Clerodane Diterpenoids

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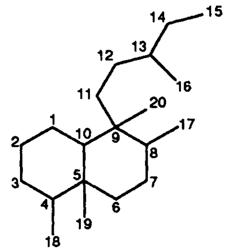
1 Introduction

During the last thirty years, over six hundred and fifty diterpenoids and nor-diterpenoids with the clerodane carbon skeleton (1) have been isolated.

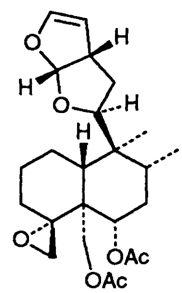
Confusion has arisen in the literature over the absolute stereochemistry of the various clerodanes isolated. The revision of the absolute stereochemistry of clerodin (2),[1] the first member of the clerodane series,[2] has led to those compounds with the same absolute stereochemistry as clerodin being termed *neo*-clerodanes and those compounds enantiomeric to clerodin being termed *ent-neo*-clerodanes. A further division of the clerodanes has been to *cis* and *trans* compounds, depending on the stereochemistry of the decalin ring junction.

Biosynthetically, the clerodanes appear to be related to the labdanes, *via* a series of methyl and hydride shifts. The labdane skeleton (4) is itself derived from geranylgeranylpyrophosphate (3) (Scheme 1),[3] although this represents a simplification of the overall biogenetic route, involving many parallel pathways to yield the multitude of clerodane natural products.

The *trans* clerodanes can arise *via* a concerted migration process to intermediate (5), whilst the *cis* compounds require a stepwise process, with a 'pause' at intermediate (6). This can then lead to either *cis* or *trans* compounds, depending on which of the C-4 methyl groups migrate.[4] This proposed biosynthetic pathway is supported, for example, by the isolation of the partially rearranged labdane compounds chettaphanin (7) from *Adenochlaena siamensis* (Compositae)[5] and salmantic acid (8) from *Cistus laurifolius* (Cistaceae).[6]



(1)



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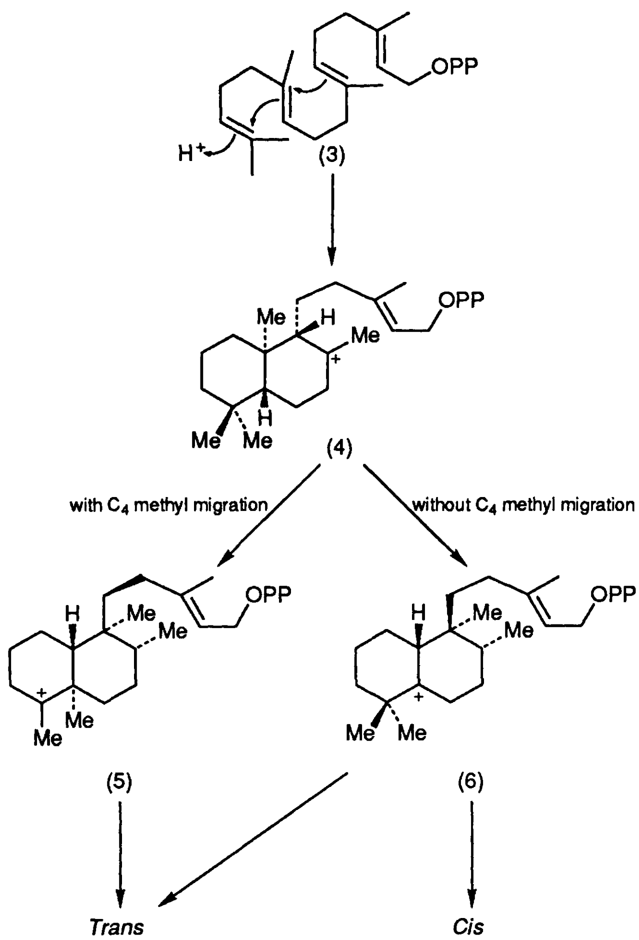
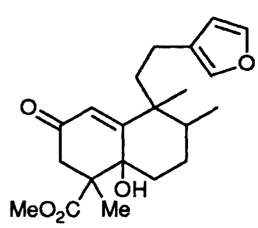


Scheme 1



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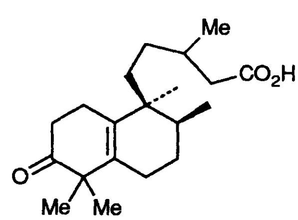

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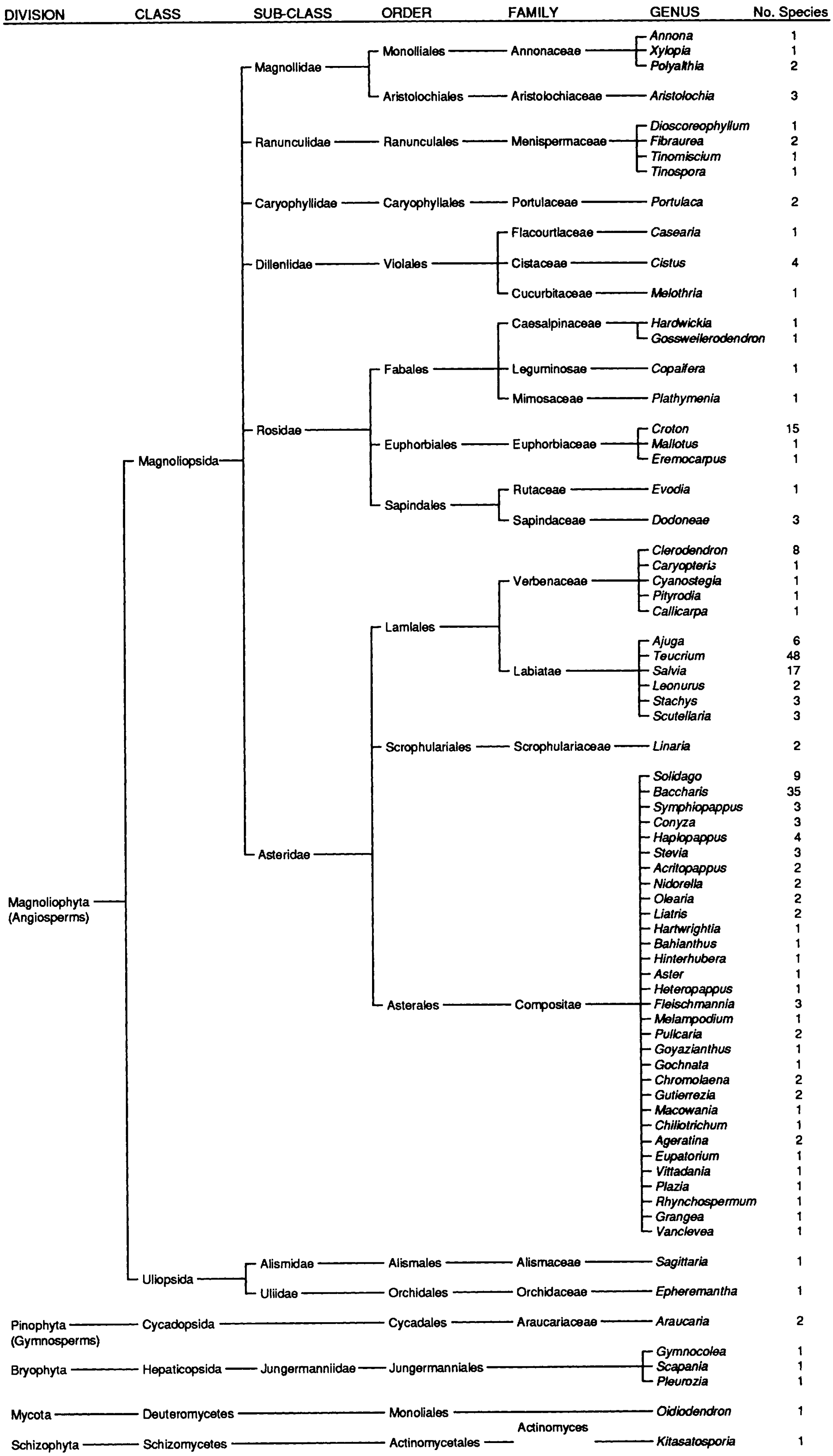

DIVISION CLASS SUB-CLASS ORDER FAMILY GENUS No. Species
Magnoliidae
Monoliales Annonaceae Annona 1
Xylopia 1
Polyalthia 2
Aristolochiales Aristolochiaceae Aristolochia 3
Ranunculidae Ranunculales Menispermaceae Dioscoreophyllum 1
Fibraurea 2
Tinomiscium 1
Tinospora 1
Caryophyllidae Caryophyllales Portulaceae Portulaca 2
Dillenidae Violales Flacourtiaceae Casearia 1
Cistaceae Cistus 4
Cucurbitaceae Melothria 1
Rosidae
Fabales Caesalpinaceae Hardwickia 1
Gossweilerodendron 1
Leguminosae Copaifera 1
Mimosaceae Plathymenia 1
Euphorbiales Euphorbiaceae Croton 15
Mallotus 1
Eremocarpus 1
Sapindales Rutaceae Evodia 1
Sapindaceae Dodoneae 3
Magnoliopsida
Asteridae
Lamiales Verbenaceae Clerodendron 8
Caryopteris 1
Cyanostegia 1
Pityrodia 1
Callicarpa 1
Labiatae Ajuga 6
Teucrium 48
Salvia 17
Leonurus 2
Stachys 3
Scutellaria 3
Scrophulariales Scrophulariaceae Linaria 2
Asterales Compositae Solidago 9
Baccharis 35
Symphiopappus 3
Conyza 3
Haplopappus 4
Stevia 3
Acritopappus 2
Nidorella 2
Olearia 2
Liatris 2
Hartwrightia 1
Bahianthus 1
Hinterhubera 1
Aster 1
Heteropappus 1
Fleischmannia 3
Melampodium 1
Pulicaria 2
Goyazianthus 1
Gochnata 1
Chromolaena 2
Gutierrezia 2
Macowania 1
Chiliotrichum 1
Ageratina 2
Eupatorium 1
Vittadania 1
Plazia 1
Rhynchospermum 1
Grangea 1
Vanclevea 1
Magnoliophyta (Angiosperms)
Uliopsida
Alismidae Alismales Alismaceae Sagittaria 1
Uliidae Orchidales Orchidaceae Epheremantha 1
Pinophyta (Gymnosperms) Cycadopsida Cycadales Araucariaceae Araucaria 2
Bryophyta Hepaticopsida Jungermanniidae Jungermanniales Gymnocolea 1
Scapania 1
Pleurozia 1
Mycota Deuteromycetes Moniliales Oidiodendron 1
Schizophyta Schizomycetes Actinomycetales Actinomyces Kitasatosporia 1

Scheme 2

Several synthetic approaches to the clerodanes have appeared in the literature, but these have been reviewed elsewhere[7] and are beyond the scope of this article. This review will instead consider the isolation, structural elucidation, and reported biological activity of the large number of clerodanes reported in the literature.

2 Taxonomy

The taxonomic relationships of the clerodane producing plants are shown in Scheme 2, to the rank of genera. The scheme is based on the system of Cronquist,[8] extended beyond the angiosperms by the systems of Holmes.[9] The vast majority of clerodanes have been isolated from dicotyledonous plants (the Magnoliopsida), with examples from all but one of the relevant sub-classes. Below sub-class, however, a greater degree of specificity occurs, with only a small fraction of orders and families apparently producing clerodanes. This appears to go against normal taxonomic trends, where one might expect a pyramidal relationship leading down from sub-class to genus. It is possible that the various genera/families developed independently the capacity to biosynthesize the clerodanes, or simply that there are a large number of families producing as yet unisolated clerodanes.

The independent development of synthetic ability is supported by the occurrence of the non-dicotyledonous producers, with two genera of monocotyledonous species (class Liliopsida), one genus of a gymnosperm, three genera of liverworts (Bryophyta), one genus of fungi (Mycota), and one strain of bacteria (Schizophyta). Although these have only been shown to produce a limited range of clerodanes, their ability to do so, considered alongside the large taxonomic differences, lends support to an independent synthetic development.

In the following sections, the individual families will be tabulated, with reference to any family or genera related trends, and they will be considered in the evolutionary order for the Magnoliopsida, as proposed by Cronquist,[8] reading from top to bottom of Scheme 2. Within individual families and genera, however, the species have been grouped to indicate chemical similarities of the isolated natural products, or trends in the productivity of species, rather than adhering to strict taxonomic ordering.

3 Isolation and Elucidation

The elucidation of the clerodane structures, and specifically the stereochemical relationship of substituents, has not been consistent in the literature. Several of the compounds have proved suitable for *X*-ray structural analysis, whilst others have been assigned by extensive spectral and correlation techniques. Many compounds, however, have been presented with only a minimal amount of spectral data to support the structural assignments. Only those compounds established by *X*-ray techniques have been indicated in the comments in the following tables. In addition, in many cases there is confusion between acidic and ester groupings in the natural products, due to the isolation techniques utilized and readers are advised to refer to the source references for possible further clarification. Finally, any cross family connections are also indicated in the comments section.

3.1 Family Annonaceae

Three genera have been shown to yield clerodanes, with only *trans* compounds being produced, as shown in Table 1.

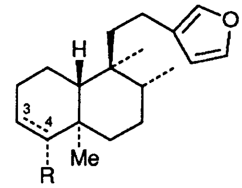
3.2 Family Aristolochiaceae

Genus-*Aristolochia*

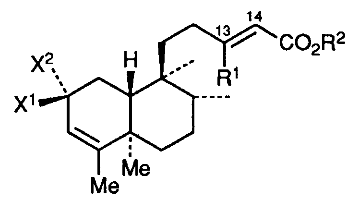
This genus has been shown to produce open chain C-11–C-16 compounds, often 'common' compounds found in other families (Table 2).

Table 1 Clerodanes obtained from Annonaceae

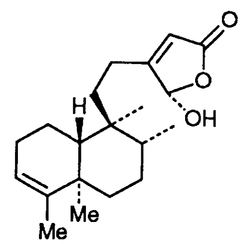
Genus – *Annona* Species	Compounds	Ref.	Comments
A. coriacea	(9), (10)	10	(9) see Compositae
Genus – *Xylopia* Species			
X. aethiopica	(11)	11	see Aristolochiaceae
Genus – *Polyalthia* Species			
P. longifolia	(12), (15)	12	(15) see Compositae, *X*-Ray structure
P. viridis	(15)	13	see Compositae



(9) R = Me, 3–4 = double
(10) R = CO_2H, 3–4 = Single



(11) R^1 = Me, R^2 = H, X^1,X^2 = =O, 13–14 = *E*
(12) R^1 = CHO, R^2 = H, X^1 = X^2 = H, 13–14 = *Z*
(13) R^1 = R^2 = Me, X^1,X^2 = =O, 13–14 = *E*
(14) R^1 = R^2 = Me, X^1 = OOH, X^2 = H, 13–14 = *E*



(15)

3.3 Family Menispermaceae

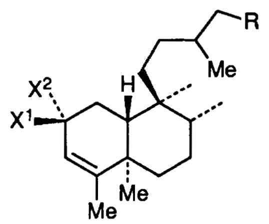
Four genera are of interest here, giving fifteen clerodanes (Table 3). Fourteen of these have been shown by chemical and spectral methods to be *cis*-clerodanes, whereas the other compound remains unassigned. All the compounds contain an unusual fused δ-lactone ring at C-8–C-9, incorporating the C-11–C-16 side chain.

3.4 Family Portulacaceae

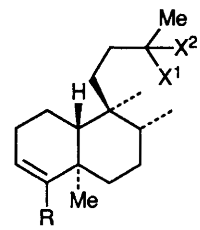
Clerodanes obtained from Portulaceae are given in Table 4.

Table 2 Clerodanes obtained from Aristolochiaceae

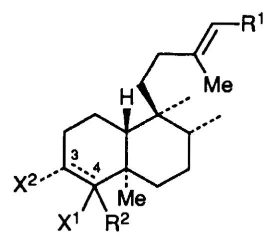
Genus – *Aristolochia* Species	Compounds	Ref.	Comments
A. galeata	(16) populifolic acid	14	see Cistaceae, Compositae
	(17)		see Cistaceae
	(28) kolaveelool		see Compositae, Caesalpinaceae
	(30) kolavenol		see Compositae, Caesalpinaceae
	(31) kolavenic acid		see Compositae, Caesalpinaceae
A. esperanzae	(13), (14), (18)—(20), (32)	15	(32) see Compositae
A. brasiliensis	(11), (16) populifolic acid	15	(11) see Annonaceae
	(19), (31) kolavenic acid		
	(36)—(38)		



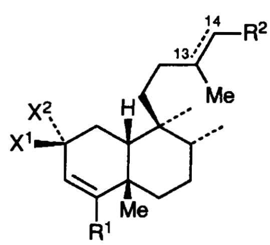
(16) R = CO_2H, $X^1 = X^2$ = H
(17) R = CO_2H, X^1,X^2 = =O
(18) R^1 = CO_2Me, $X^1 = X^2$ = H
(19) R^1 = CO_2Me, X^1,X^2 = =O
(20) R^1 = CO_2Me, X^1 = OOH, X^2 = H
(21) R^1 = CO_2H, X^1 = H, X^2 = OAc
(22) R^1 = CH_2OH, X^1,X^2 = =O
(23) R^1 = CH_2OH, X^1 = H, X^2 = OH
(24) R^1 = CO_2H, X^1 = H, X^2 = OH
(25) R^1 = CO_2H, X^1 = OH, X^2 = H
(26) R^1 = CO_2H, X^1 = OMe, X^2 = H
(27) R^1 = CO_2H, X^1 = H, X^2 = OMe



(28) R = Me, X^1 = OH, X^2 = Vinyl
(29) R = CO_2H, X^1,X^2 = =O



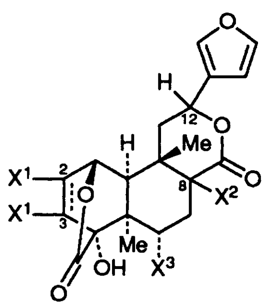
(30) R^1 = CH_2OH, R^2 = Me, X^1 = -, X^2 = H, 3–4 = Double
(31) R^1 = CO_2H, R^2 = Me, X^1 = -, X^2 = H, 3–4 = Double
(32) R^1 = CO_2Me, R^2 = Me, X^1 = -, X^2 = H, 3–4 = Double
(33) R^1 = CO_2H, R^2 = Me, X^1 = OH, X^2 = H, 3–4 = Single
(34) $R^1 = R^2$ = CO_2H, X^1 = -, X^2 = H, 3–4 = Double
(35) R^1 = CH_2OH, R^2,X^1 =CH_2, X^2 = OH, 3–4 = Single

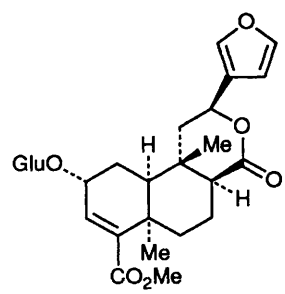


(36) R^1 = Me, R^2 = CO_2H, X^1,X^2 = = O, 13–14 = Single
(37) R^1 = Me, R^2 = CO_2Me, X^1,X^2 = =O, 13–14 = Double
(38) R^1 = Me, R^2 = CO_2H, $X^1 = X^2$ = H, 13–14 = Double
(39) $R^1 = R^2$ = CH_2OH, $X^1 = X^2$ = H, 13–14 = Single
(40) $R^1 = R^2$ = CO_2H, $X^1 = X^2$ = H, 13–14 = Single
(41) R^1 = CH_2OAc, R^2 = CO_2H, $X^1 = X^2$ = H, 13–14 = Single
(42) R^1 = CO_2H, R^2 = CH_2OAc, $X^1 = X^2$ = H, 13–14 = Single
(43) R^1 = CO_2H, R^2 = CH_2OH, $X^1 = X^2$ = H, 13–14 = Single
(44) R^1 - CH_2OH, R^2 = CO_2H, $X^1 = X^2$ = H, 13–14 = Single
(45) R^1 = CH_2OAc, R^2 = CO_2Me, X^1 = OH, X^2 = H, 13–14 = Single
(46) R^1 = CH_2OAc, R^2 = CO_2Me, X^1 = OMe, X^2 = H, 13–14 = Single
(47) R^1 = CH_2OAc, R^2 = CO_2Me, X^1,X^2 = =O, 13–14 = Single
(48) R^1 = CHO, R^2 = CO_2Me, X^1,X^2 = =O, 13–14 = Single
(49) R^1 = Me, R^2 = CO_2Me, X^1,X^2 = =O, 13–14 = Single

Table 3 Clerodanes from Menispermaceae

Genus – Species	Compounds	Ref.	Comments
Genus – *Dioscoreophyllum*			
Species			
D. cumminsii	(50) columbin	16	see Cucurbitaceae
	(51) jateorin		
	(52) chasmanthin		
	(53) palmarin		
Genus – *Fibraurea*			
Species			
F. chloroleuca	(56) fibleucin	17	
	(57) fibraurin (58)	18	
F. tinctoria	(56) fibleucin	19	
	(57) fibraurin		
	(59) fibleucinoside		
	(60) fibruarinoside		
	(61) tinophylloside		
Genus – *Tinomiscium*			
Species			
T. philippinense	(62) tinophyllone	20	unassigned sterochemistry
Genus – *Tinospora*			
Species			
T. cordifolia	(63)	21	
	(54)	22, 23	
	(55)	24	
	(64)	25	





(61)

(50) $X^1 = X^2 = X^3 = H$, 2–3 = Double, C-8–X^2 = β, C-12–H = α

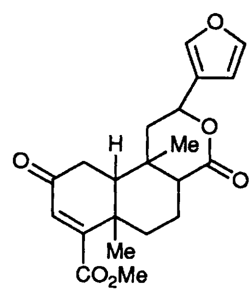
(51) X^1 = –O–, $X^2 = X^3 = H$, 2–3 = Single, C-8–X^2 = β, C-12–H = α

(52) X^1 = –O–, $X^2 = X^3 = H$, 2–3 = Single, C-8–X^2 = β, C-12–H = β

(53) X^1 = –O–, $X^2 = X^3 = H$, 2–3 = Single, C-8–X^2 = α, C-12–H = β

(54) X^1 = –O–, X^2 = OH, X^3 = H, 2–3 = Single, C-8–X^2 = β, C-12–H = α

(55) X^1 = –O–, X^2 = H, X^3 = OH, 2–3 = Single, C-8–X^2 = α, C-12–H = β



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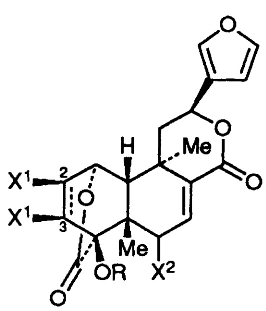


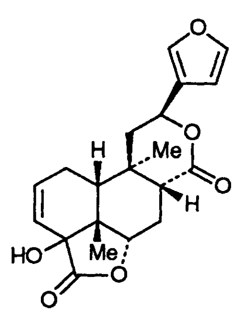
(56) R = H, $X^1 = X^2 = H$, 2–3 = Double

(57) R = H, X^1 = –O–, X^2 = H, 2–3 = Single

(58) R = H, X^1 = –O–, X^2 = OH, 2–3 = Single

(59) R = Gluc, $X^1 = X^2 = H$, 2–3 = Double

(60) R = Gluc, X^1 = –O–, X^2 = H, 2–3 = Single



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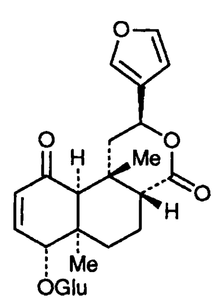
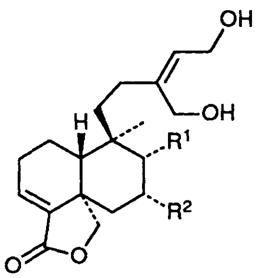


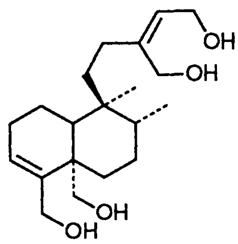
(64)

Table 4 Clerodanes from Portulacaceae

Genus – *Portulaca* Species	Compounds	Ref.	Comments
P. cv Jewel	(65) portulide A	26	
	(66) portulide B		
	(67) portulide C		
	(68) portulide D		
	(69) jewenol A	27	*X*-Ray structure
P. grandiflora Hook	(65) portulide A	28	



(65) $R^1 = CH_2OH$, $R^2 = H$
(66) $R^1 = Me$, $R^2 = H$
(67) $R^1 = Me$, $R^2 = OH$
(68) $R^1 = CHO$, $R^2 = H$



(69)

3.5 Family Flacourtiaceae

All the compounds produced from the Genus *Casearia* are highly oxygenated *cis* compounds; *e.g.* *C. sylvestris* yields compounds (70)—(75).[29]

3.6 Family Cistaceae

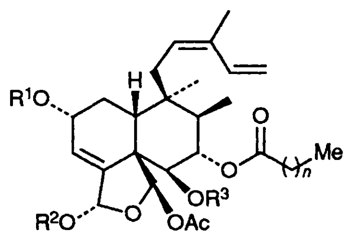
Clerodanes obtained from this Family are shown in Table 5. Both cis and trans compounds are produced with saturated open chain arrangements of C-11–C-16.

3.7 Family Cucurbitaceae

Columbin (50) (see Menispermaceae) has been isolated from *Melothria maderospatuna*.[16]

3.8 Family Caesalpinaceae

Table 6 lists the clerodanes found in Caesalpinaceae.



(70) $R^1 = Me$, $R^2 = Ac$, $R^3 = H$, $n = 2$
(71) $R^1 = Me$, $R^2 = R^3 = Ac$, $n = 2$
(72) $R^1 = H$, $R^2 = R^3 = Ac$, $n = 8$
(73) $R^1 = R^3 = H$, $R^2 = COPr$, $n = 2$
(74) $R^1 = R^2 = H$, $R^3 = Et$, $n = 8$
(75) $R^1 = R^2 = H$, $R^3 = Et$, $n = 2$

Table 5 Clerodanes from Cistaceae

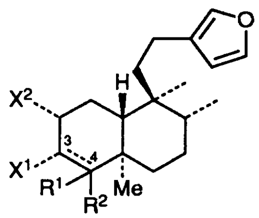
Genus – *Cistus* Species	Compounds	Ref.	Comments
C. monspeliensis	(39) cistidiol	30, 31	
	(40) cistidioic acid		
C. laurifolius	(39)—(48)	32	
C. palinhae	(49)	33	
C. populifolius	(16) populifolic acid	34—36	see Compositae, Aristolochiaceae
	(21)—(27)		
	(17)	37	see Aristolochiacaea

Table 6 Clerodanes from Caesalpinaceae

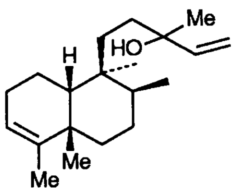
Genus – *Hardwickia* Species	Compounds	Ref.	Comments
H. pinnata	(28) kolavelool	38—40	see Compositae, Aristolochiaceae for all compounds
	(29) kolavonic acid		
	(30) kolavenol		
	(31) kolavenic acid		
	(33) kolavenolic acid		
	(34) kolavic acid		
	(76) hardwickiic acid		
Genus – *Gossweilerodendron* Species			
G. balsiferum	(34) kolavic acid	41	see Compositae
	(35) agbanindiol A		
	(76) hardwickiic acid		see Compositae, Leguminosae
	(77) agbanindiol B		
	(78) agbaninol		

3.9 Family Leguminosae

From *Copaifera officinales*[42] hardwickiic acid (76) has been obtained (see Compositae, Caesalpinaceae).



(76) $R^1 = CO_2H$, R^2 = -, $X^1 = X^2$ = H, 3–4 = Double
(77) $R^1,R^2 = {=}CH_2$, $X^1 = X^2$ = OH, 3–4 = Single
(78) $R^1,R^2 = {=}CH_2$, X^1 = OH, X^2 = H, 3–4 = Single



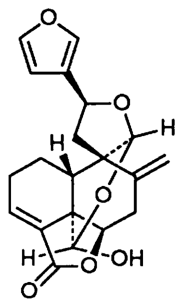
(79)

3.10 Family Mimosaceae

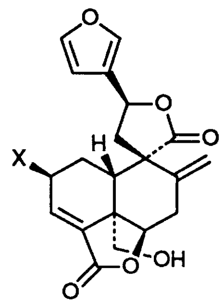
Plathymenia reticulata has yielded plathyterpol (79).[43,44]

3.11 Family Euphorbiaceae

Three genera of this family produce clerodanes, with the genus *Croton* being the most prolific (Table 7). All but two of the compounds isolated are of the *trans* variety, with a strong family trend to produce structures with a C-12-furan substituted C-9 spiro-γ-lactone, or compounds arising from rearrangements of this structure.



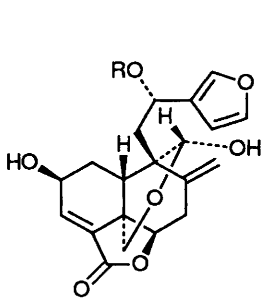
(80)



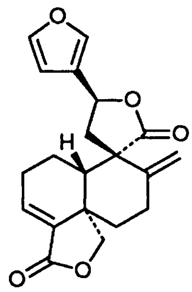
(81) X = H
(82) X = OH

Table 7 Clerodanes from Euphorbiaceae

Genus – *Croton* Species	Compounds	Ref.	Comments
C. sublyratus Kurz	(80) plaunol A	45—51	*X*-Ray structure
	(81) plaunol B		
	(82) plaunol C		
	(83) plaunol D		
	(84) plaunol E		
	(85) plaunolide		*X*-Ray structure
C. joufra	(83) plaunol D	47	
	(85) swassin	52	also plaunolide
C. caudatus	(86) crotocaudin	53, 54	
	(87) isocrotocaudin		
	(88) teucvidin		see Labiatae
C. corylifolius Lam	(90) corylifuran	55	*X*-Ray structure
C. sonderianus	(91) sonderianin	56	*X*-Ray structure
C. verreauxii Baill.	(92) croverin	57	*X*-Ray structure
	(93) dihydrocroverin		
C. pyramidalis	(94)	58	
C. penduliflorus	(95) penduliflaworosin	59	
C. ajucara	(97) dehydrocrotonin	60	
	(98) t-crotonin	61	
C. californicus	(76) hardwickiic acid	62	see Caesalpinaceae
	(100) methyl barbascoate	3	
C. aromaticus	(76) hardwickiic acid	63	see Caesalpinaceae
C. oblongifolus	(76) hardwickiic acid	64	see Caesalpinaceae
	(101) dehydrohardwickiic acid		
C. eleuteria	(102) cascarillin	65	
	(104) cascarillin A		
	(105) cascarillone	66	
C. lucidus	(99) crotonin	67—69	*X*-Ray structure
C. argyrophylloides	(106)	70	
Genus – *Mallotus* Species			
M. repandus	(89) mallotucin A	71, 72	see Labiatae, named teucvin
	(96) mallotucin B		
	(107) mallotucin C		
	(108) mallotucin D		
Genus – *Eremocarpus* Species			
E. setigerus	(103) hautriwaic acid	73	see Compositae
	(109) eremone		



(83) R = H
(84) R = Ac



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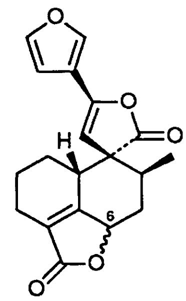
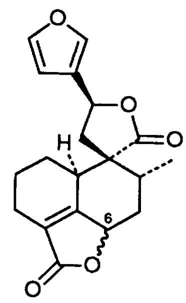
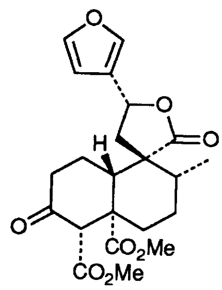


(86) C_6–O = β
(87) C_6–O = α



(88) C_6–O = β
(89) C_6–O = α



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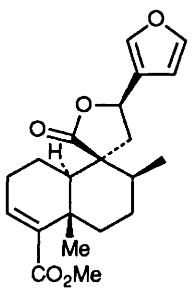

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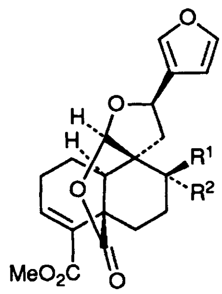
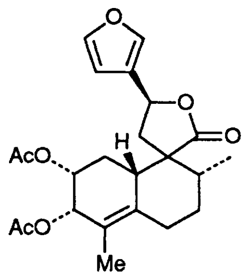
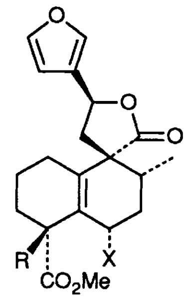


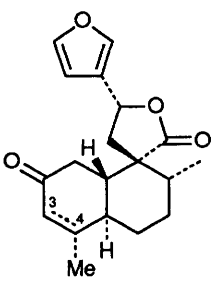
(92) R^1,R^2 = =CH_2
(93) R^1 = Me, R^2 = H



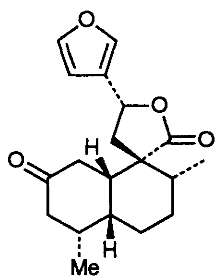
(94)



(95) R = Me, X = H
(96) R = CO_2Me, X = OAc



(97) 3–4 = Double
(98) 3–4 = Single



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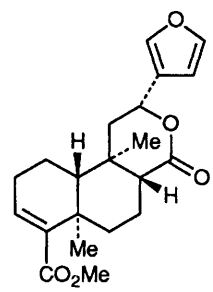

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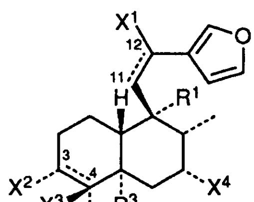
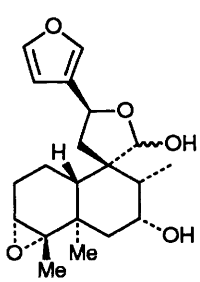


(76) R^1 = R^3 = Me, R^2 = CO_2H, X^1 = X^2 = X^4 = H, X^3 = -, 3–4 = Double, 11–12 = Single
(101) R^1 = R^3 = Me, R^2 = CO_2H, X^1 = X^2 = X^4 = H, X^3 = -, 3–4 = Double, 11–12 = Double
(102) R^1 = CHO, R^2 = R^3 = Me, X^1 = X^2 = X^3 = OH, X^4 = OAc, 3–4 = Single, 11–12 = Single
(103) R^1 = Me, R^2 = CO_2H, R^3 = CH_2OH, X^1 = X^2 = X^4 = H, X^3 = -, 3–4 = Double, 11–12 = Single



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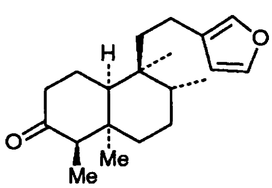

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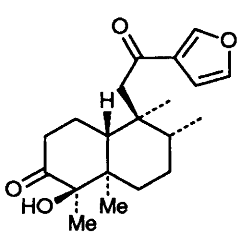

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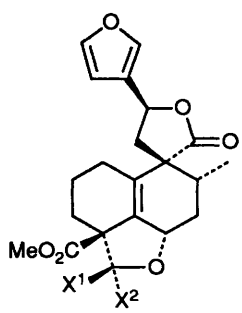
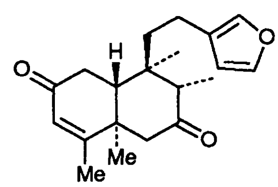


(107) X^1 = OH, X^2 = H
(108) X^1 = H, X^2 = OH

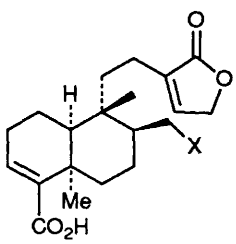


(109)

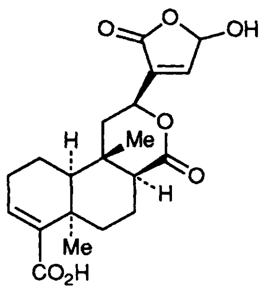
Table 8 Clerodanes from Rutaceae

Genus – *Evodia*

Species	Compounds	Ref.	Comments
E. floribunda Baker	(110) floridolide A	74	
	(111) floridolide B (112),		
	(113) floribundic acid	75	
	(114) floridiolic acid	76, 77	*X*-Ray structure



(110) X = H
(111) X = OH



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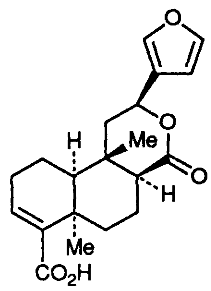

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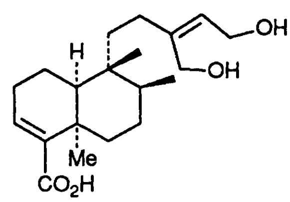
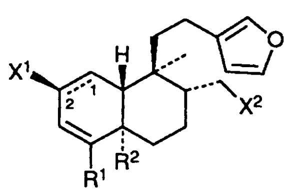


(114)

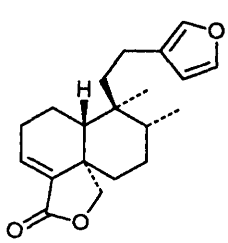
Table 9 Clerodanes from Sapindaceae

Genus – *Dodoneae*

Species	Compounds	Ref.	Comments
D. boroniaefolia	(115)—(118)	78	
D. attenuata	(118)—(120)	79, 80	
D. viscosa	(103) hautriwaic acid	81	see Compositae, Euphorbiaceae



(103) $R^1 = CO_2H$, $R^2 = CH_2OH$, $X^1 = X^2 = H$, 1–2 = Single
(115) $R^1 = CH_2OH$, $R^2 = Me$, $X^1 = X^2 = H$, 1–2 = Single
(116) $R^1 = CH_2OH$, $R^2 = Me$, $X^1 = OH$, $X^2 = H$, 1–2 = Single
(117) $R^1 = CO_2H$, $R^2 = Me$, $X^1 = OH$, $X^2 = H$, 1–2 = Single
(118) $R^1 = CO_2H$, $R^2 = CH_2OH$, $X^1 = X^2 = H$, 1–2 = Double
(119) $R^1 = CO_2H$, $R^2 = CH_2OH$, $X^1 = H$, $X^2 = OAc$, 1–2 = Single



(120)

3.12 Family Rutaceae

Clerodanes obtained from Rutaceae are given in Table 8.

3.13 Family Sapindaceae

Three species of the genus *Dodoneae* have been shown to produce clerodanes, with all the compounds possessing the *trans* arrangement, and the C-11–C-16 chain existing as a furylethyl substituent (Table 9).

3.14 Family Verbenaceae

Five genera of this family have thus far been shown to produce clerodanes, with the *Clerodendron* and *Caryopteris* genera the most prolific.[82] The compounds isolated from these two genera all possess a bis-tetrahydrofuranyl C-11–C-16 side chain, with varying levels of oxidation at C-14–C-15, and a common arrangement of 6α-acetoxy, 19-acetoxy, C-4–C-18 α-epoxide on the 'southern' portion of the decalin (the term 'southern' is here used to identify the decalin substituent pattern from C-3–C-7).

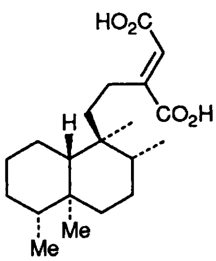
Clerodin (2) was the first compound of the clerodane family to be isolated and identified[2], thus lending its name to the whole series, with its structure assigned by X-ray analysis (Table 10).[1,83]

3.15 Family Labiatae

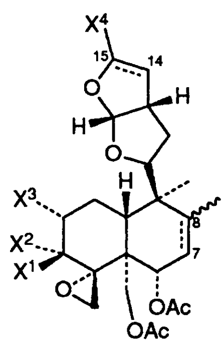
Six genera of this family have been shown to produce clerodanes (Table 11). The genera *Ajuga* and *Scutellaria* produce compounds closely related, structurally, to those from the *Clerodendron* and *Caryopteris* genera (Verbenaceae), with similar

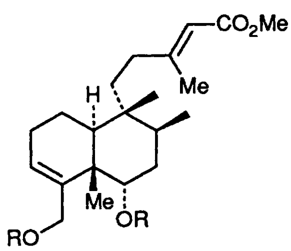
Table 10 Clerodanes from Verbenaceae

Genus – *Clerudendron* Species	Compounds	Ref.	Comments
C. infortunatum Linn.	(2) clerodin	2, 83	*X*-Ray structure
C. colebrookium	(2) clerodin	84	
C. phlamoides	(2) clerodin (124) clerodendrin A	84	
C. tricotomum Thumb	(124) clerodendrin A (125) clerodendrin B	85—89	*X*-Ray structure
C. cryptophyllum	(124) clerodendrin A	82	
C. fragrans	(126) 3-epicaryoptin	82	
C. calamitosum	(126) 3-epicaryoptin	90	
C. inerme	(126) 3-epicaryoptin	1	*X*-Ray structure
Genus – *Caryopteris* Species			
C. divaricata Maxim	(2) clerodin (127), (128), (126) 3-epicaryoptin (129) caryoptin (130), (131), (132) caryoptinol (133)	91—95	
Genus – *Cyanostegia* Species			
C. angustifolia	(121)	78	
Genus – *Pityrodia* Species			
P. lepidota	(122), (123)	96	(123) *X*-Ray structure
Genus – *Callicarpa* Species			
C. maingayii	(134) maingayic acid	97	



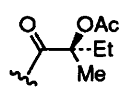
(121)

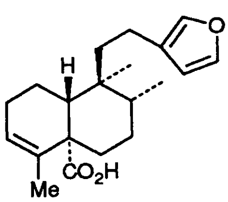




(122) R = H
(123) R = Ac

(2) $X^1 = X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Double, C-8–Me = α
(124) X^1 = OR, $X^2 = X^4$ = H, X^3 = OH, 7–8 = Double, 14–15, = Double, C-8–Me = -
(125) X^1 = OR, $X^2 = X^4$ = H, X^3 = OH, 7–8 = Single, 14–15 = Double, C-8–Me = α
(126) $X^1 = X^3 = X^4$ = H, X^2 = OAc, 7–8 = Single, 14–15 = Double, C-8–Me = α
(127) $X^1 = X^2 = X^3$ = H, X^4 = OH, 7–8 = Single, 14–15 = Single, C-8–Me = α
(128) $X^1 = X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Single, C-8–Me = α
(129) X^1 = OAc, $X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Double, C-8–Me = α
(130) X^1 = OAc, $X^2 = X^3$ = H, X^4 = OH, 7–8 = Single, 14–15 = Single, C-8–Me = α
(131) X^1 = OAc, $X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Single, C-8–Me = α
(132) X^1 = OH, $X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Double, C-8–Me = α
(133) X^1 = OH, $X^2 = X^3 = X^4$ = H, 7–8 = Single, 14–15 = Single, C-8–Me = α

R = 



(134)

Table 11 Clerodanes from Labiatae

Species	Compounds	Ref.	Comments
Genus – *Ajuga*			
A. remota	(138) ajugarin I	104—108	*X*-Ray structure
	(139) ajugarin II		
	(135) ajugarin III		
	(136) ajugarin IV		
	(140) ajugarin V		
A. nipponensis	(141) ajugamarin A1	109—112	*X*-Ray structure
	(142) ajugamarin B1		
	(143) ajugamarin B2		
	(144) ajugamarin B3		
	(145) ajugamarin C1		
	(137) ajugamarin D1		
A. reptans	(146) ajugareptansone A	113—115	
	(147) ajugareptansone B		*X*-Ray structure
	(149) ajugareptansin		*X*-Ray structure
A. iva	(150) ivain I	116	*X*-Ray structure
	(151) ivain II		
	(152) ivain III		
	(153) ivain IV		
A. chamaepitys	(154) ajugapitin (155), (156), (157), (158)	117—119	
A. pseudoiva	(155), (159)	120	
Genus – *Teucrium*			
T. chamaedrys	(160) teucrin A	121, 122	
	(170) teucrin B		
	teucrins C and D	123—128	No structures
	(171) teucrin E		
	(180) teucrin F		
	(183) teucrin G		
	(89) teuchamaedryn A	129	also known as teucvin, mallotucin A see Euphorbiaceae
	(172) teuchamaedryn B		also known as
	(184) teuchamaedryn C	130	teucrin H2
	(161) 6-epiteucrin A	131	
	(162) 6-epiteucvin		also known as
	(173) teugin, (174)		teuflin
	(88) teucvidin		see Euphorbiaceae
	(163) teuflidin	132	
	(164) isoteuflidin		
	(185) teucroxide	133	
	(187) chamaedroxide	134	*X*-Ray structure
T. lucidum	(180), (183) teucrins F, G	135	
	(88) teucvidin		
	(162) teuflin, (174)		
T. barbeyanum	(160) teucrin A	135	
	(180), (183) teucrins F, G		
T. subspinosum	(89) teuchamaedryn A	136	
	(172) teuchamaedryn B		
	(162) teuflin (174)		
T. webbianum	(160) teucrin A	137	
	(163) teuflidin (165)		
T. viscidum	(89) teucvin	138, 139	*X*-Ray structure
sub *miquelianum*	(88) teucvidin	140, 141	*X*-Ray structure
	(162) teuflin	142, 143	*X*-Ray structure
	(89) teucvin	135	
T. intricatum			
T. cubense	(89) teucvin	144, 145, 146	named eugarzasadine
T. fragile	(173) teugin	147	
T. heterophyllum	(88) teucvidin	148	
T. polium	(189) picropolin	149	
	(190), (223) isopicropolin	150	
	(224) teucrin P1	151	
T. polium	(189) picropolin	152	
sub *capitatum*	(230) picropolinone	153	
	(191) capitatin	154	*X*-Ray structure
	(192) teucapitatin		*X*-Ray structure
	(193), (231) picropolinol	152	
	(160) teucrin A	119	
	(194) teucrin H3	155	
	(232) lolin		*X*-Ray structure
	(195) teucjaponin B (196)	152	

Table 11 Clerodanes from Labiatae (*continued*)

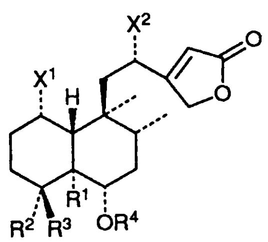
Genus – *Ajuga* Species	Compounds	Ref.	Comments
T. polium sub *polium*	(194), (224) teucrin P1	156, 157	
	(197) teupolin I		
	(198) teupolin II	158	
	(225) teupolin III	159	
	(199) teupolin IV	160	
	(238) teupolin V		
	(239) montanin B	158	
	(242) montanin E	160	
	(269) teulamifin B	161	identical to teubotryn (ref. 162)
T. polium sub *aureum*	(194), (224) teucrin P1	98	
	(200) gnaphalidin		
	(241) auropolin	163	*X*-Ray structure
T. polium sub *pilosum*	(201)	164	
T. polium sub *belion*	(194), (241) auropolin	119	(241) *X*-Ray structure
T. polium sub *album*	(202) montanin C	156, 165	
T. polium sub *vincentum*	(194), (203) eriocephalin	166	
	(204) isoeriocephalin (205)		
	(260) teuvincentin A		
	(245) teuvincentin B		
	(246) teuvincentin C		
T. asiaticum	(162) teuflin	119	
	(241) auropolin		*X*-Ray structure
T. turredanum	(194), (203) eriocephalin	167	
	(204) isoeriocephalin		
T. montanum sub *skorpilii*	(247) montanin A	168	
	(239) montanin B		
	(202) montanin C	169	
	(186) montanin D	171, 172	
	(242) montanin E	170	
	(206) montanin F		also known as teucjaponin A
	(207) montanin G	173	
T. japonicum	(206) teucjaponin A	174	also known as montanin F
	(195) teucjaponin B		
	(89) teucvin		
T. scorodonia sub *scorodonia*	(233) teuscorodol	175	
	(234) teuscorodal		
	(248) teuscorodonin,	176	
	(181) teuscorodin (167)		
	(166) teuscorolide	175	
	(197) teupolin I	135	
	(162) teuflin		
T. scorodonia sub *euganum*	(162) teuflin	135	
T. massiliense	(202), (206) montanins C and F	177	
	(148), (252) teumassilin (253)		
	(254) fruticolone	178, 179	*X*-Ray structure
T. fruticans	(255) isofruticolone (256)		
T. gnaphalodes	(194), (200) gnaphilidin	180	
	(208) gnaphalin		
	(224) teucrin P1	182	*X*-Ray structure
	teucrin P2		no structure
	(258) teugnaphalodin	181	
T. eriocephalin	(203) eriocephalin	183	*X*-Ray structure
T. chartaginense sub *homotrichum*	(194), (203) eriocephalin	135	
T. lanigerum	(197) teupolin I	156	
	(203) eriocephalin	184, 185	
	(204) isoeriocephalin		
	(205), (209), (261),		
	(210) teulanigen		
	(262) teulanigeral		
	(264) teulanigerin		
	(265) teulanigeridine		
T. pyrenaicum	(211) teupyreinin	186, 187	
	(212) teupyreinidin		
	(226) teupyrenone		
	(266) teupyrin A	136	*X*-Ray structure
	(257) teupyrin B		

Table 11 Clerodanes from Labiatae (*continued*)

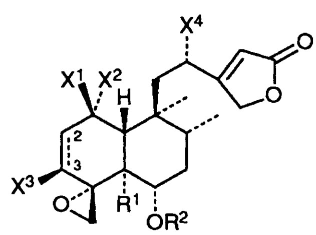
Genus – *Ajuga* Species	Compounds	Ref.	Comments
T. flavum	(162) teuflin	188	*X*-Ray structure
sub *flavum*	(163) teuflidin	189	*X*-Ray structure
T. flavum	(162) teuflin	156, 187,	
sub *glaucum*	(163) teuflidin (168)	190	
	(213) teuflavin		
	(240) teuflavoside		
T. carolipaui sub *carolipaui*	(194), (230) picropolinone	148	
T. marum	(214) teumarin	191	
T. scordium	(185) teucroxide	192	
	(242) montanin E	169	
	(170), (171) teucrin E	192	
	(173) teugin (176), (178),		
	(182), (216), (217),		
	(174), (175), (179),	193, 194	
	(177) teuscordinon	195	
	(169) teucrin H4, (249),	196	
T. creticum	(194), (195) teucjaponin B	197	also known as
	(253), (263) teucretol		*T. rosmarinifolium* Lam
T. lamiifolium D'urv	(162) teuflin	161, 198	
	(177) teuscordinon (194),		
	(202) montanin C (218),		
	(269) teulamifin B		identical to teubotryn (ref. 162)
T. divaricatum	(160), (170), teucrins A, B	199	
sub *canescens*	(180), (183) teucrins F, G		
	(172) teuchamaedryn B		also teucrin H2
	(162) teuflin		
	(163) teuflidin, (175),		
	(186) montanin D, (188)		
T. micro podioides Rouy	(219), (220) teumicropodin,	200	
	(227) teumicropin, (228), (229)		
T. hyrcanicum	(163) teucrin H1	201, 202	also teuflidin
	(172) teucrin H2		also teuchamaedryn B
	(194) teucrin H3	203—208	
	(169) teucrin H4		
T. spinosum	(194), (250) teuspinin, (251)		*X*-Ray structure (251)
T. botrys	(88) teucvidirn, (175),	162	
	(184) teuchamaedryn C		
	(186) montanin D		
	(235), (269) teubotryn		identical to teulamifin B (ref. 161)
T. africanum	(243) tafricanin A	209	
	(244) tafricanin B		*X*-Ray structure
T. salviastrum	(88) teucvidin	210	
	(185) teucroxide		
	(267) teusalvin A		
	(268) teusalvin B		
	(236) teusalvin C		
	(237) teusalvin D		
	(270) teusalvin E		
	(271) teusalvin F		*X*-Ray structure
T. lepicephalum	(221) teulepicin, (222)	211	
	(259) teulepicephin		
T. buxifolium	(194), (222)	211	
Genus – *Salvia* Species			
S. rubescense	(272)	212	no stereochem.
S. coccinea	(273) salviacoccin	213	
S. plebia	(273) salviacoccin, (276)	214	
S. greggii	(277)	215	
S. splendens	(274) salviarin,	216	
	(275) splendidin		
S. lineata	(278), (279), (282)	217, 218	
S. gesneraefolia	(283) gesnerofolin A	219	no stereochem.
	(284) gesnerifolin B		no stereochem.
S. sousae Ramamoorthy	(280), (285)	220	
S. languidula	(281) languiduline	221	
S. divinorum	(286) salvinorin	222	also divinorin A,
	(287) divinorin B	223	*X*-Ray structure
S. semiatratha	(288) semiatrin	224	*X*-Ray structure
	(289)	225	see Compositae

Table 11 Clerodanes from Labiatae (*continued*)

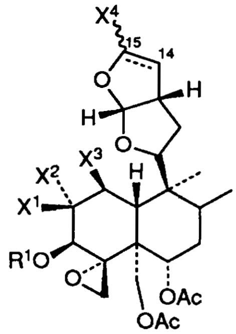
Species	Compounds	Ref.	Comments
Genus – *Ajuga*			
S. keerlii	(290) kerlinolide	226	
	(291) kerlin		*X*-Ray structure
	(292) kerlinic acid	227	
S. lasiantha	(293) lasianthin	228	
S. breviflora	(295) brevifloralactone	229	
	(296)		
S. melissodora	(295) brevifloralactone	230, 231	
	(289), (294),		
	(297)—(305)		
	(67) portulide C		see Portulacaceae
S. microphylla	(289)	232	
S. farinacea	(306) salvifaricin	233—235	
	(307) salvifarin		*X*-Ray structure
Genus – *Leonurus*			
L. cardiaca	(308)	236	
L. marrubiastrum	(309) marrubiaside	237	
	(310) marrubialactone		
Genus – *Stachys*			
S. annua	(311) stachysolone		also annuanone
	(312) stachylone	238—241	
	(313) stachone		
S. recta	(314)—(316)	242, 243	
Genus – *Scutellaria*			
S. woronowii	(318) jodrellin A	244	
Juz	(319) jodrellin B		
S. galericulaea			
	(317) galericulin	245	
	(319) jodrellin B		
	(320) jodrellin T, (321)		
S. rivularis	scuterivulactones A, B	246—249	no structures
Wall	(322) scuterivulactone C1		also scutellone A
	(323) scuterivulactone C2		
	(324) scutellone B		
	(325) scutellone C		
	(326) scuterivulactone D		also scutellone D,
	(327) scutellone E		*X*-Ray structure
	(328) scutellone F		



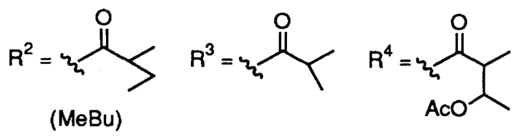
(135) $R^1 = CH_2OAc$, $R^2 = OH$, $R^3 = CH_2OH$, $R^4 = Ac$, $X^1 = X^2 = H$
(136) $R^1 = Me$, $R^2 = CO_2Me$, $R^3 = H$, $R^4 = Ac$, $X^1 = X^2 = H$
(137) $R^1 = R^3 = CH_2OAc$, $R^2 = OH$, $R^4 = H$, $X^1 = OMeBu$, $X^2 = OH$



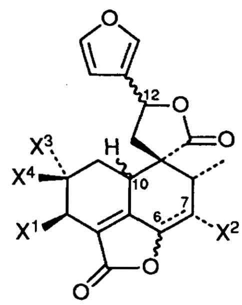
(138) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1 = X^2 = X^3 = X^4 = H$, 2–3 = Single
(139) $R^1 = CH_2OAc$, $R^2 = H$, $X^1 = X^2 = X^3 = X^4 = H$, 2–3 = Single
(140) $R^1 = Me$, $R^2 = Ac$, $X^1 = X^2 = X^3 = X^4 = OH$, 2–3 = Single
(141) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1 = OTig$, $X^2 = X^3 = X^4 = H$, 2–3 = Single
(142) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1 = OMeBu$, $X^2 = X^3 = H$, $X^4 = OH$, 2–3 = Single
(143) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1 = OMeBu$, $X^2 = X^3 = H$, $X^4 = OAc$, 2–3 = Single
(144) $R^1 = CH_2OAc$, $R^2 = H$, $X^1 = OMeBu$, $X^2 = X^3 = H$, $X^4 = OH$, 2–3 = Single
(145) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1 = X^4 = OH$, $X^2 = X^3 = H$, 2–3 = Single
(146) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1,X^2 = {=}O$, $X^3 = OMeBu$, $X^4 = H$, 2–3 = Single
(147) $R^1 = CH_2OAc$, $R^2 = Ac$, $X^1,X^2 = {=}O$, $X^3 = X^4 = H$, 2–3 = Double
(148) $R^1 = CH_2OH$, $R^2 = H$, $X^1 = X^2 = X^3 = X^4 = H$, 2–3 = Single



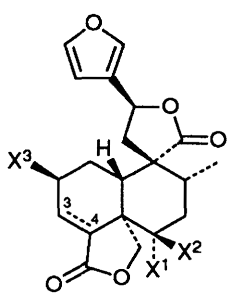
(149) $R^1 = H$, $X^1 = X^2 = X^4 = H$, $X^3 = OR^2$, 14–15 = Single
(150) $R^1 = R^3$, $X^1 = OH$, $X^2 = X^3 = X^4 = H$, 14–15 = Single
(151) $R^1 = R^3$, $X^1 = X^2 = X^3 = X^4 = H$, 14–15 = Single
(152) $R^1 = R^3$, $X^1 = OH$, $X^2 = X^3 = H$, $X^4 = OEt$, 14–15 = Single
(153) $R^1 = R^2$, $X^1 = OH$, $X^2 = X^3 = X^4 = H$, 14–15 = Single
(154) $R^1 = R^2$, $X^1 = X^3 = X^4 = H$, $X^2 = OH$, 14–15 = Double
(155) $R^1 = R^2$, $X^1 = X^3 = X^4 = H$, $X^2 = OH$, 14–15 = Single
(156) $R^1 = R^2$, $X^1 = X^3 = H$, $X^2 = OH$, $X^4 = OEt$, 14–15 = Single
(157) $R^1 = R^2$, $X^1 = X^3 = H$, $X^2 = X^4 = OH$, 14–15 = Single
(158) $R^1 = R^4$, $X^1 = X^3 = H$, $X^2 = X^4 = OH$, 14–15 = Single
(159) $R^1 = R^3$, $X^1 = OAc$, $X^2 = X^3 = X^4 = H$, 14–15 = Single



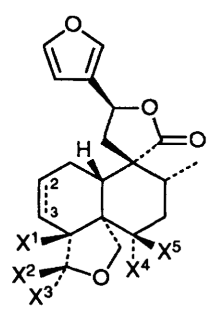
'southern' substitution patterns. This may be due to the Labiatae and the Verbenaceae families being of the same order (Lamiales). The *Teucrium* genus is the most prolific of all the clerodane producing genera, accounting for well over one hundred of the reported clerodanes, though this apparent productivity may, in part, be due to the extremely extensive investigation of this genus by the groups of Piozzi, Rodriguez, Savona, Malakov, and Papanov. Previous reviews of the clerodanes isolated from this genus have been published by Piozzi,[98,99] and Fujita,[100] along with a smaller review by Al-Hazimi and Miana.[101] These authors have also reviewed the clerodanes of the *Salvia*,[102] as has Rodriguez-Hahn and co-workers.[103] The *Teucria*, and the less prolific genera of the Labiatae, show a strong tendency to give compounds with a 3-furyl substituted spiro-γ-lactone at the C-9 position, and give almost exclusively *trans* compounds, or compounds with sp^2 hybridization at C-5. Compounds originating from *Teucrium* also all show oxidation at the C-6 position.



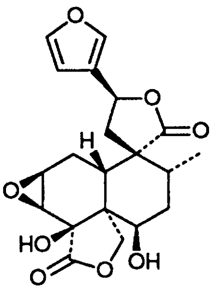
(88) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = β, C-10–H = α, C-12–Fur = β
(89) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = α, C-10–H = β, C-12–Fur = β
(160) $X^1 = X^3 = X^4 = H$, $X^2 = OH$, 6–7 = Single, C-6–O = α, C-10–H = β, C-12–Fur = β
(161) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = β, C-10–H = β, C-12–Fur = β
(162) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = β, C-10–H = β, C-12–Fur = α
(163) $X^1 = OH$, $X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = β, C-10–H = α, C-12–Fur = β
(164) $X^1 = OH$, $X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = α, C-10–H = β, C-12–Fur = β
(165) $X^1 = X^2 = X^3 = H$, $X^4 = OH$, 6–7 = Single, C-6–O = β, C-10–H = α, C-12–Fur = β
(166) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Double, C-6–O = -, C-10–H = β, C-12–Fur = β
(167) $X^1 = X^2 = X^4 = H$, $X^3 = OH$, 6–7 = Double, C-6–O = -, C-10–H = β, C-12–Fur = β
(168) $X^1 = X^2 = X^3 = X^4 = H$, 6–7 = Single, C-6–O = α, C-10–H = β, C-12–Fur = α
(169) $X^1 = X^2 = X^4 = H$, $X^3 = OH$, 6–7 = Single, C-6–O = β, C-10–H = β, C-12–Fur = β

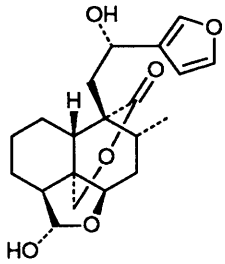


(170) $X^1 = H$, $X^2 = X^3 = OH$, 3–4 = Single, C-4–H = β
(171) $X^1 = OH$, $X^2 = X^3 = H$, 3–4 = Single, C-4–H = β
(172) $X^1 = X^3 = H$, $X^2 = OH$, 3–4 = Single, C-4–H = β
(173) $X^1 = H$, $X^2 = X^3 = OH$, 3–4 = Double, C-4–H = -
(174) $X^1 = OH$, $X^2 = X^3 = H$, 3–4 = Double, C-4–H = -
(175) $X^1 = X^3 = H$, $X^2 = OH$, 3–4 = Double, C-4–H = -
(176) $X^1 = X^3 = OH$, $X^2 = H$, 3–4 = Double, C-4–H = -
(177) $X^1,X^2 = {=O}$, $X^3 = H$, 3–4 = Double, C-4–H = -
(178) $X^1,X^2 = {=O}$, $X^3 = OH$, 3–4 = Double, C-4–H = -
(179) $X^1,X^2 = {=O}$, $X^3 = H$, 3–4 = Single, C-4–H = β



(180) $X^1 = X^5 = OH$, $X^2,X^3 = {=O}$, $X^4 = H$, 2–3 = Double
(181) $X^1 = X^3 = H$, $X^2 = OH$, $X^4,X^5 = {=O}$, 2–3 = Single
(182) $X^1 = X^5 = H$, $X^2,X^3 = {=O}$, $X^4 = OH$, 2–3 = Double


(183)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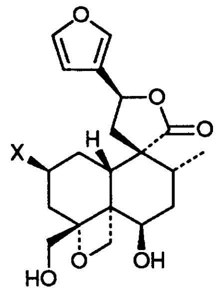
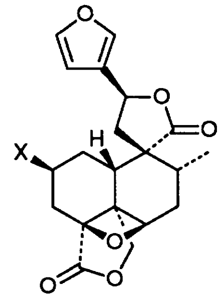
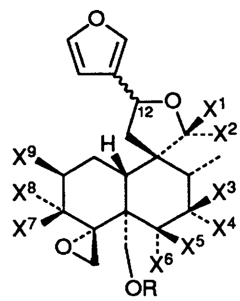
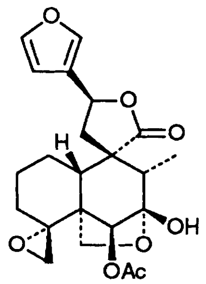

(185) X = OH
(186) X = H


(187) X = OH
(188) X = H



(189) R = Ac, X^1,X^2 = =O, X^3,X^4 = =O, X^5 = OH, $X^6 = X^7 = X^8 = X^9$ = H, C-12–Fur = β
(190) R = Ac, X^1,X^2 = =O, X^3,X^4 = =O, X^5 = OAc, $X^6 = X^7 = X^8 = X^9$ = H, C-12–Fur = β
(191) R = Ac, X^1,X^2 = =O, $X^3 = X^7 = X^8 = X^9$ = H, X^4 = OAc, X^5,X^6 = =O, C-12–Fur = β
(192) R = Ac, X^1,X^2 = =O, $X^3 = X^5 = X^7 = X^8 = X^9$ = H, X^4 = OH, X^6 = OAc, C-12–Fur = β
(193) R = Ac, X^1,X^2 = =O, $X^3 = X^7 = X^8 = X^9$ = H, X^4 = OH, X^5,X^6 = =O, C-12–Fur = β
(194) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(195) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OH, C-12–Fur = β
(196) R = Ac, $X^1 = X^5 = X^7 = X^8 = X^9$ = H, X^2 = OAc, X^3,X^4 = =O, X^6 = OH, C-12–Fur = β
(197) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OH, C-12–Fur = α
(198) R = H, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OAc, C-12–Fur = β
(199) R = H, X^1,X^2 = =O, X^3 = OAc, $X^4 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(200) R = Ac, X^1 = OAc, $X^2 = X^3 = X^4 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(201) R = Ac, X^1,X^2 = =O, X^3 = OAc, $X^4 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(202) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OAc, C-12–Fur = α
(203) R = Ac, X^1 = OAc, $X^2 = X^3 = X^7 = X^8 = X^9$ = H, X^4 = OH, X^5,X^6 = =O, C-12–Fur = β
(204) R = Ac, X^1 = OAc, $X^2 = X^5 = X^7 = X^8 = X^9$ = H, X^3,X^4 = =O, X^6 = OH, C-12–Fur = β
(205) R = Ac, X^1 = OAc, $X^2 = X^3 = X^4 = X^8 = X^9$ = H, X^5,X^6 = =O, X^7 = OAc, C-12–Fur = β
(206) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^6 = X^7 = X^8 = X^9$ = H, X^5 = OH, C-12–Fur = β
(207) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^8 = X^9$ = H, X^6 = OAc, X^7 = OH, C-12–Fur = α
(208) R = H, X^1,X^2 = =O, $X^3 = X^4 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(209) R = Ac, $X^1 = X^4$ = OH, $X^2 = X^3 = X^7 = X^8 = X^9$ = H, X^5,X^6 = =O, C-12–Fur = β
(210) R = Ac, $X^1 = X^3 = X^4 = X^8 = X^9$ = H, $X^2 = X^7$ = OAc, X^5,X^6 = =O, C-12–Fur = β
(211) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^8 = X^9$ = H, $X^6 = X^7$ = OAc, C-12–Fur = α
(212) R = Ac, $X^1 = X^3 = X^4 = X^5 = X^8 = X^9$ = H, $X^2 = X^6 = X^7$ = OAc, C-12–Fur = β
(213) R = Ac, $X^1 = X^3 = X^4 = X^6 = X^9$ = H, $X^2 = X^5$ = OH, X^7,X^8 = =O, C-12–Fur = β
(214) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^6 = X^7 = X^8$ = H, $X^5 = X^9$ = OH, C-12–Fur = β
(215) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OAc, C-12–Fur = β
(216) R = Ac, $X^1 = X^3 = X^4 = X^5 = X^8 = X^9$ = H, $X^2 = X^7$ = OAc, X^6 = OH, C-12–Fur = β
(217) R = Ac, $X^1 = X^3 = X^4 = X^5 = X^8 = X^9$ = H, $X^2 = X^6$ = OH, X^7 = OAc, C-12–Fur = β
(218) R = H, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^7 = X^8 = X^9$ = H, X^6 = OAc, C-12–Fur = α
(219) R = Ac, X^1 = OAc, $X^2 = X^3 = X^4 = X^8 = X^9$ = H, X^5,X^6 = =O, X^7 = OH, C-12–Fur = β
(220) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^5 = X^8 = X^9$ = H, X^6 = OH, X^7 = OAc, C-12–Fur = β
(221) R = H, X^1,X^2 = =O, $X^3 = X^4 = X^8 = X^9$ = H, X^5,X^6 = =O, X^7 = OH, C-12–Fur = β
(222) R = Ac, X^1,X^2 = =O, $X^3 = X^4 = X^8 = X^9$ = H, X^5,X^6 = =O, X^7 = OH, C-12–Fur = β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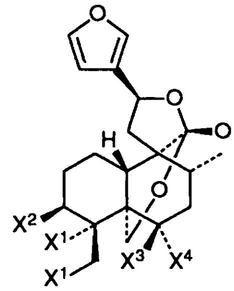
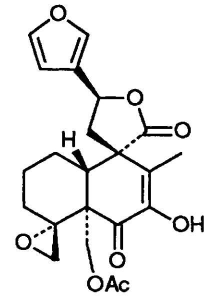

(224) X^1 = –O–, X^2 = H, X^3,X^4 = =O
(225) X^1 = OH, X^2 = H, X^3,X^4 = =O
(226) X^1 = –O–, X^2 = OAc, X^3,X^4 = =O
(227) X^1 = –O–, X^2 = X^3 = OH, X^4 = H
(228) X^1 = –O–, X^2 = OAc, X^3 = OH, X^4 = H
(229) X^1 = –O–, X^2 = OH, X^3,X^4 = =O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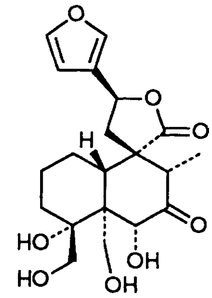
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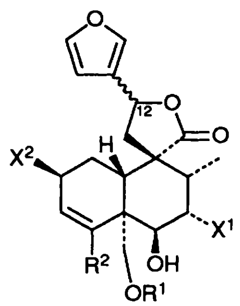
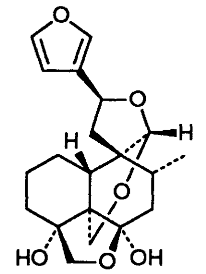

(232) R^1 = Ac, R^2 = CH_2OH, X^1 = OH, X^2 = H, C-12–Fur = β
(233) R^1 = Ac, R^2 = CH_2OH, X^1 = X^2 = H, C-12–Fur = β
(234) R^1 = Ac, R^2 = CHO, X^1 = X^2 = H, C-12–Fur = β
(235) R^1 = H, R^2 = CH_2OH, X^1 = X^2 = H, C-12–Fur = β
(236) R^1 = H, R^2 = CH_2OH, X^1 = X^2 = H, C-12–Fur = α
(237) R^1 = H, R^2 = CH_2OH, X^1 = H, X^2 = OH, C-12–Fur = β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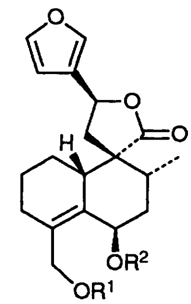
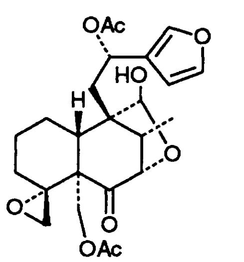

(239) R^1 = R^2 = H
(240) R^1 = Ac, R^2 = Gluc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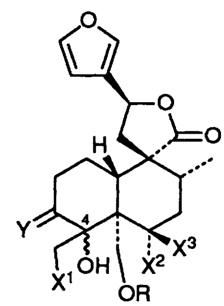
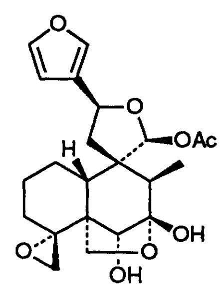

(242) R = H, X^1 = X^3 = OH, X^2 = H, Y = H_2, C-4–OH = β
(243) R = Ac, X^1 = Cl, X^2,X^3 = =O, Y = O, C-4–OH = α
(244) R = Ac, X^1 = Cl, X^2 = OAc, X^3 = H, Y = O, C-4–OH = α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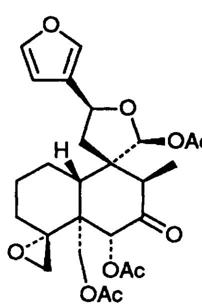
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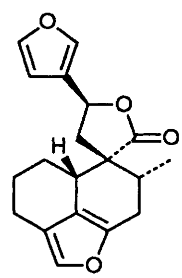
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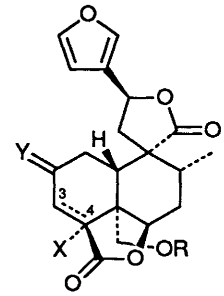
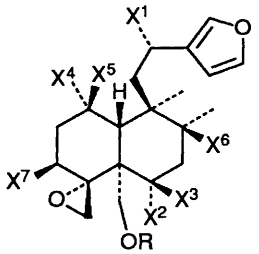
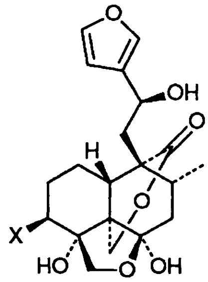
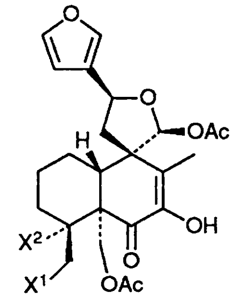

(248) R = H, X = -, Y = H_2, 3–4 = Double
(249) R = H, X = H, Y = O, 3–4 = Single
(250) R = H, X = OH, Y = H_2, 3–4 = Single
(251) R = Ac, X = OH, Y = H_2, 3–4 = Single



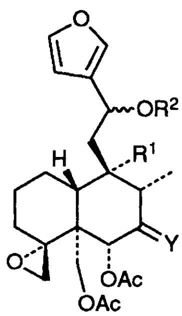
(252) R = H, $X^1 = X^2$ = OH, $X^3 = X^4 = X^5 = X^6 = X^7$ = H
(253) R = Ac, X^1 = OH, X^2 = OAc, $X^3 = X^4 = X^5 = X^6 = X^7$ = H
(254) R = Ac, $X^1 = X^5 = X^6 = X^7$ = H, X^2,X^3 = =O, X^4 = OH
(255) R = Ac, $X^1 = X^2 = X^6 = X^7$ = H, X^3 = OH, X^4,X^5 = =O
(256) R = Ac, $X^1 = X^5 = X^7$ = H, X^2,X^3 = =O, $X^4 = X^6$ = OH
(257) R = H, $X^1 = X^7$ = OH, X^2 = OAc, $X^3 = X^4 = X^5 = X^6$ = H



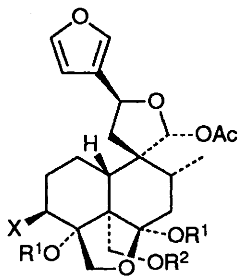
(258) X = H
(259) X = OH



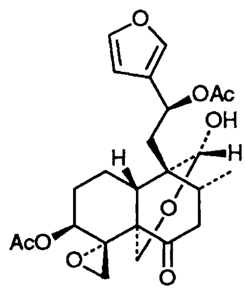
(260) X^1 = Cl, X^2 = OH
(261) X^1,X^2 = –O–



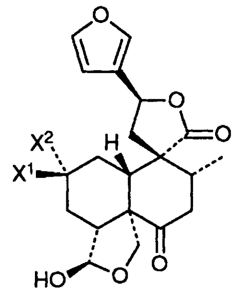
(262) R^1 = CHO, R^2 = Ac, Y = O
(263) R^1 = CH_2OH, R^2 = H, Y = H_2



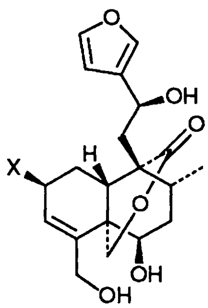
(264) R^1 = H, R^2 = Ac, X = H
(265) R^1,R^2 = MeC<, X = OH



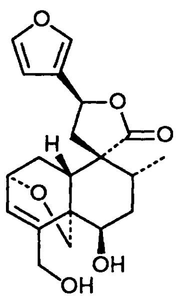
(266)



(267) X^1,X^2 = =O
(268) X^1 = OH, X^2 = H



(269) X = H
(270) X = OH



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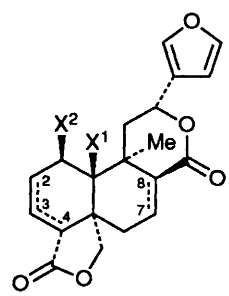
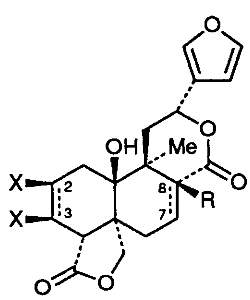
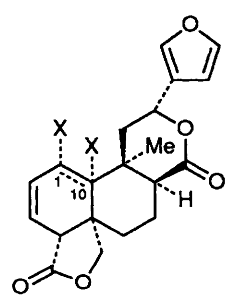


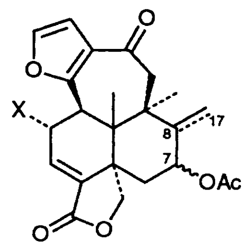
(272)* X^1 = OH, X^2 = H, 2–3 = Single, 3–4 = Double, 7–8 = Single
(273) X^1 = OH, X^2 = H, 2–3 = Double, 3–4 = Single, 7–8 = Double
(274) $X^1 = X^2$ = H, 2–3 = Double, 3–4 = Single, 7–8 = Single
(275) X^1 = H, X^2 = OAc, 2–3 = Double, 3–4 = Single, 7–8 = Single
* No assigned stereochem.



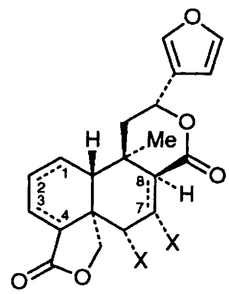
(276) R = -, X = –O–, 2–3 = Single, 7–8 = Double
(277) R = H, X = H, 2–3 = Double, 7–8 = Single



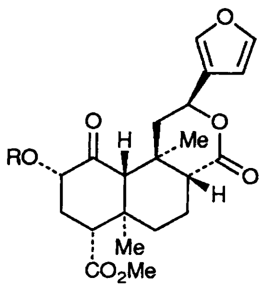
(278) X = H, 1–10 = Double
(279) X = –O–, 1–10 = Single



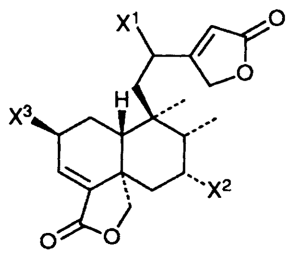
(280) X = OH, 8–17 = Single, C-7–OAc = α, C-8–Me = α
(281) X = H, 8–17 = Double, C-7–OAc = β, C-8–Me = -



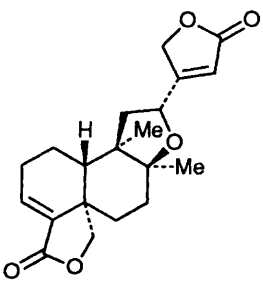
(282) X = H, 1–2 = Double, 3–4 = Double, 7–8 = Single
(283)* X = H, 1–2 = Double, 3–4 = Single, 7–8 = Single
(284)* X = H, 1–2 = Double, 3–4 = Double, 7–8 = Double
(285) X = –O–, 1–2 = Single, 3–4 = Double, 7–8 = Single
* No assigned stereochem.



(286) R = Ac
(287) R = H



(288) $X^1 = X^3$ = OH, X^2 = H
(289) $X^1 = X^3$ = H, X^2 = OH
(290) X^1 = OH, X^2 = OAc, X^3 = H



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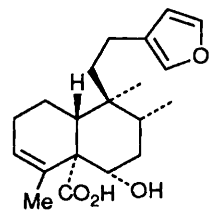

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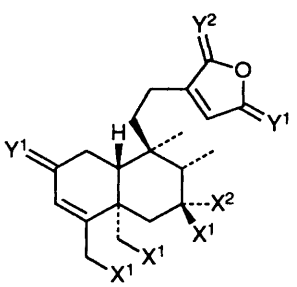
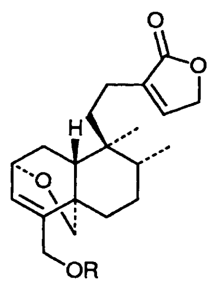
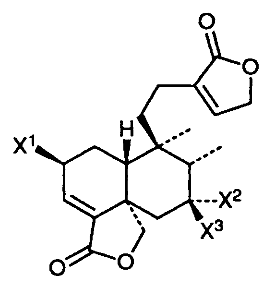


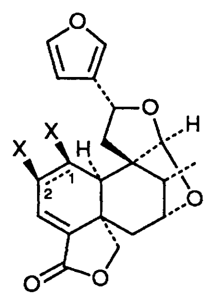
(293) X^1 = H, X^2 = OAc, Y^1 = O, $Y^2 = H_2$
(294) X^1 = OH, X^2 = H, $Y^1 = H_2$, Y^2 = O



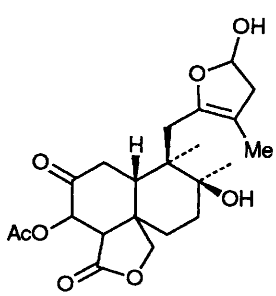
(295) R = H
(296) R = Ac



(297) X^1 = OH, X^2 = OAc, X^3 = H
(298) $X^1 = X^2$ = H, X^3 = OH
(299) $X^1 = X^3$ = H, X^2 = OH
(300) $X^1 = X^3$ = H, X^2 = OAc
(301) $X^1 = X^2$ = OH, X^3 = H
(302) X^1 = OAc, X^2 = OH, X^3 = H
(303) X^1 = H, X^2,X^3 = =O
(304) X^1 = OH, $X^2 = X^3$ = H
(305) X^1 = OH, X^2,X^3 = =O



(306) X = H, 1–2 = Double
(307) X = –O–, 1–2 = Single



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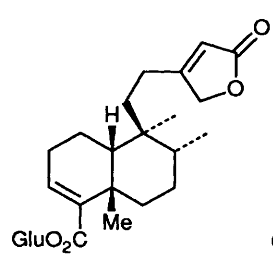

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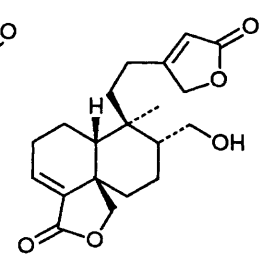

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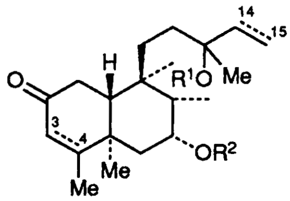
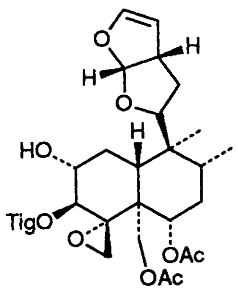
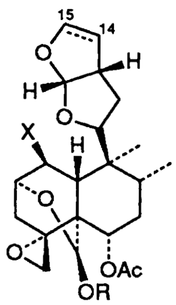


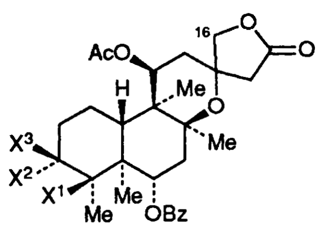
(311) $R^1 = R^2 = H$, 3–4 = Double, 14–15 = Double
(312) $R^1 = R^2 = H$, 3–4 = Single, 14–15 = Double
(313) $R^1 = R^2 = H$, 3–4 = Single, 14–15 = Single
(314) $R^1 = H$, $R^2 = Ac$, 3–4 = Double, 14–15 = Double
(315) $R^1 = Ac$, $R^2 = H$, 3–4 = Double, 14–15 = Double
(316) $R^1 = R^2 = Ac$, 3–4 = Double, 14–15 = Double



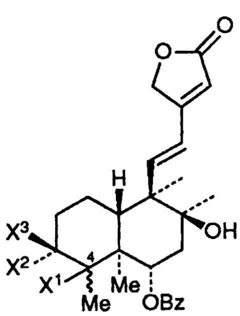
(317)



(318) R = Ac, X = H, 14–15 = Double
(319) R = CO^{i}Pr, X = H, 14–15 = Double
(320) R = Ac, X = OTig, 14–15 = Double
(321) R = Ac, X = OTig, 14–15 = Single



(322) $X^1 = X^2 = OH$, $X^3 = H$, C-16 = β
(323) $X^1 = X^2 = OH$, $X^3 = H$, C-16 = α
(324) $X^1 = H$, X^2,X^3 = =O, C-16 = β
(325) $X^1 = X^3 = OH$, $X^2 = H$, C-16 = -

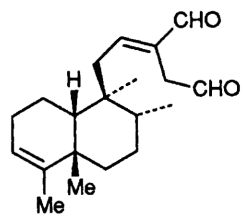


(326) $X^1 = X^2 = OH$, $X^3 = H$, C-4–Me = α
(327) $X^1 = H$, X^2,X^3 = =O, C-4–Me = α
(328) X^1,X^2 = –O–, $X^3 = H$, C-4–Me = β

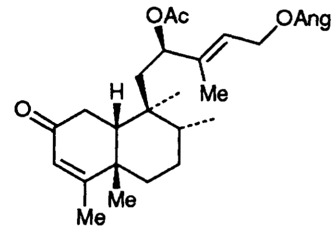
Table 12 Clerodanes from Scrophulariaceae

Genus – *Linaria*

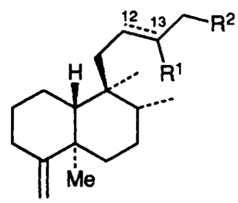
Species	Compounds	Ref.	Comments
L. japonica Miq	(329) linaridial (330) linarienone	250—254	
L. saxitalis	(331) isolinaridial (332)—(350)	255—257	



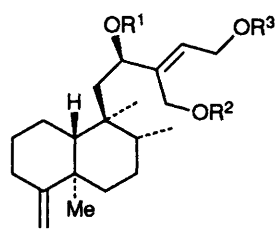
(329)



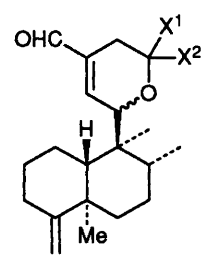
(330)



(331) $R^1 = R^2 = CHO$, 12–13 = Double
(332) $R^1 = Me$, $R^2 = CHO$, 12–13 = Double
(333) $R^1 = Me$, $R^2 = CHO$, 12–13 = Single
(334) $R^1 = R^2 = CH_2OAc$, 12–13 = Double



(335) $R^1 = R^2 = R^3 = Ac$
(336) $R^1 = H$, $R^2 = R^3 = Ac$
(337) $R^1 = R^3 = Ac$, $R^2 = H$
(338) $R^1 = R^2 = Ac$, $R^3 = H$



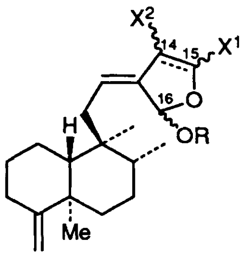
(339) X^1,X^2 = =O
(340) $X^1 = OAc$, $X^2 = H$

3.16 Family Scrophulariaceae

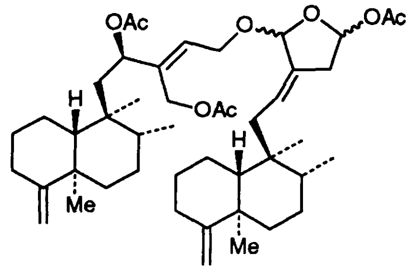
Clerodanes obtained from Scrophulariceae are shown in Table 12.

3.17 Family Compositae

As the largest family of angiosperms, with an estimated 19000 species,[8] it is not surprising that thirty-one genera have been shown to produce clerodanes (Table 13). The natural products isolated comprise both cis and trans compounds, though mainly trans clerodanes, and with a large variety of structures, though a tendency towards simple C-11–C-16 open chain



(341) R = Me, X^1 = X^2 = H, 14–15 = Double, 15/16 = -
(342) R = Me, X^1 = OMe, X^2 = H, 14–15 = Single, 15/16 = *cis*
(343) R = Me, X^1 = OMe, X^2 = H, 14–15 = Single, 15/16 = *trans*
(344) R = Ac, X^1 = OAc, X^2 = H, 14–15 = Single, 15/16 = *cis*
(345) R = Ac, X^1 = OAc, X^2 = H, 14–15 = Single, 15/16 = *trans*
(346) R = Me, X^1 = OAc, X^2 = H, 14–15 = Single, 15/16 = *cis*
(347) R = Me, X^1 = OAc, X^2 = H, 14–15 = Single, 15/16 = *trans*
(348) R = Me, X^1 = OAc, X^2 = OH, 14–15 = Single, 15/16 = *cis*
(349) R = Me, X^1 = OAc, X^2 = OH, 14–15 = Single, 15/16 = *trans*



(350)

Table 13 Clerodanes from Compositae

Genus – *Solidago* Species	Compounds	Ref.	Comments
S. altissima	(30) kolavenol,	261—263	for both see
	(31) kolavenic acid		Caesalpinaceae
	(359), (368),	264—266	Aristolochiaceae
	(369)—(372)		
	(373) solidagonic acid	261—271	
	(400) solidagolactone I		
	(351) solidagolactone II		also elongatolide C
	(352) solidagolactone III		
	(353) solidagolactone IV		also elongatolide A
	(354) solidagolactone V		
	(355) elongatolide B		
	(363) solidagolactone VI		also elongatolide D
	(364) solidagolactone VII		also elongatolide E
	(365) solidagolactone VIII		
	(13), (360)	272	see Arostolachiaceae
	(361)	273	
S. elongata Nutt	(353) elongatolide A	274	see above
	(355) elongatolide B		
	(351) elongatolide C		see above
	(363) elongatolide D		see above
	(28) kolavelool (32), (374)		see Casaelpinaceae
	(401), (402), (416), (417), (420)		Aristolochiaceae
S. vigauria	(351) solidagolactone II	275	
	(352) solidagolactone III		
	(354) solidagolactone V		
	(364) solidagolactone VII		
	(365) solidagolactone VIII		
	(356)—(358), (421)—(424)		
S. gigantea sub *serotina*	(425) solidagonic acid A	276	
	(426) solidagonic acid B	276—279	
	(427)—(438)		see *Eupatorium*
S. arguta Ait	(439)—(444)	280—284	(44) *X*-Ray structure
S. serotina Ait	(9), (445), (452), (453), (456),	284, 285	(9) see Annonaceae
	(457), (418), (471), (472)	286, 287	see *Ageratina*
S. shortii	(366), (367)	280, 288	(366) *X*-Ray structure
S. juncea Ait	(446) junceic acid, 447	289	
S. chiliensis	(446) junceic acid	290	
S. canadensis	(500) rugosolide	291	
Genus – *Baccharis* Species			
B. tricuneata	(464) bacchotricuneatin A	292, 293	*X*-Ray structure
	(510) bacchotricuneatin B		*X*-Ray structure
	(514) bacchotricuneatin C		
	(479) bacchotricuneatin D		
B. cassinaefolia D.C.	(511), (512)	294	
B. nitida	(513)	295	

Table 13 Clerodanes from Compositae (*continued*)

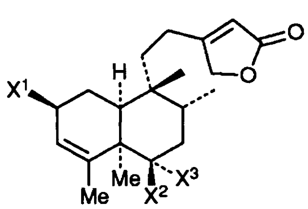
Genus – *Solidago* Species	Compounds	Ref.	Comments
B. artemisiodes	(515) bartemidiolide	296	
B. kingii	(480) kingidiol	297	
B. incarum Wedd	(115) bacchalineol	298	see Sapindaceae
	(375) bincatriol		
	(481) barticulidiol		
	(376), (403), (465), (466), (501)	299	
B. articulata	(464) bacchotricuneatin A	300	
	(482)		
B. calvescens	(103) hautriwaic acid	294	for next five see
B. chilko HBK	(103) hautriwaic acid	295	Euphorbiateae,
B. sarothroides	(103) hautriwaic acid	301	Sapindaceae
	(487)		
B. vaccinoides	(103) hautriwaic acid	301	
B. macrei	(103) hautriwaic acid	302	
	(76) hardwickiic acid		see Leguminosae,
	(516) bacchasmacranone		Casaelpinaceae,
	(517),		Euphorbiaceae
	(483), (518)	303	see *Conyza* (483)
B. boliviensis	(362), (377)—(382)	304	
(Wedd) Cuatr	(448)—(451), (473)		
	(474), (484), bacchabolivic acid		
	(485), (486)		
B. obtusifolia HBK	(516) bacchasmacranone	304	
	(519), (520)		
B. conferta	(520)	305	
B. crispa Sprengel	(103), hautriwaic acid	306, 307	see Sapindaceae,
	(519), (521)		Euphorbiaceae
B. scoparia	(522), (523)	295	
B. hutchinsonii	(9), (488)	295	(9) see Annonacea, *Solidago*
B. trimera Less	(289), (525), (526)	308	(281) see Labiatae, (289, 525,
	(404), (535)	304	and 526) all *X*-Ray structure
B. genistelloides	(289), (525), (527), (531)	309, 310	
B. microcephala	(527)	311	
B. alerternoides	(405), (406), (536), (537)	311	
B. grandicapitata	(407)	295	
B. rhomboidalis	(408)—(410), (528), (538),	312	
	(539)		
B. tucamanensis	(475) tucamanoic acid	313	
B. magellanica Pers	(510) bacchotricuneatin B	314	
	(549) bacchomagellin A		
	(550) bacchomagellin B		
	(502)	315	see *Grangea*
B. peruviana Cuatr	(549) bacchomagellin A	304	
	(550) bacchomagellin B		
B. patagonica	(549) bacchomagellin A	315	
Hook & Arn	(550) bacchomagellin B		
	(502)		see *Grangea*
B. gilliesi	(510) bacchotricuneatin B	314	
B. salicifolia	(383) bacchasalicyclic	314	
Pers	acid, (384), (385),		
	(103) hautriwaic acid	316	see Sapindaceae, Euphorbiaceae
	(118)		see Sapindaceae
	(489), (503)		(489) see *Conyza*
B. flabellata	(490)	317	see *Conyza*
B. rhetinodes	(464) bacchotricuneatin A	314	
Meyen & Walp	(482), (492)		
B. marginalis	(532)	318	
B. Pedicellata	(408), (529)	318	
B. paniculata	(411), (412)	319	
sub *floribunda*			
Genus – *Symphiopappus* Species			
S. itatiagensis	(533), (534)	320	
S. reticulatus	(386)—(392), (540), (541),	321	
	(542), (553)		
S. compressus	(413), (419), (458)	321	
Genus – *Conyza* Species			
C. ivaefolia Less	(103) hautriwaic acid	322	see Sapindaceae, Euphorbiaceae

Table 13 Clerodanes from Compositae (*continued*)

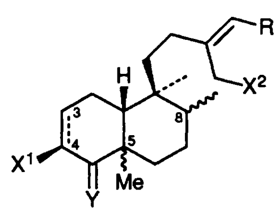
Genus – *Solidago* Species	Compounds	Ref.	Comments
C. scabrida D.C	(103) hautriwaic acid	323	see Sapindaceae, Euphorbiaceae
	(454), (455), (483), (489), (490), (504), (505), (570) (571) (493)—(495)		see *Baccharis*
C. podacephala	(467), (524)	324	
Genus – *Haplopappus*			
Species			
H. foliosus	(565) haplopappic acid	325	
H. angustifolia	(565) haplopappic acid	325	
H. ciliatus	(543) haplociliatic acid	326—328	*X*-Ray structure
H. paucindentatus Phil	(44), (566)—(568)	329	see Cistaceae
Genus – *Stevia*			
Species			
S. salicifolia	(572)	330	
S. polycephala	(573) stephalic acid	331	*X*-Ray structure
S. myriadenia	(393)	332	
Genus – *Acritopappus*			
Species			
A. hagei K & R	(394)—(397), (506), (507)	333	
A. longifolius	(15), (398), (400) solidagolactone I	334	(15) see Annonaceae see *Solidago*
Genus – *Ageratina*			
Species			
A. ixiocladon	(16) populifolic acid (17), (476), (574)—(579) (606)	335	for (16), (17) see Cistaceae, Aristolochiaceae
A. saltillensis	(418), (551), (552), (580)—(588)	285	(418) see *Solidago*
Genus – *Nidorella*			
Species			
N. agria	(589) nidorellalactone (590) isonidorellalactone	336	
N. residifolia	(591) methyl nidoresate	336	
Genus – *Olearia*			
Species			
O. muelleri	(496)	337	no sterochem at C-2 – see cpd (487)
O. heterocarpa	(530) olearin	338	
Genus – *Liatris*			
Species			
L. scariosa	(544)	339	
L. spicata	(464) bacchotricuneatin A (468)	340	see *Baccharis*
Genus – *Hartwrightia*			
Species			
H. floridana	(16) populifolic acid (459)	341	see Cistaceae
Genus – *Bahianthus*			
Species			
B. viscidus	(414), (415)	342	
Genus – *Hinterhubera*			
Species			
H. imbricata Cuatr.	(593)—(595)	343	
Genus – *Aster*			
Species			
A. alpinus	(469), (596)	344	
Genus – *Heteropappus*			
Species			
H. altaicus	(497), (600), (601)	345	
Genus – *Fleischmannia*			
Species			
F. sinclairii	(16) populifolic acid (31) kolavenic acid	346	see Cistaceae see Caesalpinaceae, Aristolochiaceae
F. microstemen K & R	(16) populifolic acid (31) kolavenic acid	347	see Cistaceae see Caesalpinaceae, Aristolochiaceae
F. gracilenta K & R	(16) populifolic acid	347	see Cistaceae
Genus – *Melampodium*			
Species			
M. divaricatum	(30) kolavenol	348	see *Solidago*, Caesalpinaceae, Aristolochiaceae

Table 13 Clerodanes from Compositae (*continued*)

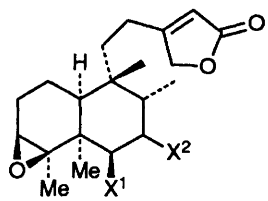
Genus – *Solidago* Species	Compounds	Ref.	Comments
Genus – *Pulicaria*			
Species			
P. gnaphalodes	(592)	349	
P. salviifolia	(399) salvicin	350, 351	*X*-Ray structure
Genus – *Goyazianthus*			
Species			
G. tetrastichus	(460)—(463), (477), (478)	352	
Genus – *Gochnata*			
Species			
G. paniculata	(554)—(557), (604), (605)	353	
Genus – *Chromolaena*			
Species			
C. laevigata	(607)—(611)	354	
C. connivens	(545)—(548)	355	
Genus – *Gutierezzia*			
Species			
G. dracunculoides	(612)	356	
G. texana	(613), (614), (615)—(622)	357, 358	(614) *X*-Ray structure
Genus – *Macowania*			
Species			
M. glandulosa	(569)	359	
Genus – *Chiliotrichium*			
Species			
C. rosmarinifolium	(623) chiliomarin	360	
Genus – *Eupatorium*			
Species			
E. cannabium	(436)	361	see *Solidago*
Genus – *Vittadinia*			
Species			
V. gracilis	(470), (624)	362	
Genus – *Plazia*			
Species			
P. daphnoides	(30) kolavenol	363	see *Solidago*, Caesalpinaceae, Aristolochiaceae
Genus – *Rhynchospermum*			
Species			
R. verticillatum	(597) rhynchosperin A (598) rhynchosperin B (599) rhynchosperin C (602) rhynchospermoside A (603) rhynchospermoside B	364	
Genus – *Grangea*			
Species			
G. maderaspatana	(76) hardwickiic acid (498), (499), (502), (508), (509), (625)	365	see Leguminosae, Caesalpinaceae (502) See *Baccharis*
Genus – *Vanclevia*			
Species			
V. stylosa	(558) vanclevic acid A (559) vanclevic acid B (560)—(564), (626)—(637)	366	



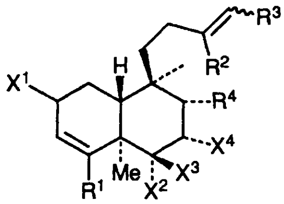
(351) $X^1 = X^3 = H$, $X^2 = OAng$
(352) $X^1 = X^3 = H$, $X^2 = OTig$
(353) $X^1 = X^3 = H$, $X^2 = OH$
(354) $X^1 = H$, $X^2,X^3 = {=}O$
(355) $X^1 = X^3 = H$, $X^2 = OAc$
(356) $X^1 = OH$, $X^2 = OAng$, $X^3 = H$
(357) $X^1 = OH$, $X^2 = OTig$, $X^3 = H$
(358) $X^1 = OH$, $X^2,X^3 = {=}O$



(359) $R = CO_2Me$, $X^1 = X^2 = H$, $Y = O$, C-5–Me = α, C-8–Me = α, 3–4 = Double
(360) $R = CO_2Me$, $X^1 = OOH$, $X^2 = H$, $Y = CH_2$, C-5–Me = α, C-8–Me = α, 3–4 = Single
(361) $R = CO_2Me$, $X^1 = OOH$, $X^2 = H$, $Y = CH_2$, C-5–Me = β, C-8–Me = β, 3–4 = Single
(362) $R = CH_2OH$, $X^1 = H$, $X^2 = OH$, $Y = CH_2$, C-5–Me = α, C-8–Me = α, 3–4 = Double

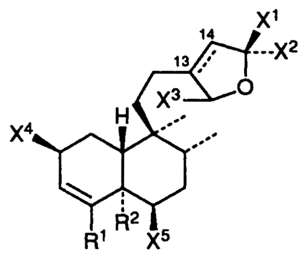


(363) X^1 = OAc, X^2 = H
(364) X^1 = OAng, X^2 = H
(365) X^1 = OTig, X^2 = H
(366) X^1 = X^2 = H
(367) X^1 = H, X^2 = OAng

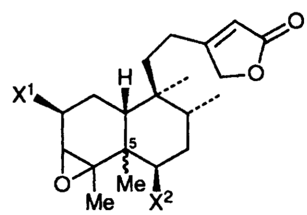


(30) $R^1 = R^2 = R^4$ = Me, R^3 = CH_2OH, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(31) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2H, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(32) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(368) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2H, $X^1 = X^2 = X^4$ = H, X^3 = OAng, R^2,R^3 = *cis*
(369) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2H, $X^1 = X^2 = X^4$ = H, X^3 = OTig, R^2,R^3 = *cis*
(370) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, $X^1 = X^2 = X^4$ = H, X^3 = OAng, R^2,R^3 = *cis*
(371) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, $X^1 = X^2 = X^4$ = H, X^3 = OTig, R^2,R^3 = *cis*
(372) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, $X^1 = X^4$ = H, X^2,X^3 = =O, R^2,R^3 = *cis*
(373) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2H, $X^1 = X^2 = X^3$ = H, X^4 = OAc, R^2,R^3 = *cis*
(374) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, $X^1 = X^2 = X^4$ = H, X^3 = OAc, R^2,R^3 = *cis*
(375) $R^1 = R^2 = R^3$ = CH_2OH, R^4 = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(376) $R^1 = R^3$ = CH_2OAc, $R^2 = R^4$ = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(377) R^1 = Me, $R^2 = R^3$ = CH_2OH, R^4 = CO_2H, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(378) R^1 = Me, $R^2 = R^3 = R^4$ = CH_2OH, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(379) R^1 = Me, $R^2 = R^3$ = CH_2OH, R^4 = CH_2OXyl, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(380) $R^1 = R^4$ = Me, R^2 = CH_2OXyl, R^3 = CH_2OH, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(381) $R^1 = R^4$ = Me, $R^2 = R^3$ = CH_2OH, X^1 = βOMe, $X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(382) $R^1 = R^2 = R^4$ = Me, R^3 = CH_2OH, X^1 = αOH, $X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(383) $R^1 = R^2$ = Me, R^3 = CH_2OH, R^4 = CO_2H, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(384) $R^1 = R^2$ = Me, R^3 = CH_2OH, R^4 = CO_2Xyl, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(385) R^1 = Me, $R^2 = R^3$ = CH_2OAc, R^4 = CO_2H, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(386) $R^1 = R^4$ = Me, R^2 = CH_2OH, R^3 = CHO, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(387) $R^1 = R^4$ = Me, R^2 = CH_2OH, R^3 = CHO, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(388) $R^1 = R^4$ = Me, R^2 = CO_2H, R^3 = CHO, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(389) $R^1 = R^4$ = Me, R^2 = CO_2H, R^3 = CHO, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(390) $R^1 = R^4$ = Me, $R^2 = R^3$ = CH_2OH, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(391) $R^1 = R^4$ = Me, R^2 = CH_2OH, R^3 = CH_2OR^1 $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(392) $R^1 = R^4$ = Me, R^2 = CH_2OH, R^3 = CH_2OR^2 $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(393) $R^1 = R^2 = R^4$ = Me, R^3 = CO_2Me, X^1 = βOAc, $X^2 = X^3 = X^4$ = H, R^2,R^3 = *trans*
(394) $R^1 = R^2$ = CH_2OH, R^3 = CO_2H, R^4 = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(395) R^1 = CHO, R^2 = CH_2OH, R^3 = CO_2H, R^4 = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(396) R^1 = CH_2OH, R^2 = CH_2OAc, R^3 = CO_2H, R^4 = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(397) R^1 = CHO, R^2 = CH_2OAc, R^3 = CO_2H, R^4 = Me, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(398) $R^1 = R^4$ = Me, R^2 = CH_2OH, R^3 = CO_2H, $X^1 = X^2 = X^3 = X^4$ = H, R^2,R^3 = *cis*
(399) R^1 = CO_2H, $R^2 = R^4$ = Me, R^3 = CH_2OH, $X^1 = X^3 = X^4$ = H, X^2 = OH, R^2,R^3 = *cis*

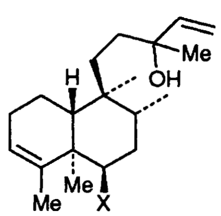
R^1 = $CO(CH_2)_{18}Me$ R^2 = $CO(CH_2)_{20}Me$



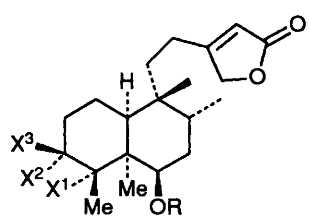
(15) $R^1 = R^2$ = Me, X^1,X^2 = =O, X^3 = OH, $X^4 = X^5$ = H, 13–14 = Double
(400) $R^1 = R^2$ = Me, X^1,X^2 = =O, $X^3 = X^4 = X^5$ = H, 13–14 = Double
(401) $R^1 = R^2$ = Me, X^1,X^2 = =O, $X^3 = X^4$ = H, X^5 = OAc, 13–14 = Double
(402) $R^1 = R^2$ = Me, X^1,X^2 = =O, $X^3 = X^4$ = H, X^5 = OAng, 13–14 = Double
(403) R^1 = CH_2OAc, R^2 = Me, X^1,X^2 = =O, X^3 = OMe, $X^4 = X^5$ = H, 13–14 = Double
(404) R^1 = CH_2OMal, R^2 = Me, X^1,X^2 = H,OMe, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(405) R^1 = CH_2OMal, R^2 = Me, $X^1 = X^3 = X^4 = X^5$ = H, X^2 = OH, 13–14 = Single
(406) R^1 = CH_2OMal, R^2 = Me, X^1 = OH, $X^2 = X^3 = X^4 = X^5$ = H, 13–14 = Single
(407) R^1 = CH_2OAc, R^2 = Me, X^1,X^2 = H,OMe, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(408) R^1 = CH_2OH, R^2 = Me, X^1,X^2 = H,OMe, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(409) $R^1 = R^2$ = CH_2OH, X^1,X^2 = H,OMe, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(410) $R^1 = R^2$ = CH_2OAc, X^1,X^2 = H,OMe, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(411) $R^1 = R^2$ = CH_2OH, X^1,X^2 = =O, $X^3 = X^4 = X^5$ = H, 13–14 = Double
(412) $R^1 = R^2$ = CH_2OAc, X^1,X^2 = =O, $X^3 = X^4 = X^5$ = H, 13–14 = Double
(413) $R^1 = R^2$ = Me, X^1,X^2 = =O, $X^3 = X^5$ = H, X^4 = OH, 13–14 = Double
(414) $R^1 = R^2$ = Me, X^1,X^2 = =O, $X^3 = X^4 = X^5$ = H, 13–14 = Single
(415) $R^1 = R^2$ = Me, X^1,X^2 = =O, X^3 = OH, $X^4 = X^5$ = H, 13–14 = Single



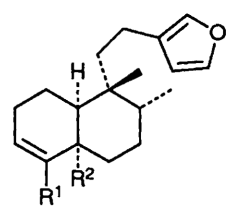
(416) X^1 = H, X^2 = OAc, O = α, C-5–Me = α
(417) X^1 = H, X^2 = OAng, O = α, C-5–Me = α
(418) $X^1 = X^2$ = H, O = β, C-5–Me = β
(419) X^1 = OH, X^2 = H, O = α, C-5–Me = α



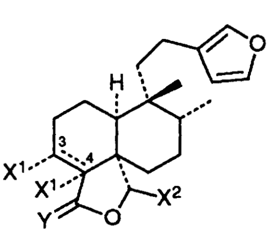
(28) X = H
(420) X = OAng



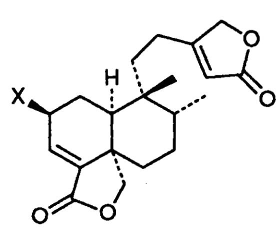
(421) R = Ang, $X^1 = X^2$ = OH, X^3 = H
(422) R = Tig, $X^1 = X^2$ = OH, X^3 = H
(423) R = Ang, X^1 = H, X^2,X^3 = =O
(424) R = Tig, X^1 = H, X^2,X^3 = =O



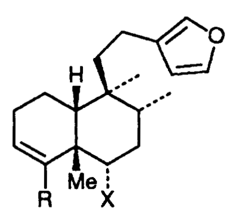
(425) R^1 = Me, R^2 = CO_2H
(426) R^1 = CH_2OAng, R^2 = CO_2H
(427) R^1 = Me, R^2 = CHO
(428) $R^1 = R^2$ = CHO
(429) R^1 = Me, R^2 = CH_2OH
(430) R^1 = CH_2OH, R^2 = Me
(431) $R^1 = R^2$ = CH_2OH



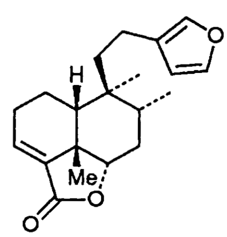
(432) X^1 = -, X^2 = H, Y = O, 3–4 = Double
(433) X^1 = -, X^2 = OH, Y = H_2, 3–4 = Double
(434) X^1 = –O–, X^2 = OH, Y = H_2, 3–4 = Single
(435) $X^1 = X^2$ = OH, Y = H_2, 3–4 = Single



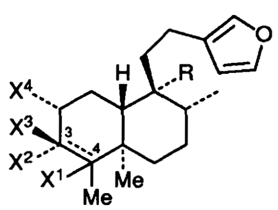
(436) X = H
(437) X = OH
(438) X = OGluc



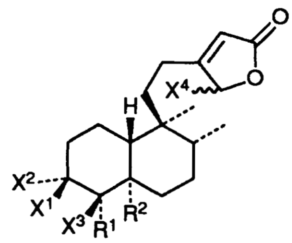
(439) R = CH_2OH, X = H
(440) R = CH_2OAc, X = H
(441) R = Me, X = H
(442) R = CH_2OH, X = OH
(443) R = CH_2OAc, X = OH



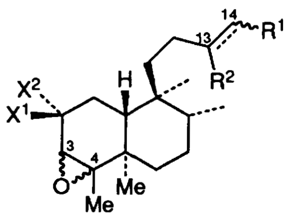
(444)



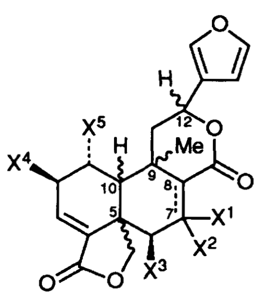
(445) R = Me, X^1,X^2 = —O—, X^3 = X^4 = H, 3–4 = Single, C-4–Me = β
(446) R = CO_2H, X^1,X^2 = -, X^3 = X^4 = H, 3–4 = Double, C-4–Me = -
(447) R = CO_2H, X^1,X^3 = —O—, X^2 = X^4 = H, 3–4 = Single, C-4–Me = α
(448) R = Me, X^1 = X^2 = X^4 = OH, X^3 = H, 3–4 = Single, C-4–Me = α
(449) R = Me, X^1 = H, X^2,X^3 = =O, X^4 = OH, 3–4 = Single, C-4–Me = α
(450) R = Me, X^1,X^2 = —O—, X^3 = H, X^4 = OH, 3–4 = Single, C-4–Me = β
(451) R = Me, X^1,X^2 = —O—, X^3 = H, X^4 = OMe, 3–4 = Single, C-4–Me = β



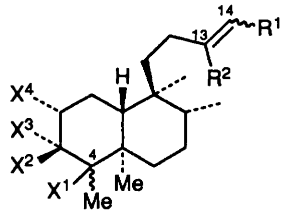
(452) R^1 = R^2 = Me, X^1 = X^4 = H, X^2 = X^3 = OH
(453) R^1 = R^2 = Me, X^1 = X^2 = =O, X^3 = X^4 = H
(454) R^1 = CO_2H, R^2 = CH_2OH, X^1 = X^2 = X^3 = H, X^4 = αOH
(455) R^1 = CO_2H, R^2 = CH_2OH, X^1 = X^2 = X^3 = H, X^4 = βOH



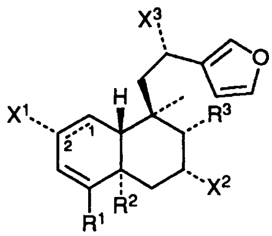
(456) R^1 = CHO, R^2 = Me, X^1 = X^2 = H, 13–14 = Double(*E*), O = α
(457) R^1 = CHO, R^2 = Me, X^1 = X^2 = H, 13–14 = Double(*Z*), O = α
(458) R^1 = CH_2OH, R^2 = Me, X^1 = OH, X^2 = H, 13–14 = Single, O = α
(459) R^1 = CO_2H, R^2 = Me, X^1,X^2 = =O, 13–14 = Single, O = β
(460) R^1 = CH_2OAc, R^2 = Me, X^1 = H, X^2 = OH, 13–14 = Double(*E*), O = β
(461) R^1 = CH_2OAc, R^2 = Me, X^1 = H, X^2 = OAc, 13–14 = Double(*E*), O = β
(462) R^1 = CH_2OAc, R^2 = CH_2OH, X^1 = H, X^2 = OH, 13–14 = Double(*Z*), O = β
(463) R^1 = R^2 = CH_2OAc, X^1 = H, X^2 = OAc, 13–14 = Double(*Z*), O = β



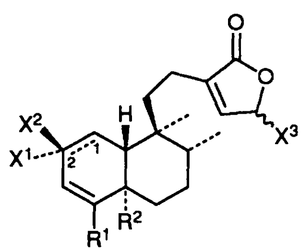
(464) X^1 = X^2 = X^3 = X^4 = X^5 = H, 7–8 = Single, C-8–H = α, C-10–H = α, C-12–H = α, C-9–Me = β, C-5–CH_2 = β
(465) X^1 = αOH, X^2 = X^3 = X^4 = X^5 = H, 7–8 = Single, C-8–H = β, C-10–H = β, C-12–H = β, C-9–Me = α, C-5–CH_2 = α
(466) X^1 = X^2 = X^3 = X^4 = H, X^5 = OH, 7–8 = Single, C-8–H = β, C-10–H = β, C-12–H = β, C-9–Me = α, C-5–CH_2 = α
(467) X^1 = OH, X^2 = -, X^3 = X^4 = X^5 = H, 7–8 = Double, C-8–H = -, C-10–H = β, C-12–H = α, C-9–Me = α, C-5–CH_2 = α
(468) X^1 = X^4 = X^5 = H, X^2 = -, X^3 = OH, 7–8 = Double, C-8–H = -, C-10–H = β, C-12–H = β, C-9–Me = α, C-5–CH_2 = α
(469) X^1 = X^2 = X^3 = X^4 = X^5 = H, 7–8 = Double, C-8–H = -, C-10–H = β, C-12–H = β, C-9–Me = α, C-5–CH_2 = α
(470) X^1 = X^2 = X^3 = X^5 = H, X^4 = OH, 7–8 = Single, C-8–H = β, C-10–H = β, C-12–H = α, C-9–Me = α, C-5–CH_2 = α



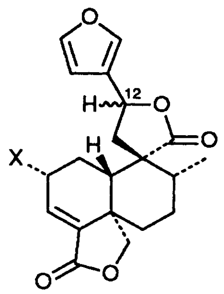
(471) R^1 = CHO, R^2 = Me, X^1 = X^4 = H, X^2,X^3 = =O, R^1/R^2 = *cis*, C-4–Me = α
(472) R^1 = CHO, R^2 = Me, X^1 = X^4 = H, X^2,X^3 = =O, R^1/R^2 = *trans*, C-4–Me = α
(473) R^1 = R^2 = CH_2OH, X^1 = X^3 = OH, X^2 = X^4 = H, R^1/R^2 = *cis*, C-4–Me = α
(474) R^1 = R^2 = CH_2OH, X^1 = H, X^2,X^3 = =O, X^4 = OH, R^1/R^2 = *cis*, C-4–Me = α
(475) R^1 = CO_2H, R^2 = Me, X^1, X^3 = X^4 = OH, X^2 = H, R^1/R^2 = *trans*, C-4–Me = α
(476) R^1 = CO_2H, R^2 = Me, X^1 = OH, X^2 = X^3 = X^4 = H, R^1/R^2 = *trans*, C-4–Me = β
(477) R^1 = CH_2OAc, R^2 = Me, X^1 = OH, X^2 = H, X^3 = X^4 = OAc, R^1/R^2 = *cis*, C-4–Me = α
(478) R^1 = R^2 = CH_2OAc, X^1 = OH, X^2 = H, X^3 = X^4 = OAc, R^1/R^2 = *cis*, C-4–Me = α



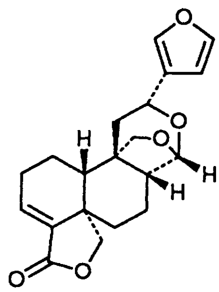
(9) R^1 = R^2 = R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(76) R^1 = CO_2H, R^2 = R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(103) R^1 = CO_2H, R^2 = CH_2OH, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(115) R^1 = CH_2OH, R^2 = R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(479) R^1 = CH_2OH, R^2 = R^3 = Me, X^1 = X^3 = H, X^2 = OH, 1–2 = Single
(480) R^1 = R^2 = CH_2OH, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(481) R^1 = R^2 = CH_2OAc, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(482) R^1 = CH_2OMal, R^2 = CH_2OAc, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(483) R^1 = CO_2H, R^2 = CH_2OAc, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(484) R^1 = R^2 = Me, R^3 = CO_2H, X^1 = X^2 = X^3 = H, 1–2 = Single
(485) R^1 = R^2 = Me, R^3 = CO_2Xyl, X^1 = X^2 = X^3 = H, 1–2 = Single
(486) R^1 = R^2 = Me, R^3 = CH_2OMal, X^1 = X^2 = X^3 = H, 1–2 = Single
(487) R^1 = CO_2H, R^2 = CH_2OH, R^3 = Me, X^1 = βOH, X^2 = X^3 = H, 1–2 = Single
(488) R^1 = R^2 = Me, R^3 = CHO, X^1 = X^2 = X^3 = H, 1–2 = Single
(489) R^1 = CO_2H, R^2 = CHO, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(490) R^1 = CO_2H, R^2 = CH_2OAc, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Double
(492) R^1 = CH_2OH, R^2 = CH_2OMal, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(493) R^1 = CO_2H, R^2 = CH_2OAng, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(494) R^1 = CO_2H, R^2 = CH_2OVal, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(495) R^1 = CO_2H, R^2 = CH_2OMe, R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(496) R^1 = CO_2H, R^2 = CH_2OH, R^3 = Me, X^1 = OH, X^2 = X^3 = H, 1–2 = Single
(497) R^1 = CO_2H, R^2 = R^3 = Me, X^1 = X^2 = H, X^3 = OMeBu, 1–2 = Single
(498) R^1 = CO_2H, R^2 = R^3 = Me, X^1 = αOAc, X^2 = X^3 = H, 1–2 = Single
(499) R^1 = CO_2H, R^2 = R^3 = Me, X^1 = X^2 = X^3 = H, 1–2 = Double



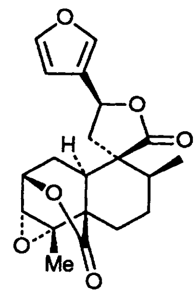
(500) R^1 = R^2 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(501) R^1 = CH_2OAc, R^2 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(502) R^1 = CO_2H, R^2 = Me, X^1 = X^2 = X^3 = H, 1–2 = Single
(503) R^1 = CO_2H, R^2 = CH_2OH, X^1 = H, X^2 = -, X^3 = OH, 1–2 = Double
(504) R^1 = CO_2H, R^2 = CH_2OH, X^1 = X^2 = H, X^3 = αOH, 1–2 = Single
(505) R^1 = CO_2H, R^2 = CH_2OH, X^1 = X^2 = H, X^3 = βOH, 1–2 = Single
(506) R^1 = R^2 = Me, X^1 = X^3 = H, X^2 = OH, 1–2 = Single
(507) R^1 = R^2 = Me, X^1,X^2 = =O, X^3 = H, 1–2 = Single
(508) R^1 = CO_2H, R^2 = Me, X^1 = X^2 = H, X^3 = OMe, 1–2 = Single
(509) R^1 = CO_2H, R^2 = Me, X^1 = X^2 = H, X^3 = OMe, 1–2 = Double



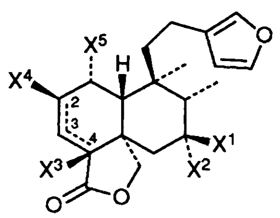
(510) X = H, C-12–H = β
(511) X = OSen, C-12–H = β
(512) X = OMeBu, C-12–H = β
(513) X = OAng, C-12–H = α



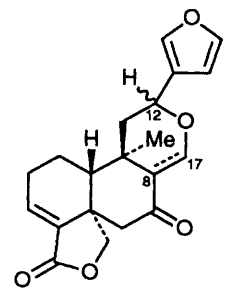
(514)



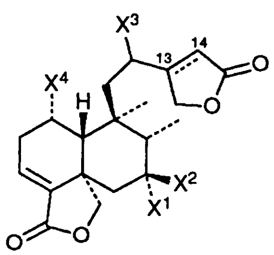
(515)



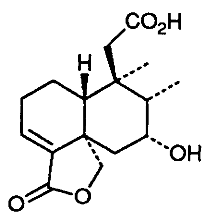
(516) X^1,X^2 = =O, X^3 = -, X^4 = X^5 = H, 2–3 = Single, 3–4 = Double
(517) X^1,X^2 = =O, X^3 = -, X^4 = OH, X^5 = H, 2–3 = Single, 3–4 = Double
(518) X^1 = X^2 = X^4 = X^5 = H, X^3 = OH, 2–3 = Double, 3–4 = Single
(519) X^1 = X^4 = X^5 = H, X^2 = OH, X^3 = -, 2–3 = Single, 3–4 = Double
(520) X^1 = X^2 = X^4 = H, X^3 = -, X^5 = OH, 2–3 = Single, 3–4 = Double
(521)* X^1 = X^5 = OH, X^2 = X^4 = H, X^3 = -, 2–3 = Single, 3–4 = Double
*(No assigned stereochem.)



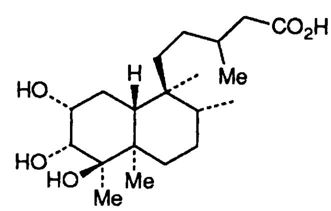
(522) 8–17 = Double, C-8–H = -, C-12–H = β
(523) 8–17 = Single, C-8–H = β, C-12–H = β
(524) 8–17 = Double, C-8–H = -, C-12–H = α



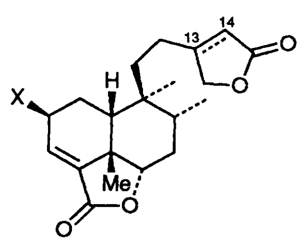
(289) X^1 = OH, X^2 = X^3 = X^4 = H, 13–14 = Double
(525) X^1 = OH, X^2 = X^3 = X^4 = H, 13–14 = Single
(526) X^1 = X^2 = X^3 = X^4 = H, 13–14 = Single
(527) X^1,X^2 = =O, X^3 = X^4 = H, 13–14 = Single
(528) X^1 = X^2 = X^3 = H, X^4 = OH, 13–14 = Double
(529) X^1 = X^2 = X^3 = X^4 = H, 13–14 = Double
(530) X^1 = X^2 = X^4 = H, X^3 = OH, 13–14 = Double



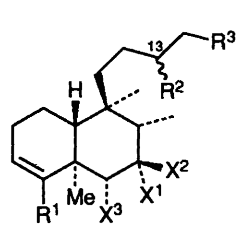
(531)



(532)

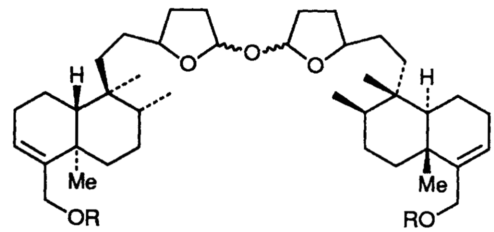


(533) X = H, 13–14 = Double
(534) X = OH, 13–14 = Single

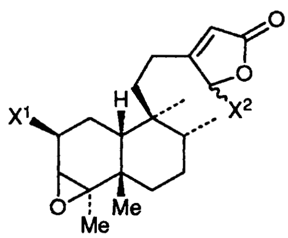


(16) $R^1 = R^2 = Me$, $R^3 = CO_2H$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(535) $R^1 = CH_2OMal$, $R^2 = R^3 = CH_2OAc$, $X^1 = OH$, $X^2 = X^3 = H$, C-13–R^2 = -
(536) $R^1 = CH_2OMal$, $R^2 = Me$, $R^3 = CH_2OH$, $X^1 = X^2 = X^3 = H$, C-13–$R^2 = \alpha$
(537) $R^1 = CH_2OMal$, $R^2 = Me$, $R^3 = CH_2OH$, $X^1 = X^2 = X^3 = H$, C-13–$R^2 = \beta$
(538) $R^1 = R^2 = R^3 = CH_2OAc$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(539) $R^1 = R^3 = CH_2OAc$, $R^2 = Me$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(540) $R^1 = Me$, $R^2 = CH_2OAc$, $R^3 = CH_2OR^4$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(541) $R^1 = Me$, $R^2 = CH_2OAc$, $R^3 = CH_2OR^5$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(542) $R^1 = Me$, $R^2 = CHO$, $R^3 = CH_2OH$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(543) $R^1 = R^3 = CO_2H$, $R^2 = Me$, $X^1 = X^2 = X^3 = H$, C-13–$R^2 = \beta$
(544) $R^1 = CH_2OAc$, $R^2 = Me$, $R^3 = CO_2H$, $X^1 = X^2 = X^3 = H$, C-13–R^2 = -
(545) $R^1 = R^2 = Me$, $R^3 = CO_2H$, $X^1 = H$, $X^2 = OAc$, $X^3 = OAng$, C-13–R^2 = -
(546) $R^1 = R^2 = Me$, $R^3 = CO_2H$, $X^1 = H$, $X^2 = OAc$, $X^3 = OCOBu^i$, C-13–R^2 = -
(547) $R^1 = R^2 = Me$, $R^3 = CO_2H$, $X^1 = H$, $X^2 = OAc$, $X^3 = OMeBu$, C-13–R^2 = -
(548) $R^1 = R^2 = Me$, $R^3 = CO_2H$, $X^1 = H$, $X^2 = X^3 = OAc$, C-13–R^2 = -

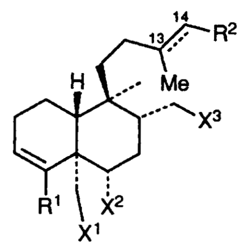
$R^4 = CO(CH_2)_{18}Me$ $R^5 = CO(CH_2)_{20}Me$



(549) R = Mal
(550) R = Succ

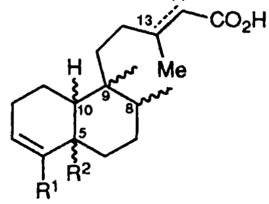


(418) $X^1 = X^2 = H$
(551) $X^1 = H$, $X^2 = OH$
(552) $X^1 = OH$, $X^2 = H$

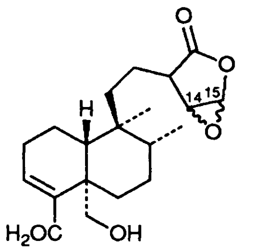


(553) $R^1 = Me$, $R^2 = CHO$, $X^1 = X^2 = H$, $X^3 = OH$, 13–14 = Single
(554) $R^1 = CHO$, $R^2 = CH_2OH$, $X^1 = H$, $X^2 = OH$, $X^3 = OAc$, 13–14 = Single
(555) $R^1 = R^2 = CH_2OH$, $X^1 = H$, $X^2 = OH$, $X^3 = OBz$, 13–14 = Single
(556) $R^1 = CH_2OH$, $R^2 = CO_2H$, $X^1 = H$, $X^2 = OH$, $X^3 = OAc$, 13–14 = Double
(557) $R^1 = CH_2OH$, $R^2 = CO_2H$, $X^1 = H$, $X^2 = OH$, $X^3 = OBz$, 13–14 = Double
(558) $R^1 = Me$, $R^2 = CH_2OH$, $X^1 = X^2 = H$, $X^3 = OMal$, 13–14 = Double
(559) $R^1 = Me$, $R^2 = CH_2OH$, $X^1 = OMal$, $X^2 = X^3 = H$, 13–14 = Double
(560) $R^1 = Me$, $R^2 = CH_2OAc$, $X^1 = X^2 = H$, $X^3 = OMal$, 13–14 = Double
(561) $R^1 = Me$, $R^2 = CH_2OAc$, $X^1 = OMal$, $X^2 = X^3 = H$, 13–14 = Double
(562) $R^1 = Me$, $R^2 = CH_2OR^3$, $X^1 = X^2 = H$, $X^3 = OMal$, 13–14 = Double
(563) $R^1 = Me$, $R^2 = CH_2OR^3$, $X^1 = OMal$, $X^2 = X^3 = H$, 13–14 = Double
(564) $R^1 = Me$, $R^2 = CH_2OMal$, $X^1 = OMal$, $X^2 = X^3 = H$, 13–14 = Double

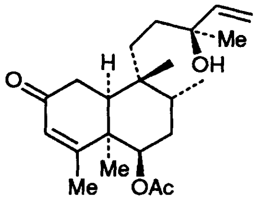
$R^3 = CO(CH_2)_{22}Me$



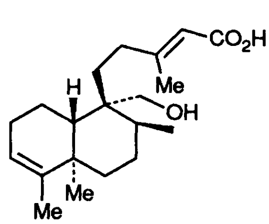
(44) $R^1 = CH_2OH$, $R^2 = Me$, 13–14 = Single, C-5–$R^2 = \beta$, C-8–Me = α, C-9–Me = α, C-10–H = β
(565) $R^1 = CO_2H$, $R^2 = Me$, 13–14 = Double, C-5–$R^2 = \beta$, C-8–Me = α, C-9–Me = α, C-10–H = β
(566) $R^1 = CH_2OH$, $R^2 = Me$, 13–14 = Double, C-5–$R^2 = \beta$, C-8–Me = α, C-9–Me = α, C-10–H = β
(567) $R^1 = CH_2OAc$, $R^2 = Me$, 13–14 = Double, C-5–$R^2 = \beta$, C-8–Me = α, C-9–Me = α, C-10–H = β
(568) $R^1 = Me$, $R^2 = CH_2OH$, 13–14 = Single, C-5–$R^2 = \beta$, C-8–Me = α, C-9–Me = α, C-10–H = β
(569) $R^1 = R^2 = Me$, 13–14 = Single, C-5–$R^2 = \alpha$, C-8–Me = β, C-9–Me = β, C-10–H = α



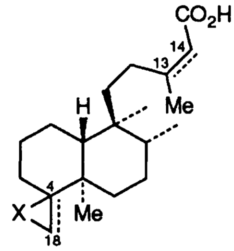
(570) —O— = α
(571) —O— = β



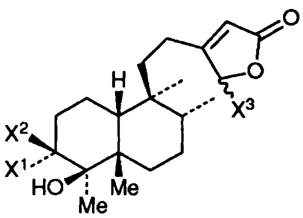
(572)



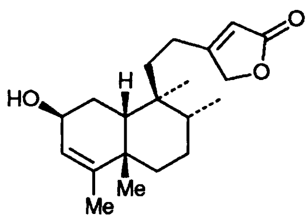
(573)



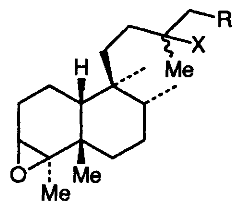
(574) X = -, 4–18 = Double, 13–14 = Double
(575) X = -, 4–18 = Double, 13–14 = Single
(576) X = αO, 4–18 = Single, 13–14 = Double
(577) X = βO, 4–18 = Single, 13–14 = Double
(578) X = αO, 4–18 = Single, 13–14 = Single
(579) X = βO, 4–18 = Single, 13–14 = Single



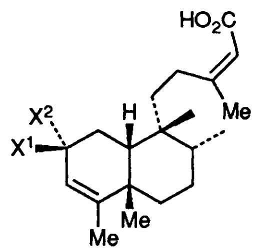
(580) $X^1 = X^3 = OH$, $X^2 = H$
(581) $X^1 = OH$, $X^2 = X^3 = H$
(582) $X^1 = OMe$, $X^2 = X^3 = H$
(583) $X^1,X^2 = {=}O$, $X^3 = H$



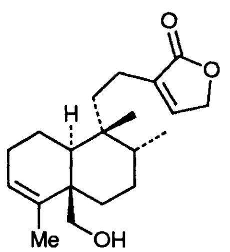
(584)



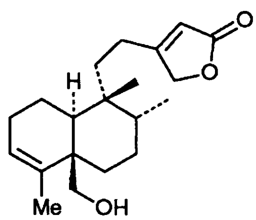
(585) R = CO_2H, X = H
(586) R = CH_2OH, X = OH



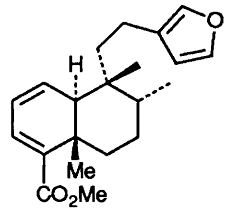
(587) $X^1,X^2 = {=}O$
(588) $X^1 = OH$, $X^2 = H$



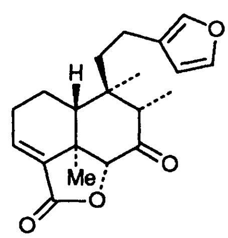
(589)



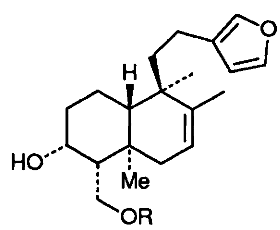
(590)



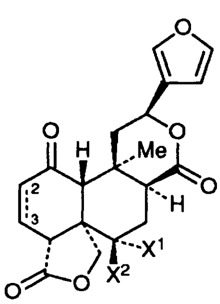
(591)



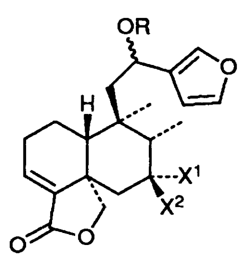
(592)



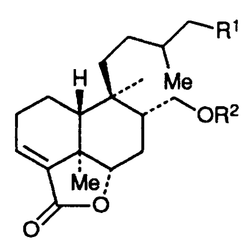
(593) R = $COPr^i$
(594) R = MeBu
(595) R = Tig



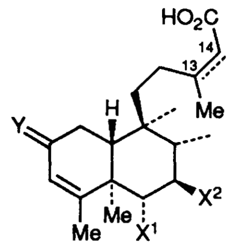
(596) X^1 = OAng, X^2 = H, 2–3 = Single
(597) $X^1 = X^2 = H$, 2–3 = Double
(598) X^1 = H, X^2 = OH, 2–3 = Double
(599) X^1 = H, X^2 = OTig, 2–3 = Double



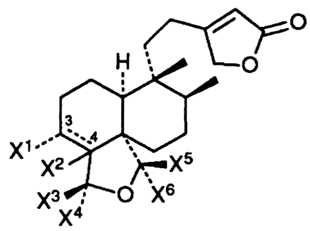
(600) R = H, $X^1 = X^2 = H$, C-12–OR = α
(601) R = H, X^1 = OH, X^2 = H, C-12–OR = α
(602) R = Gluc, $X^1,X^2 = {=}O$, C-12–OR = α
(603) R = Gluc, $X^1,X^2 = {=}O$, C-12–OR = β



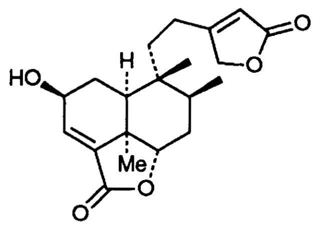
(604) $R^1 = CH_2OH$, R^2 = Ac
(605) $R^1 = CO_2H$, R^2 = Bz



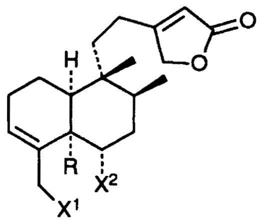
(606) $X^1 = X^2 = H$, $Y = O$, 13–14 = Double
(607) $X^1 = X^2 = OAc$, $Y = H_2$, 13–14 = Double
(608) $X^1 = OAng$, $X^2 = OAc$, $Y = H_2$, 13–14 = Double
(609) $X^1 = OCOPr^i$, $X^2 = OAc$, $Y = H_2$, 13–14 = Double
(610) $X^1 = X^2 = OH$, $Y = O$, 13–14 = Double
(611) $X^1 = OCOPr^i$, $X^2 = OAng$, $Y = H_2$, 13–14 = Single



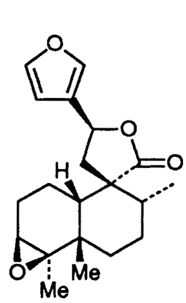
(612) $X^1 = Cl$, $X^2 = OH$, $X^3 = X^4 = X^6 = H$, $X^5 = OMe$, 3–4 = Single, C-4–X^2 = β
(613) $X^1 = X^5 = X^6 = H$, X^2 = -, X^3,X^4 = =O, 3–4 = Double, C-4–X^2 = -
(614) $X^1 = X^3 = X^4 = X^5 = H$, X^2 = -, $X^6 = OH$, 3–4 = Double, C-4–X^2 = -
(615) X^1,X^2 = –O–, $X^3 = X^4 = X^5 = H$, $X^6 = OH$, 3–4 = Single, C-4–X^2 = α
(616) X^1,X^2 = –O–, $X^3 = X^6 = OH$, $X^4 = X^5 = H$, 3–4 = Single, C-4–X^2 = α
(617) X^1,X^2 = –O–, X^3,X^4 = =O, $X^5 = H$, $X^6 = OH$, 3–4 = Single, C-4–X^2 = α
(618) $X^1 = X^2 = X^6 = OH$, $X^3 = X^4 = X^5 = H$, 3–4 = Single, C-4–X^2 = β



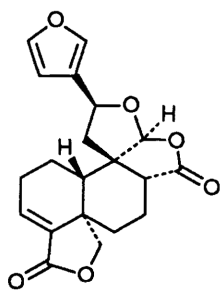
(619)



(620) R = Me, $X^1 = X^2 = OH$
(621) R = CH_2OH, $X^1 = OH$, $X^2 = H$
(622) R = CO_2Arab, $X^1 = X^2 = H$



(623)



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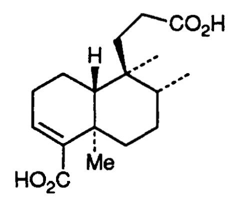

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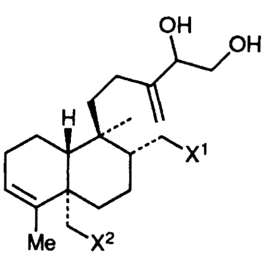
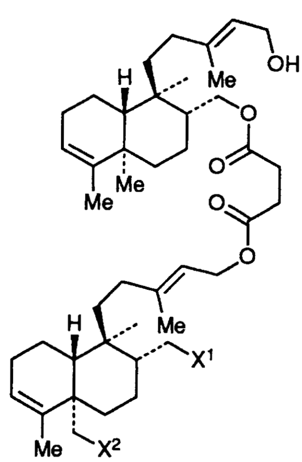
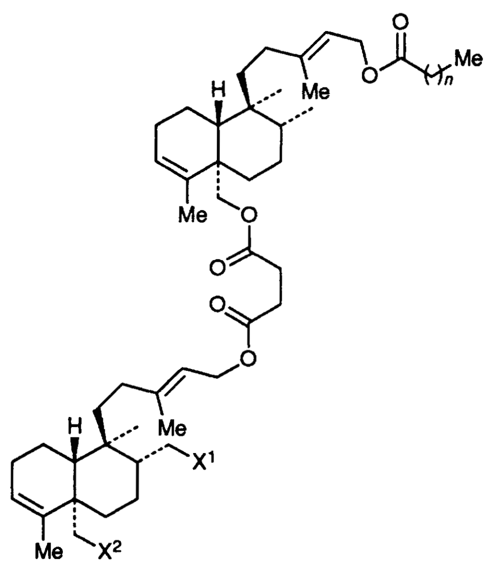


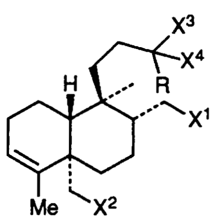
(626) $X^1 = H$, X^2 = Succ
(627) X^1 = Succ, $X^2 = H$



(632) $X^1 = H$, X^2 = Succ
(633) X^1 = Succ, $X^2 = H$



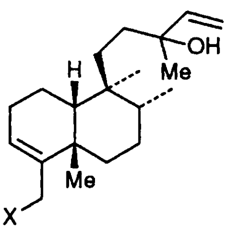
(634) $X^1 = H$, X^2 = Succ, $n = 0$
(635) X^1 = Succ, $X^2 = H$, $n = 0$
(636) $X^1 = H$, X^2 = Succ, $n = 22$
(637) X^1 = Succ, $X^2 = H$, $n = 22$



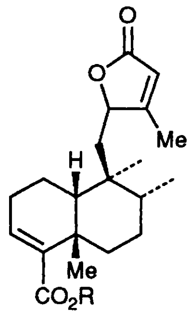
(628) R = Me, $X^1 = H$, X^2 = Succ, X^3,X^4 = =O
(629) R = CO_2Me, $X^1 = H$, X^2 = Succ, X^3,X^4 = $=CH_2$
(630) R = CO_2Me, $X^1 = X^4 = H$, X^2 = Succ, $X^3 = Me$
(631) R = CO_2Me, X^1 = Succ, $X^2 = X^4 = H$, $X^3 = Me$

Table 14 Clerodanes from Jungermanniales

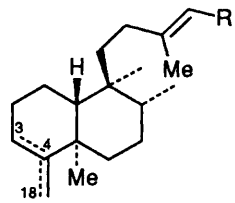
Species	Compounds	Ref.	Comments
Genus – *Gymnocolea*			
G. inflata	(644) gymnocolin	373	
Genus – *Scapania*			
S. bolanderi	(645)	374	no stereochem
Genus – *Pleurozia*			
P. acinosa	(28) kolaveelool	375	see Compositae, Caesalpinaceae



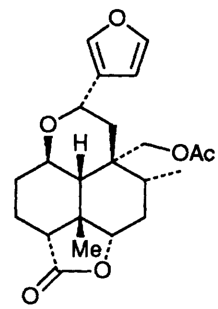
(638) X = H
(639) X = OH



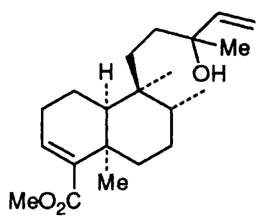
(640) R = H
(641) R = Gluc



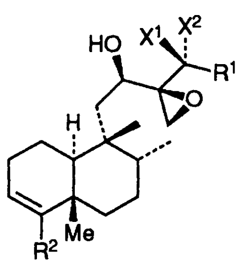
(32) R = CO_2Me, 3–4 = Double, 4–18 = Single
(642) R = CO_2Me, 3–4 = Single, 4–18 = Double
(643) R = CH_2OH, 3–4 = Single, 4–18 = Double



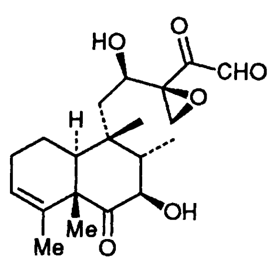
(644)



(645)



(646) $R^1 = CH_2OH$, $R^2 = CHO$, $X^1 = OH$, $X^2 = H$
(647) $R^1 = R^2 = CH_2OH$, $X^1 = OH$, $X^2 = H$
(648) $R^1 = R^2 = CH_2OH$, $X^1 = H$, $X^2 = OH$
(649) $R^1 = R^2 = CHO$, X^1,X^2 = =O



(650)

substitution is evident. The presence of clerodane natural products in the Compositae has been partially reviewed during a symposium of the biology and chemistry of the Compositae,[258] and in a review tabulating one hundred and sixty five clerodane diterpenes.[259] The presence of clerodanes in the genus *Solidago* (Table 13) has been partially detailed in an article in an A.C.S. symposium on allelochemistry and it's role in agrochemistry.[260]

3.18 Family Alismaceae

Sagittaria sagittifolia has yielded compounds (638) and (639).[367,368]

3.19 Family Orchidaceae

Ephermeranthus comata[369] has yielded ephemeric acid (640) and ephemeroside (641).

3.20 Family Araucariaceae

This family has yielded the following compounds: from *Araucaria bidwilli*,[370,371] methylkolavenate (32) and (642) (See Compositae, Aristolochiaceae); and *A. hunsteinii* gave (643).[372]

3.21 Order Jungermanniales

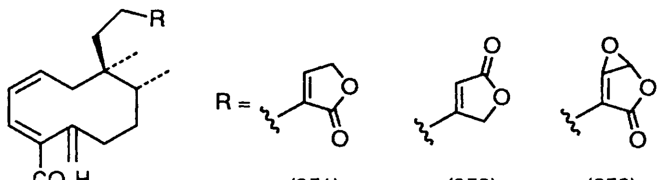
These are the liverworts, with three genera shown to yield clerodanes (Table 14).

3.22 Order Moniliales

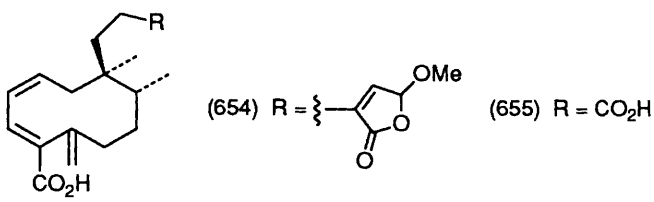
Only one species of fungi has been reported as producing clerodanes, namely *Oidiodendron truncatum*, which has yielded compounds (646)—(649).[376,377]

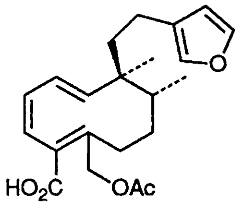
3.23 Family Actinomyces

Only one strain of bacteria has so far been shown to yield clerodanes: *Kitasatosporia* species MF-730-N6, which produced (650).[378,379]



(651) (652) (653)





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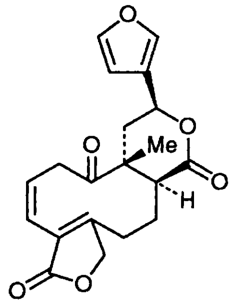
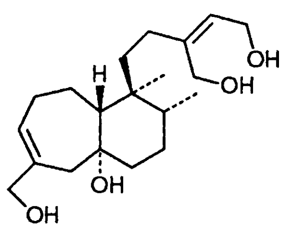


(657)



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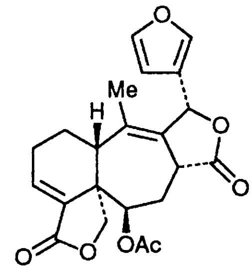


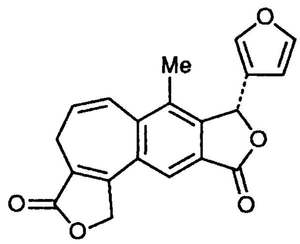
(659)

4 Clerodane Derived Diterpenes

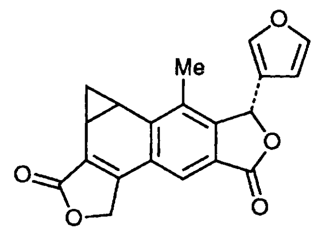
Several examples of diterpenes apparently related to the clerodanes have also been isolated. Some may arise by separate biosynthetic routes, but in several cases the related compounds have been found in the same species as clerodane natural products. *Pulicaria angustifolia* (Compositae), already shown to produce (592), yields a series of diterpenes with the decalin system opened to give a 5-*exo*-methylene carbocyclic system as in structures (651)—(653).[380] Similarly opened compounds have also been obtained from *Grangea maderaspatana* (Compositae), butenolide (654), and acid (655),[365] as have furyl (656) from *Baccharis flabellata* (Compositae),[317] and cardiophyllidan (657) from *Salvia cardiophylla* Benth (Labiatae).[381]

Ring expanded compounds have also been isolated, with *Portulaca cv* Jewel (Portulacaceae) yielding the [7.6] system in jewenol B (658).[27] The *Salvia* genus (Labiatae) has been shown to produce several clerodanes and *Salvia fulgens* also produces [6.7] compound salvigenolide (659),[382] whilst *Salvia puberula* yields the [7.6] isopuberulin (660), along with cyclopropyl puberelin (661).[383]

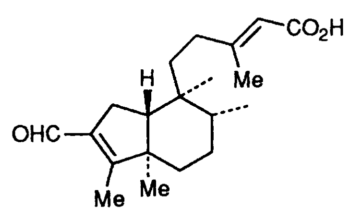
Ring contracted compounds have not been found, except in one case, from *Solidago altissima* (Compositae) with a [5.6] ring system, (662).[384]



(660)



(661)



(662)

5 Biological Activity

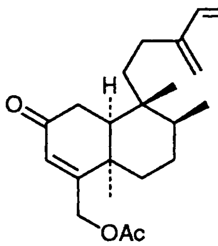
Only a small number of the clerodanes listed in Section 3 have been shown to exhibit any biological activity. However, only a handful of compounds have been reported as having no activity in the tests carried out, thus leaving the large majority as simply untested or unreported. The clerodanes are best known for their insect antifeedant properties, and related insecticidal properties, with an emphasis placed on the safety aspects of such natural insect antifeedants in relation to mammalian and piscial life.[385,386] All the compounds isolated from the *Clerodendron* and *Caryopteris* genera (Verbenaceae) (2,124—133) have proved active against certain plant pests, notably the tobacco cut worm (*Spodoptera litura*) and the African army worm (*Spodoptera exempta*), but not effective as general antifeedants.[85,86,387,388] Of the compounds obtained from the *Ajuga* genus (Labiatae), ajugarins I—III (138,139,135) showed antifeedant activity towards the African army worm and African desert locust (*Schisticerea gregaria*)[389] and against *Phaedon cochleariae*, *Plutella xylostella* and *Myzus persicae*,[390] whilst ajugarin IV (136) has been shown to act as an insecticide against *Bombyx mori*,[105] though ajugarin V (140) appears inactive.[389,391] The ivains I—IV (150—153) have demonstrated antifeedant activity in a crude mixture form,[116] whilst ajugareptansin (149), ajugapitin (154), dihydroajugapitin (155), and 2-acetylivain I (159) have all shown activity against the Egyptian cotton leafworm (*Spodoptera litteralis*), along with the purified fraction of ivains I—IV.[392] Ajugareptansone A (146), however, proved inactive in the same study. Several compounds from the *Teucrium* genus (Labiatae) have shown antifeedant activity, tafricanins A and B (243,244) against *Locusta migratoria*,[209] montanin F (206) against *Prodenia litura*,[174] and 6,19-diacetylteumassilin (253), shown by our studies to be active against *Spodoptera litteralis*, along with Teucjaponin B (195), eroicephalin (203), and 12-epiteucvin (168).[393,394] Jodrellins A and B (318,319) from *Scutellaria woronowii* (Labiatae) have also shown activity against the Egyptian cotton leafworm (*Spodoptera litteralis*).[244] Finally kolavenol (30), described from many sources (Caesalpinaceae, Aristolochiaceae, and Compositae), has been reported as having activity against leaf cutter ants (*A. cephalotes*), as well as against their mutualistic attine fungus,[395] whilst hardwickiic acid (76) (Caesalpinaceae, Euphorbiceae, and Compositae) is described as insecticidal against *Aphis*

Table 15 Clerodanes recently isolated

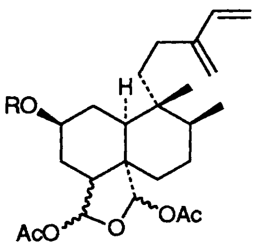
Family / Species	Compounds	Ref.
Family Annonaceae		
Species		
Monodora brevipes Benth	(663)—(665)	397
Polyalthia viridis Craib	(666)—(670)	398
Family Menispermaceae		
Species		
Tinospora cordifolia	(671)	399
Family Flacourtiaceae		
Species		
Casearia pitumba Pleumer	(672)	400
Casearia corymbosa	(673)—(681)	401
Zuelania guidonia (Sw.) Britton et Millsp.	(682)—(693)	402, 403
Family Euphorbiaceae		
Species		
Croton cajucara Benth	(694), (695)	404
Croton sonderianus Muell. Arq.	(76), (91), (696), (697)	405
Croton haumanianus J. Leonard	(698)	406
Croton megalocarpus	(699)	407
Family Verbenaceae		
Species		
Clerodendron brachyanthum Schauer	(2), (700)—(704)	408, 409
Clerodendron inerme L.	(705)	410
Family Labiatae		
Species		
Ajuga chamaepitys	(154), (255), (706), (707)	411
Ajuga decumbens Thunb	(143), (708)—(715)	412, 413
Ajuga ciliata Bunge var *villosior* A. Gray	(136), (716)—(724)	414
Teucrium kotschyanum Poech. (synonym *T. smyrnaeum* Boiss.)	(88), (162), (169), (172), (181), (186), (248), (725)—(728)	415, 416
Teucrium bicolor L.E.Sm.	(89), (168), (172), (197), (202), (218), (729)	417
Teucrium canadense L.	(88), (89), (162), (197), (218), (234), (730), (731)	418
Teucrium abutiloides L'Herit (synonym *T. umbrosum* Buch.)	(202), (218), (734), (735)	420
Teucrium pestallazae	(243), (732), (733), (736), (737)	419, 421
Teucrium odontites Boiss. & Bal.	(172), (186), (233)	421
Teucrium microphyllum	(160), (170), (173), (183)	421
Scutellaria rivularis	(738)—(741)	422
Family Compositae		
Species		
Conyza welwitschii S. Moore	(742)—(753)	423
Conyza blinii Levl.	(754)	424
Nardophyllum lanatum Cabr.	(755), (756)	425
Pteronia eenii S. Moore	(757)—(762) (767)—(771)	426
Pteronia incana DC	(757)—(759) (763)—(766)	426
Pteronia divaricata Less.	(759)	426
Pteronia paniculata Thunb	(772)—(776)	426
Microglossa pyrrhopappa A. Rich	(777)—(783)	427
Platychaete aucheri Boiss.	(784)—(787)	428
Family Jungermanniaceae		
Species		
Jungermannia infusca	(788)—(793)	429, 430

craccivora,[63] and two compounds from *Polyalthia longifolia* (Annonaceae), (12) and (15), are described as having antifeedant potential.[12]

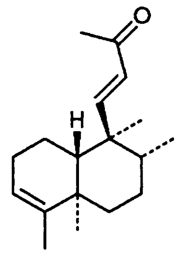
Antiviral and Antitumour properties have been demonstrated by a crude extract of *Baccharis tricuneata* (Compositae) containing bacchotricuneatins A—D (464,510,514,479),[293] whilst antibiotic and antitumour properties have been reported for terpentecin (650) from *Kitasatosporia* MF-730-N6 (Actinomyces),[378,379] and clerocidin (649) from *Oidiodendron truncatum* (Moniliales) has shown antibiotic potential.[376,377] Kolavenic acid (31), isolated from several sources (Aristolochiaceae, Caesalpinaceae, Compositae), has been reported as antimicrobial,[262,263] whilst teucvin (89), isolated from the *Mallotus* (Euphorbiaceae) and *Teucrium* (Labiatae) genera, has been shown to be amoebicidal, and act as a root development inhibitor,[146] though showing no antitumour potential, as is the case with the structurally similar teucvidin (88).[396] The compounds isolated from *Scutellaria rivularis* Wall (322—328) (scutellones A—F and scuterivulactone C2) are part of the Chinese drug Ban-Zhi-Lian, used in the treatment of tumours, hepatitis, cirrhosis, and other diseases.[248] *Tinospora cordifolia* Miers (Menispermaceae) yields (55) which is used in agurvedic medicine (India) against jaundice, urinary disease, and rheumatism.[24] Two compounds from *Casearia sylvestris* Flacour-



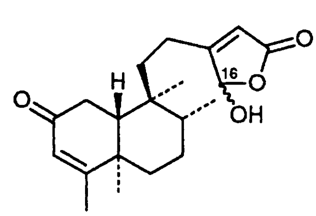
(663)



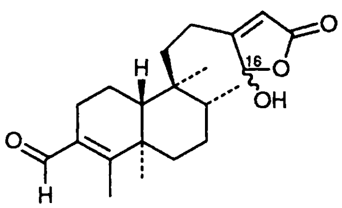
(664) R = Ac
(665) R = Pr^{i}CO



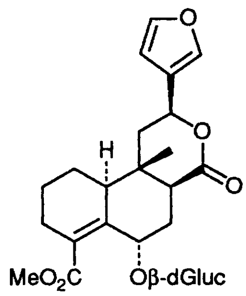
(666)



(667) 16–OH = α
(668) 16–OH = β



(669) 16–OH = α
(670) 16–OH = β



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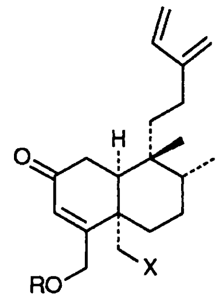
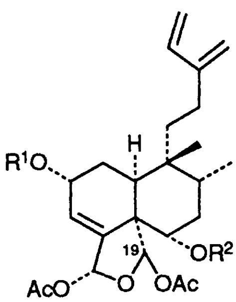
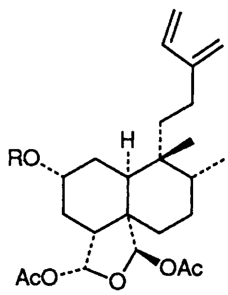


(677) R = H, X = H
(678) R = Ac, X = OAc



(672) R^1 = H, R^2 = R^{3}CO, 19–O = α
(673) R^1 = Bu^{i}CO, R^2 = H, 19–O = β
(674) R^1 = Pr^{i}CO, R^2 = H, 19–O = β
(675) R^1 = Bu^{i}CO, R^2 = Me, 19–O = β
(676) R^1 = Pr^{i}CO, R^2 = Me, 19–O = β



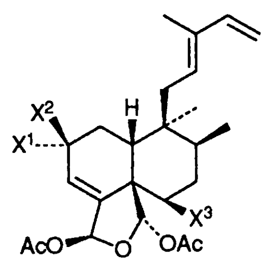
(679) R = H
(680) R = Ac
(681) R = Bu^{i}CO

tiaceae), (71 and 73), have demonstrated antitumour potential against sarcoma in mice.[29]

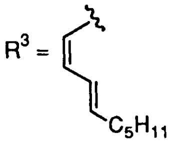
The pluanols B-E (81—84), isolated from the Thai folk drug Plaunoi *Croton sublyratus* (Euphorbiaceae) have all shown anti-peptic ulcer properties,[45] though plaunol A (80) shows no activity.[46] Divinorin A (salvinoron, 286), from the hallucinogenic Mexican mint *Salvia divinorum* (Labiatae), has shown psychotropic activity.[223] Finally, solidagolactones IV—VI and VIII (353,354,363,365) from various *Solidago* species (Compositae) are the only *cis* compounds with reported activity, as piscicidal agents.[269,270]

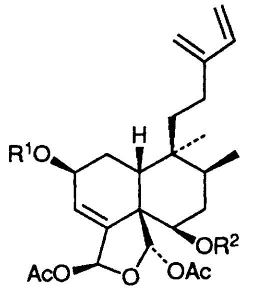
6 Recent Isolations

Since the initial preparation of this report several further isolations of novel clerodane products have appeared in the literature, and these are reported here (Table 15). The isolated compounds are reported in the same order as the main part of the manuscript. However, no attempt has been made to indicate any structural or taxonomic trends, either within this section or related to Section 3, and the specific species are not included in the taxonomic relationship diagram (Scheme 2).

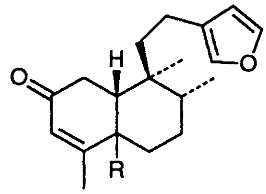


(682) X^1 = OH, X^2 = H, X^3 = OCinn
(683) X^1 = OCinn, X^2 = H, X^3 = OH
(684) X^1 = H, X^2 = OH, X^3 = OCinn
(685) X^1 = OAc, X^2 = H, X^3 = OH
(686) X^1 = OOct, X^2 = H, X^3 = OH
(687) X^1 = H, X^2 = OOct, X^3 = OH
(688) X^1 = H, X^2 = OBz, X^3 = OH
(689) X^1 = OH, X^2 = H, X^3 = OBz
(690) X^1 = OH, X^2 = H, X^3 = O–3OH–Oct
(691) X^1 = X^3 = H, X^2 = OBz

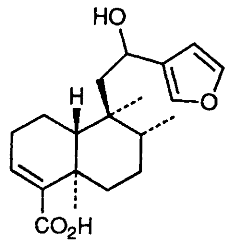




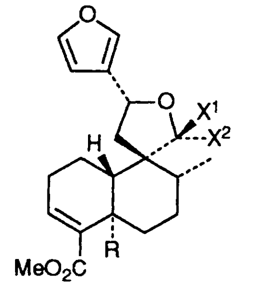
(692) R^1 = Ac, R^2 = Cinn
(693) R^1 = Bz, R^2 = H



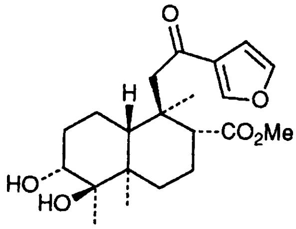
(694) R = α-CHO
(695) R = β-H



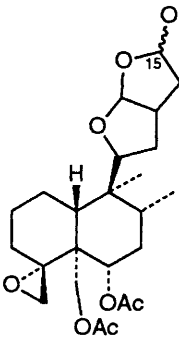
(696)



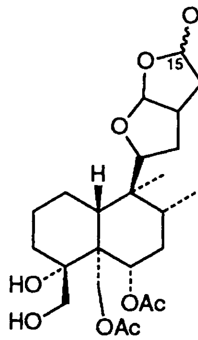
(697) R = Me, X^1 = OH, X^2 = H
(698) R = CO_2Me, X^1,X^2 = =O



(699)



(700) R = Me, 15–Me = α
(701) R = Me, 15–Me = β
(702) R = Et, 15–Me = α
(703) R = Et, 15–Me = β



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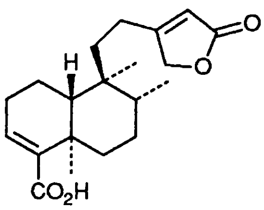

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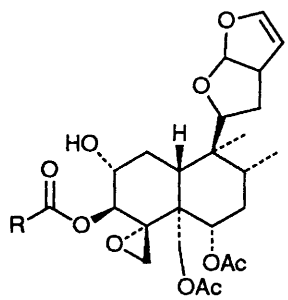
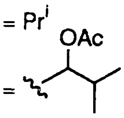
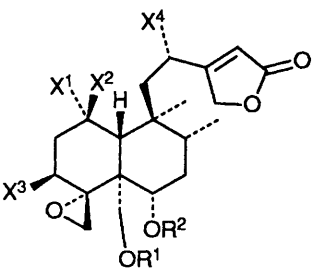
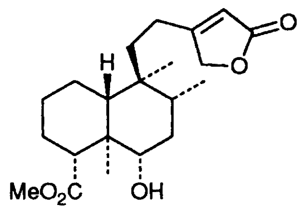


(706) R = Pr^i

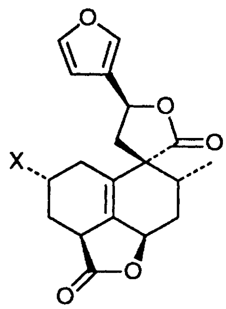
(707) R = 



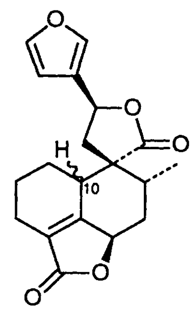
(708) $R^1 = R^2$ = Ac, $X^1 = X^3$ = H, X^2 = OTig, X^4 = OAc
(709) $R^1 = R^2$ = Ac, $X^1 = X^3$ = H, X^2 = OTig, X^4 = OMeBu
(710) $R^1 = R^2$ = Ac, $X^1 = X^3$ = H, X^2 = OMeBu, X^4 = OTig
(711) $R^1 = R^2$ = Ac, $X^1 = X^2 = X^3$ = H, X^4 = OMeBu
(712) R^1 = Tig, R^2 = Ac, $X^1 = X^2 = X^3 = X^4$ = H
(713) R^1 = Tig, R^2 = H, $X^1 = X^2 = X^3 = X^4$ = H
(714) R^1 = Tig, R^2 = Ac, $X^1 = X^3$ = OAc, $X^2 = X^4$ = H
(715) R^1 = Tig, R^2 = Ac, $X^1 = X^2 = X^4$ = H, X^3 = OH
(716) R^1 = H, R^2 = Ac, $X^1 = X^3$ = H, X^2 = OMeBu, X^4 = OH
(717) R^1 = H, R^2 = Ac, $X^1 = X^3$ = H, X^2 = OMeBu, X^4 = OAc
(718) R^1 = H, R^2 = Ac, $X^1 = X^3$ = H, X^2 = OH, X^4 = OMeBu
(719) R^1 = Ac, R^2 = H, $X^1 = X^3$ = H, X^2 = OH, X^4 = OMeBu
(720) $R^1 = R^2$ = Ac, $X^1 = X^3$ = H, X^2 = OH, X^4 = OMeBu
(721) $R^1 = R^2$ = H, $X^1 = X^2 = X^3$ = H, X^4 = OMeBu
(722) R^1 = H, R^2 = Ac, $X^1 = X^2 = X^3$ = H, X^4 = OMeBu
(723) R^1 = Ac, R^2 = H, $X^1 = X^2 = X^3$ = H, X^4 = OMeBu



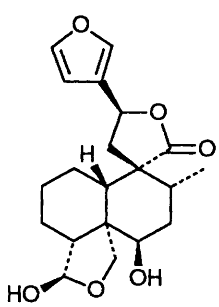
(724)



(725) X = OH
(731) X = H



(726) 10–H = α
(727) 10–H = β



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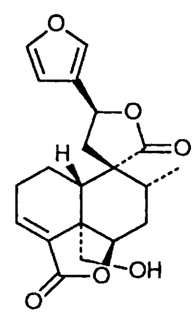

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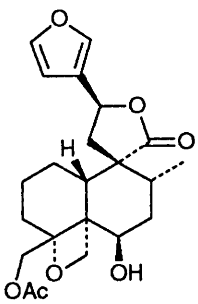

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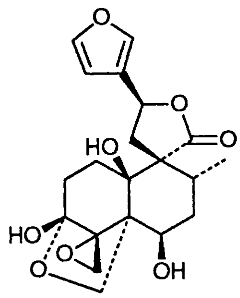
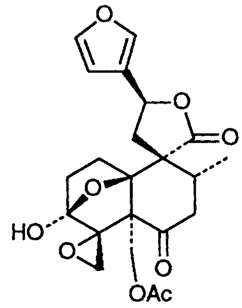
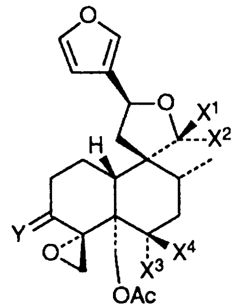


(732)



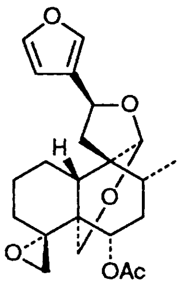
(733)



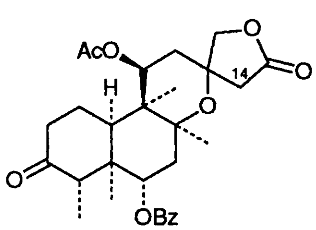
(735) $X^1 = X^3 = OAc$, $X^2 = X^4 = H$, $Y = H_2$

(736) $X^1,X^2 = {=}O$, $X^3,X^4 = {=}O$, $Y = O$

(737) $X^1,X^2 = {=}O$, $X^3 = H$, $X^4 = OH$, $Y = O$

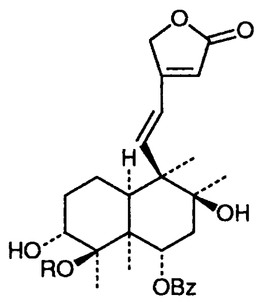


(734)



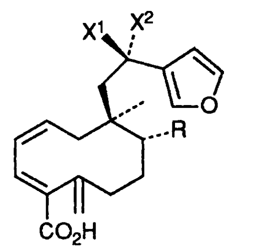
(738) C-14 = α

(739) C-14 = β



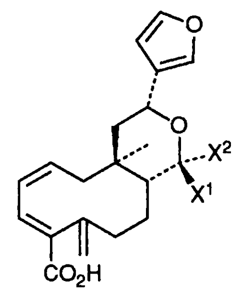
(740) R = Me

(741) R = Et



(742) $X^1 = OH$, $X^2 = H$, R = Me

(743) $X^1,X^2 = {=}O$, $R = CO_2H$



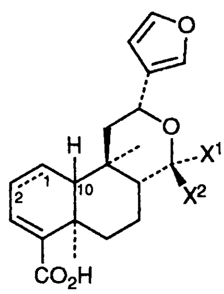
(744) $X^1 = OH$, $X^2 = H$

(745) $X^1 = H$, $X^2 = OH$

(746) $X^1 = OMe$, $X^2 = H$

(747) $X^1 = H$, $X^2 = OMe$

(748) $X^1,X^2 = {=}O$



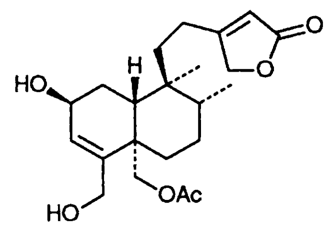
(749) $X^1,X^2 = {=}O$, 10–H = α, 1–2 = Double

(750) $X^1,X^2 = {=}O$, 10–H = β, 1–2 = Double

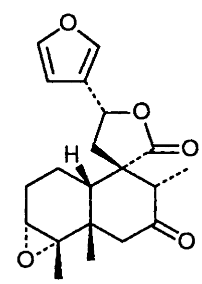
(751) $X^1 = OH$, $X^2 = H$, 10–H = β, 1–2 = Double

(752) $X^1 = H$, $X^2 = OH$, 10–H = β, 1–2 = Double

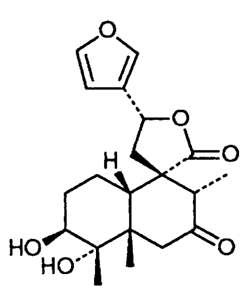
(753) $X^1,X^2 = {=}O$, 10–H = β, 1–2 = Single



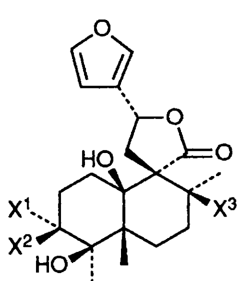
(754)



(755)



(756)

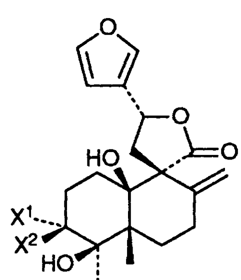


(757) $X^1 = OH$, $X^2 = X^3 = H$

(758) $X^1 = X^3 = OH$, $X^2 = H$

(759) $X^1 = OAc$, $X^2 = H$, $X^3 = OH$

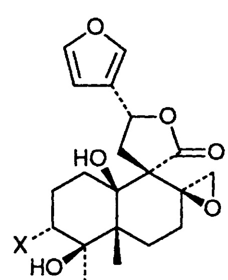
(760) $X^1,X^2 = {=}O$, $X^3 = OH$



(761) $X^1 = OH$, $X^2 = H$

(762) $X^1 = OAng$, $X^2 = H$

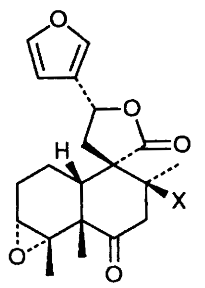
(763) $X^1,X^2 = {=}O$



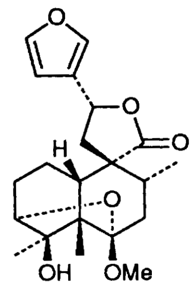
(764) X = OH

(765) X = OAc

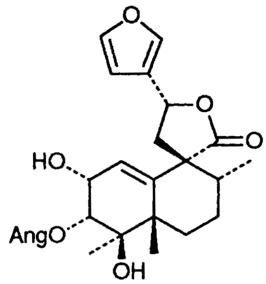
(766) X = OAng



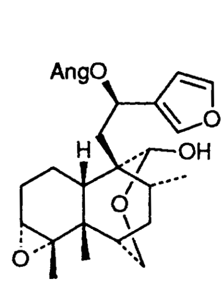
(767) X = H
(768) X = OH



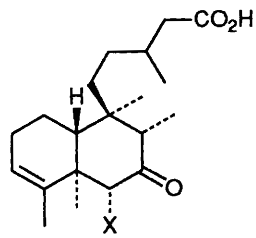
(769)



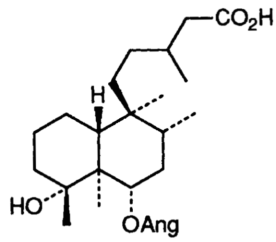
(770)



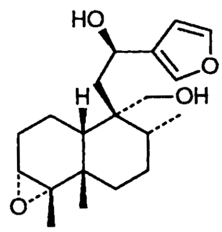
(771)



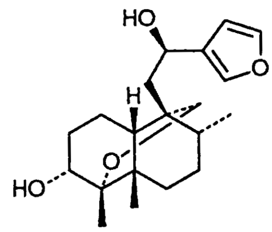
(772) X = H
(773) X = OH
(774) X = OAng
(775) X = OBu^{i}



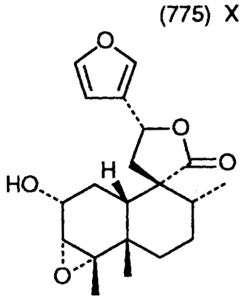
(776)



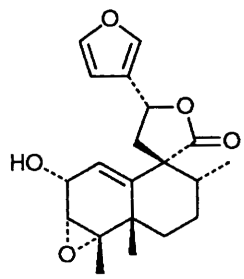
(777)



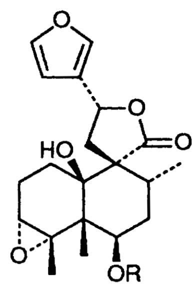
(778)



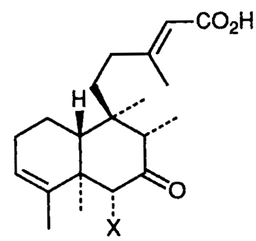
(779)



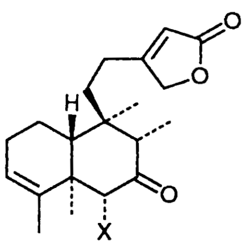
(780)



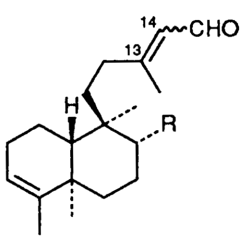
(781) R = H
(781) R = Ang
(783) R = MeBu



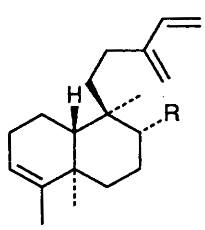
(784) X = H
(785) X = OH



(786) X = H
(787) X = OH



(788) R = CO_2H, 13–14 = *E*
(789) R = CHO, 13–14 = *E*
(790) R = CO_2H, 13–14 = *Z*
(791) R = CHO, 13–14 = *Z*



(792) R = CHO
(793) R = CO_2H

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