	29.2	29.3	29.6	71.8	71.7	71.9
4	44.1	44.2	43.9	48.9	48.4	49.2
5	59.8	59.9	59.3	59.4	59.5	57.6
6	57.3	57.1	61.7	62.7	60.1	62.7
7	28.4	28.3	74.5	72.0	73.1	67.6
8	49.6	48.3	46.9	49.0	48.9	49.5
9	49.6	50.7	56.4	52.4	52.3	48.6
10	56.4	56.8	54.1	55.3	55.5	56.5
11	70.5	70.5	63.2	74.6	74.1	71.0
12	58.8	58.7	61.0	45.9	45.3	60.0
13	207.0	206.0	208.8	73.7	73.8	206.2
14	51.6	51.7	50.6	39.3	39.2	53.8
15	70.7	71.3	28.9	29.4	29.0	30.1
16	142.1	137.5	133.5	141.5	140.6	136.8
17	117.6	120.7	115.7	111.3	111.6	113.9
18	26.4	26.6	26.1	22.9	22.8	23.3
19	195.0	195.9	196.6	190.5	191.7	196.4
20	66.6	66.5	67.2	64.6	63.9	66.0
21	33.0	33.1	34.9	35.0	34.2	33.6

TABLE XLXIX (*continued*)

AⅧ1-1: 170.7, 21.5; 169.4, 21.1 (2×OAc), 165.4 (COO), 129.6 (2', 6'), 128.6 (3', 5'), 133.3 (4'); AⅧ1-2: 170.7, 21.5; 170.7, 21.2; 169.3, 21.2 (3×OAc), 165.3 (COO), 129.6 (1'), 129.6 (2', 6'), 128.6 (3', 5'), 133.3 (4'); AⅧ1-3: 170.0, 20.9; 170.0, 20.6 (2×OAc), 165.3 (COO), 129.6 (1'), 129.6 (2', 6'), 128.6 (3', 5'), 133.5 (4'); AⅧ1-4: 170.7, 170.0, 169.3; 21.6, 21.2, 20.6 (3×OAc), 165.5, 164.0 (2×OAc), 129.4 (2×1'), 129.0 (2×(2', 6')), 128.3 (2×(3', 5')), 133.1 (2×4'); AⅧ1-5: 170.5, 169.5, 169.3, 169.0; 21.3, 20.9, 20.3, 20.3 (4×OAc), 165.5, 163.9 (2×COO), 129.3 (2×1'), 128.8 (2×(2', 6')), 133.0 (2×4'); AⅧ1-6: 170.6, 170.2, 169.3; 21.5, 20.9, 20.6 (3×OAc); 164.9 (COO), 129.2 (1'), 129.8 (2', 6'), 128.8 (3', 5'), 133.7 (4')

TABLE XLXX

^{13}C NMR OF VEATCHINE TYPE DITERPENOID ALKALOIDS (B I)

carbon	B I 1a-1 (*296, 297*) (veatchine)	B I 1a-2 (*306*) (garryfoline)	B I 1a-3 (*306*) (ovatine)	B I 1a-4 (*310*) (cuauchichicine)
1	41.7[a](41.3)[b]	41.9[a] (41.6)[b]	41.9[a] (41.6)[b]	41.6
2	18.6 (19.2)	19.3 (20.0)	18.2 (19.5)	18.4
3	37.1 (37.1)	37.6 (37.6)	37.6 (37.6)	38.4
4	34.1 (34.1)	34.2 (34.1)	34.2 (34.1)	34.0
5	52.8 (52.3)	52.3 (53.1)	52.2 (53.2)	52.4
6	18.6 (17.4)	18.9 (17.5)	18.5 (17.2)	17.9
7	33.9 (33.9)	35.1 (35.1)	35.3 (35.1)	32.6
8	47.3 (47.5)	45.4 (45.7)	45.7 (46.0)	52.0
9	51.6 (51.1)	43.9 (43.2)	45.4 (44.8)	47.7
10	40.6 (40.3)	40.2 940.10	40.8 (40.3)	40.5
11	22.7 (21.8)	22.8 (21.9)	22.8 921.9)	22.7
12	31.2 (30.3)	32.0 (30.9)	32.2 (30.9)	22.4
13	42.4 (42.4)	40.4 (40.4)	40.6 (40.2)	33.7
14	35.1 (35.1)	37.4 (37.0)	37.6 (37.6)	34.7
15	82.8 (84.3)	83.1 (83.1)	82.1 (82.4)	224.7
16	160.7 (161.2)	159.3 (159.3)	154.5 (154.9)	49.5
17	107.4 (107.8)	104.4 (106.0)	105.7 (105.5)	10.0
18	25.9 (26.4)	26.0 (26.5)	26.0 (26.6)	25.5
19	56.4 (55.9)	56.6 (56.1)	56.6 (56.1)	56.7
20	92.6 (93.3)	93.2 (94.5)	93.2 (94.4)	92.7
21	50.2 (49.8)	50.5 (49.4)	50.5 (49.5)	50.5
22	64.3 (58.8)	64.6 (59.0)	64.6 (59.0)	64.5
OAc	—	—	171.7 (171.7)	—
	—	—	21.3 (20.4)	—

a: 20-R; b: 20-S; B II 1-1: 55.6 (OCH_3)

TABLE XLXX (*continued*)

carbon	B I 1a-5 (*296, 297*) (garryine)	B I 1a-6 (*309*) (isogarryfoline)	B I 1a-7 (*310*) (isocuauchichicine)	B I 1b-1 (*305*) (lindheimerine)
1	40.6	40.7	40.6	
2	20.6	21.3	20.1	
3	40.6	40.5	39.7	
4	40.3	39.9	40.6	
5	50.6	48.7	50.6	
6	18.2	18.2	18.0	
7	33.8	33.0	33.0	
8	47.4	45.5	52.4	45.2
9	49.1	42.8	47.9	
10	35.9	36.1	35.9	
11	22.3	22.4	22.3	
12	32.4	37.2	24.9	
13	41.7	39.7	38.5	
14	36.8	37.6	34.6 (34.2)	
15	82.7	82.6	224.7	81.6
16	159.6	158.1	48.8	153.8
17	108.5	105.2	10.1	106.8
18	24.4	24.5	24.3	
19	98.2	98.6	98.4 (96.8)	
20	51.1	51.3	48.4	167.1
21	54.8	54.9	54.9 (56.5)	
22	58.7	58.8	58.8 (64.9)	

TABLE XLXXI

^{13}C NMR OF NAPELLINE TYPE DITERPENOID ALKALOIDS (B II)

carbon	B II 1-1 (*315*) (liangshanine)	B II 1-3 (*316, 317*) (napelline)	B II 1-4 (*316, 330,331*) (12-epi-napelline)	B II 1-5 (*316*) (1-epi-napelline)	B II 1-7 (*201*) (lucidusculine)	B II 1-8 (*318*) (12-acetyl lucidusculine)
1	80.7	70.5[a] (69.5[b])	69.5	77.0	69.9	69.6
2	25.8	31.9 (31.2)	31.5	31.2	31.6	31.7
3	38.1	32.4 (36.1)	32.4	32.4	30.5	36.8
4	34.5	34.7 (34.2)	35.2	35.3	34.0	34.0
5	50.7	49.4 (48.0)	51.6	49.1	47.7	48.4
6	23.3	23.6 (23.2)	24.3	24.1	23.7	23.6
7	44.6	45.0 (43.9)	45.1	45.8	43.7	43.6
8	51.4	50.3 (50.0)	51.6	51.0	49.6	49.4
9	38.2	38.2 (36.6)	39.6	38.1	37.7	37.2
10	51.4	53.5 (52.9)	53.8	54.0	52.5	52.6
11	28.8	29.4 (30.7)	33.6	29.7	29.1	25.9
12	67.4	76.2 (75.8)	71.8	76.7	75.5	77.5
13	44.4	49.9 (47.1)	45.7	50.6	48.8	44.7
14	32.6	38.4 (28.6)	38.8	38.5	36.5	29.3
15	77.0	77.8 (77.4)	78.1	78.4	77.5	77.1
16	155.4	160.8 (158.9)	154.8	160.0	153.1	151.7
17	111.1	107.4 (108.6)	112.2	108.4	109.5	111.1
18	26.0	26.4 (26.3)	26.7	26.8	26.4	26.3
19	57.0	57.7 (58.1)	58.9	59.0	57.9	57.9
20	66.3	66.2 (65.4)	67.3	67.0	65.7	65.5
21	51.2	51.6 (51.4)	52.1	52.1	50.8	50.9
22	13.5	13.3 (12.7)	13.7	13.7	13.4	13.4
OAc	—	—	—	—	170.6, 21.6	170.7, 170.5

B II 1-3: a: py-d_5; b: $CDCl_3$

TABLE XLXXI (*continued*)

carbon	B II 1-9 (*340*) (turpelline)	B II 1-11 (*331*) (songorine)	B II 1-13 (*315*) (liangshanone)	B II 1-16 (*347*) (karakonine)	B II 1-17 (*348*) (chuanfunine)	B II 2a-1 (*142, 316*) (dehydronapelline)
1	68.9	70.1	80.4	69.0	68.0	67.9
2	30.2	31.5	25.8	31.5	30.2	29.9
3	31.2	31.9	37.9	35.0	37.5	24.4
4	36.8	34.0	34.3	33.4	34.8	37.8
5	48.4	49.0	50.4	47.7	52.9	32.5
6	23.6	23.0	22.9	22.7	70.4	24.0
7	45.8	43.4	44.1	39.7	46.1	46.7
8	55.2	49.7	49.8	54.0	43.2	50.4
9	46.8	35.1	35.9	43.0	50.8	45.9
10	55.5	52.1	51.3	52.6	53.2	51.9
11	73.5	37.3	38.0	30.6	23.8	27.8
12	82.7	209.6	210.7	67.5	21.0	76.4
13	46.8	33.6	54.1	40.4	43.5	48.8
14	37.2	38.0	31.7	30.0	28.8	30.4
15	77.4	76.9	77.3	221.9	85.4	77.5
16	158.6	150.3	151.3	38.9	80.0	157.7
17	109.8	111.1	111.4	16.4	69.1	109.5
18	25.6	26.0	26.0	26.3	25.5	19.0
19	59.2	57.2	56.9	58.1	55.0	93.1
20	66.8	65.8	66.4	66.0	68.8	66.0
21	51.5	50.8	51.1	50.9	54.3	48.4
22	10.7	13.5	13.6	13.6	10.5	14.3

B II 1-13: 55.5 (OCH_3)

TABLE XLXXI (*continued*)

carbon	B II 2a-2 (*331*) (12-epi-19-dehydronapelline)	B II 2a-3 (*134, 331a*) (dehydrolucidusculine)	B II 2a-4 (*331*) (12-epi-acetyl-dehydronapelline)	B II 2a-5 (*134*) (12-acetyldehy-drolucidusculine)	B II 2a-6 (*350*) (12-epi-acetylde-hydrolucidusculine)	B II 2a-7 (*351*) (subdesucline)
1	67.9	67.6	67.9	67.6	67.4	67.7
2	30.0	29.7	29.8	29.8	29.6	29.7
3	24.8	24.5	24.5	24.5	24.5	24.4
4	37.9	37.7	38.0	37.8	37.5	37.7
5	48.9	33.7	49.0	45.9	45.6	45.9
6	24.2	23.8	24.2	23.9	23.8	23.9
7	46.0	46.8	46.1	48.3	48.1	48.7
8	50.9	49.4	50.9	49.3	49.4	50.2
9	33.3	45.8	33.8	33.6	34.9	32.2
10	52.1	51.7	52.1	51.8	51.6	51.8
11	30.9	28.1	27.1	26.3	26.8	26.3
12	67.5	76.1	72.3	77.4	71.9	76.8
13	42.6	48.3	40.2	43.3	40.0	43.0
14	31.9	30.2	31.6	28.6	31.4	28.1
15	77.3	77.7	77.2	77.9	77.9	77.2
16	154.0	151.7	153.9	150.7	147.7	156.5
17	112.6	110.4	111.8	111.8	112.6	110.5
18	19.1	18.9	19.1	19.0	18.8	18.9
19	93.1	92.2	93.2	92.8	92.6	92.9
20	66.1	65.6	66.0	65.6	65.3	65.9
21	48.5	48.3	48.5	48.3	48.1	48. 3
22	14.4	14.1	14.4	14.2	14.0	14. 2
OAc	—	170.7, 21.5	170.8, 21.5	170.8, 170.4;	170.8, 170.5;	170.4
	—	— —	— —	21.5, 21.3	21.5, 21.1	21.3

TABLE XLXXI (*continued*)

carbon	B II 2a-8 (*134, 331a*) (*N*-deethyldehydro-lucidusculine)	B II 2a-9 (*331, 341*) (songoramine)	B II 3-1 (*142*) (flavamine)	B II 3-2 (*355*) (12-epi-napelline *N*-oxide)	B II 3-4 (*142, 354*) (flavadine)
1	67.8	67.9	68.1	67.2	68.0
2	29.6	29.9	30.1	30.5	29.9
3	23.7	24.4	35.3	32.6	31.1
4	37.8	37.9	36.2	35.2	36.4
5	34.0	48.7	48.5	46.6	47.2
6	23.5	24.1	22.9	22.8	23.5
7	46.8	46.1	47.3	46.3	47.2
8	49.4	50.4	49.8	49.8	49.6
9	45.5	31.6	39.1	39.0	40.7
10	50.6	51.9	55.5	54.2	55.2
11	28.1	31.4	31.3	28.9	29.9
12	76.1	209.0	76.7	66.6	76.4
13	48.1	53.3	48.5	43.8	48.4
14	30.2	37.5	29.6	34.9	35.2
15	77.7	77.1	77.6	76.4	77.8
16	151.6	149.9	158.9	153.6	154.3
17	110.5	111.9	109.3	112.7	110.8
18	19.0	19.0	26.5	26.5	26.3
19	87.8	93.1	75.3	74.8	74.8
20	57.5	66.4	81.5	80.3	81.1
21	—	48.5	67.9	67.2	68.0
22	—	14.4	7.8	7.8	7.9
OAc	170.6, 21.5	—	—	—	172.3, 231.3

TABLE XLXX II

^{13}C NMR OF ANOPTERINE TYPE DITERPENOID ALKALOIDS (BIII)

carbon	BIII1-1 (*359, 360*) (anopterine)	BIII1-2 (*358, 360*) (dihydroxy-anopterine)	BIII1-3 (*358, 360*) (hydroxyanopterine)	BIII2-1 (*358*) (anopterimine)	BIII3-1 (*358*) (anopterimine *N*-oxide)
1	41.6	82.7	82.6	40.5	40.1
2	71.4	75.7	76.0	21.6	21.3
3	42.9	41.7	41.8	36.5	37.8
4	36.6	36.6	36.2	40.5	41.5
5	78.5	78.2	77.9	44.8	45.6
6	66.2	65.4	66.5	24.4	23.7
7	39.8	38.9	38.8	34.1	33.6
8	51.7	52.6	52.3	53.2	50.7
9	57.0	55.8	56.1	58.7	53.9
10	48.2	47.2	47.0	51.4	50.3
11	73.0	73.3	73.4	71.0	70.4
12	70.3	70.8	70.3	76.2	75.6
13	54.3	54.3	54.2	54.6	53.4
14	53.3	53.5	53.2	53.2	51.8
15	36.6	37.4	36.2	36.5	36.0
16	148.8	148.5	148.2	149.7	148.4
17	108.3	108.9	108.7	107.7	108.4
18	24.4	24.4	24.5	23.8	24.3
19	61.8	61.5	61.6	168.5	143.8
20	65.6	65.4	64.9	63.2	70.4
21	42.9	42.8	42.8	—	—

TABLE XLXXIII

^{13}C NMR OF REARRANGED TYPE DITERPENOID ALKALOIDS (C II, CIII, CIV)

carbon	C II 1-1 (*367*) (kusnesoline)	CIII1-2 (*370*) (ajabicine)	CIV1-1 (*371*) (racemulosine)[a]
1	94.1	73.3	76.0
2	71.3	30.8	49.9
3	70.8	32.7	142.3
4	69.6	33.3	58.0
5	66.6	47.1	54.1
6	64.5	26.3	25.5
7	64.1	46.7	47.6
8	58.8	80.8	76.0
9	53.2	48.5	46.6
10	51.0	49.8	47.8
11	46.7	35.8	27.4
12	41.3	38.8	35.9
13	39.9	33.5	34.6
14	38.7	33.3	32.5
15	38.1	51.8	44.7
16	37.9	156.6	51.3
17	36.8	103.2	179.5
18	31.5	27.5	113.2
19	39.5	60.2	56.0
20	28.5	62.8	63.1
21	-	48.6	48.3
22	-	13.3	13.4

TABLE XLXXIV

^{13}C NMR OF REARRANGED ATISINE—HETIDINE TYPE BISDITERPENOID ALKALOIDS (D II)

carbon	D II 1-1 (*373, 374*) (staphidine)	D II 1-2 (*373, 375*) (staphisine)	D II 1-3 (*374, 376*) (staphirine)	D II 1-4 (*374, 376*) (staphigine)	D II 1-5 (*373, 374*) (staphimine)	D II 1-6 (*373, 374*) (staphinine)
4	34.2	34.2	44.7	44.6	41.5	41.5
8	37.6	37.4	38.7	38.4	38.3	38.1
10	45.5	46.0	44.3	44.6	43.7	44.3
13	—	89.4	—	90.3	—	91.2
16	73.6	72.2	73.5	72.2	73.8	72.3
19	60.4	60.7	175.0	175.1	167.6	168.1
20	77.0	74.4	77.0	72.9	75.8	73.1
21	43.5	43.9	46.9	46.9	—	—
OCH_3	—	57.8	—	57.0	—	56.4
4'	34.4	34.5	34.5	34.5	34.5	34.4
5'	135.6*	135.6*	136.1*	135.6*	135.7*	135.5*
8'	41.6	41.8	41.9	41.8	41.6	41.6
9'	127.7*	127.6*	128.1*	128.2*	127.9*	127.7*
10'	135.8*	135.6*	136.4*	136.1*	135.7*	135.5*
11'	112.7	112.9	113.1	113.7	113.3	112.9
15'	77.6	78.1	78.1	78.5	77.9	78.5
16'	29.3	29.5	29.4	29.7	29.4	29.5
19'	62.4$^{\Delta}$	62.5$^{\Delta}$	62.7$^{\Delta}$	62.5$^{\Delta}$	62.3$^{\Delta}$	62.5$^{\Delta}$
20'	64.5$^{\Delta}$	64.7$^{\Delta}$	64.8$^{\Delta}$	64.7$^{\Delta}$	64.4$^{\Delta}$	64.7$^{\Delta}$
21'	46.3	46.6	46.6	46.4	46.4	46.3

*, Δ exchangeable

TABLE XLXXV
^{13}C NMR OF DENUDATINE—DENUDATINE AND HETERATISINE—HETIDINE TYPE BISDITERPENOID ALKALOIDS (DIII, DIV)

DIII1-1 (pukeeosine) (*377*)			DIV1-1 (tangirine) (*378*)		
δ_C			δ_C		
19.5	34.4	53.9	30.5 (C-1)	82.3 (C-1')	13.5 (C-21')
20.6	35.8	56.0 (C-21')	27.4 (C-2)	26.7 (C-2')	55.0 (1"-OCH_3)
22.0	36.0	57.1 (C-19')	30.6 (C-3)	36.3 (C-3')	166.6 (6"-COO)
23.5	37.0	58.7 (C-22)	45.0 (C-4)	34.7 (C-4')	130.8 (1")
24.8	39.6	68.1 (C-17)	44.3 (C-5)	55.9 (C-5')	130.2 (2"', 6"')
25.2	39.9	70.9 (C-20)	20.6 (C-6)	74.0 (C-6')	128.2 (3"', 5"')
26.0	40.6	71.4 (C-20')	31.5 (C-7)	44.7 (C-7')	132.3 (4"')
26.1 (C-18)	45.3	72.6 (C-22')	43.1 (C-8)	78.7 (C-8')	
26.6 (C-18')	45.4	76.4 (C-15')	46.4 (C-9)	48.2 (C-9')	
28.2	47.1	94.2 (C-19)	44.9 (C-10)	43.0 (C-10')	
29.7	47.6	108.8 (C-17')	28.4 (C-11)	48.8 (C-11')	
31.1	48.8 (C-21)	157.3 (C-16')	31.5 (C-12)	29.2 (C-12')	
31.2	49.2		42.8 (C-13)	75.1 (C-13')	
34.0	51.7		72.5 (C-14)	173.2 (C-14')	
			127.8 (C-15)	31.2 (C-15')	
			146.0 (C-16)	29.7 (C-16')	
			60.4 (C-17)	62.9 (C-17')	
			19.0 (C-18)	25.9 (C-18')	
			169.2 (C-19)	57.4 (C-19')	
			80.3 (C-20)	48.8 (C-20')	

TABLE XLXXVI

^{13}C NMR OF ATISANE DITERPENES (A I ')

carbon	A I '-1 (*104*) atisenol	A I '-2 (*89*) spiramilactone	A I '-3 (*105*) spiramilactone C	A I '-4 (*105*) spiramilactone D	A I '-5 (*98*) spiraminol
1	40.2	40.9	40.1	53.3	34.5
2	20.2	20.3	20.8	42.8	23.2
3	37.5	37.5	39.9	38.2	30.0
4	42.7	32.7	42.6	47.2	34.3
5	49.6	46.7	47.7	47.9	45.9
6	20.5	13.0	15.3	23.0	26.0
7	29.7	80.6	81.1	82.2	71.1
8	37.3	41.6	41.8	39.4	38.5
9	40.0	46.5	44.8	39.3	44.1
10	36.0	45.8	36.6	34.4	42.2
11	27.3	28.4	29.0	22.0	23.2
12	31.0	35.9	36.2	52.7	37.6
13	26.4	26.6	28.3	21.1	21.3
14	23.3	24.5	26.8	20.4	20.8
15	76.5	76.8	77.4	71.0	73.9
16	155.6	157.0	155.4	70.3	156.0
17	110.3	107.7	109.9	31.0	111.0
18	28.9	23.5	23.6	27.0	23.0
19	176.7	76.4	175.7	174.7	94.3
20	74.7	174.3	74.1	76.3	98.5

TABLE XLXXVI (*continued*)

carbon	A Ⅰ'-6 (*105*) spiramacetal	A Ⅰ'-7 (*106*) spiramilactone B	A Ⅰ'-8 (*105*) spiramadol
1	34.5	40.0	42.6
2	25.3	25.5	32.3
3	29.8	29.1	35.4
4	37.5	45.8	53.8
5	55.7	45.9	52.4
6	69.8	26.2	69.1
7	71.4	70.3	80.8
8	41.0	41.5	39.2
9	51.5	44.2	48.9
10	35.8	33.5	47.8
11	21.8	25.3	25.6
12	37.5	36.8	35.9
13	20.9	20.2	22.6
14	29.4	19.6	19.4
15	132.2	74.1	27.3
16	139.1	154.6	149.9
17	21.1	112.8	106.6
18	22.7	21.5	27.4
19	95.4	175.7	206.0
20	97.3	101.7	200.0

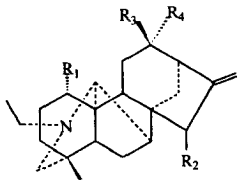
A Ⅰ'-6: 169.9, 169.9; 20.7, 20.4 (2×OAc); A Ⅰ'-8: 170.4, 21.3 (OAc)

E. MASS SPECTROMETRY

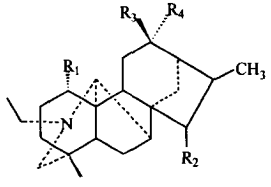
In 1970, Yunusov *et al.* (*341*) first reported the characteristic fragmentation of ring A in the mass spectra of napelline-type diterpenoid alkaloids. Sultankhadzaev *et al.* (*332*) later studied the mass spectra of napelline and its derivatives. Wang and Liang (*160*) also reported the mass spectrometry features for the hetidine-type alkaloid episcopalidine and its analogues. Studies on the mass spectra of hetisine-type alkaloids were reported independently by Rashkest *et al.* (*194*) and Mil'grom and co-workers (*422*). Several scientists, Edwards (*10*), Pelletier (*4*), and Yunusov (*33, 37*), have reviewed the mass spectra of C_{20}-diterpenoid alkaloids reported in the literature before 1992. Here we would like to summarize the field, covering the literature until the end of 2000.

1. Napelline-type Alkaloids

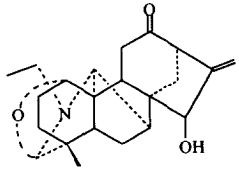
Because the whole ring systems of the napelline-type diterpenoid alkaloids are stable, their mass spectra show predominant fragmentation of substituent groups in the high mass range, and the songorine-type fragmentation of ring A with the loss of C-1-C-3 in the middle mass range. The latter may be derived from rearrangement of the radical group induced by the nitrogen atom after cleavage of the C-20-C-7 bond (*341*).



57 $R_1=R_2=OAc$ $R_3+R_4=O$
58 $R_1=OAc$ $R_2=R_3=OH$ $R_4=H$
60 $R_1=R_2=OH$ $R_3+R_4=O$
61 $R_1=R_3=OH$ $R_2=OAc$ $R_4=H$



59 $R_1=R_2=OAc$ $R_3+R_4=O$
62 $R_1=R_2=H$ $R_3+R_4=O$

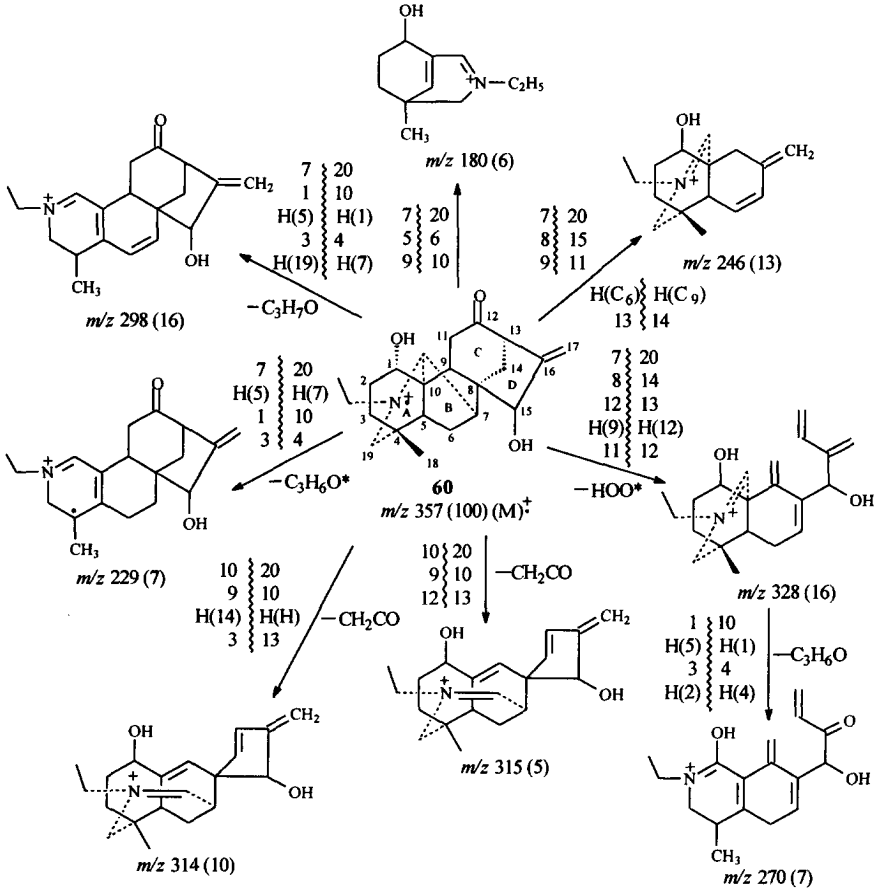


63

a. Molecular ion peak and base peak. The mass spectra of the napelline-type diterpenoid alkaloids generally show significant molecular ion peaks depending on

the types of substituent group at C-1. In general, alkaloids with the ester groups at C-1, e.g., alkaloids **57~62**, exhibited the base peaks at (M-O_2CR, R=CH_3) The mass spectra of the *N,O*-mixed acetal [C-1-O-C-19-*N*]-containing alkaloids, e.g., songoramine (**63**), generally had the molecular ion as the base peak.

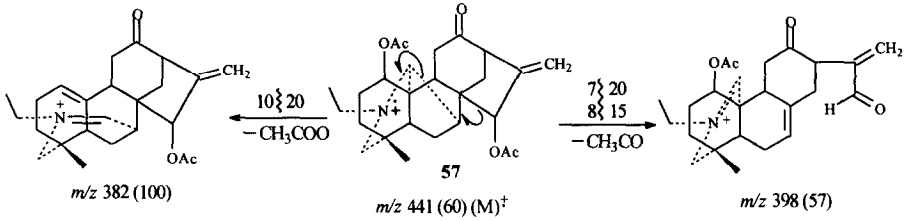
b. Skeletal fragmentation. The most important features in the mass spectra of napelline-type alkaloids are songorine-type fragmentation of ring A. As shown in the mass spectrum of songorine **60** (*341*), a characteristic fragment ion peak at *m/z*



Scheme 17

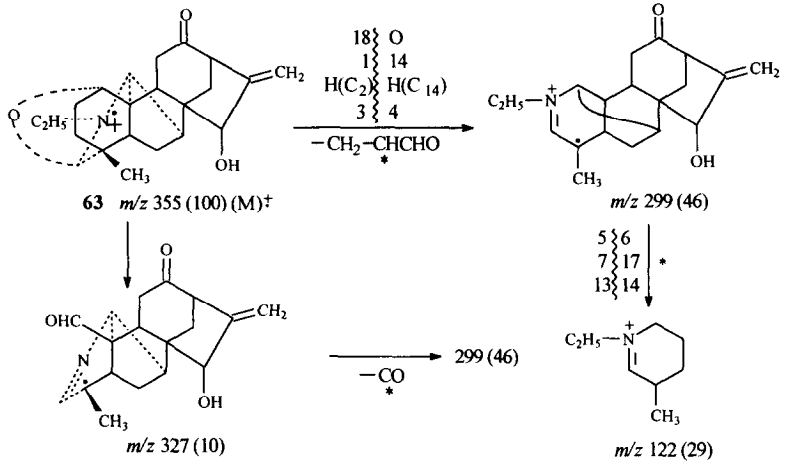
298 (M-59) is derived from cleavage of the C-20-C-7 and C-1-C-10 bonds with the subsequent loss of the C-1-C-3 unit. In addition, the fragment ion peak at *m/z* 246 may be formed by elimination of rings C and D. This has been confirmed by metastable techniques, while another valuable fragment ion peak at *m/z* 180 comes from the fragmentation of ring B (Scheme 17).

In the mass spectrum of diacetylsongorine (**57**), in addition to the songorine-type fragmentation of ring A, other important fragment ion peaks at *m/z* 382 [M-C-1-OAc, 100%] and *m/z* 398 (M-CH_3, 57%) with ring D opening may be observed (Scheme 18).



Scheme 18

The fragmentation of ring A of songoramine (**63**) (*341*) with an *N,O*-mixed acetal unit may be carried out by the cleavage of the C-19-O bond followed by loss

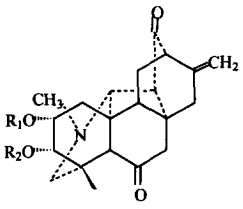


Scheme 19

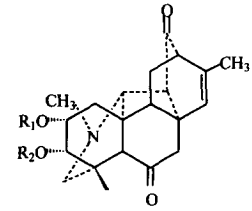
of C-1-C-3 to form the fragment ion peak at *m/z* 299, which is simultaneously derived from the fragment ion peak at *m/z* 327 with loss of CO. This coincidence was established by the corresponding metastable ions. The fragment ion at *m/z* 299 further fragments to give the peak at *m/z* 122 (Scheme 19).

2. Hetidine-type alkaloids

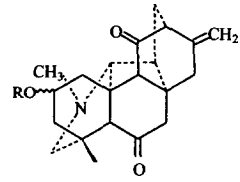
In 1985, Wang and Liang (*160*) studied the mass spectra of episcopalidine (**46**), a hetidine-type alkaloid from *Aconitum contortum*, and its analogues (**64-76**). In addition to the weak ion peaks from fragmentation of the skeletons in the middle-lower mass range, there appeared predominantly the fragmentation of substituent groups in the high mass range. The nitrogen atom becomes the fragmentation center.



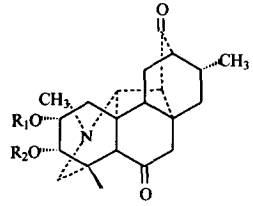
46 R_1 = Ac R_2 = PhCO
64 R_1 = R_2 = H
65 R_1 = R_2 = Ac
66 $R_1 + R_2$ =



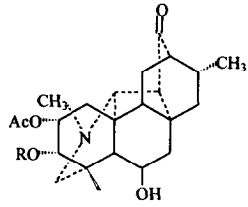
67 R_1 = Ac R_2 = PhCO
68 R_1 = R_2 = Ac



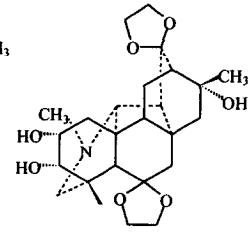
69 R = Ac
70 R = H



71 R_1 = R_2 = H
72 R_1 = Ac R_2 = PhCO
73 R_1 = Ac R_2 = OC



74 R = PhCO
75 R = OC



76

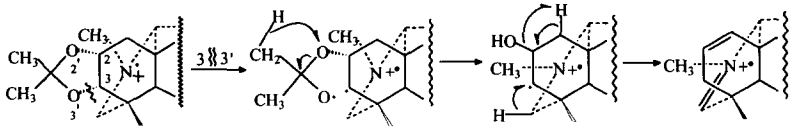
a. Molecular ion peak and base peak. The substituent groups, especially the

ester group, of episcopalidine and its derivatives, significantly affect the relative abundance of the molecular ion peaks. In general, alkaloids with ester groups, e.g., alkaloids **46**, **65**, **66**, **67**, and **72~76**, exhibited weak molecular ion peaks, and the alkaloids, e.g., **66** and **70**, fairly strong ones. The base ion peaks for these alkaloids come from either the M-C-2-OR, e.g., **72~75**, or the fragmentation of substituent groups as **46**.

b. Important fragment ion peaks derived from the substituent groups and skeleta. Characteristic fragment ion peaks at *m/z* M-17, M-18, M-CO, M-43, M-59, M-60, and M-121 were often observed in their mass spectra. The oxygenated groups at C-3 and C-2, e.g., **46**, **64**, **65**, **66**, **67**, and **71~76**, always give rise to intense ion peaks.

For alkaloids possessing the β, γ-unsaturated keto group in rings C and D (**46**, **64~70**), elimination of CO takes place in the first or second step.

In ring A, with the loss of C-1-C-3, ions at *m/z* 282 (**46**, **64~70**), *m/z* 284 (**71**, **72**), and *m/z* 286 (**74**, **75**), may be discerned. It is of interest to note that another fragmentation of ring A with the loss of C-2-C-3 in the mass spectrum of hetidine (**59**), also may be observed (Scheme 20).



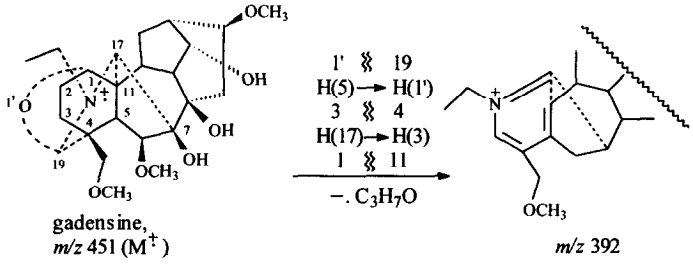
66 *m/z* 397 (3) $(M)^{+\bullet}$ *m/z* 340 (4) *m/z* 322 (4)

Scheme 20

To our knowledge, the C_{20}-diterpenoid alkaloids with the songorine-type fragmentation of ring A are: napelline-type, e.g., songorine (**60**), songoramine (**63**), norsongoramine (*353*); denudatine-type, e.g., dictysine (*10*, *194*), and some carbinolamine ether-containing C_{19}-diterpenoid alkaloids, e.g., gadensine (*419*) and pentagydine (*423*). Careful examination of the mass spectra of five C_{18}-type, twenty

C_{19}-type, as well as two denudatine-type diterpenoid alkaloids, showed that only the napellines, denudatines, hetidines, and some *N,O*-mixed acetal-containing diterpenoid alkaloids, except for the hetisines and the non-carbinolamine ether-containing C_{18}-, C_{19}-, and lactone-type alkaloids, give rise to the songorine-type fragmentation of ring A.

The songorine-type fragmentation of ring A of the hetidine-type alkaloids may be derived from the rearrangement of a radical group induced by the nitrogen atom after cleavage the C-20-C-14 bond instead of the C-20-C-7 bond, as in the napellines and denudatines. Because the predominant fragmentation of C_{18}-, C_{19}- or lactone-type diterpenoid alkaloids is the elimination of the substituent groups at C-1 (*33*, *37*), resulting in prohibiting cleavage of the C-17-C-7 bond, the absence of songorine-type fragmentation of ring A has been observed. Songorine-type fragmentation of ring A for gadensine (*419*), an *N,O*-mixed acetal-containing C_{19}-diterpenoid alkaloid, is represented possibly as in Scheme 21. But, the non-songorine-type fragmentation of ring A of the hetisine-type alkaloids has not been interpreted so far.

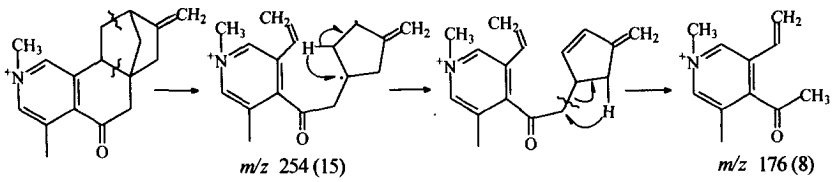


gadensine, *m/z* 451 (M^+)

m/z 392

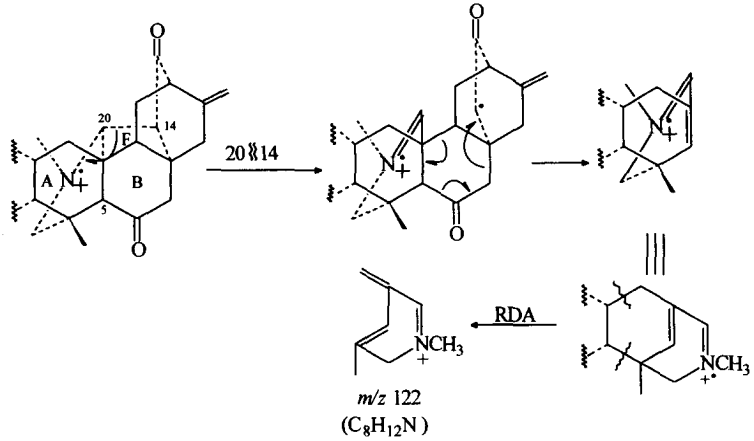
Scheme 21

In addition, fragmentation derived from other ring systems in the mass spectra of the hetidine-type alkaloids has also been displayed in the lower mass range (Scheme 22). For example, the fragmentation of *m/z* 254→176 in the mass spectrum of **64** is possibly from the cleavage of rings B and C (Scheme 23). A characteristic ion peak at *m/z* 122 in the mass spectra of episcopalidine and all of its



Scheme 22

analogues, except for **73** and **75**, was observed, which is possibly derived from the extrusion of the rings A, B, and F (Scheme 23). From the foregoing discussion, we may conclude that characteristic ion peaks in the mass spectra of episcopalidine and its derivatives are mainly at *m/z* 282 (254, 122), e.g., **46**, **64**~**70**; *m/z* 284 (256, 122), e.g., **71**-**73**; and *m/z* 286 (258, 122), e.g., **74**, **75**.

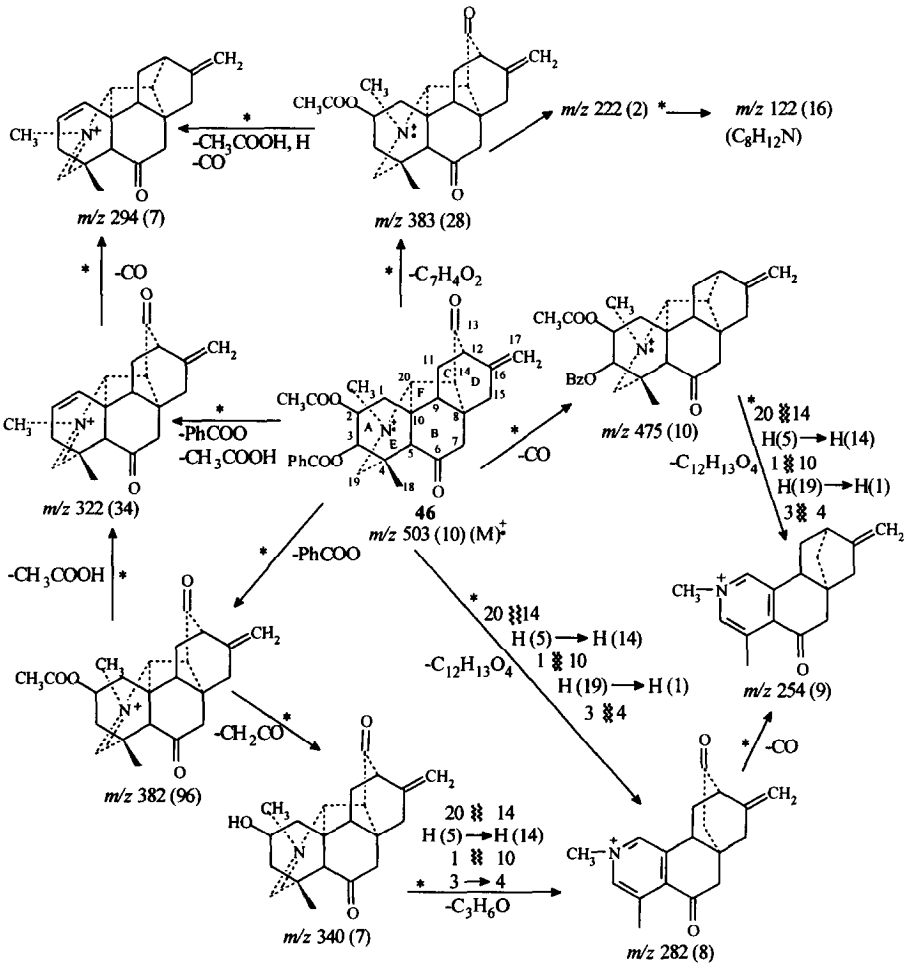


Scheme 23

Finally, as exemplified by episcopalidine (**46**), hetidine (**64**), and deacetylpanicutine (**70**), the important patterns of the fragmentation were supported by both HRMS and metastable techniques and are illustrated below (*160*).

(a) Episcopalidine (**46**). Many intense fragment ion peaks in its MS spectrum come from the fragmentation of substituent groups, while the fragment ion peaks at *m/z* 262 (M-$C_{12}H_{13}O_4$), and 254 (475-$C_{12}H_{13}O_4$ or 340- C_3H_6O) were

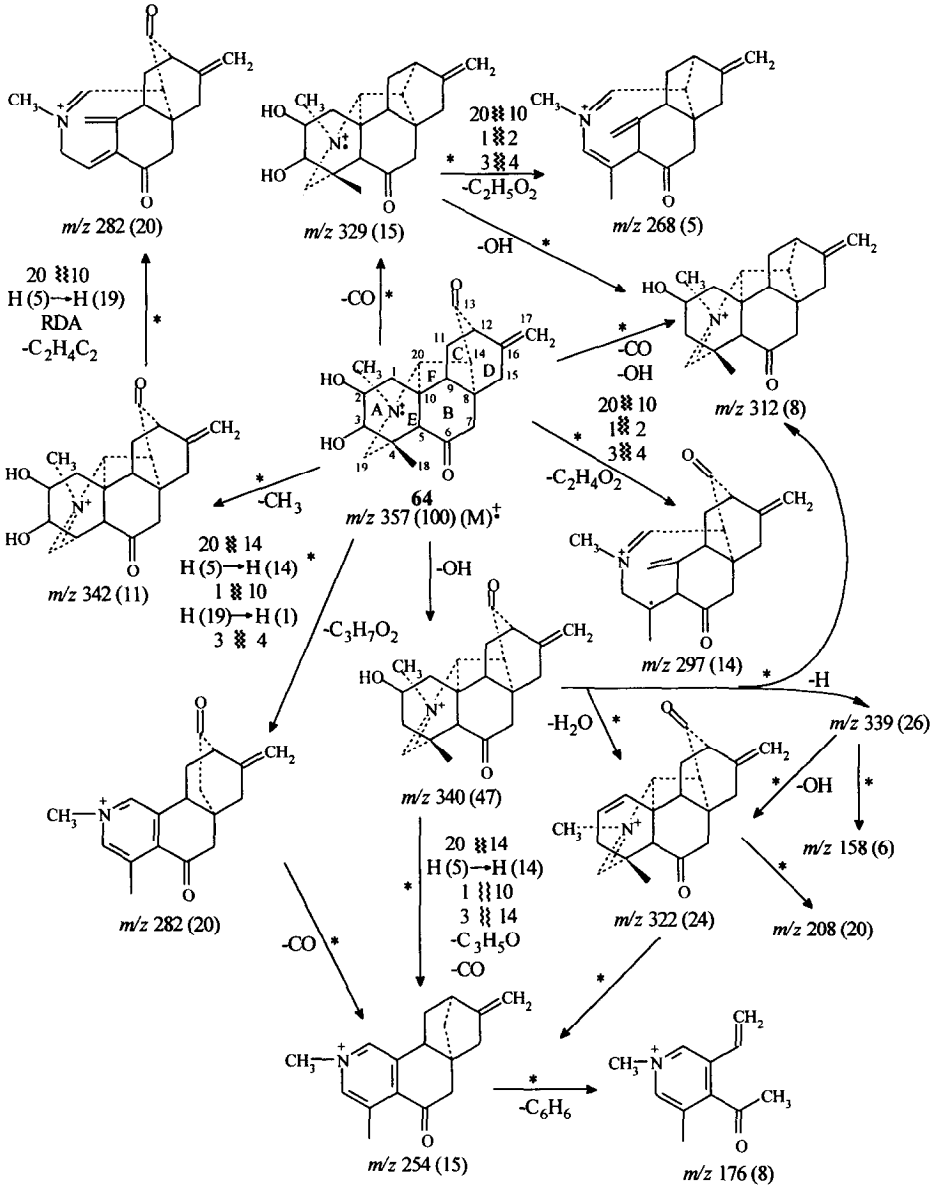
observed from the songorine-type fragmentation of ring A (Scheme 24).



Scheme 24

(b) Hetidine (**64**). In addition to the fragmentation of the substituent groups, the fragmentation of ring A passes through additional pathways. Three fragment ion peaks at *m/z* 297, 282, and *m/z* 254, with the loss of C-21-C-3 and an important ion peak are also observed (Scheme 25). Another important fragment ion at *m/z* 176 is

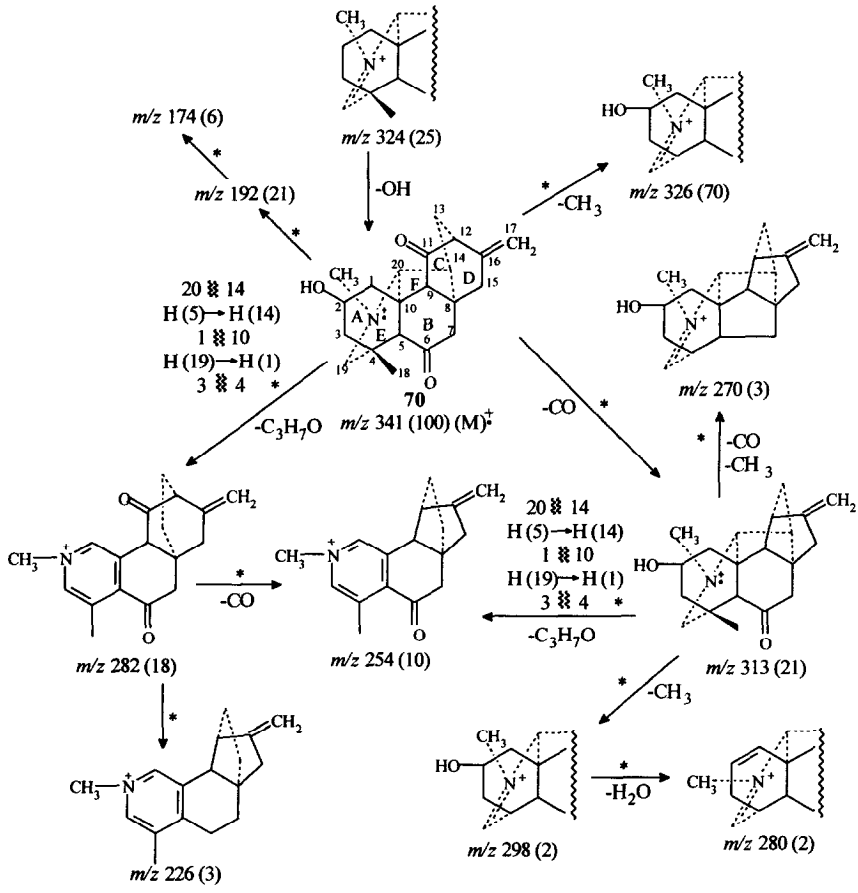
possibly derived from the fragmentation of the rings B and C.



Scheme 25

(c) Deacetylpanicutine (**70**). The fragmentation of the ring A in the mass

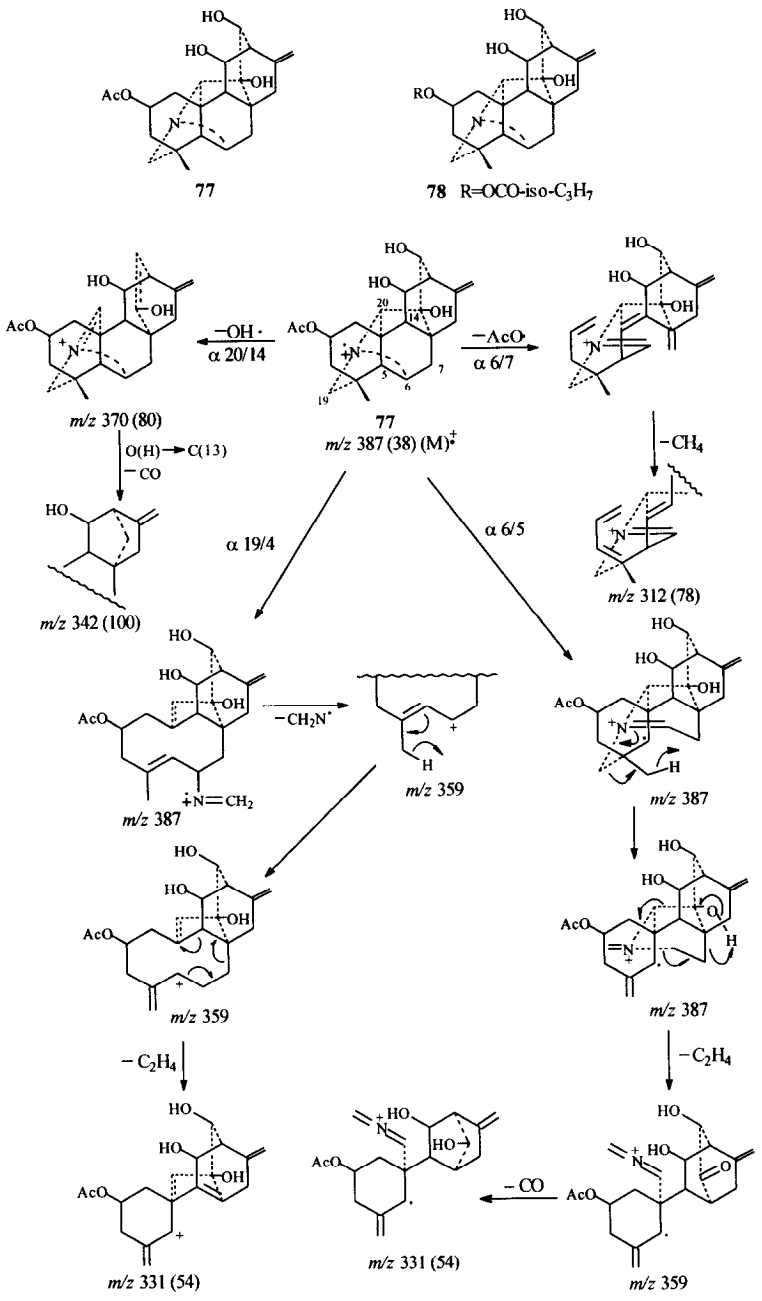
spectrum of deacetylpanicutine (**70**) is very similar to episcopalidine and hetidine (Scheme 26). But the possible formation process of the fragment ion peaks at *m/z* 341→192 and *m/z* 192→174 has not been made clear. The fragmentation pattern of deacetylpanicutine (**70**) shown in Scheme 26 has been established by HRMS and metastable techniques.



Scheme 26

3. Hetisine-type Diterpenoid Alkaloids

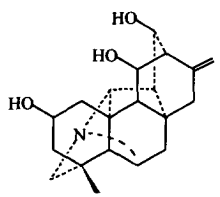
In 1986, Reinecke *et al.* (*229*) studied the mass spectra of two hetisine-type alkaloids, the guan-fu bases Z (**77**) and Y (**78**) from *Aconitum coreanum*, displaying


77
78 R=OCO-iso-C_3H_7
−OH·
α 20/14
−AcO·
α 6/7
m/z 370 (80)
O(H)→C(13)
− CO
m/z 342 (100)
77
m/z 387 (38) $(M)^+$
α 19/4
α 6/5
−CH_4
m/z 312 (78)
−$CH_2N^•$
m/z 359
m/z 387
m/z 387
m/z 359
m/z 387
−C_2H_4
−C_2H_4
m/z 331 (54)
m/z 331 (54)
− CO
m/z 359

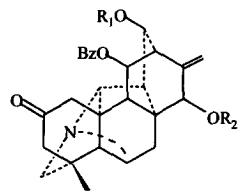
Scheme 27

the fragmentation feature around the nitrogen atom (Scheme 27). Because of the presence of the 14-OH group, the base peaks for these alkaloids are derived from M-45, and the fragment ion peaks from M-28, with the loss of the neutral fragment C_2H_4 or the radical CH_2N. Studies on the mass spectra of a number of the hetisine-type alkaloids with the 14-hydroxyl group were reported independently by Rashkes *et al.* (*194*) and Mil'grom *et al.* (*422*) using a combination of HRMS, MD, and B/E linked metastable techniques. In addition, Mil'grom *et al.* (*422*) also revised some of the fragmentations in the MS reported by Reinecke *et al.* (*229*), and showed that the fragment ion peak at M-28 was actually derived from the loss of CO, instead of C_2H_4 or CH_2N (Scheme 27).

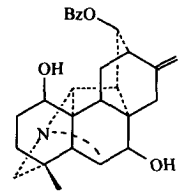
a) Molecular ion peak and base peak. The mass spectra of the hetisine-type alkaloids display intense molecular ion peaks, especially with the absence of a hydroxyl group at C-14, depending upon the oxygenated groups at C-11 and at C-9 as **79**~**81** (*194*). Alkaloids having hydroxyl groups at C-1 or C-9, e.g., **82**, **83**, or **84**, **85** (*194*), gave molecular ion peaks with the moderate abundance possibly *via* α-fragmentation (Scheme 28). The molecular ion peaks for the hetisine-type alkaloids with the 14-hydroxyl instead of the 1-OH groups generally are base peaks



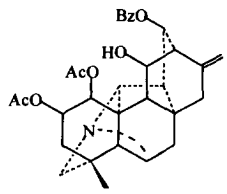
79



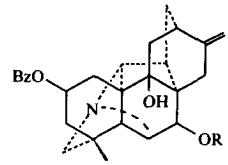
80 $R_1 = R_2 = H$
81 $R_1 = R_2 = OAc$



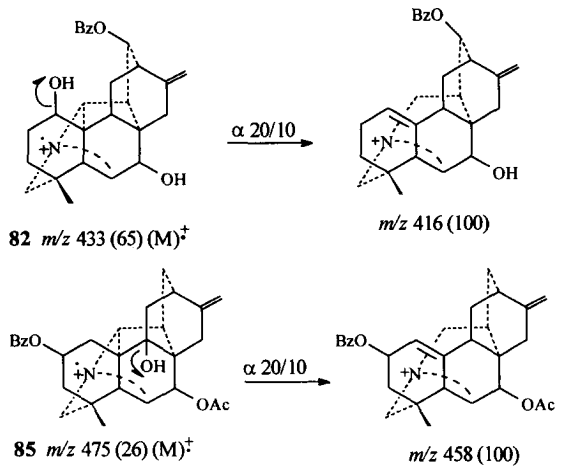
82



83

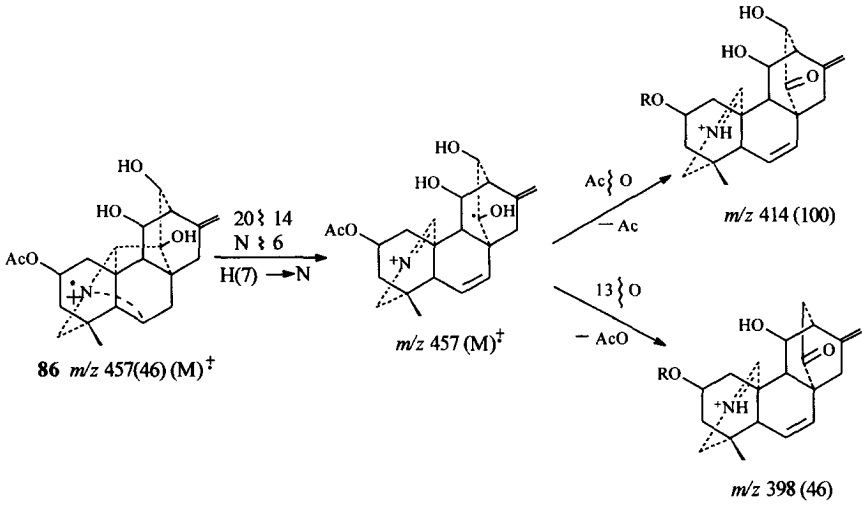


84 R = H
85 R = Ac



Scheme 28

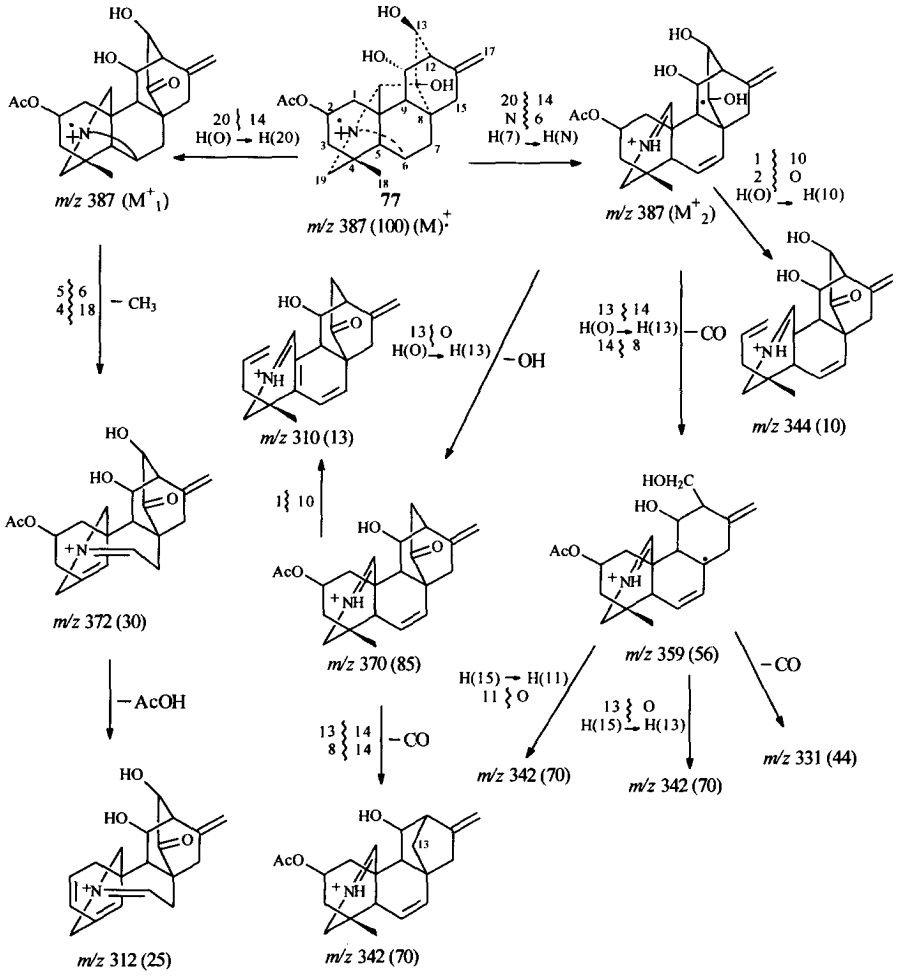
or rather strong ions, apparently depending on the measurement conditions (*229, 190*), but still followed by α-fragmentation. It is worth pointing out that, in many cases, the base peaks of the alkaloids, e.g., **77** and **86**, were affected by the oxygenated groups at C-13 (Schemes 29 and 30).



Scheme 29

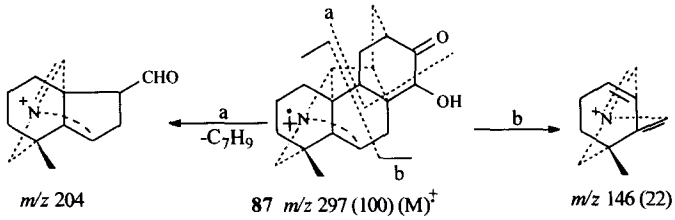
b) Fragmentation derived from the skeleta. Characteristic

α-fragmentations around the nitrogen atom, and predominant fragmentations with the loss of substituent groups, may often be observed. As exemplified by guan fu base Y (**77**) and nominine (**87**) (*422, 194*), these fragmentations are illustrated in Schemes 30 and 31. The fragment ion peaks at *m/z* 342 (M-45) for the hetisine-type alkaloids with the 14-hydroxyl group may be formed by three paths (Fig. 30). The fragment ion peak at *m/z* 372 (M-CH_3) (Fig. 30) was proved to be a consequence of fragmentation of the C-4-C-18 bond by HRMS and metastable techniques. Similarly,



Scheme 30

the key fragments formed in the breakdown of the skeletal bonds of other hetisine-type alkaloids, e. g., hetisine, talatisine and their derivatives, have also been observed (*194*).



Scheme 31

F. X-RAY CRYSTALLOGRAPHY

In 1987, Pelletier and Joshi (*423*) reviewed the X-ray crystallographic analysis of some C_{19}-diterpenoid alkaloids. However, no review has so far appeared on the X-ray crystallographic studies of the C_{20}-diterpenoid alkaloids.

Lucidusculine (*328, 329*) was the first C_{20}-diterpenoid alkaloid confirmed by X-ray crystallographic analysis. The X-ray crystallographic analysis of about 56 naturally-occurring C_{20}-diterpenoid alkaloids has been reported (Table XLXXVII). The most important role for elucidating the structures by X-ray analysis is in establishing novel skeleta, with representative examples such as denudatine (*110, 111*), hetidine (*156*), coryphine (*174*), anhydroignavinol (*248*), hypognavine (*222*), vakognavine (*215*), lucidusculine (*328, 329*), acofine (*349*), anopterine (*361*), kusnezoline (*365*), actaline (*369*), racemulosine (*371*), and staphisine (*375*). In a few cases, e.g., cuauchichicine (*308*), gaun-fu base A (*234*), and veatchine (*77*), some structural revisions were accomplished by X-ray analysis. The X-ray analysis of C_{20}-diterpenoid alkaloids was performed in the early days on their salts, e.g., methiodide, hydroiodide, hydrochloride, in contrast to the more convenient direct method on the free bases.

TABLE XLXXVII
LIST OF NATURALLY-OCCURRING
C_{20}-DITERPENOID ALKALOIDS STUDIED BY X-RAY ANALYSIS

type	alkaloid	code	*ref*
atisine-type	dihydroatisine	A I 1-1	*77*
	atidine	A I 1-5	*65*
	spiramine G	A I 1-6	*68, 69*
	isoatisine	A I 2a-2	*77*
	spiramine A	A I 2c-2	*86, 87*
	thalicsiline	A I 2c-9	*91*
	atisine chloride	A I 3-2	*77*
denudatine-type	denudatine	A II 1-2	*110, 111*
	dictysine	A II 1-11	*125, 126*
	dehydrodictysine	A II 1-15	*125, 126*
	gomadonine	A II 1-16	*132*
	paniculamine	A II 2-2	*139*
hetidine-type	panicutine	AIV 1a-10	*151*
	heterophylloidine	AIV 1a-12	*154*
	hetidine	AIV 1a-13	*156*
	episcopalidine	AIV 1a-14	*157*
	contorine	AIV 1a-15	*161*
	contorsine	AIV 1a-16	*161*
	contortine	AIV 1a-17	*161*
	miyaconitine	AIV 1a-20	*164*
	vilmorrianone	AIV 1a-21	*163*
	coryphine	AIV 2a-2	*174*
	spiteine*	AIV 2a-11	*180*
	talassimine	AIV 3-3	*184*
hetisine-type	spirasine XI	AVII 1a-1	*190*
	sanyonamine	AVII 1a-5	*197*
	kobusine	AVII 1a-6	*192*
	hetisine	AVII 1a-7	*203*
	ryosenamine	AVII 1a-17	*221*
	guan-fu base A	AVII 1a-26	*233, 234*
	zeravshanisine	AVII 1a-29	*237*
	guan-fu base G	AVII 1a-30	*232*
	hypognavinol	AVII 1a-31	*238*
	hypognavine	AVII 1a-32	*222*
	tadzhaconine	AVII 1a-36	*246*
	3-epi-ignavinol	AVII 1a-37	*247*

TABLE XLXXVII (*continued*)

hetisine-type	delatisine	AVII2a-1	*264*
	delnuttaline	AVII2b-23	*224*
	septentriosine	AVII2c-6	*282*
	2-acetylseptentriosine	AVII2c-7	*283*
	talatisine	AVII2c-9	*398*
	13-acetyl-14-hydroxy-2-isobutylhetisine *N*-oxide (guan-fu base *F N*-oxide)	AVII3-2	*287*
vakognavine-type	vakognavine	AVIII1-2	*215*
	barbaline	AVIII1-6	*295*
veatchine-type	veatchine	B I 1a-1	*77*
	cuauchichicine	B I 1a-4	*308*
napelline-type	lucidusculine	B II 1-7	*328, 329*
	finetianine	B II 1-14	*298*
	acofine	B II 1-18	*349*
anopterine-type	anopterine	BIII1-1	*361*
delnudine-type	delnudine	C I 1-1	*364*
kusnesoline-type	kusnesoline	C II 1-1	*365*
	guan-fu base K	C II 1-2	*368*
actaline-type	actaline	CIII1-1	*369*
racemulosine-type	racemulosine	CIV1-1	*371*
rearranged atisine-hetidine type	staphisine	D II 1-2	*375*

1. Atidine and Spiramine A

The first two atisine-type alkaloids studied by X-ray analysis were dihydroatisine (*77*) and isoatisine (*77*).

The X-ray diffraction analysis of atidine (*65*) showed that there were intramolecular hydrogen bonds between the 22-OH group and the oxygen of the C-7 group, and between the 15-OH and the oxygen of C-2 in the crystalline state.

Spiramine A (*86, 87*) is the first of a series of C_{20}-diterpenoid alkaloids from *Spiraea* plants by Hao and co-workers. The five-membered ring in spiramine A has a distorted half chair conformation with the C_2-axis bisecting the *N*-C-19 bond. In

addition, the nitrogen atom has a pyramidal sp^3 configuration with normal *N*-C distances. The naturally-occurring alkaloids which have been correlated with spiramine A are: spiramines C (*86*), D (*86~88*), E (*68, 69*), F (*68, 69*), and R (*93*).

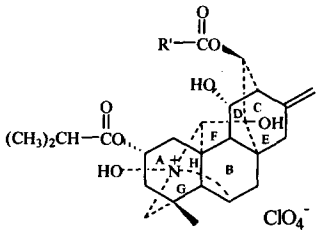
2. Dihydrodictysine

This alkaloid belongs to the denudatine-type. Denudatine (*110, 111*) itself was structurally established by X-ray analysis, thus leading to the structural elucidation of many denudatine-type alkaloids.

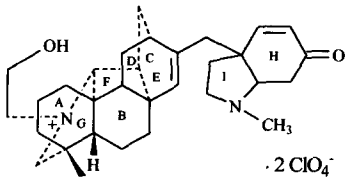
The X-ray diffraction analysis of dihydrodictysine (*125, 126*) showed the following conformations of the rings: A, E-chair; B, C, D-distorted boat (twist); and F-envelope.

3. 13-Acetyl-14-hydroxy-2-isobutyryl hetidine *N*-oxide and Coryphine

Hetidine (*156*) is the first alkaloid among the hetidine-type confirmed by X-ray analysis. The X-ray analysis of 13-acetyl-14-hydroxy-2-isobutyryl hetidine *N*-oxide (**88**) (*287*) indicated that rings A and B were in chair forms, and rings C, D, E formed a bicyclo[2.2.2]octane system, where the boat conformation suffered appreciable distortion in rings C and D. In addition, rings F, G, and H in this alkaloid adopted envelope conformations and rings K and L was in boat and chair forms, respectively. There are intramolecular hydrogen bonds between the $\overset{+}{N}$-OH and 14-OH, and between the 11-OH and the 13-ester carbonyl group.



88



coryphine perchlorate

Coryphine (*174*) is the first hetidine-type alkaloid having an oxazolidine ring with a C-14-C-20 bridge and consists of two main parts: hetidine part having a rigid

structure consisting of seven rings, and a hexahydro-*N*-methylindolin-6-one fragment. The X-ray analysis of coryphine perchlorate showed that the six-membered rings A and B occurred in chair forms; rings C, D, and E formed a bicyclo [2.2.2] octane system with boat forms; the heterocyclic G and the six-membered ring H were present in the half-chair forms characteristic for cyclohexane rings; and the five-membered rings F and I had an envelope conformation.

4. Talatisine, Septetriosine, Zeravshanisine, and Delnuttaline

The X-ray crystallographic analysis of talatisine (*398*) established the following: ring A (C-1, C-2, C-3, C-4, C-5, C-6) is a $^{1e}C_5$ chair form; ring B (C-5, C-6, C-7, C-8, C-9, C-10) occurs in a distorted $^{6}C_9$ chair conformation; ring C is a distorted ^{8,12} C boat; rings E (C-5, C-6, C-7, C-8, C-9, C-10, C-20, N) and F (C-4, C-5, C-6, C-19, N) are an ^{e}E envelope conformation differing somewhat from the ideal ^{e}E envelope, and ring G (C-8, C-9, C-10, C-14, C-20) is an almost ideal ^{e}E envelope. These four alkaloids belong to the hetisine-type. X-Ray crystallographic study of the only ignavine derivative, anhydroignavinol (*248*), provided a basis for the structural elucidation of many hetisine-type diterpenoid alkaloids.

The structure of septetriosine (*282*) was elucidated by the X-ray analysis of its hydrochloride.

The structure and conformation of zeravshanisine (*237*) were established by the X-ray crystallographic analysis of its hydriodide. Rings A and B are in chair forms; rings C, D, and E adopt distorted boat conformations, while rings F, G, and H occur in the envelope form. The heterocyclic ring K has a boat conformation.

The structure and stereochemistry of delnuttaline from *D. nuttalianum* were confirmed by X-ray crystallography (*224*). Its structure is stabilized through a network of hydrogen bonds involving nitrogen and hydroxy groups with O---O and O---*N* separation in the range 2.688 (7)-2.903 (8) $\mathring{A}$.

5. Veatchine and Cuauchichicine

There are two veatchine-type alkaloids with structures confirmed by X-ray analysis. The absolute configuration of veatchine (*77*) was shown to be 4*S*, 5*S*, 8*R*, 10*R*, 13*R*, 15*R*, and 20*SR*, where the *SR* indicates a predominance of the 20*S* epimer. In contrast to veatchine, cuauchichicine (*308*) exists as only one C-20 epimer in the solid state. The conformational differences between the two alkaloids are in rings D and F. Ring D in veatchine and cuauchichicine occurs in an envelope form with C-14 at the flap, and the twist conformation, respectively. The oxazolidine ring F in veatchine is disordered with both in the twist conformation and in the envelope conformation with C-20 at the flap.

6. Lucidusculine

As described previously, lucidusculine (*328, 329*) is the first C_{20}-diterpenoid alkaloid studied by X-ray crystallography. It provided a basis for establishing the structures of several related alkaloids, e.g., napelline (*316~329*), songorine (*331, 341*), and songoramine (*261, 331, 341*).

7. Delnudine, Vakoganvine, and Staphisine

These three alkaloids are the skeletal representatives of the delnudines, vakognavines, and the rearranged atisine--hetidine type alkaloids, respectively. Delnudine, the only member of the delnudine-type alkaloids, and isolated from *D. denudatum* by Wiesner and co-workers (*363*), is considered biogenetically to arise from hetisine. The stereochemistry of delnudine hydrochloride was confirmed by X-ray analysis as the following: ring A is the only chair form with the hydroxyl group in the axial position stabilized by a hydrogen bond to the chloride ion; ring C is an envelope form; ring D (C-8, C-9, C-11, C-12, C-13, C-14) adopts the chair conformation, while in hetisine it occurs in the boat form (*364*).

Vakognavine (*215*) is the first example of an *N*,19-*seco*-C_{20}-diterpenoid alkaloid reported. Its structure and conformation was confirmed by X-ray

crystallographic analysis, differing from hetisine only by the absence of ring E (C-19, C-4, C-5, C-10, C-20, N).

Staphisine is also the first bisditerpenoid alkaloid, consisting of one rearranged atisine- and one hetidine-type unit. Its structure and stereochemistry were established by X-ray analysis of its monomethiodide (*375*). The central oxygen-containing ring occurs in the chair conformation with C-8 in unit B equatorial and C-12 in unit A axial, thus keeping the separation of the two units of the molecule. The ring E of unit A is in a boat conformation. In contrast to atisinum chloride (*77*) and dihydroatisine (*77*), the C-D ring fragments in unit A of staphisine have an atypical conformation for a bicyclo[2.2.2]octane because the dihedral angles for this moiety deviate from the their ideal values of 0.60, or -60° by an average of 11.5°.

V. Stereochemistry and Reactions

The chemistry, mainly including the stereochemistry and reactions, of the C_{20}-diterpenoid alkaloids before 1991 was reviewed systematically by us in Volume 42 of this treatise. Thereafter, some interesting progress on the chemistry of these alkaloids was conducted by Pelletier and his colleagues, and by two Chinese research groups, Hao' s group at Kumming Institute of Botany, and our group.

A. STEREOCHEMISTRY

1. The iso-type oxazolidine ring/19-OR or 19-R-containing Diterpenoid Alkaloids

   a. Stereochemical representention at C-19 and C-20. The absolute configurations at C-19 and C-20 of the iso-type oxazolidine ring-containing alkaloids, like the atisines and hetidines, are usually stereochemically designated by *S* and *R*. Some of these alkaloids exist as mixtures of epimeric pairs, e.g., spiredine D (*175*), spirasines I (*176*), II (*176*), III (*176*), VII (*178*), and spirasine VIII (*178*), spiredine (*178*), thalicsiline (*91, 92*), and

isocuauchichicine (*307*, *311*). Some others were isolated as single epimers, e.g., spiramines A (*86~88*), B (*86, 87*), C (*86, 87*), D (*86, 87*), F (*89*), G (*89*), J (*100*), K (*100*), L (*100*), M (*100*), N (*98*), O (*70*), P (*94*), Q (*93, 94*), T (*90*), U (*90, 94*), W (*95*) and Z (*85*), spiratine B (*419*), and 19-*O*-deethyl spiramine N (*75*) of the atisine-type; spirasines V (*177*) and VI (*177*) of the hetidine-type; and garryine (*296, 297*) and isogarryfoline (*306, 314*) of the veatchine-type, etc.

The absolute configuration of C-19 is mostly unspecified in the literature. Most authors use structures a and b, some use c and d, as shown in Fig. 8. It is seen that the path of O-C-19-N-C-21-C-22 in structure a is counter-clockwise, while that in c is clockwise. Thus we are viewing different "faces" of the oxazolidine ring in a and c. The same is true for b and d. Accordingly, in this kind of structure representations we have a≡c and b≡d, where, for instance, the 19-H appears, as "β" in a and "α" in c.

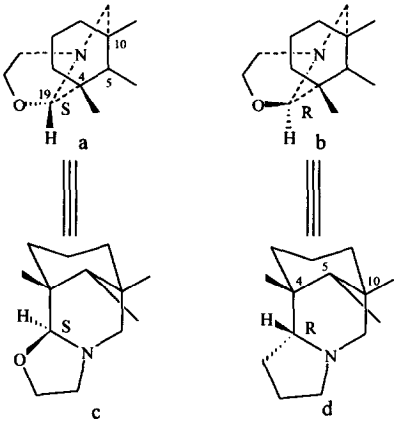
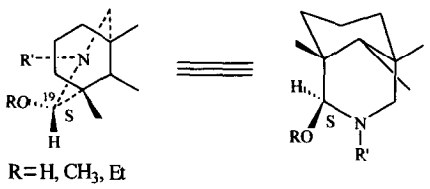


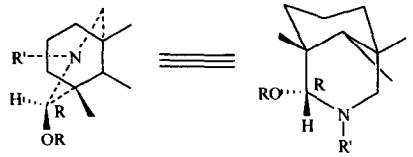
Fig. 8

Similarly, the absolute configurations of C-19 with alkoxy or alkyl groups can be illustrated as shown in Fig. 9 for spiramines O (*70*), N (*98*), and J (*100*).

The absolute configurations of C-20 can be treated in a similar fashion, as shown in Fig. 10.



R=H, CH_3, Et



R=H, CH_3, Et

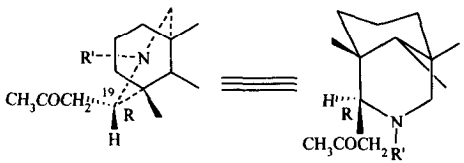


Fig. 9

e.g. cuauchichicine

(*306, 311*) etc.

Fig. 10

In addition, the configurational designations of α and β for the C-13 substituents in some hetisine-type alkaloids tend to be confusing, although they are in accord with literature practice. They become unequivocal if one flattens out any of the six-membered rings containing C-13 with the α-atom away from the viewer (*26, 27*) (Fig. 11).

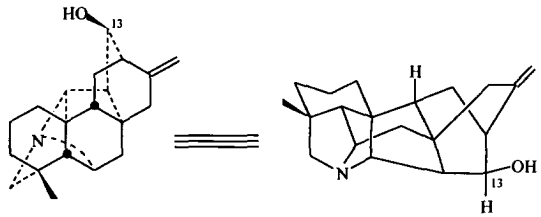
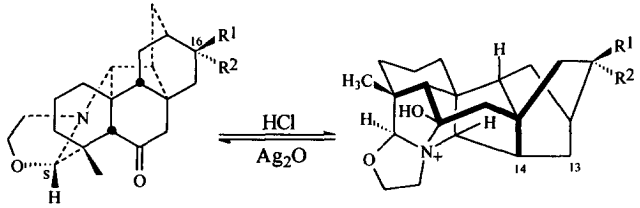


Fig. 11. Configurational designation of α and β for the C-13 substituents in some hetisine-type alkaloids

b. Epimerization. In 1986, Liang and co-workers (*177*) observed with the aid of $^{1}H(^{13}C)$ NMR spectroscopy that both spirasines V (**89**) and VI (**90**), as isoatisine (*63,73*) and thalicsessine (*182, 91*), exist as a single epimer with the 19*S* configuration only in the solid state, and that fast equilibration occurs in solution to form a pair of C-19 epimers in an approximate ratio of 1:1.

Treatment of spirasines V or VI with HCl gave the corresponding salts **91** or **92** of the carbinolamine type where only one epimeric form (19*S*) is possible because of the constraints of the newly formed *N* to C-6 bond. Apparently, the 19*R* epimer was converted to 19*S* *via* the intermediate immonium ion formed by opening the oxazolidine ring. The salt shows no carbonyl absorption in the IR and can be reconverted to the free base by treatment with silver oxide (Scheme 32).



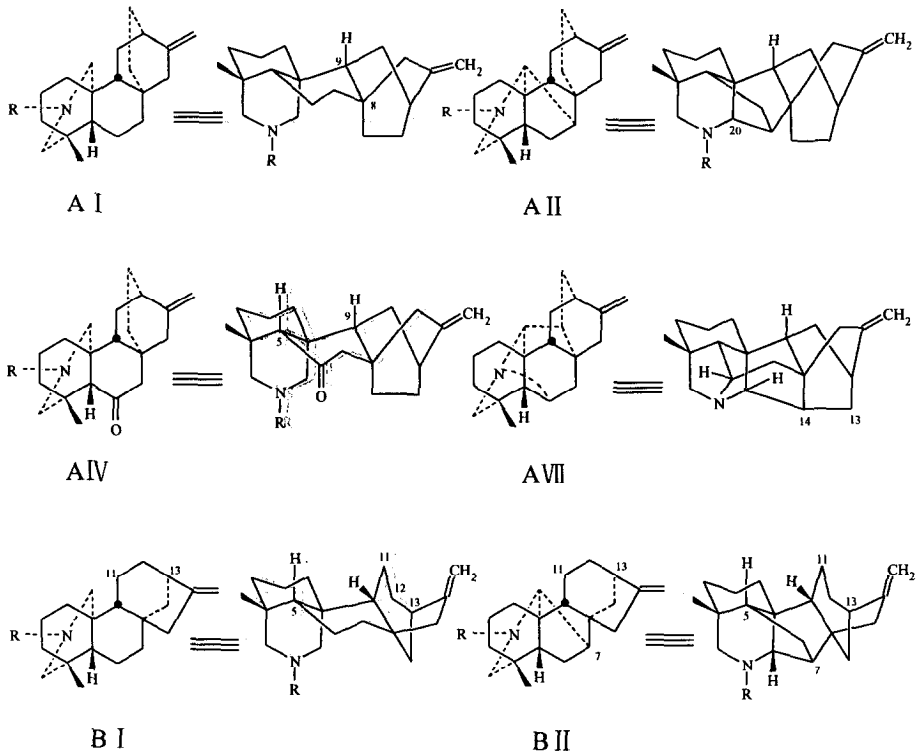
89 R1=CH_3 R2=OH
90 R1=OH R2=CH_3

91 R1=CH_3 R2=OH
92 R1=OH R2=CH_3

Scheme 32

Examination of C_{20}-diterpenoid alkaloids having the iso-type oxazolidine ring or 19-substitution (OH, OMe, OEt, CH_2COCH_3) revealed an interesting fact. A few alkaloids, like spiramines V (*177*) and VI (*177*), exist as single epimers in the solid state, but easily suffer epimerization in solution. Those without the 6-CO group, like most of the atisine-type, e.g., spiramine A (*86, 87*), tend to retain the pure epimeric form, even in solution. It is suggested that the 6-CO might be responsible for inducing epimerization.

2. Stereo-structures for the Major Types of C_{20}-Diterpenoid Alkaloids. These were depicted in Fig. 12.



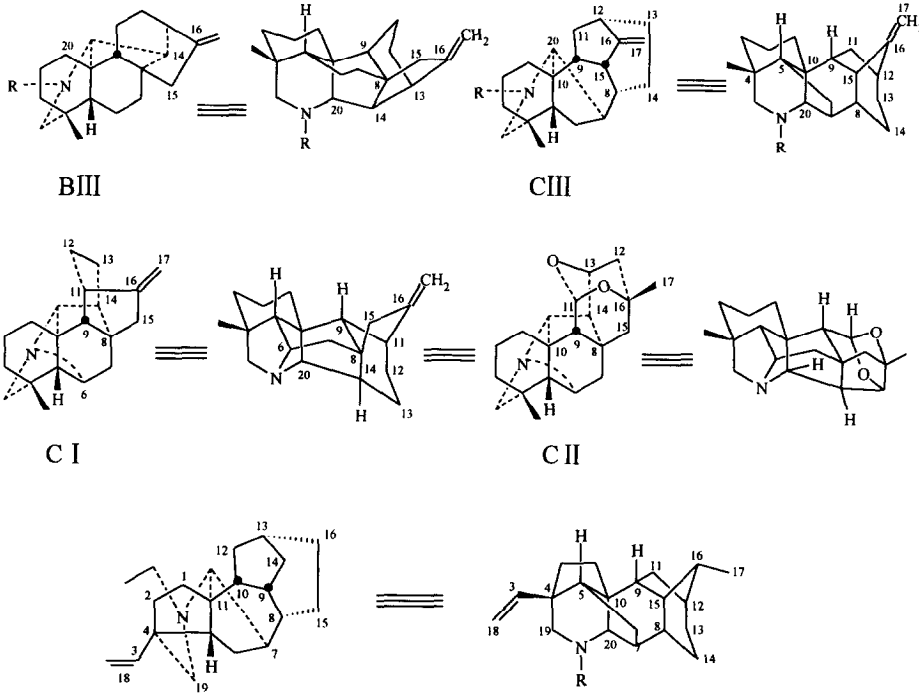
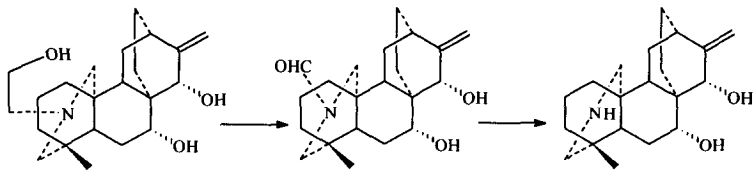


Fig. 12. Stereo-structures of the important types of C_{20}-diterpenoid alkaloids

A. REACTIONS

1. *N*-Deethanolation

Treatment of compound **93**, a reduction product of spiramine C (*86*), with active MnO_2 at room temperature for 90 min gave **94**, which was hydrolyzed with 10% KOH under reflux conditions for 16h to afford the *N*-deethanolic compound **95**, without specifying the yield (*70*) (Scheme 33).

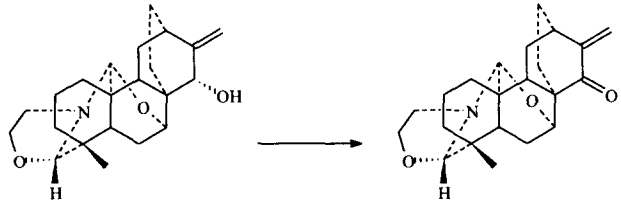


93 **94** **95**

Scheme 33

2. Allylic Secondary Alcohol System

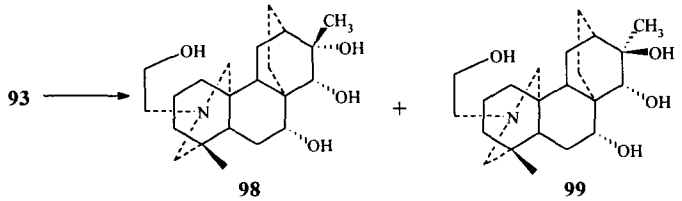
a. Oxidation. Spiramine C (**96**), isolated from *Spiraea japonica* var. *acuminata* by Hao *et al.* (*86*), was treated with active MnO_2 at room temperature for 3 days to produce an α, β-unsaturated ketone dehydrospiramine C (**97**) (Scheme 34) (*87*) without involving the oxazolidine ring unit in **96**.



96 **97**

Scheme 34

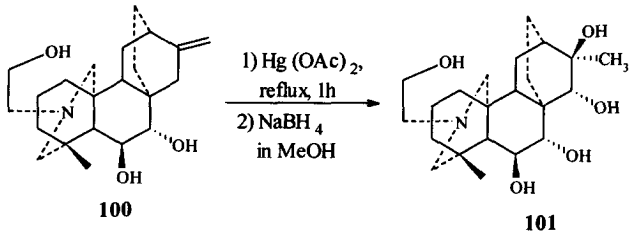
b. Oxymercuration-Demercuration. Treatment of compound **93** with $Hg(OAc)_2$ under reflux conditions for 1h, followed by reduction with $NaBH_4$ for only 2 min, gave a pair of epimers at C-16 (**98** and **99**) (Scheme 35) (*90*).



98 **99**

Scheme 35

Similarly, compound **100**, a reductive derivative of spiramine F (*68, 69*) from *Spiraea japonica* var. *acuminata*, was treated successively with $Hg(OAc)_2$ and $NaBH_4$ to afford the hydroxylated product **101** in 46% yield (Scheme 36) (*90*).

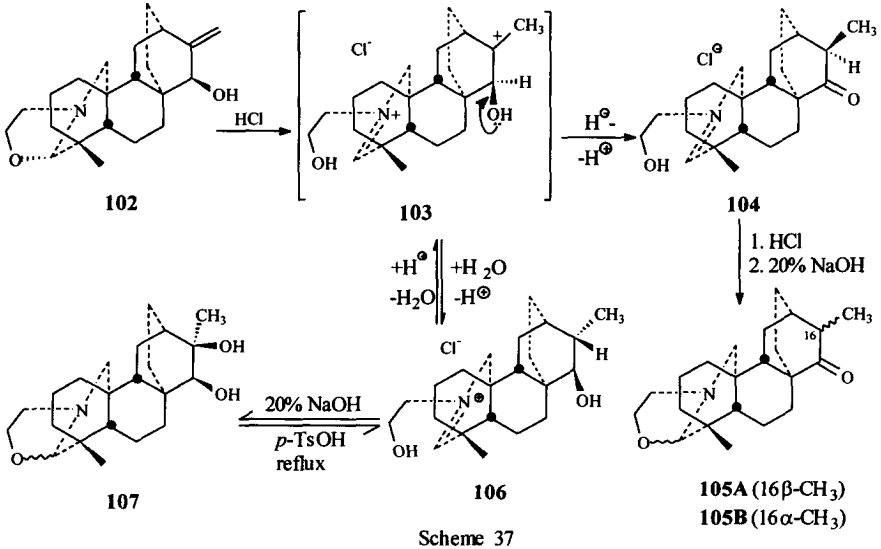


100 **101**

Scheme 36

c. Rearrangement

a) In 1990, further investigation on the acid-catalyzed rearrangement of isoatisine (**102**) by Pelletier *et al.* (*76*) led to interesting results. Treatment of isoatisine (**102**) with 7% HCl at room temperature for 7 days afforded a pair of epimeric methyl ketones **105** (**A+B**), and a diol **107** (50%). The latter can also be converted into a mixture of **105** (**A+B**) in 93% yield when refluxed with *p*-TsOH overnight. A mechanism for the formation of these compounds **105** (**A+B**) and **107** was proposed. As showed in Scheme 37, protonation of the double bond $\Delta^{16(17)}$ of isoatisine (**102**) generates a key intermediate **103**, at room temperature or under refluxing conditions, **103** gave **107** *via* **106** following the basic workup, or a



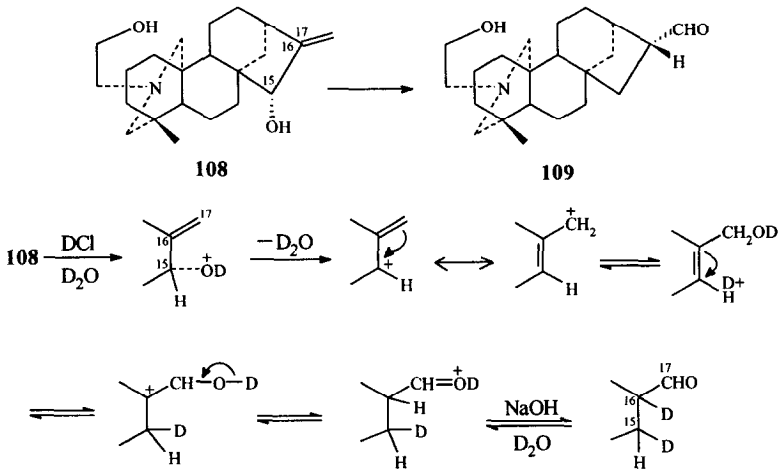
102 **103** **104**

107 **106** **105A** (16β-CH_3)
105B (16α-CH_3)

Scheme 37

mixture of **105** (**A**+**B**) through a pinacol-type hydride shift (**103**→**104**), and epimerization of **104** *via* an enol in acidic medium and basic workup, respectively.

b) In continuing the study on the chemical reactions of the veatchine-type diterpenoid alkaloids (*4, 76, 424~426*), in 1997, Pelletier and colleagues (*427*) found that treatment of dihydroveatchine (**108**) with 6 N HCl under reflux conditions for 45 min afforded a single major compound, aldehyde **109**, in 81% yield, which was fully characterized by spectral analysis. A plausible pinacol-type mechanism, that involved dehydration, rehydration, and an allylic rearrangemeant for **108**, has been suggested by Pelletier *et al.* on the basis of deuterium labeling experiments (Scheme 38).

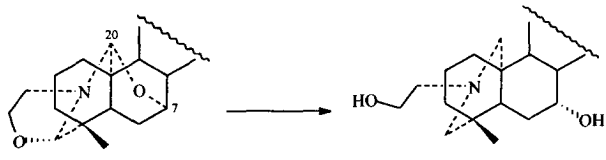


Scheme 38

3. Oxazolidine Ring System with *N,O*-Mixed Ketal [*N*-C-20-*O*- *C-7*]

In recent years, a number of the C_{20}-diterpenoid alkaloids from *Spiraea* spp. plants grown in Yunnan province, China, were isolated by Hao *et al.*, many of which contain *N,O*-mixed ketal [*N*-C-20-*O*- *C-7*] moieties.

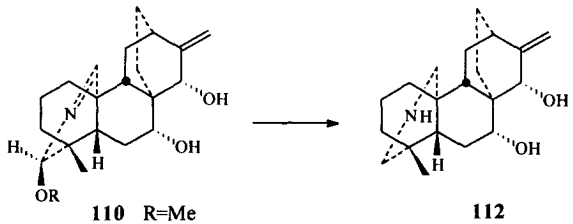
a. Reduction. The C_{20}-diterpenoid alkaloids having an oxazolidine ring system with the *N,O*-mixed ketal [*N*-C-20-*O*-*C*-7]moiety (A), e.g., spiramines A (*87*), C (*70, 94*), F (*68, 94*), and U (*94*), and dihydrospiramine C (*87*), were reduced with $NaBH_4$ at room temperature for 3-8h to the corresponding products **B** (Scheme 39).



A **B**

Scheme 39

Similarly, treatment of the C_{20}-diterpenoid alkaloids possessing an imine [*N*=C-20] moiety, e.g., spiramines O (**110**) (*70*) and *N* (**111**) (*75*), with $NaBH_4$ gave the same *N*-dealkoxy derivative **112** (Scheme 40).

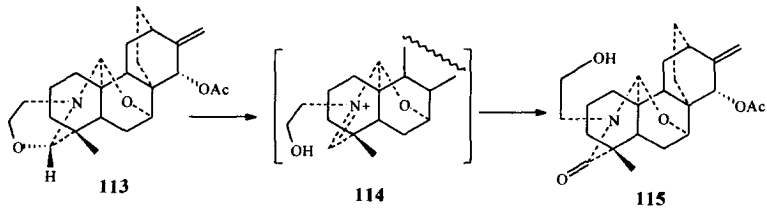


110 R=Me
111 R=Et

112

Scheme 40

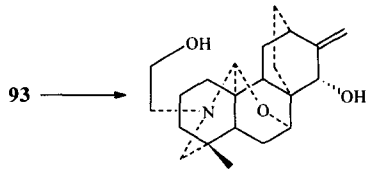
b. Oxidation. Spiramine **A** (**113**) from *Spiraea japonica* var. *acuminata* and *S. japonica* var. *glabra* (*86~88*) was oxidized with CrO_3-pyridine first at 0℃ followed by room temperature for 4h gave a lactam **115** in 40% yield *via* a possible intermediate **114** by opening the oxazolidine ring (Scheme 41) (*93*).



113 **114** **115**

Scheme 41

c. Formation of a *N,O*-Mixed Ketal [*N*-C-20-*O*-*C*-7] System. One example of forming this moiety was reported by Hao *et al.* (*68*). Compound **93** was oxidized with $K_3Fe(CN)_6$ in 8% KOH at room temperature for 30 min to afford the *N,O*-mixed ketal-containing compound **116** (Scheme 42). It is of interest to note that in this case no oxazolidine ring-containing compounds were produced.



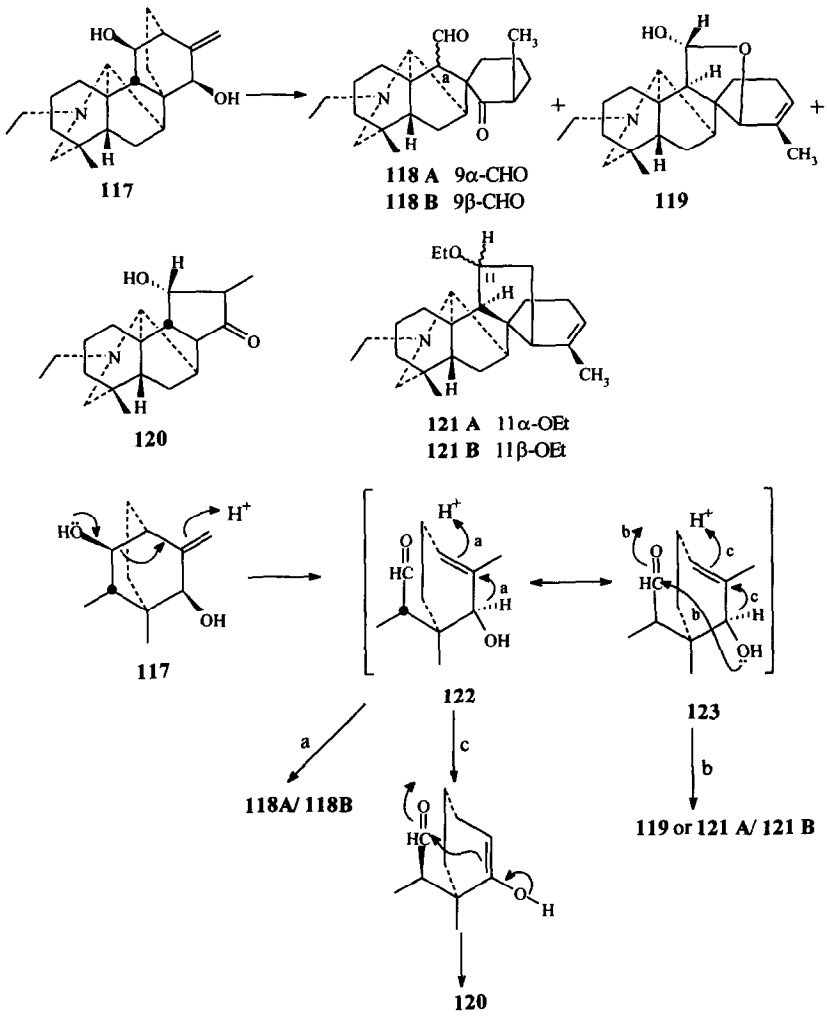
116

Scheme 42

4. Rearrangements of Denudatine

Denudatine (**117**), a hetidine-type diterpenoid alkaloid, was isolated from several *Aconitium* and *Delphinium* plants (*108, 114, 115, 140*). After reporting the rearrangements of denudatine (*428~431*), we have further studied the interconvension among its rearrangement products (*432*). Here we wish to summarize these interesting reactions of denudatine.

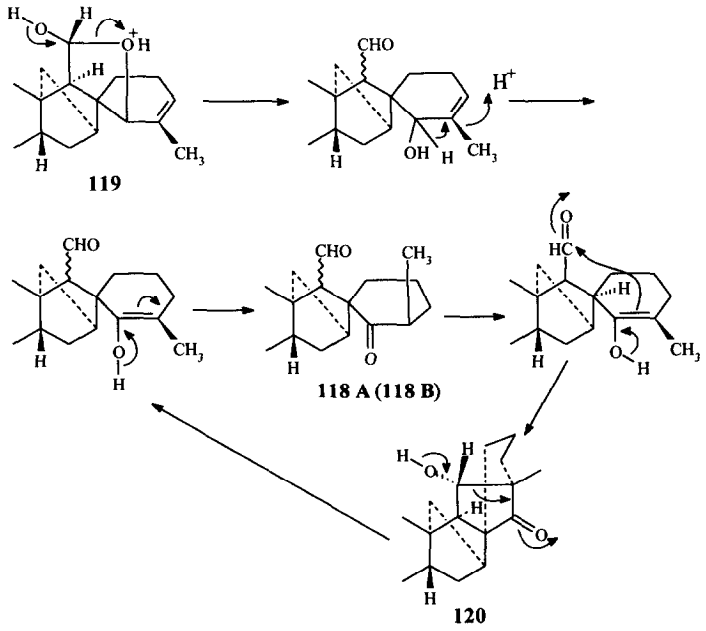
Treatment of denudatine (**117**) with 10% HCl at 30~50 ℃ leads to rearrangement to a pair of epimers, **118A** and **118B** (72% yield), as well as **119** (10% yield) and **120** (10% yield). However, treatment of **117** with 10% HCl containing a little ethanol at 30-40℃ gave only the pair of epimers **121A** and **121B** in 40% yield, with no detectable **118A** and **118B** in the resulting solution. The reaction processes involve the initial cleavage of the C-11-C-12 bond, followed by conversion to the key intermediate **122** or **123**, *via* inversion of the 9α-formyl group at C-9, and finally, rearrangement or condensation to the corresponding compounds through the path a, b and c, respectively (Scheme 43).



Scheme 43

We have also studied the interconversions among these rearrangement compounds **118A (118B)**, **119**, and **120**. Treatment of **119** with 10% HCl at 82-84℃ for 28h afforded compounds **118A (118B)** and a little **120**. Refluxing a mixture of **118A (118B)** with 10% HCl for 3 days leads to almost quantitative conversion to **120** (Scheme 44). However, treatment of **120** with NaOH-DMF at 120-126℃

overnight instead of 10% HCl under vigorous conditions *via* a retroaldol reaction afforded **118A (118B)** (ratio=1:1, totally 50% yield for both compounds) besides the starting material. Scheme 44 shows the possible mechanism of the aforementioned conversions.



Scheme 44

The possible rearrangement mechanism depicted in Scheme 44 indicates that cleavage between the C-11-C-12 bond under acidic conditions, as in hetisine and its derivatives (*34, 35*), as well as similar reactions reported in the literature (*429*), may involve the step as shown in Fig. 13.

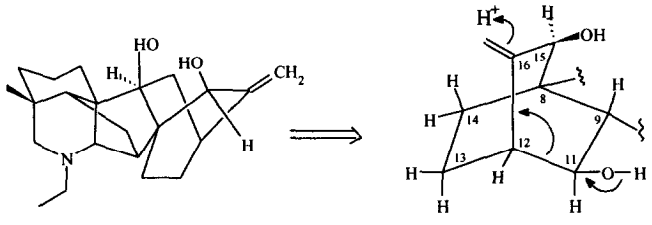
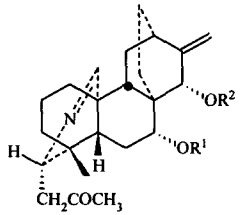


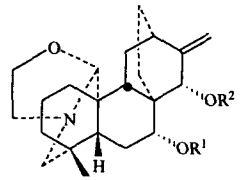
Fig. 13

5. Acyl Migration

Hao *et al.* (*100, 97*) have isolated four atisine-type diterpenoid alkaloids spiramines L (**124**) and M (**125**), S (**126**), and V (**127**), as two pairs of regioisomers, from *Spiraea japonica* var. *acuminata*, probably attributable to 1,3-acyl migration. Other similar examples. e.g., guan-fu base A (*233, 234*), were also reported.



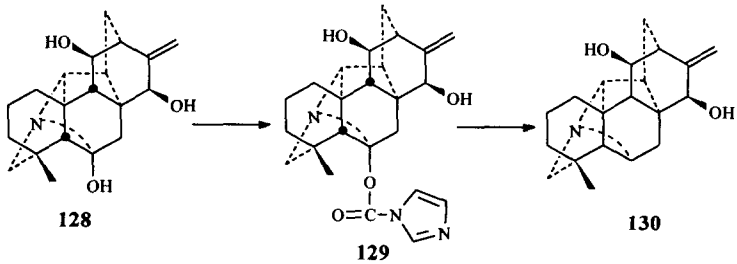
124 R^1=H R^2=Ac
124 R^1=Ac R^2=H



126 R^1=H R^2=Ac
127 R^1=Ac R^2=H

6. Conversion of Pseudokobusine to Kobusine

This conversion was achieved by Japanese scientists (*433*) employing the following steps. Reaction of pseudokobusine (**128**) in dichloromethane with *N*, *N'*-thiocarbonyl diimidazole at room temperature for 21h afforded compound **129** (94%), which, by reduction with tri-*n*-butyltin hydride at 50℃ for 7h, gave kobusine (**130**) in 89% yield (Scheme 45).



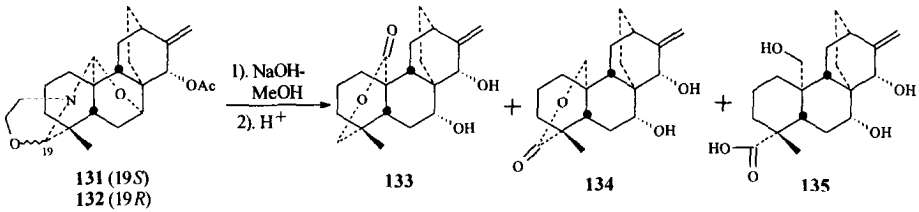
128 **129** **130**

Scheme 45

7. Interconversion between the C_{20}-Diterpenoid Alkaloids and the Diterpenes

Edwards *et al.* (*434*), Pelletier *et al.* (*435~437*), and Okamoto *et al.* (*438*) have reported the conversion of imino-containing C_{20}-diterpenoid alkaloids into the

diterpenes in poor yields using HNO_2 (*22*). Following these reports, Chinese scientists Hao *et al.* (*406, 407*) also reported the interconversion of the C_{20}-diterpenoid alkaloids and the diterpenes. Treatment of spiramines A (**131**) and B (**132**), with NaOH under refluxing conditions for 14h gave the corresponding diterpenes spiramilactone (**133**) (26.7%), spiramilactone C (**134**) (13.3%), and **135** (15.2%) (Scheme 46).

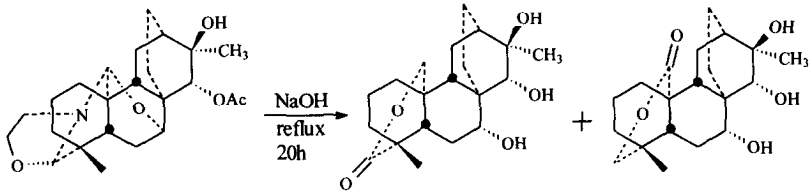


131 (19*S*)
132 (19*R*)

133 **134** **135**

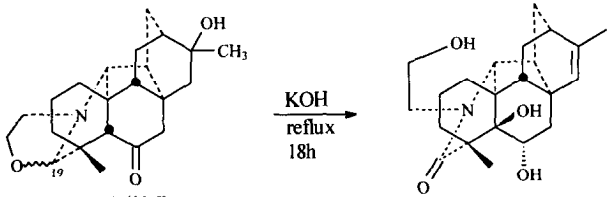
Scheme 46

Under similar conditions, spiramine U (**136**) was converted into the diterpenes **137** (26%) and **138** (16.5%) (Scheme 47) (*407*).



136 **137** **138**

Scheme 47



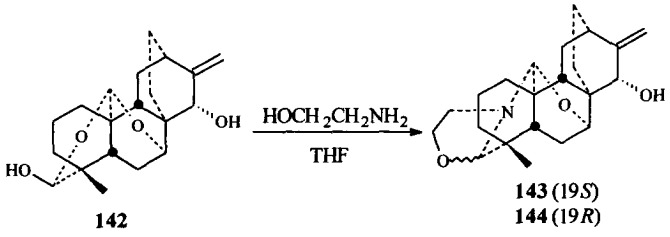
139 (19*S*)
140 (19*R*)

141 (25%)

Scheme 48

However, the hetidine-type alkaloids spirasines **139** and **140**, without the distinctive structural features of spiramines A and B, under similar conditions afforded only the lactam **141**, instead of the corresponding diterpenes (Scheme 48) (*407*), which clearly involves a more complex reaction process.

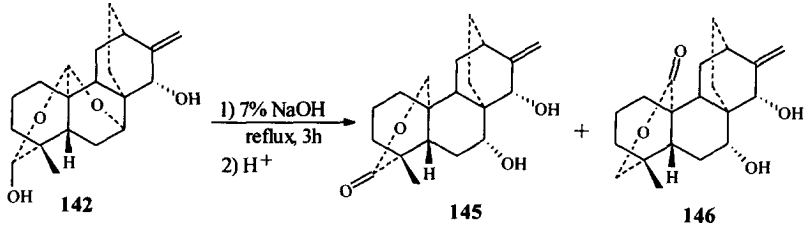
The afore-mentioned interesting reactions led Hao *et al.* (*406, 407*) to propose the biomimetic correlation of the diterpenes and the C_{20}-diterpenoid alkaloids. Treatment of spiraminol (**142**), instead of the diterpenes not having the acetal groups at C-19 or C-20 such as spiramilactone **133**, with ethanolamine, first at room temperature overnight, then by refluxing for 4h, afforded spiramines C (**143**) and D (**144**) in 74.6% total yield (Scheme 49), possibly *via* a double Mannich process.

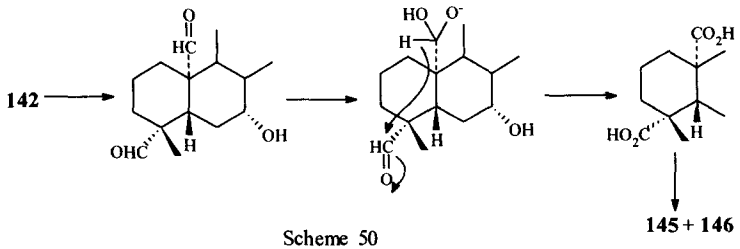


Scheme 49

8. Intramolecular Cannizzaro Reaction of Diterpenes

It is of interest to note that eight atisane-type diterpenes (Table XXII) were isolated from *Spiraea* plants by Pelletier *et al.* (*104*) and Hao *at al.* (*98, 105, 106, 112*). When spiraminol (**142**), an atisane-type diterpene from *Spiraea japonica* var. *incisa* (*98*), was treated with 7% KOH under reflux for 3h, two lactones **145** and **146** were afforded, possibly *via* a so-called Cannizzaro reaction mechanism (Scheme 50) (*406*).





Scheme 50

VI. **Pharmacology**

In many countries, especially including China, Japan, Russia, Mongolia, and India, the diterpenoid alkaloids, as the components of numerous prescriptions in traditional medicine, are used for the treatment of plaque, sepsis, intoxication, cold- and immunosuppression-induced ailments, rheumatoid arthritis, and various types of pain, including migraine, swelling induced by trauma and fracture, and facial paralysis. In recent years, Tashkent and Chinese scientists have determined and studied fruitfully the antiarrhythmic activities of many diterpenoid alkaloids.

In 1983, Benn (*439*) provided an excellent review of the biological activities of the C_{19}-diterpenoid alkaloids. After this, only a few reviews in this field were reported (*440, 441*). The present review is a summation of the toxicity and biological activity of the C_{20}-diterpenoid alkaloids.

A. TOXICITY

Acute lethal doses (LD_{50}) of about thirty-six C_{20}-diterpenoid alkaloids and their derivatives are shown in Table XLXXVIII. However, only a few alkaloids, e.g., guan-fu bases A and G have been reported in detail (see later).

B. BIOLOGICAL ACTIVITY

1. Anti-inflammatory

Guau-fu base A (98 mg/kg, ip) from *Aconitum coreanum* inhibited inflammatory exudation, edema, granuloma, and leukocyte migration, and had

similar antiinflammatory effects as sodium salicylate (400 mg/kg) (*459, 496*).

2. Antiarrhythmic

In 1977, the Russian scientists Dzhakhangirov and Sadritdinov (*460*) first reported the powerful antiarrhythmic actions of napelline and heteratisine, leading to broad screening among about 180 various structural types of the diterpenoid alkaloids and their derivatives (*461*). These efforts discovered many C_{20}-diterpenoid alkaloids with pronounced antiarrhythmic activities including the atisines, denudatines, hetidines, hetisines, veatchines, and napellines (Table XLXXⅧ). Among the alkaloids investigated, the most powerful antiarrhythmic and antifibrillation activities were shown by furoylheteratisine, *N*-acetylseparaconitine, deacetyllappaconitine, 6-benzoylheteratisine, 1-benzoylnapelline, ranaconitine, lappaconitine, 14-benzoyl talatisamine, and zeravshanizine. Based on their activity and favorable selectivity (LD_{50}/ED_{50}), with unique of pharmacodynamics and pharmacokinetics, metabolism and mechanism of antiarrhythmic action (*442, 462~470*), these alkaloids are of great interest compared with existing remedies (Table XLXXⅨ) (*461*). From them, "Allapinine" (lappaconitine hydrochloride) (*464, 465, 470*) and "Actezine" (alkaloids of *Aconitum leukostomum*) (*461*), as a new class of antiarrhythmic drugs, were introduced into clinical practice. 1-Benzoylnapelline hydrochloride (*469*) and 14-benzoyltalatisamine hydrochloride (*470*) may be used in human and veterinary medicine as antidotes in cases of poisoning by aconitine-like alkaloids, while 6-benzoylheteratisine hydrochloride ("Benzerafin") (*442*) is undergoing clinical trials for treatment of arrhythmia.

TABLE XLXXVIII
TOXICITIES AND ANTIARRHYTHMIC ACTIVITIES OF
C_{20}-DITERPENOID ALKALOIDS ON MODEL ACONITINE ARRHYTHMIAS IN RATS

Alkaloid (*Refs*)	iv, mg/kg		LD_{50} / ED_{50}	Notes
	LD_{50}	ED_{50}		
A. Atisine-type (A I)				
atidine (*443*)	58.0	5	11.6	
atisine (*443*)	9.0	—	—	
dihydroatisine (*444, 457*)	38.0	1	38.0	
isoatisine (*444, 457*)	8.0	—	—	possesses a brief curaremimetic action, blocks the transmission of a nervous impulse from the sciatic nerve to the gastrocnemius muscle of the anti-depolarizing type
B. Denudatine-type (A II)				
denudatine (*57*)	207.0 (s.c.)			
dictysine (*442, 444, 457*)	165 (mice)			brief hypotensive action due to a peripheral
	155.0	15.0	10.3	gangliolytic and spasmolytic effect
dictysine acetate (*442*)	45.0	17.0	2.6	
lepenine (*446*)	132.5 (mice)	—	—	weak H-cholinolytic, membrane-stabilizing, and antiarrhythmic action
talatizine (*447*)	110.8 (mice)	—	—	antiarrhythmic, local anesthetic, and
	300 (ip, mice)			anti-inflammatory action, and H-antidepolarizing effect on vegetative ganglia. Superior in activity to quinidine and procainamide.

TABLE XLXXVIII (*continued*)

Alkaloid (*Refs*)	iv, mg/kg			Notes
	LD_{50}	ED_{50}	LD_{50} / ED_{50}	
C. Hetidine-type (AIV)				
episcopalidine (*458*)	7.0 (ip, mice) 10.0 (s.c, mice)	—		prevents the death of mice poisoned by the iv administration of a lethal dose of yunnaconitine
D. Hetisine-type (AVII)				
guan-fu base A (*57, 459, 490*)	582.2 (ip, mice) 134 (mice)	81.87	7.11	
guan-fu base A hydrochloride (*475*)	163.9 (mice)	12.4	13.2	
guan-fu base G (*57, 490*)	185.50 (ip, mice)	9.53	19.46	
guan-fu base Z *N*-oxide (*448*)	230			weak hopytensive and H-cholinobloking effect
hetisine (*443*)	26.0	1	26.0	
nominine (*449*)	68	5	13.6	membrane-stabilizing, local anesthetic, antinflammatory, and antiarrhythmic action
tetrapropinyl guan-fu alcoholamine (*493*)	42 (mice)			
tadzhaconine (*450*)	12.8	0.3	42.7	pronounced antiarrhythmic action. Superior in activity to quinidine, procainamide, ajmaline, etc.
zeravschanizine (*451*)	34.1	0.5	68.0	pronounced antiarrhythmic and local anesthetic and activity

TABLE XLXXVIII (*continued*)

Alkaloid (*Refs*)	iv, mg/kg		Notes
	LD_{50}	ED_{50}	LD_{50} / ED_{50}
E. Veatchine-type (B Ⅰ)			
1-acetylsongorine (*442*)	150.0 420 (ip, mice)	15.0	10.0
1-benzoylsongorine (*442*)	41.0	0.38	107.9
1, 15-diacetylsongorine (*442*)	131.0 805 (ip, mice)	18.0	7.3
dehydrosongorine (*442*)	120.0 450 (ip, mice)	12.0	10.0
norsongorine (*453*)	150 (mice)		hypotensive, weak ganglioblocking and pronounced antiarrhythmic action
songoramine (*442*)	120.0 420 (ip, mice)	8.2	14.5
songorine (*57, 442*)	142.5 480 (ip, mice)	7.3	19.4
songorine *N*-oxide (*442*)	550.0 >2000 (ip, mice)	20.0	27.5 feebly active, weak antiarrhythmic and H-cholinoblocking action
songorine 12-semicarbazone (*442*)	90.0 289 (ip, mice)	10.0	9.0

TABLE XLXXVIII (*continued*)

Alkaloid (*Refs*)	iv, mg/kg		Notes	
	LD_{50}	ED_{50}	LD_{50} / ED_{50}	
F. Napelline-type (B II)				
1-acetylnapelline (*442*)	100.0 310 (ip, mice)	15.0	6.7	
12-acetylnapelline (*442*)	101.0	15.0	6.7	
1-benzoylnapelline (*442*)	30.0 135 (ip, mice)	0.24	133.3	
12-epinapelline (*442, 455*)	82.0 >250 (ip, mice)	8.0	10.3	hypotensive, H-cholinoblocking, anti-inflammatory, antiarrthymic action
napelline (*442, 456*)	88.0 280 (ip, mice)	10.0	8.8	
napelline-1-butyrate (*442*)	66.0	20.0	3.3	
napelline-1-methacrylate (*442*)	100.0	25.0	4.0	
napelline *N*-oxide (*442, 457*)	725.0 >2000 (ip, mice)	28.0	25.8	
11,12,15-tribenzoyl-napelline (*442*)	175.0	20.0	8.8	

TABLE XLXXIX

COMPARATIVE ANTIARRHYTHMIC EFFECTS BETWEEN SELECTED DITERPENOID ALKALOIDS AND KNOWN DRUGS (*461*)

Compound	iv, mg/kg		LD_{50} / ED_{50}
	LD_{50}	ED_{50}	
furoylheteratisine	16.2	0.07	231.4
N-acetylseparaconitine	15.0	0.07	214.3
N-desacetyllappaconitine	7.3	0.05	146.0
6-benzoylheteratisine	5.0	0.035	142.9
1-benzoylnapelline	30.0	0.24	133.3
ranaconitine	6.2	0.05	124.0
lappaconitine	5.9	0.05	118.0
actezine	14.5	0.13	111.5
14-benzoyltalatisamine	25.0	0.26	96.2
zeravshanizine	34.1	0.5	68.0
rytmilen	42.0	4.0	10.5
etmozine	12.0	1.25	9.6
ajmaline	33.0	5.0	6.6
mexitil	35.0	7.0	5.0
lidocaine	39.0	10.0	3.9
quinidine	66.0	20.0	3.3
novocainamide	138.0	60.0	2.3

Clinical investigations over many years by Tashkent scientists (*461*) showed that allapinine and actezine possess high antiarrythmic effect in the therapy of ventricular and supraventricular extrasystoles, paroxysms of a trial fibrillation and flutter paroxysmal ventricular and supraventricular tachycardia, including Wolf-Parkinson-White (WPW) syndrome cases. As compared with the known antiarrhythmic drugs, allapinine and actezine proved to be more effective in the therapy of chronic and dangerous ventricular and supraventricular tackyarrhythmic

cases. Both drugs have a number of important advantages over other drugs due to effectiveness in the therapy of well-manifested sinus brachycardia, weak sinus node syndrome, and the syndrome of broadening of Q-T interval cases during the reduced arterial pressure. In addition, in the course of prolonged treatment, their antiarrhythmic actions are still retained and do not bring about arrhythmogenic or other toxic effects.

TABLE XLXXX

TOXICITIES AND ANTIFIBRILLATORY ACTIVITIES OF C_{20}-DITERPENOID ALKALOIDS ON CARDIAC FIBRILLATION IN ALERT MICE (*442*)

Alkaloid	iv, mg/kg		LD_{50} / ED_{50}
	LD_{50}	ED_{50}	
1-benzoylnapelline	135	3	45
dihydrosongorine	450	28	15.3
12-epi-napelline	>250	20	>12.5
napelline	280	17.8	15.7
songorine	480	25	19.4

In 1985, observation of the activity of the total alkaloids, episcopalisine (*157, 161*) and episcopalidine (*157, 161*) from *Aconitum contortum* (*161*) in the model of yunnaconitine (LD_{50}: 0.59 mg/kg, ip, mice)-induced arrhythmias in mice (*458*) showed that the total alkaloids (30 mg/kg, ip; 10 mg/kg, s.c.), and espiscopalisine (30 mg/kg, s.c) exhibited effective antagonism to yunnaconitine, and were established to have the poisoning preventive action described in Chinese folk-medicine.

For more than 10 years, Chinese scientists, mainly those from China Pharmaceutical University, have carefully scrutinized the antiarrhythmic activities of guan-fu base A first reported by Heu and Liu *et al.* (*459, 471, 472*) in 1981. At

the present time, guan-fu base A hydrochloride is undergoing the Phase III clinical trials in China.

The 1981 paper of Heu *et al.* (*471*) was followed by a series of investigations by other researchers (*459, 472~475*).

Chen *et al.* (*459*) reported that pretreatment of rats with guan-fu base A (GFA) (20 or 30 mg/kg iv) significantly reduced the incidence of ventricular fibrillation induced by $CaCl_2$ (130 mg/kg) and also reduced the mortality. Prior iv treatment with GFA (2.5-20 mg/kg, 2 min) in anesthetized rats, led to an increasing dose of beiwutine necessary to produce cardiac arrhythmias. GFA (30 mg/kg iv) also markedly increased the ouabain dose necessary to cause ventricular premature beats, ventricular fibrillation, and cardiac arrest in anesthetized guinea pigs. The ventricular fibrillation threshold to electrical stimulation was elevated in anesthetized cats by giving GFA (2-8 mg/kg iv). GFA produced bradycardia even after vafotomy, and did not block the isoproterenol-induced tachycardia and hypertension in cats. In Langendorff's guinea pig hearts, GFA (4 mg/kg) caused a 32% reduction of heart rate, a 27% reduction of coronary flow, and a 33% diminution of the amplitude of cardiac contractions.

Harris low-stage left anterior ligation was performed in anesthetized dogs. After 12h, severe ventricular arrhythmia was recorded in the conscious state. Cumulative iv administration of GFA from 10 to 40 mg/kg produced a remarkable antiarrhythmic effect lasting over 30 min and the Q-T interval of the sinus rhythm were significantly altered. The antiarrhythmic potency of GFA in this model was found to be one third that of quinidine (*472*).

GFA (10 mg/kg iv) reduced the heart rate of anesthetized or non-anesthetized dogs (*473*). The inhibitory effects of GFA on heart automatoticity and conductivity in anesthetized rabbits are beneficial to block tachyarrhythmia and re-entry (*474*). Guan-fu base A hydrochloride (GFAHC) at 10, 25, and 40 mg/kg iv significantly

prevents the ventricular arrhythmia induced by aconitine in rats (*475*).

GFA possessed the electrophysiological properties of antiarrhythmic drugs such as quinidine, mexiletine (*476, 480, 482*), and could block the fast Na^+ channels (*477, 479*) or act as a sodium channel blocker with slow kinetics (*483*) to exhibit the antiarrhythmic action. GFA (8.6 μ mol/L) decreased the action potential amplitude and maximal rate of depolarization (Vmax) of isolated guinea pig papillary muscles, significantly prolonged ERP (*478*). GFA has inhibitory effects on Ik, contributing to the prolongation of cardiac repolarization (*481*). The bradycardia induced by GFA is mechanically directly on the sinoatrial node, but calcium chloride or beta adenoceptor blocks (*484~486*).

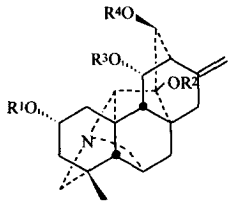
The phamacokinetic and pharmacodynamic profiles of GFA were analysed by the integrated PK-PD model following iv dosing to dogs. The values of Emax, S, Keo and EC_{50} for GFA are 1.11 ± 0.01, 1.06 ± 0.43, 0.097 ± 0.046 min^{-1} and $1.50 \times 10^{-6} \pm 0.92 \times 10^{-6}$ μg/ml, respectively (*487*). GFA also can reduce myocardial oxygen consumption and improve myocardiac blood supply in anesthetized rats (*488*).

In general pharmacological studies with GFAHC, there were no significant drug-related changes on the neural and respiratory systems in mice, rabbits, and rats. However, GFAHC (5, 10, and 15 mg/kg iv) can produce a brief hypotensive action on anesthetized cats (*489*).

In 1987, Luo and Heu *et al.* (*490*) reported that guan-fu bases G (GFG) and Z (GFZ) isolated from *Aconitum coreanum* are effective in several experimental arrhythmic models, and their antiarrhythmic activities, as compared with GFA, were GFG (LD_{50}/ED_{50}=19.46)>GFA (LD_{50}/ED_{50}=7.11)>>GFZ (ED_{50}=189.9 mg/kg) (ip, mice), thus suggesting a close connection with the molecular hydrophilic feature.

These interesting results encouraged Chinese scientists to undertake further studies on the structure-antiarrhythmic activity relationships for gaun-fu base

alkaloids (*491, 492*). Six derivatives of GFA, were prepared, but only compounds **147~149** markedly inhibited the arrhythmic action induced by aconitine in rats. A comparative study of antiarrhythmic activities between tetrapropionyl guan-fu base A (TPGFA) (**148**) and GFA by Zhu *et al.* (*493*) showed that TPGFA (**148**) (1.2, 4 mg/kg iv) significantly counteracted arrhythmia induced by aconitine in rats, and



147 R^1=R^2=R^3=R^4=Ac

148 R^1=R^2=R^3=R^4=$COCH_2CH_3$

149 R^1=R^4=Ac R^2=R^3=$COCH_2CH$

reduced the doses of strophanthin G to produce ventricular premature beats (VP), ventricular tachycardia (VT), ventricular fibrillation (VF), and cardiac arrest (CA) in guinea pigs. Pre-treatment of rats with TPGFA (**148**) at 7 and 10 mg/kg iv significantly reduced the incidence of VF induced by $CaCl_2$ and reduced the mortality as well. The ventricular fibrillation threshold for electrical stimulation was elevated by TPGFA (**148**) at 4 and 8 mg/kg iv in rabbits. VT and VFF due to coronary artery ligation and reperfusion could be prevented by TPGFA (4.5, 6 and 8 mg/kg, iv) in anesthetized rats, thus showing that the antiarrhythmic activities of TPGFA were more potent than those of GFA. Examination of the stereochemical model of GFA with a rigid system indicated that GFA was apparently composed of two layers, a hydrogenated phenanthrene ring and the alkylamino chain containing

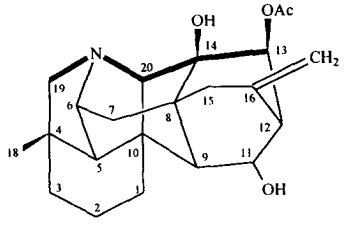
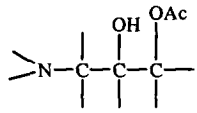
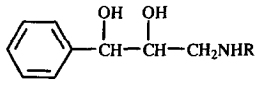


Fig. 13

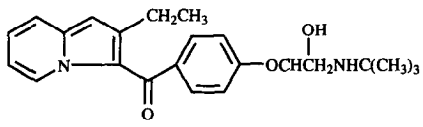
hydroxy and acetyl groups (), and that the latter was probably a pharmacophore contributing to the biological activities (Fig. 13). This conclusion led Peng *et al.* (*494*) to design and synthesize fourteen derivatives of phenylpropane-diolamine as congeners of GFA. Screening tests for these compounds showed that six of the phenylpropane-diolamines (**150~155**) and one indolizine derivative **156** markedly antagonized the arrhythmias induced by chloroform in rats. It is note worthy that compounds **151**, **152**, **153**, and **154** appeared to be more potent than GFA. On the basis of the afore-mentioned preliminary screening results, Peng *et al.* (*495*) designed and synthesized twenty-one (erythro)–2-alkyl-3-phenylpropan-2,3-diolamine compounds, eight of which possessed antiarrhythmic effects on aconitine-induced arrhythmia in rats.



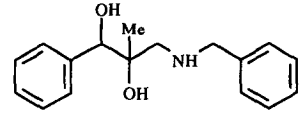
150 R=CH(CH$_3$)$_2$ **153** R=CH(CH$_3$)$_3$

151 R=CH$_2$(CH$_2$)$_2$CH$_3$ **154** R= 

152 R=  **155** R=NH 



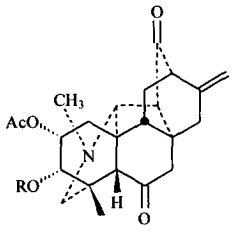
156

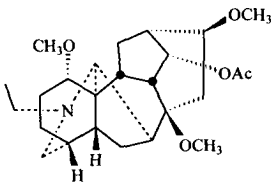


157

Among them, the antiarrhythmic activity of compound **154** was similar to that of GFA. This is very important progress in establishing the structure-activity relationships of the antiarrhythmic effects for the C_{20}-diterpenoid alkaloids.

In the course of the continuing investigation of *Aconitum contortum* (*157~160*), Japanese and Chinese Scientists Niitsu and Chen *et al.* (*161, 497, 498*) have isolated some new alkaloids (**158~161**) and developed these alkaloid-containing formulations for the treatment of heart failure. The hydrochloride salt of alkaloid **160** at 10^{-5} M concentration showed 50.4% inhibition of the contractile force of isolated right artrium of guinea pig heart. While other alkaloids also showed inhibitory effects and may therefore be useful for the treatment of angina pectoris and cardiac infarction (*497*). At the same concentration, the hydrochloric acid salt of **159** inhibited the contractile force by only 39.4% and the heart rate by 26.47%, as compared with 31.3% and 0.44% for the control compound 20-ethyl-1α, 8β,16β-trimethoxyaconitine in each case (*498*).





contorsine **158** R=COCH$(CH_3)_2$ **161**

contortine **159** R=COCH$(CH_3)_2CH_3$

contorine **160** R=CO−C_6H_4−CH_3 (p)

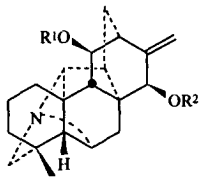
3. Antifibrillatory

Tashkent scientists (*442*) reported that some C_{20}-diterpenoid alkaloids possessed pronounced antiarrhythmic actions (Tables XLXXⅧ~XLXXⅨ), and also exhibited powerful antifibrillatory effects (Tables XLXXⅩ). In addition, GFA also showed an effect on the electrical stimulation-induced ventricular fibrillation in rabbits (*471*), and GFA at 30 mg/kg iv markedly increased the ouabain doses to cause ventricular fibrillation in anesthetized guinea pigs (*459*).

4. Effects of Kobusine and Pseudokobusine Derivatives on Cutaneous Blood

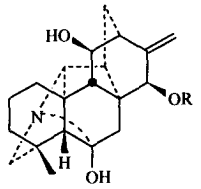
Flow in Mice

In 1997, Wada *et al.* (*499*) reported that the hetisine-type alkaloids kobusine (**162**) and pseudokobusine (**163**) caused marked increases in cutaneous blood flow in the hind foot of mice. Later, their continuing study (*500*) revealed that alkaloids **162** and **163** of 11 and 15-derivatives showed significant activity, while other alkaloids had only mild to moderate activity. The prospect that esterification of the hydroxyl groups of **162** and **163** may contribute to enhancement of the activity of the parent alkaloids led Wada *et al.* (*501*) to synthesize a series of the esterified derivatives of both kobusine and pseudokobusine for active screening test on cutaneous blood flow in mice using a Doppler-type laser blood flowmeter. The



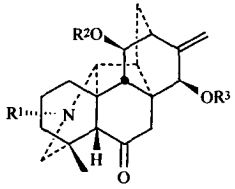
	R1	R2
162	H	H
164	H	As
165	Vr	H
166	H	Vr
167	Nt	H
168	H	Nt

As=COC_6H_4-OCH_3 (4)
Vr=$COC_6H_3(OCH_3)_2$ (3, 4)
Nt=COC_5H_4N

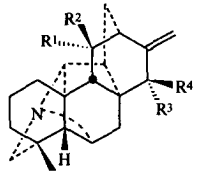


163 R=H
169 R=As
170 R=Vr
171 R=NB

NB=COC_6H_4-NO_2 (4)



172 R1=Me R2=R3=H
173 R1=Me R2=H R3=Vr
174 R1=Ac R2=R3=H
175 R1=R2=R3=Ac

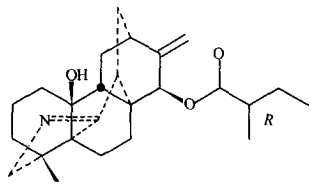


176 R1=H R2=OVr R3+R4=O
177 R1+R2=O R3=H R4=OVr

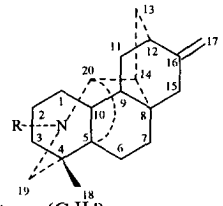
results showed that compounds **164~168** were significantly effective at the low dose of 0.5 or 0.05 mg/kg, while pseudokobusine derivatives were all active at 1.0, 0.5, or 0.05 mg/kg, and the effects of compounds **169~171** at 0.1 mg/kg were truly remarkable. Yesoline (**173**) from *Aconitum yesoense* var. *macroyesoense* (*142*) and **175** were significantly effective at a low dose of 1 mg/kg, whereas yesonine (**172**) from *Aconitum yesoense* var. *macroyesoense* (*143*) and **174** were inactive. Dehydrokobusine derivatives **176** and **177** were significantly effective at low doses of 0.5 or 0.1 mg/kg. From the afore-mentioned results, it was concluded that the hydroxyl groups of these alkaloids, especially a free OH group of **163** at C-6, are important for action on the peripheral vasculature leading to dicatation, and that the alkaloids with a 15-aromatic ester groups, e.g., OAs, OVr, or ONB, may have enhanced activity compared with the parent alkaloids.

Ⅶ. Addendum

1. Four hetisine-type alkaloids (9-hydroxynominine, 11,13-diacetyl hetisine, sadosine, and 13-acetyl hetisinone) could be supplemented in Tables IX, XXXIII, and XLXVIII.
2. Tashkhodzhaev, *et al* (*508*) recently reported a new type C_{20}-diterpenoid alkaloid arcutin. With respect to our classification criteria, it was assigned to the



arcutin (C Ⅱ'-1)

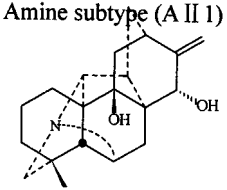


arcutine-type (C Ⅱ')

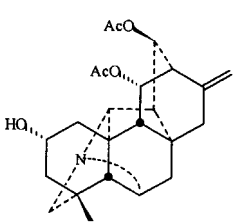
$C_{25}H_{35}NO_3$
MW=397
mp 225-226℃ (hexane)
NMR (no reported)
Aconitum arcuatum Maxim

TABLE IX (*supplement*)
HETISINE TYPE DITERPENOID ALKALOIDS (AVII)

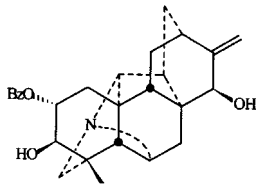
a. Amine subtype (A II 1) / group



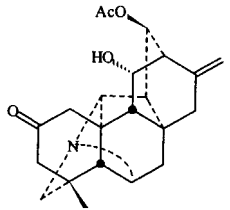
AVII1a-65



AVII1a-66



AVII1a-67



AVII1a-68

code (name)	formula	MW	mp	$[\alpha]_D$	plant	ref
AVII1a-65 (9-hydroxynominine)	$C_{20}H_{37}NO_2$	313	287-291	+68.5	*Aconitum ibukiense* Nakai	*502*
AVII1a-66 (11,13-diacetyl hetisine)	$C_{24}H_{31}NO_5$	413	225-227	+26.1	*Delphinium nuttalianum* Pritz	*503, 504*
AVII1a-67 (sadosine)	$C_{27}H_{31}NO_6$	465	222-224	+53.1	*A. japonicum* Thunb	*505*
AVII1a-68 (13-acetyl hetisinone)	$C_{22}H_{27}NO_4$	369			*D. cardiopetalum*	*205*
					D. gracile DC	*507*
					D. peregrinum var. *elongatum* Boiss	*506*

TABLE XXXIII (*supplement*)

Code (name) (*ref*)	δ_H
AVII1a-65 (9-hydroxynominine) (*502*)	1.02 (3H, s, H_3-18), 2.22, 2.44 (each 1H, d, *J*=17.0 Hz, H_2-19), 4.02 (1H, s, H-15α), 5.00, 5.01 (each 1H, s, H_2-17)
AVII1a-66 (11,13-diacetyl hetisine) (*504*)	1.00 (3H, s, H_3-18), 2.12, 2.23 (each 3H, s, 2×OAc), 4.20 (1H, brs, H-2β), 4.82, 5.00 (each 1H, s, H_2-17)
AVII1a-67 (sadosine) (*505*)	1.19 (3H, s, H_3-18), 3.67 (1H, d, *J*=3.0 Hz, H-3α), 4.44 (1H, d, *J*=4.0Hz, H-7β), 4.52 (1H, brs, H-15α), 5.00 (2H, brs, H_2-17), 5.40 (1H, m, H-2β)

TABLE XLXVIII (*supplement*)

carbon	AVII1a-65 (*502*) (9-hydroxy-nominine)	AVII1a-66 (*504*) (11,13-diacetyl hetisine)	AVII1a-68 (*204*) (13-acetyl hetisinone)	carbon	AVII1a-65 (*502*) (9-hydroxy-nominine)	AVII1a-66 (*504*) (11,13-diacetyl hetisine)	AVII1a-68 (*204*) (13-acetyl hetisinone)
1	28.9	32.0	45.2	13	33.4	73.2	73.6
2	19.6	67.4	213.0	14	41.5	50.4	49.9
3	33.4	40.6	50.2	15	73.2	34.1	33.7
4	37.3	36.8	42.8	16	154.6	143.9	144.5
5	54.6	61.4	60.9	17	109.9	109.8	109.9
6	64.8	64.5	65.3	18	29.0	29.8	28.7
7	24.5	36.2	36.0	19	62.4	63.9	64.7
8	45.1	44.0	44.7	20	72.3	68.7	70.7
9	79.2	53.3	54.7	OAc		170.4	170.3
10	52.8	50.6	55.5			170.8	21.1
11	38.5	76.1	74.4			21.3	
12	35.1	45.2	48.4			21.6	

AVII1a-67 (*505*)(sadosine) (CD_3OD): 25.6, 25.7, 34.0, 36.1, 37.6, 39.9, 41.7, 48.3, 50.0, 51.4, 62.3, 65.0, 67.7, 71.1, 71.3, 74.6, 75.6, 80.6, 110.1, 129.5, 130.1, 134.2, 155.4, 166.5.

rearranged-class (C) named as the arcutine-type (C II '), and given the code number as C II '-1.

Arcutine--type (C II '): heptacyclic, which may be considered as a rearrangement product of the hetidine- or hetisine-type alkaloids, leading to lacking a C(10)-C(20) bridge and the appearance of an unusual C(5)-C(20) one.

The X-ray diffraction of arcutin showed that there were the A/B-trans and B/C-cis fussions. But chiral centers C-5 and C-20 change sign compared with known C_{20}-diterpenoid alkaloids, leading to HO-10 to be β-axial, C(5)-C(20) to be α-axial. The six-menbered rings A and B in arcutin have the 2β,5α-chair and 5,8α-boat conformation, respectively. The rings C, D, and E have the 8,12α-boat conformations. The new six-membered rings G (C_5, C_{10}, C_9, C_8, C_{14}, C_{20}) and H (C_5, C_6, C_7, C_8, C_{14}, C_{20}) have slightly distorted 5,8α-boat conformations.

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