REVIEW PAPER

^{13}C NMR Spectroscopy of Lignan and Neolignan Derivatives*

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^{13}C NMR shielding data for about 300 compounds are tabulated, and critical spectral features are discussed as a guide to the use of the technique in structure elucidation and stereochemical allocations of lignan, neolignan and their derivatives. Unanalysed reported data have been analysed and, wherever necessary, ^{13}C signal assignments have been revised on the basis of more recent evidence and to obtain consistency throughout the series.

The term lignan was introduced by Haworth[2] around 1940 for a category of plant products having a common constitutional feature of two C_6–C_3 (*n*-propylbenzene) residues linked by a bond connecting the central (β) carbon atoms of each side-chain. In 1969, McCredie *et al.*[3] proposed that the definition of lignans should be extended to cover all natural products of low molecular weight that arise primarily from the oxidative coupling of *p*-hydroxyphenylpropane units. The term neolignan was introduced to designate compounds in which the two C_6–C_3 units are not linked by a β—β' bond.[4] According to the most recent definition, lignans are formed by oxidative coupling of cinnamyl alcohols and/or cinnamic acids, whereas neolignans are formed by oxidative coupling of 1-propenylphenols and/or allylphenols.[5] Lignans and neolignans have attracted much interest over the years, both on account of their widespread occurrence in nature[6] and their broad range of biological activities[7] (anti-tumour substances, hypertensive, sedative and anti-bacterial activity, plant germination inhibitors, growth inhibitors and antifungal agents). Of possibly even greater importance is the recent isolation of lignans from animals, including humans.[8] As a consequence, various reviews[9] have appeared, including a book,[6] covering the literature up to 1976 and dealing with various aspects of this class of natural products. The most recent review deals with the synthesis of these compounds.[10]

From a survey of the literature it is evident that, after the appearance of the first report[19] in 1974, ^{13}C NMR spectroscopy has played a distinctive role in structure elucidation and assignment of stereochemistry, and has also contributed to the revision of some structures which were derived from limited information gained from ^{1}H NMR and MS data. ^{13}C shielding data, however, are still scattered in the literature and so far there is no systematic compilation. This may be one of the reasons why most publications dealing with the isolation and chemical investigation of such compounds ignore ^{13}C NMR spectral analysis, despite its potential. A review of the available ^{13}C NMR literature for this important class of natural products was therefore considered to be timely. The assignments in some cases have been revised in the light of more recent evidence. Similarly, based on various facts, the stereochemistry of some of the compounds has been assigned and/or revised.

Instrumental and theoretical aspects of the ^{13}C NMR technique are not discussed here because detailed information is already available.[11–15] In general, ^{13}C NMR spectra are recorded with proton-noise (broad band) decoupling, which leads to loss of splitting owing to ^{13}C,^{1}H interactions and, hence, the ^{13}C signals appear as narrow singlets. Information regarding the number of attached H atoms to each C atom can be obtained by single frequency off-resonance decoupling (SFORD), where all CH couplings are reduced to such an extent that only the largest coupling constants [^1J(CH)] give rise to small residual splittings. (J, r) with gated decoupling, each C exhibited splitting due to one- and multiple-bond interactions. In some cases, both techniques lead to signal overlap. New techniques, such as the recording of J-coupled spin echoes,[16] attached proton polarization transfer (INEPT) and distortionless enhancement by polarization transfer (DEPT), have therefore been developed, where information on the number of attached hydrogens to an individual C atom can be inferred from the signal phases and intensities.[17]

Lanthanide shift reagents (LSR) have been increasingly used to simplify NMR spectra and for the purpose of ^{13}C signal assignments; however, their application to lignans is limited owing to their multifunctional behaviour. Recently, we have shown that Yb(fod)$_3$ is a very suitable ^{13}C NMR shift reagent with many advantages over other LSRs, and is of wide applicability owing to its definitive pattern of normalized shift values (RS values). For podophyllotoxin[18] it complexed preferentially to the trimethoxy grouping (C-4/C-α) rather than to the lactone carbonyl and hydroxyl groups (Fig. 1).

* ^{13}C NMR spectral Investigations, Part 9. For Part 8, see Ref. 1; for Part 5, see Ref. 63.

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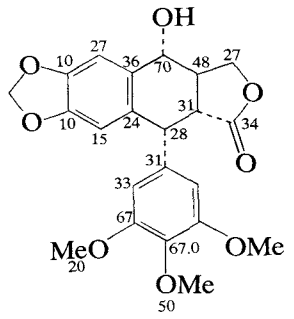


Figure 1. Yb(fod)$_3$-induced ^{13}C NMR shifts [C-α (C-4) in ppm, *S*; other carbons in %, *RS*] in podophyllotoxin.

All the ^{13}C shielding data for over 300 compounds, reported up to 1982, have been classified into different groups for convenience of discussion.[6] The term miscellaneous lignan has been used for those dimeric molecules formed from coupling of one C_6–C_3 unit with some member of another category of natural products such as flavonoids, xanthones and coumarins. These could be classified further according to the name of the adjoining non-lignan moiety.

The whole of the representation has been divided into three major parts. The first part (Sections 1–6) deals with a general discussion, divided into subcategories for lignan and neolignan derivatives. The second part (Section 7) discusses the effect of derivatization, such as acetylation, methylation and glycosylation, on the chemical shifts for spectral assignments purposes, and the ^{13}C chemical shift data of all the compounds are tabulated in the last part (Section 8, Table 1).

The classification of lignan and neolignan derivatives in Sections 1–6 is as follows.

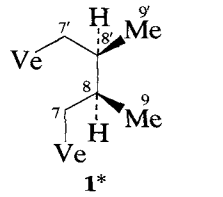
1. Lignan
   - 1.1. Derivatives of butane
   - 1.2. Derivatives of butanolide
   - 1.3. Derivatives of tetrahydrofuran
   - 1.4. Derivatives of 3,7-dioxabicyclo[3.3.0]octane
2. Cyclolignans
   - 2.1. Derivatives of tetrahydronaphthalene
   - 2.2. Derivatives of tetrahydronaphthalene lactone
   - 2.3. Derivatives of naphthalene lactone
3. Isolignan and benzofuran types of neolignan
   - 3.1. Derivatives of dihydrobenzofuran
   - 3.2. Derivatives of benzofuran
4. Dibenzocyclooctadiene lignan
   - 4.1. *R*-Biphenyl configuration
   - 4.2. *S*-Biphenyl configuration
5. Neolignan
   - 5.1. Hydrobenzofuranoid type
   - 5.2. Benzodioxane type
   - 5.3. Bicyclo[3.2.1]octane type
   - 5.4. Carinatane type
   - 5.5. Heterotropanone type
   - 5.6. Asatone type
   - 5.7. Other types
6. Miscellaneous lignans
   - 6.1. Flavonolignan
   - 6.2. Xanthonolignan
   - 6.3. Coumarinolignan

1. LIGNAN

This category is characterized by its typical β–β' or C-8–C-8′ coupling of two C_6–C_3 units, which may undergo additional couplings to generate various skeletal types. These have therefore been grouped into the following sections.

1.1. Derivatives of butane

The C-8–C-8′ coupling of the two C_6–C_3 units results in the formation of disubstituted (methyl or hydroxymethyl) diarylbutane derivatives in which, commonly, vicinal substituents possess a *trans*-stereochemical relationship. In a few cases the hydroxymethyl grouping is modified to a methoxymethyl grouping, as in phyllanthin (**8**), which introduces into the spectrum a distinctive signal at *ca* 58 ppm, corresponding to the aliphatic OCH_3 function.[22]



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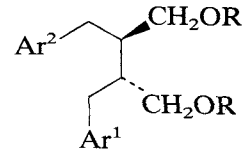
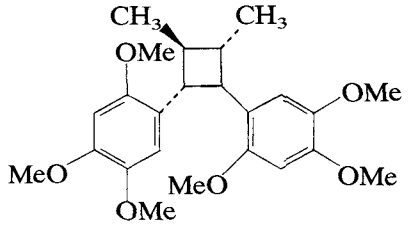


2 $Ar^1 = Ar^2 =$ Gu, R = H
3 $Ar^1 = Ar^2 =$ GuAc, R = Ac
4 $Ar^1 =$ Gu, $Ar^2 =$ Ve, R = H
5 $Ar^1 =$ GuAc, $Ar^2 =$ Ve, R = Ac
6 $Ar^1 = Ar^2 =$ Ve, R = H
7 $Ar^1 = Ar^2 =$ Ve, R = Ac
8 $Ar^1 = Ar^2 =$ Ve, R = Me
9 $Ar^1 = Ar^2 =$ Pi, R = H
10 $Ar^1 = Ar^2 =$ Pi, R = Me
11 $Ar^1 = Ar^2 =$ Pi, R = Ac



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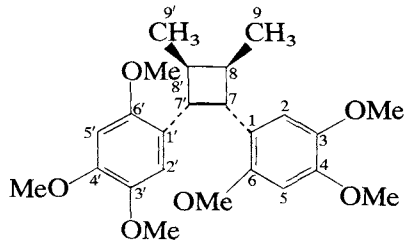

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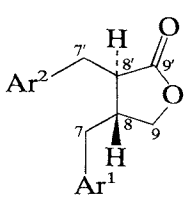
An additional α–α' or C-7–C-7′ coupling gives rise to cyclobutane types of lignans in which the relative stereochemistry could be deduced by comparison with the ^{13}C shielding data reported for cyclobutane derivatives.[25c] Thus, the appearance of the 9,9′-CH_3 signal at 19.3 ppm in acoradin[24] (**12**) suggests a *trans* orientation of the methyl groups; hence, the stereochemistry

* See footnote to Table 1 for abbreviations used in formulae.

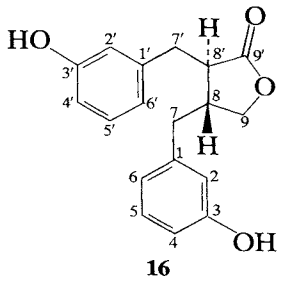
of acoradin could be depicted as shown in **12**. By analogy, the ^{13}C spectral data[25a] for heterotropan (**13**) could be analysed.

1.2. Derivatives of butanolide

Usually, benzyl substituents on a butyrolactone moiety possess a *trans* relationship, and the ^{13}C resonances for C-7 and C-7′ were observed at 38.3±0.7 and 34.5±0.3 ppm, respectively, while these were shielded by about 4–5 ppm in *cis* compounds,[28a] e.g. isoarctigenin monoacetate (**34**), owing to γ-steric interactions between the methylenic hydrogen atoms. Hence, the relative configuration of the diarylbutyrolactone lignans could be determined. ^{13}C NMR spectral data reported[28c] for yatein (**19b**) indicate the chemical shift of 3″-OMe at 65.1 ppm, which is unusually downfield even in the presence of one free *ortho*-position; moreover, it should be equivalent in its shielding pattern to 5″-OMe (56.1 ppm) (this may be a printing error and, hence, we have reported it as 56.1 instead of 65.1 ppm).



14 $Ar^1 = Ar^2 = Gu$
15 $Ar^1 = Ar^2 = GuAc$
17 $Ar^1 = Pi$, $Ar^2 = Gu$
18 $Ar^1 = Pi$, $Ar^2 = GuAc$
19 $Ar^1 = Ar^2 = Pi$
20 $Ar^1 = Tp$, $Ar^2 = Gu$
21 $Ar^1 = Tp$, $Ar^2 = Ve$
22 $Ar^1 = Tp$, $Ar^2 = GuAc$
23 $Ar^1 = Ar^2 = Ve$
24 $Ar^1 = Ve$, $Ar^2 = Tp$
25 $Ar^1 = Ve$, $Ar^2 = Gu$



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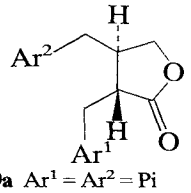
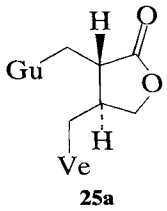
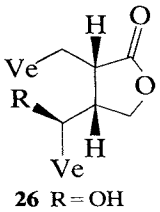


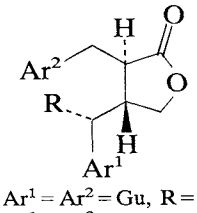
19a $Ar^1 = Ar^2 = Pi$
19b $Ar^1 = Tp$, $Ar^2 = Pi$



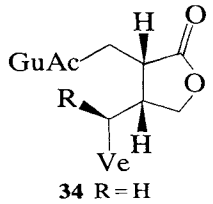
25a



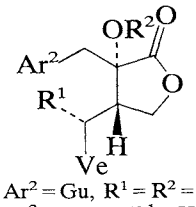
26 R = OH
27 R = OAc



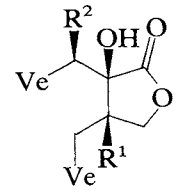
28 $Ar^1 = Ar^2 = Gu$, R = OH
29 $Ar^1 = Ar^2 = GuAc$, R = OAc
30 $Ar^1 = Ar^2 = Ve$, R = OH
31 $Ar^1 = Ar^2 = Ve$, R = OAc
32 $Ar^1 = Ar^2 = Pi$, R = OH
33 $Ar^1 = Ar^2 = Pi$, R = OAc



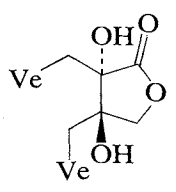
34 R = H
35 R = OAc



36 $Ar^2 = Gu$, $R^1 = R^2 = H$
37 $Ar^2 = GuAc$, $R^1 = H$, $R^2 = Ac$
38 $Ar^2 = Gu$, $R^1 = OH$, $R^2 = H$
39 $Ar^2 = GuAc$, $R^1 = OAc$, $R^2 = Ac$



40 $R^1 = H$, $R^2 = OH$
41 $R^1 = OH$, $R^2 = H$



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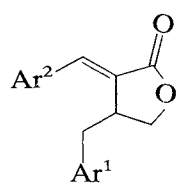
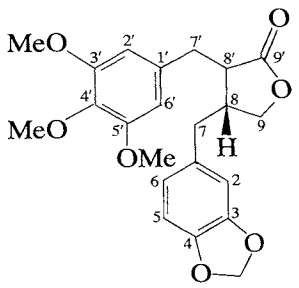


43 $Ar^1 = Ar^2 = Ve$
43a $Ar^1 = Ar^2 = Pi$



43b

The comparison of the shifts for methylarctigenin (**23**) with 7-hydroxymatairesinol dimethyl ether (**30**) provided the SIS (substituent-induced shifts), i.e. 37.0, 3.2 and 2.6 ppm downfield for C-7, C-1′ and C-8, and upfield shifts of 2.8 and 1.5 ppm for the C-9 and C-8′ signals, respectively, due to the introduction of the hydroxy group at C-7.[28a]

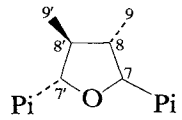
Introduction of a hydroxy group on the adjacent position (C-8′) to the butyrolactone carbonyl [arctigenin (**25**) to trachelogenin (**36**)] causes a 30 ppm downfield shift of C-8′, an unsymmetrical β-effect of +7.4 ppm for the 7′-methylene and +2.8 ppm for the 8-methine, and a negligible effect on the carbonyl shift. An interesting upfield shift (*ca* 4 ppm) for the signal of C-1′, even in the absence of a γ-hydrogen atom, provided a means of differentiating the C-1 and C-1′ signals, and hence definitive assignments for these carbons could be achieved.

The assignment of the signals of 109.04 and 121.87 ppm to an oxyaryl carbon (C-5′) and to an arylmethine (C-6′), respectively, of the 3′,4′,5′-trimethoxybenzylidene unit of nemerosin (**43b**), reported by Turabelidze *et al.*,[28b] seems to be untenable since C-3′, C-5′ and C-2′, C-6′ should be magnetically equivalent as observed in other similar cases; therefore, the assignments have been revised for the carbon atoms of the piperonyl and trimethoxyphenyl moieties.

1.3. Derivatives of tetrahydrofuran

These compounds can be grouped into the following three types.

1.3.1. 7,7′-Monoepoxy lignan. In general, an axial orientation of an aryl ring leads to a 5.5±0.6 ppm shielding of the functional α-carbon in comparison to its equatorially substituted equivalent carbon. The benzyloxy carbons were observed at 82±0.8 ppm in the case of an axially oriented aryl ring and at 87.2±0.7 ppm for equatorial substitution. Thus, the chemical shifts of these carbon atoms is sensitive to the orientation of the aryl rings and could be of



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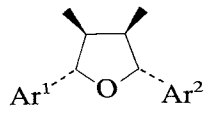
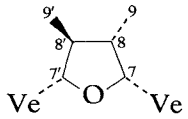


45 $Ar^1 = Ar^2 = Ve$
46 $Ar^1 = Gu$, $Ar^2 = Ve$



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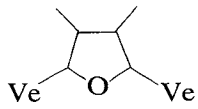

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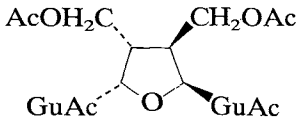

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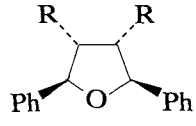
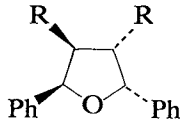
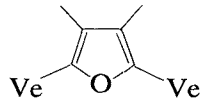


50 $R = CH_2OH$
51 $R = COOC_2H_5$



51a $R = COOC_2H_5$



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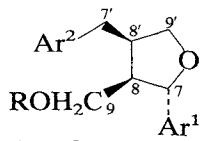
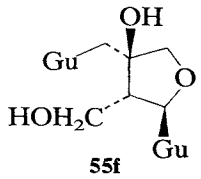
diagnostic importance for the conformational analysis of such systems.[32a] The C-9 and C-9′ carbon atoms, either as methyl or hydroxymethyl groups, substituted on the tetrahydrofuran nucleus also show shielding dependence on the mutual stereochemical relationship and, hence, *trans*-oriented vicinal substituents exhibit higher α-effects than the *cis*-epimer. The C-8,8′ signals were observed[32a] at 50.9 ppm in galbacin (**44**), 44.3 ppm in galgravin (**45**) and 41.2 in di-*O*-methyltetrahydrofuroguaicin B (**48**). This shielding variation could be correlated to the mutual *cis* or *trans* vicinal interactions as well as to the disposition of the hydrogen on these carbons with respect to the aryl substituent. A higher shielding has been observed if the hydrogen on C-8 has a *trans* relationship with respect to the aromatic ring.

The proposed configurational assignments for synthetic lignans **50** and **51** which were reported to possess symmetrical *trans–meso* structures,[35a] have been revised based on these observations. The chemical shift of the oxybenzylic carbon suggests a pseudo-axial orientation of the aryl rings, thus the *r*-2, 3*t*, 4*c*, 5*t* forms $^3T_4$ and V_4 of the cycle of pseudo-rotation (CYCLOPS)[35b] represents the most probable conformations. Similarly, the unsymmetrical pattern of the tetrahydrofuran ring signals led to the proposal of the *r*-2, 3*c*, 4*t*, 5*t* form for **51a**.

1.3.2. 7,9′-Monoepoxy lignan. In this category, the ^{13}C resonance for C-7 was found at 82.6 ± 0.3 ppm. Probably, this reflects a preferred axial orientation of the aromatic ring owing to the resemblance of the shift to those of 7,7′-monoepoxy lignans (see above). The hydroxy substitution at 7′ and/or 8′ shows the expected shift change.



53 $Ar^1 = Ar^2 = Gu$, R = H
54 $Ar^1 = Ar^2 = GuAc$, R = Ac
55 $Ar^1 = Ar^2 = Ve$, R = H
55a $Ar^1 = Ar^2 = Ve$, R = Ac
55b $Ar^1 = Gu$, $Ar^2 = Ve$, R = H
55c $Ar^1 = GuAc$, $Ar^2 = Ve$, R = Ac
55d $Ar^1 = Ve$, $Ar^2 = Gu$, R = H
55e $Ar^1 = Ve$, $Ar^2 = GuAc$, R = Ac



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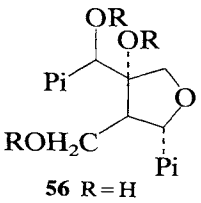
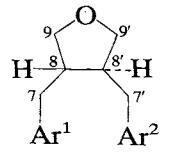
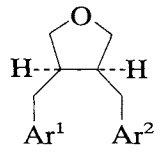


56 R = H
57 R = Ac

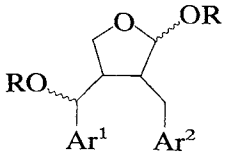
1.3.3. 9,9′-Monoepoxy lignan. The ^{13}C shifts for C-7,7′, C-8,8′ and C-9,9′ vary significantly depending on the stereochemical relationship between the benzyl substituents, and are indicative of the stereochemical assignments. In *cis*- (**60**) and *trans*-burseran (**61**) these carbon signals were downfield in the *trans* compared



58 $Ar^1 = Ar^2 = Gu$
59 $Ar^1 = Ar^2 = HdAc$
61 $Ar^1 = Tp$, $Ar^2 = Pi$
62 $Ar^1 = Ar^2 = Pi$



60 $Ar^1 = Tp$, $Ar^2 = Pi$

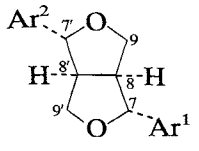


63 $Ar^1 = Ar^2 = GuAc$, R = Ac

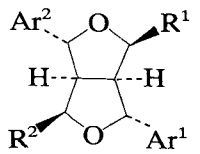
with the *cis* isomer owing to steric interactions in the latter.[36a] The epimeric shift difference (**61**−**60**) was 5.9 ± 0.1, 2.7 ± 0.3 and 1.2 ± 0.1 ppm for C-7,7′, C-8,8′ and C-9,9′, respectively. Hence, with the consistency of the shielding of these signals,[19] a *trans* stereochemistry could be proposed for **58**, **59** and **62**, which is in agreement with the similar behaviour reported for *cis*- and *trans*-2,3-dimethyltetrahydrofuran.[36b]

1.4. Derivatives of 3,7-dioxabicyclo[3.3.0]octane

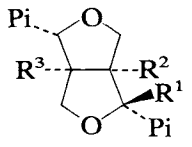
^{13}C NMR spectrometry has proved to be very useful for determining the structure and stereochemistry of these lignans. The values of the chemical shifts for C-1 and C-1′, in particular, are characteristic of the stereochemistry of the attachment to the basic skeleton.[41] Thus, the chemical shift of C-1 of equatorial 3,4-dimethoxyphenyl, 3,4-methylenedioxyphenyl and 3,4,5-trimethoxyphenyl groups are in the ranges 133.4–134.1, 134.9–135.6 and 136.6–137.6 ppm, respectively, whereas for a similar axial substituent they appear at 130.8–131.4, 132.6 and 134.1 ppm, respectively. This indicates an average shielding increase of 2.3–3.0 ppm for C-1 in going from an equatorial to an



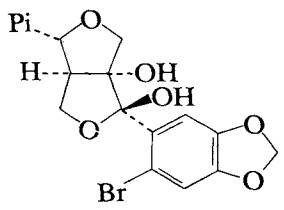
64 $Ar^1 = Ar^2 = Hy$
65 $Ar^1 = Ar^2 = Gu$
66 $Ar^1 = Ar^2 = GuAc$
67 $Ar^1 = Ve$, $Ar^2 = Gu$
68 $Ar^1 = Ve$, $Ar^2 = GuAc$
69 $Ar^1 = Ar^2 = Ve$
70 $Ar^1 = Ar^2 = Ve$
71 $Ar^1 = Ar^2 = Pi$
72 $Ar^1 = Pi$, $Ar^2 = Ve$
73 $Ar^1 = Ar^2 = Tp$
74 $Ar^1 = Ar^2 = Hd$
75 $Ar^1 = Pi$, $Ar^2 = Tp$



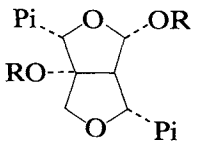
76 $Ar^1 = Ar^2 = Pi$, $R^1 = OH$, $R^2 = H$
77 $Ar^1 = Ar^2 = Pi$, $R^1 = OAc$, $R^2 = H$
78 $Ar^1 = Ar^2 = Gu$, $R^1 = R^2 = OH$
79 $Ar^1 = Ar^2 = GuAc$, $R^1 = R^2 = OAc$
80 $Ar^1 = Ar^2 = Gu$, $R^1 = R^2 = OMe$
81 $Ar^1 = Ar^2 = GuAc$, $R^1 = R^2 = OMe$
82 $Ar^1 = Ar^2 = Pi$, $R^1 = R^2 = OH$
83 $Ar^1 = Ar^2 = Pi$, $R^1 = R^2 = OAc$
84 $Ar^1 = Ar^2 = Ve$, $R^1 = R^2 = OH$
85 $Ar^1 = Ar^2 = Ve$, $R^1 = R^2 = OAc$
86 $Ar^1 = Ar^2 = Ve$, $R^1 = R^2 = OMe$



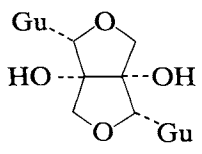
87 $R^1 = R^3 = H$, $R^2 = OH$
88 $R^1 = R^3 = H$, $R^2 = OAc$
89 $R^1 = R^2 = OH$, $R^3 = H$
93 $R^1 = H$, $R^2 = R^3 = OH$
94 $R^1 = H$, $R^2 = R^3 = OH$
95 $R^1 = H$, $R^2 = R^3 = OAc$



90



91 R = H
92 R = Ac

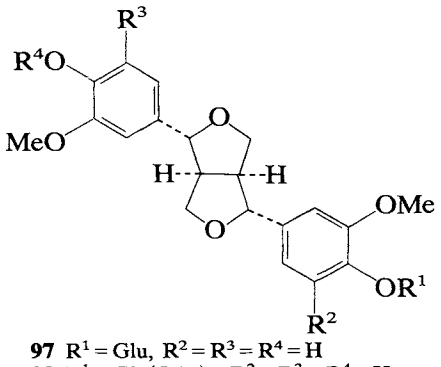


96

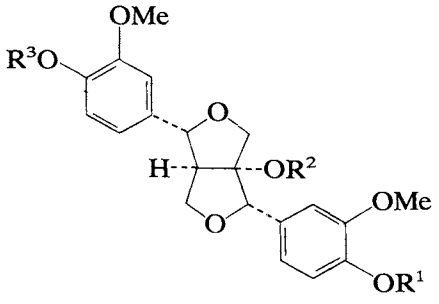
axial aryl substituent. The same is true for the *epi* series, in which, when any of the aryl groups change from an equatorial to an axial position, there is an average upfield shift of 2.5–2.7 ppm for the C-1 signal. These criteria, therefore, could be used to establish the stereochemistry of both the aryl groups in the molecule.

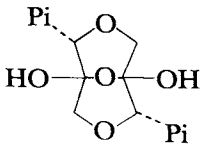
The chemical shifts for C-7,7′, C-8,8′ and C-9,9′ are also dependent on the stereochemistry of the molecule. In compounds **64–75** with both aryl groups equatorially oriented, these carbon atoms appeared in the ranges 85.3–85.9, 53.7–54.4 and 71.3–72.0 ppm, respectively. On the other hand, these signals were observed at 83.9, 49.5 and 68.7 ppm, respectively, in dieudesmin (**126**), which is the only example with both aryl groups axially oriented.[41] These shifts remain unaltered on the acetylation of the phenolic hydroxyl groups.

The hydroxy group in 9- or 9′-monohydroxylated or 9,9′-dihydroxylated compounds,[42,51] such as in some of the **76–86** series, causes downfield shifts of 29.0 ± 0.5 and 7.3 ± 0.6 ppm of the α- and β-carbons, respectively, while C-1 shows a downfield shift of 1.5 ± 0.7 ppm. In 8-hydroxy compounds, as in paulownin[43] (**87**), the hydroxy group causes downfield shifts of 37.5, 1.9 and 6.4 ppm for C-8, -7 and -8′, respectively, and an upfield shift of *ca* 5.5 ppm for C-1, with no significant effect on the remaining carbons. Introduction of a further hydroxy group at C-7, which



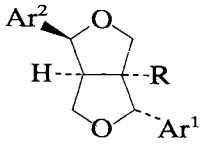
97 $R^1 = Glu$, $R^2 = R^3 = R^4 = H$
98 $R^1 = Glu(OAc)_4$, $R^2 = R^3 = R^4 = H$
99 $R^1 = Glu$, $R^2 = R^3 = H$, $R^4 = Me$
100 $R^1 = R^4 = Glu$, $R^2 = R^3 = OMe$



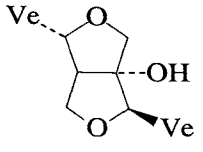


108

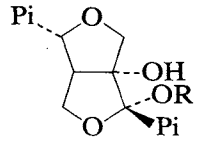
101 $R^1 = Glu$, $R^2 = Ac$, $R^3 = H$
102 $R^1 = Glu$, $R^2 = Ac$, $R^3 = Me$
103 $R^1 = Glu$, $R^2 = R^3 = H$
104 $R^1 = Glu$, $R^2 = H$, $R^3 = Me$
105 $R^1 = Glu(OAc)_4$, $R^2 = H$, $R^3 = Me$
106 $R^1 = Glu(OAc)_4$, $R^2 = Ac$, $R^3 = Me$
107 $R^1 = Glu(OAc)_4$, $R^2 = R^3 = Ac$



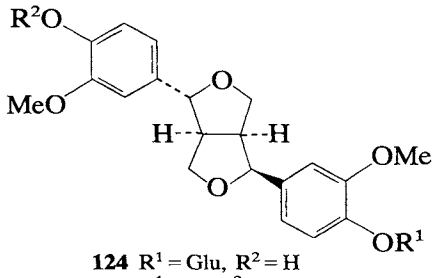
109 $Ar^1 = Ar^2 = Ve$, R = H
110 $Ar^1 = Ar^2 = Ve$, R = H
111 Ar^1 = 3-OH-4-OMe-Ph, $Ar^2 = Pi$, R = H
112 $Ar^1 = Ar^2 = Pi$, R = H
113 $Ar^1 = Ar^2 = Ve$, R = OH
118 $Ar^1 = Pi$, $Ar^2 = Tp$, R = H
119 $Ar^1 = Ve$, $Ar^2 = Tp$, R = H
120 $Ar^1 = Gu$, $Ar^2 = Ve$, R = H
121 $Ar^1 = Gu$, $Ar^2 = Ve$, R = H
122 $Ar^1 = GuAc$, $Ar^2 = Ve$, R = H
123 $Ar^1 = GuAc$, $Ar^2 = Ve$, R = H



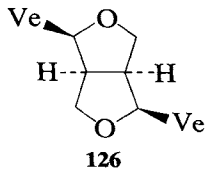
114



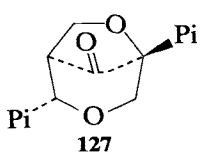
115 R = H
116 R = CH_3
117 R = C_2H_5



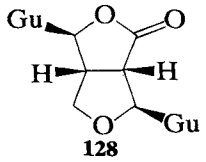
124 $R^1 = Glu$, $R^2 = H$
125 $R^1 = H$, $R^2 = Glu$



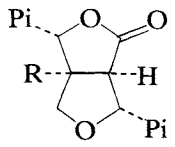
126



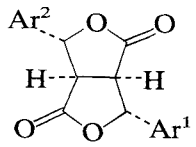
127



128



129 R = H
130 R = OH



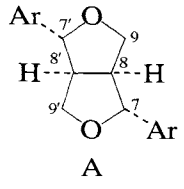
131 $Ar^1 = Ar^2 = Pi$
132 $Ar^1 = Ar^2 = Gu$
133 $Ar^1 = Ar^2 = Ve$
134 $Ar^1 = Ar^2 = GuAc$

acquires a pseudo-axial orientation as in isoarboreol[37] (**89**), leads to downfield shifts of 15.2, 3.3, 5.2 and 5.6 ppm for C-7, -8, -9 and -1, respectively.

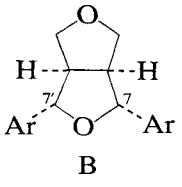
Chiba *et al.*[48a] isolated phillyrin (**125**), a 4′-*O*-glucoside of phillygenin, from *Forsythia suspensa* and assigned structure **120** to phillygenin. Banerji and Pal[48c] later isolated an identical compound from *Piper sylvaticum*, and named it as sylvatesmin (**121**). A close examination of the spectral data proved that these two compounds are identical in all respects.

Pelter *et al.*[51] assigned a signal at 108.8 or 108.5 ppm to C-5 in pinoresinol (**65**), which is in contrast to the assignments for pinoresinol at 114 ppm reported by Fonseca *et al.*[21] The latter signal at *ca* 114 ppm is characteristic of guaicyl-containing lignans. The acetylation-induced shifts supported the assignment at 114.4 ppm, as if the 108 ppm assignment were correct then the *ortho*-downfield effect on C-5 due to acetylation is 13.7 ppm, which is too high. Therefore, the assignments reported in Ref. 21 are regarded as standard for C-5.

A distinction between the two isomeric forms, A and B, of 3,7-dioxabicyclo[3.3.0]octane lignans can be deduced on the basis of the chemical shifts of C-7 and C-7′, as these are 1 ppm to lower field in B in comparison with similar carbon atoms in the A series. In general, C-7, 7′ resonances appear at 85.8±0.1 ppm in the A series, and at 87.0±0.2 ppm in the B series.[49,52]



A



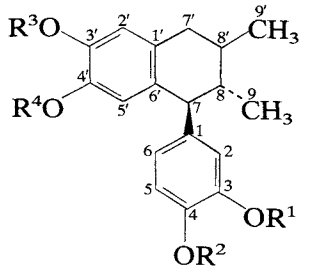
B

2. CYCLOLIGNANS

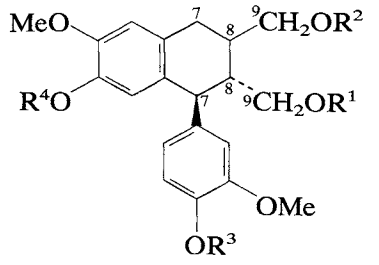
The usual C-8,8′ coupling and, in addition, coupling of an aromatic ring carbon atom of one C_6–C_3 unit with C-7 of the other C_6–C_3 unit generates a tetrahydronaphthalene or naphthalene type of skeleton, which constitute this category of lignans. These could be classified into the following three types.

2.1. Derivatives of tetrahydronaphthalene

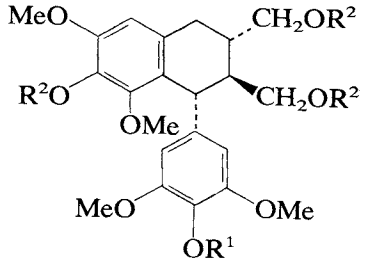
The C-9 atoms in this category may be methyl or hydroxymethyl, which commonly possess a *trans* relationship with their vicinal substituent. A comparison of the shifts for galbulin[22a] (**135**) with isolariciresinol 4,4′-dimethyl ether[20] (**139**) leads to the shifts induced by hydroxy substitution at the 9,9′-methyl groups. This indicated the usual α- and β-effects and significant shielding, 6.2±0.3 ppm, of the γ-carbon atoms C-7,7′, which could be valuable in evaluating a preferred conformation. Consideration of the phenyl substituent-induced shifts resulting from the comparison of the ^{13}C data for **135** with *trans*-2,3-dimethyltetralin,[22b] in conjunction with the shielding (−2.4 ppm) of 3-CH_3, leads to the prediction that **135** exists in a preferred conformer in which the aryl ring and the methyl group acquire a pseudo-equatorial or equatorial orientation, which is again in line with the preferred equatorial orientation of the methyl groups in *trans*-2,3-dimethyltetralin.[22b] The occurrence of severe 1,3-diaxial interaction between the substituents will certainly destabilize a conformer with axial substituents. An upfield shift (5.9–6.4 ppm) of C-7,7′ due to substitution of one of the methyl group hydrogens by a hydroxy group (as in **139** compared with **135**)



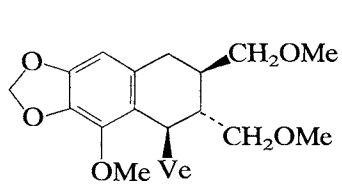
135 $R^1 = R^2 = R^3 = R^4 = Me$
136 $R^1 = R^2 = Me$, $R^3 + R^4 = CH_2$
136a $R^1 + R^2 = CH_2$, $R^3 = R^4 = Me$



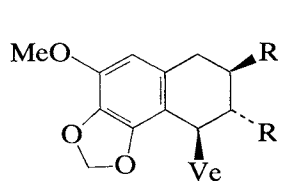
137 $R^1 = R^2 = R^3 = R^4 = H$
138 $R^1 = R^2 = R^3 = R^4 = Ac$
139 $R^1 = R^2 = H$, $R^3 = R^4 = Me$
140 $R^1 = R^2 = Ac$, $R^3 = R^4 = Me$
141 $R^1 = R^2 = R^4 = H$, $R^3 = Me$
142 $R^1 = R^2 = R^4 = Ac$, $R^3 = Me$
143 $R^1 = R^2 = R^3 = H$, $R^4 = Me$
144 $R^1 = R^2 = R^3 = Ac$, $R^4 = Me$
145 $R^1 = R^2 = R^3 = R^4 = Me$
152 $R^1 = Xyl(OAc)_3$, $R^2 = R^3 = R^4 = Ac$



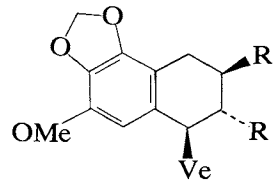
146 $R^1 = R^2 = H$
147 $R^1 = R^2 = Ac$
153 $R^1 = Glu$, $R^2 = H$
154 $R^1 = Glu(OAc)_4$, $R^2 = H$



148

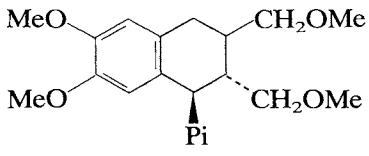


149

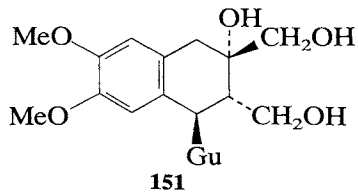


149a

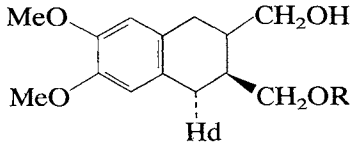
R = CH_2OMe



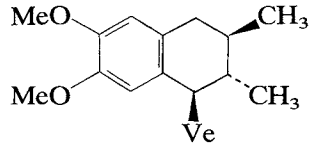
150



151



155 R = Xyl



155a

gives information about the preferred rotamer population of the CH_2OH group. The most populated form is one in which the hydroxy groups of the CH_2OH moieties acquire such a position in space that they have a *gauche* relationship with C-7,7′ and reduced methylenic interactions between the vicinal CH_2OH groups.

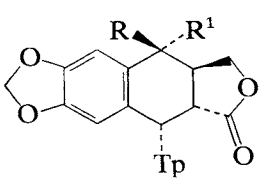
The alcoholic methoxy group absorbed distinctively at 58.0 ± 0.4 ppm and, therefore, could be readily distinguished from the aryl methoxy groups (see below).

The structure of hypophyllanthin (**149**), based on ^{13}C NMR spectral analysis,[23a] was revised to **149a**; however, x-ray analysis[23b] and synthetic studies[23c] supported the alternative proposed structure **149**.

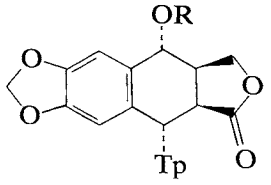
2.2. Derivatives of tetrahydronaphthalene lactone

The cyclization of hydroxymethyl and carboxylic group moieties at C-8,8′ leads to the formation of a lactone ring. The fusion of the lactone ring to the tetrahydronaphthalene ring is normally *trans*, but in some cases it may be *cis*. A distinction between the two could be made on the basis of the ^{13}C shifts, as the carbonyl signal exhibits a 3–4 ppm deshielding in the case of the *cis*-epimer compared with that for the *trans*-epimer.[58] Introduction of a 7′-OH group causes a chemical shift variation depending on the orientation of the substituent. In epipodophyllotoxin (**159**) there is a downfield shift of C-8′,9′ compared with podophyllotoxin (**157**), which shows that the 7′-OH group acquires a pseudo-axial orientation in **159** compared with a pseudo-equatorial orientation in **157**.[58]

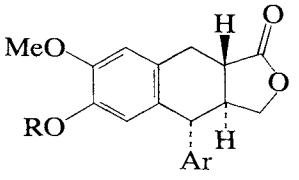
In some cases the lactone carbonyl, C-9′, becomes modified to a hydroxy or alkoxy group whose orientation could be determined on the basis of the chemical shift of the dioxygenated C-9′ methine. This gives rise to a signal at *ca* 103 ppm in the case of a pseudo-equatorial orientation, but absorbs at *ca* 101 ppm for



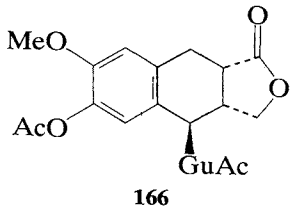
156 R = R^1 = H
157 R = H, R^1 = OH
158 R = H, R^1 = OAc
159 R = OH, R^1 = H
160 R = OAc, R^1 = H
163 R + R^1 = O



161 R = H
162 R = Ac



164 R = H, Ar = Gu
165 R = Ac, Ar = GuAc



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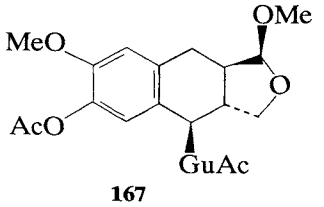
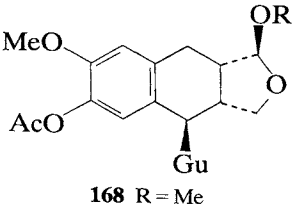
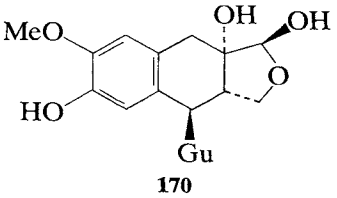


167

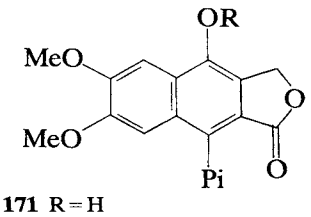


168 R = Me
169 R = C_2H_5

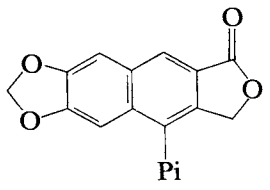


170

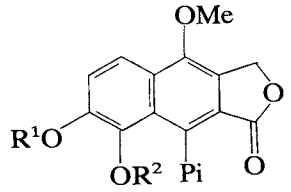
a pseudo-axial orientation.[59,60a] The chemical shift of the γ-C-7′ exhibits shielding in the case of a *gauche* relationship with the substituent at C-9′ and, hence, is indicative of the stereochemistry at the C-9′ substituent.



171 R = H
172 R = Xyl-3,4$(OCH_3)_2$
173 R = Xyl-2(OAc)-3, 4$(OCH_3)_2$
174 R = Xyl$(OCH_3)_3$
174a R = Xyl$(OCH_3)_3$(furanose)



171a



171b R^1 = Me, R^2 = H
171c R^1 = R^2 = H
171d R^1 = H, R^2 = Me

2.3. Derivatives of naphthalene lactone

The signal at 169.4 ± 1.0 ppm of the lactone carbonyl is very characteristic of this type of lignan, while the oxymethylene of the lactone ring gives rise to a signal in the range 66.6–69.8 ppm.[60c] Based on the chemical shifts of the aryl methoxy groups, the structure of a new lignan, (**171d**), has been revised to **171b** (see below).

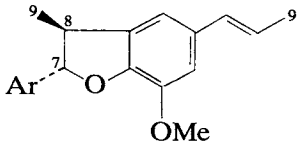
3. ISOLIGNAN AND BENZOFURAN TYPES OF NEOLIGNAN

The coupling of C-8 of one of the C_6–C_3 units with the aryl carbon (C-5′) of the other C_6-C_3 unit, in addition to the coupling of C-7 of the first with C-4′ of the second unit through oxygen, produces a benzofuran nucleus, which is a common structural feature for this category. This could be subdivided into the following two types.

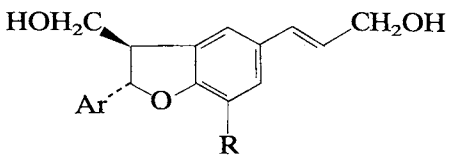
3.1. Derivatives of dihydrobenzofuran

The ^{13}C NMR data reported so far are for those dihydrobenzofuran derivatives which have been shown to have a *trans* mutual relationship between the 9-CH_3 or 9-CH_2OH group and the C-7 aryl ring. The compounds containing a 9-CH_3 group exhibit characteristic shifts of 93.8 ± 0.8, 45.9 ± 0.7 and 17.5 ± 0.3 ppm for C-7, C-8 and C-9, respectively, whereas these shifts are 87.7 ± 0.7, 55.5 ± 1.0 and 65.0 ± 0.5 ppm, respectively, in compounds containing a 9-CH_2OH grouping. The benzofuran types of neolignan also exhibit a similar chemical shift pattern to that discussed above.

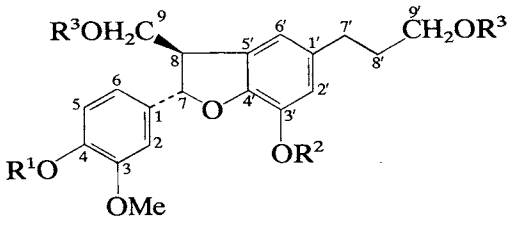
Taking a half-chair conformation for the dihydrobenzofuran moiety into consideration, the conformer with both the aryl and CH_3 or CH_2OH groups



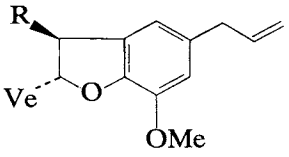
175 Ar = Gu
176 Ar = Gu
177 Ar = Gu
178 Ar = Pi



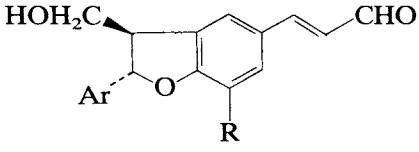
179 Ar = Gu, R = H
180 Ar = Gu, R = OMe
188a Ar = (4-O-Glu)Gu, R = OMe



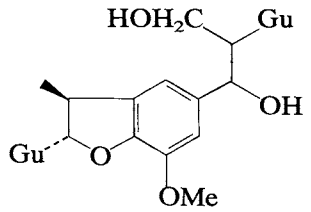
181 R^1 = R^2 = R^3 = H
182 R^1 = R^3 = H, R^2 = Me
183 R^1 = R^2 = R^3 = $COCH_3$
184 R^1 = R^3 = $COCH_3$, R^2 = Me
185 R^1 = Glu, R^2 = R^3 = H
186 R^1 = Glu$(OAc)_4$, R^2 = R^3 = $COCH_3$
187 R^1 = Glu$(OAc)_4$, R^2 = Me, R^3 = $COCH_3$



188b R = CH_3
188d R = CH_2OH



188c Ar = Gu, R = OMe
189 Ar = Ca, R = OH



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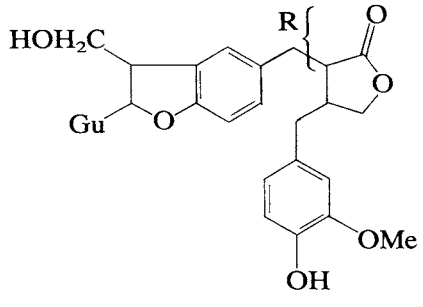

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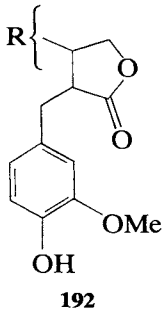

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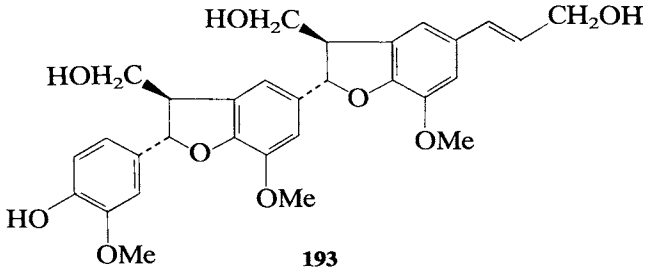
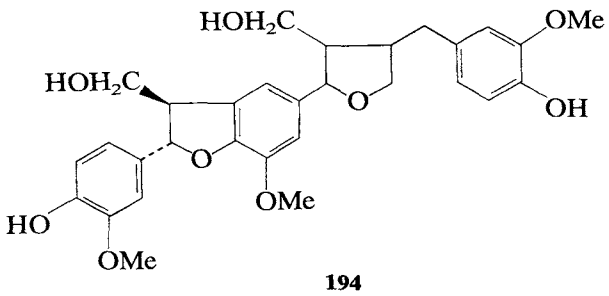
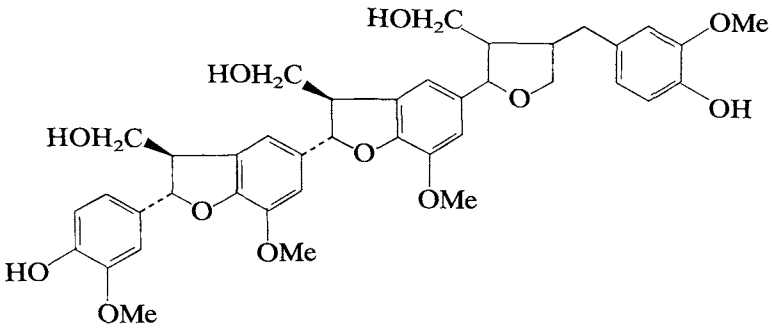


193



194



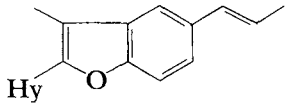
195

in an equatorial orientation is preferred over the conformer in which these are axially oriented.

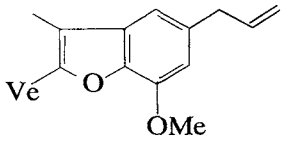
A typical chemical shift for C-7 at *ca* 88 ppm in lignans containing a 9-CH_2OH group led to the prediction of a *trans* stereochemistry for the sesquilignans **190–193** and the dilignan **194**.[65,66]

3.2. Derivatives of benzofuran

So far, the only examples known in this category possess a CH_3 group linked to the benzofuran nucleus; this absorbs at 9.5 ± 0.2 ppm. As the introduction of an OMe into the aryl ring (Ar^1) will not have a remarkable effect on the chemical shift of C-7, the C-7 signal assignment in carinatin (**195b**)[83a] has been revised in the light of the assignments reported[67] for ratanhiaphenol II (**189a**).



195a



195b

4. BENZOCYCLOOCTADIENE

The coupling of the aryl carbon atoms (C-6,6′), adjacent to the side-chain of both C_6–C_3 units, together with the usual C-8,8′ coupling, leads to a benzocyclooctadiene skeleton. This series could be classified into two groups:

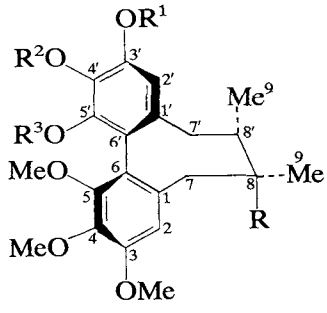
4.1. With an *R*-biphenyl configuration.
4.2. With an *S*-biphenyl configuration.

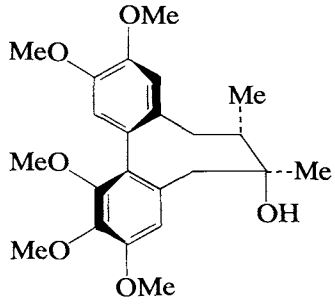
4.1. *R*-Biphenyl configuration

These can be divided into the following subgroups, depending on the substitution on the cyclo-octane ring:

4.1.1. (+)-Deoxyschizandrin group.
4.1.2. Schizandrin group with a hydroxy group at C-8.
4.1.3. Schizandrin group with a keto function at C-7.

4.1.1. (+)-Deoxyschizandrin group. The methyl signals observed at 12.7 ± 0.2 and 21.8 ± 0.2 ppm can be assigned to an axial and equatorial methyl, respectively.[70,74] The benzylic methylene at δ35.7 ± 0.2 ppm was assigned to the C-7 methylene carbon of the





201

196 R = H, $R^1 = R^2 = R^3 = Me$
197 $R = R^1 = H$, $R^2 = R^3 = Me$
198 R = H, R^1 = Ac, $R^2 = R^3 = Me$
199 $R = R^3 = H$, $R^1 = R^2 = Me$
200 R = H, $R^1 + R^2 = CH_2$, R^3 = Ac
202 R = H, R^3 = Ac, $R^1 = R^2 = Me$
203 R = OH, $R^1 + R^2 = CH_2$, $R^3 = Me$
204 R = OH, $R^1 = R^2 = Me$, $R^3 = H$

equatorial 9-methyl side, whereas the remaining methylene (C-7′) resonates at 33.6 ± 0.2 ppm, (the 9′-axial methyl side). The methine carbon (C-8′) carrying an axial methyl group appeared at δ38.9 ± 0.3 ppm while the methine carbon (C-8) carrying an equatorial methyl absorbed at δ40.8 ± 0.3 ppm.

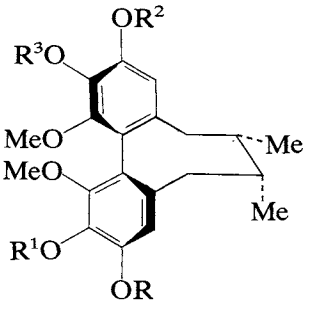
4.1.2. Schizandrin group with a hydroxy group at C-8. The introduction of a hydroxy group (axial) at C-8 as in **201–203** causes a downfield shift of 30 ppm for C-8, shifts the axial 9′-methyl 3 ppm downfield in spite of the *γ-trans* position, thus appearing at $\delta 15.8 \pm 0.1$ ppm, while the equatorial tertiary methyl (C-9) shifts to 29.8 ± 0.1 ppm due to the β-effect of the hydroxy group.

4.1.3. Schizandrin group with a keto function at C-7. This is described in Section 4.2.5 (see below).

4.2. *S*-Biphenyl configuration

These compounds can be divided into the following sub-groups:

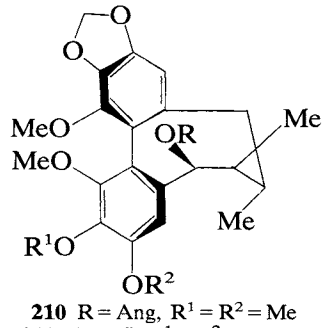
4.2.1. Gomisin J group.
4.2.2. Gomisin O group with a hydroxy group at C-7.
4.2.3. Gomisin B group with two hydroxy groups at C-7 and C-8.
4.2.4. Derivatives of benzocyclooctadiene lactone.
4.2.5. Gomisin group with a keto function at C-7.



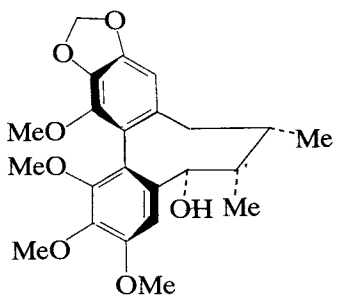
205 $R = R^1 = Me$, $R^2 + R^3 = CH_2$
205a $R + R^1 = R^2 + R^3 = CH_2$
206 $R = R^1 = R^3 = Me$, $R^2 = H$
207 $R = R^1 = R^3 = Me$, $R^2 = Ac$
208 $R = R^1 = R^2 = R^3 = Me$
209 $R^1 = R^2 = H$, $R = R^3 = Me$

4.2.1. Gomisin J group. The chemical shift pattern for the methyl groups and benzylic methylenes was found to be similar to that discussed in Section 4.1.1.

4.2.2. Gomisin O group with a hydroxy group at C-7. The chemical shifts of both methyls differed significantly from those of the other lignans possessing the twist–boat–chair (TBC) conformation, and the ^{13}C data support a boat conformation. In epigomisin O,



210 R = Ang, $R^1 = R^2 = Me$
210a R = H, $R^1 = R^2 = Me$
210b R = H, $R^1 + R^2 = CH_2$



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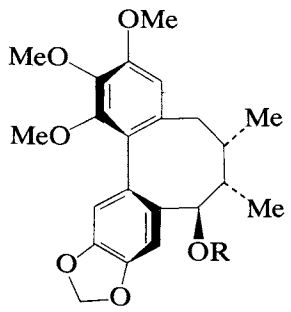
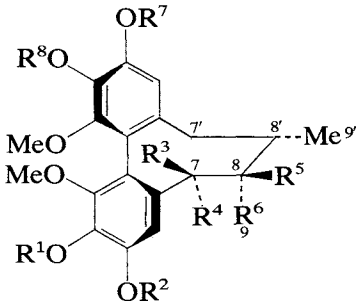


211a R = H
211b R = Benz

the equatorial 9′-methyl was observed at $\delta 22.0$ while the axial methyl (C-9) absorbed at $\delta 7.8$ ppm.

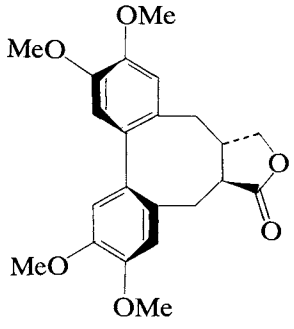
4.2.3. Gomisin B group with two hydroxy groups at C-7 and C-8. The methyl carbon at $\delta 18.8$ and 16.0 ppm of Gomisin P (**214**) were assigned to the 9′-methyl (equatorial) and 9-methyl (axial), respectively. The methyl signals at around δ 18.8 and 28.6 ppm in



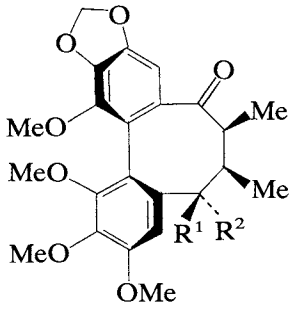
212 $R^1 = R^2 = R^{5'} = Me$, $R^3 = R^6 = OH$, $R^4 = H$, $R^7 + R^8 = CH_2$
212a $R^1 + R^2 = R^7 + R^8 = CH_2$, $R^3 = OH$, $R^4 = H$, $R^6 = OH$, $R^5 = Me$
213 $R^1 + R^2 = R^7 + R^8 = CH_2$, $R^3 = R^6 = OH$, $R^4 = H$, $R^5 = Me$
214 $R^1 = R^2 = R^6 = Me$, $R^3 = H$, $R^4 = R^5 = OH$, $R^7 + R^8 = CH_2$
215 $R^1 = R^2 = R^5 = R^7 = R^8 = Me$, $R^3 = R^6 = OH$, $R^4 = H$

deangeloylgomisin B (**212**) and deangeloylgomisin F (**213**) were assigned to C-9′ and C-9, respectively, in comparison with the data for **214** and with the lignans in Section 4.1.2.

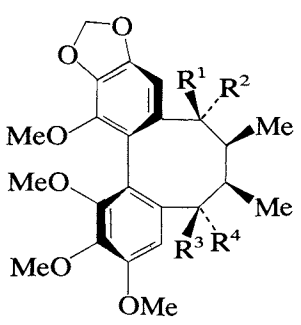
4.2.4. Derivatives of benzocyclooctadiene lactone. The ^{13}C NMR spectral analysis has been reported for only one compound (**216**) of this category; the lactone carbonyl (C-9) resonates at 176.5 ppm, and the oxymethylene (C-9′) at 70.5 ppm.[73]

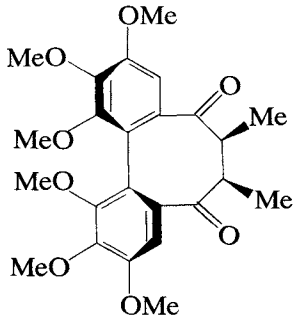


216



216a $R^1 + R^2 = O$
216b $R^1 = OH$, $R^2 = H$



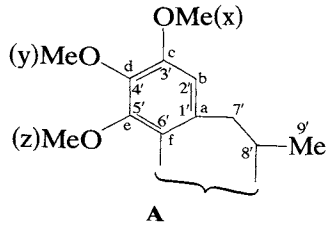


216g

216c $R^1+R^2=R^3+R^4=O$
216d $R^1=OH$, $R^2=H$, $R^3+R^4=O$
216e $R^1+R^2=O$, $R^3=OH$, $R^4=H$
216f $R^1=OAc$, $R^2=R^3=R^4=H$

4.2.5. (and 4.1.3.) With a keto function at C-7 and/or C-7′. The carbonyl absorption at 209.6 and 201.1 ± 0.8 ppm can be attributed to the conjugated and non-conjugated carbonyl groups, respectively. A conjugated carbonyl implies a TB conformation and a non-conjugated carbonyl a TBC conformation. The chemical shifts of C-2,2′ are strongly dependent on the substitution of the adjacent benzyl carbon, and appear at *ca* 7 ppm upfield when the function is a non-conjugated carbonyl compared with the conjugated compound. It appears, therefore, that a non-conjugated ketone imparts a stronger γ-effect on protonated aromatic carbon atoms, whereas with a nearly coplanar carbonyl group this effect is almost completely balanced by the deshielding caused by electron withdrawal from the ring.

Four predictions were made for the chemical shifts of the protonated aromatic carbons of lignans possessing the partial structure **A** and the twist-boat–chair conformation of the cyclooctadiene ring. (a) When the methyl group is in an axial orientation, the protonated aromatic carbon appears at δ 110 ± 0.3 ppm, and when the methyl group is equatorial, it appears at δ 107.3 ± 0.3 ppm. (b) The replacement of OMe (x) by a hydroxy or acetoxy group produces a downfield shift of *ca* 3 ppm or *ca* 10 ppm, respectively, for the protonated C-2′ aromatic carbon. (c) The replacement of OMe (z) by a hydroxy or acetoxy group produces an upfield shift of *ca* 3 ppm for the protonated aromatic carbon or a downfield shift for C-2′. (d) the replacement of OMe (x and y) by the methylenedioxy moiety produces an upfield of *ca* 4 ppm for the protonated C-2′ aromatic carbon.



A

Among the above lignans, gomisin O possesses a TB conformation of the cyclooctadiene ring whereas the others possess a TBC conformation.[70]

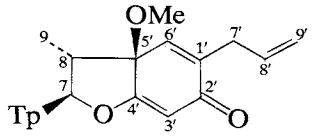
5. NEOLIGNAN

The oxidative coupling of the propenyl and/or allyl phenols occurs in several ways to produce a variety of skeletal types, which are discussed in the following sections.

5.1. Hydrobenzofuranoid type

In these cases, the aromatic ring of one of the C_6–C_3 units becomes modified to a cyclohexadienone or cyclohexenone ring and is coupled with another C_6–C_3 unit to form a furan ring. These may be of three types, as follows.

5.1.1. Angularly methoxylated hydrobenzofuranoid type. These usually possess a *trans* relationship between the aryl ring and the 9-CH_3, while the angular OCH_3 group may be *cis* or *trans* with respect to the 9-CH_3. The chemical shift of the 9-CH_3 can be utilized for the determination of the stereochemical relationship between the OCH_3 and 9-CH_3. Thus, in mirandin B (**218**), the 9-CH_3 absorbed at 6.9 ppm owing to the *cis*



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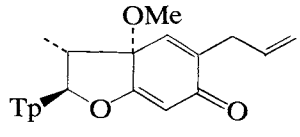
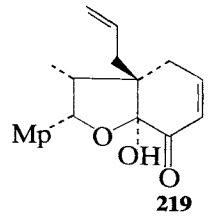


218

relationship between these two substituents, whereas this absorption was at 16.1 ppm in mirandin A (**217**), which possesses a *trans* relationship.[26] The chemical shift of the OCH_3 remains unaffected by the stereochemistry, and its signal was observed at 50.3–51.1 ppm.

5.1.2. Angularly allylated hydrobenzofuranoid type. The chemical shifts of C-9 (9-CH_3) and the methylene (C-7′) of the allyl side-chain exhibit a strong dependence on their mutual relationship and, thus, are conclusive for the configurational analysis.[26] The allylic methylene C-7′ and C-9 were found to be shifted approximately 7.00 and 3.00 ppm, respectively, upfield in the *cis* compounds **220–222** compared with the



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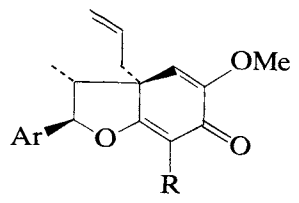
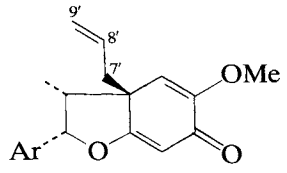
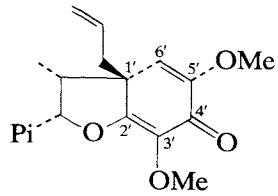


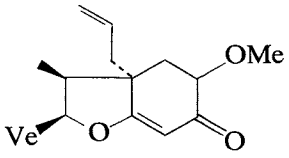
220 Ar = Pi, R = H
221 Ar = Ve, R = H
222 Ar = Ve, R = OMe



223 Ar = Pi
224 Ar = Mp
225 Ar = Tp



226



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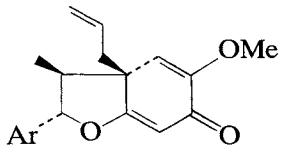
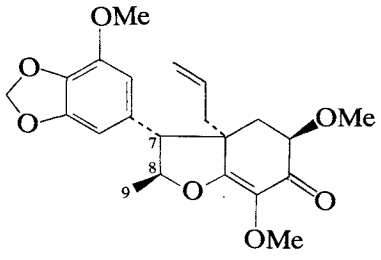


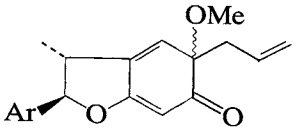
228 Ar = Ve
229a Ar = Tp



229b

trans compounds **223–225**. Similarly, the mutual relationship between the 9-CH_3 and the C-7 aryl ring determines the chemical shift of C-7 and, therefore, it absorbs at 91.2 ± 0.3 ppm in *cis* compounds and at 87.1 ± 0.1 ppm in the *trans* isomers. The introduction of an additional conjugated double bond to the cyclohexanone type (where the carbonyl absorbs around 192 ppm) results in an upfield shift by about 10 ppm, which thus appears at around 181 ppm in the cyclohexadienone type.[80,81]

5.1.3. Linearly allylated and methoxylated hydrobenzofuranoid type. The allyl and methoxy groups are substituted on the same position, C-1′, which usually absorbs at 80.7 ± 0.1 ppm. The carbonyl exhibits extended conjugation with two double bonds and, therefore, absorbs at 199.2 ppm.[26] The stereochemical relationship between the 7-aryl and the 9-CH_3 could be

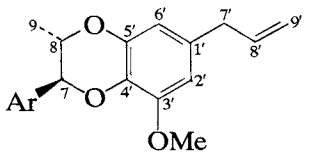


229c Ar = Pi
229d Ar = Tp

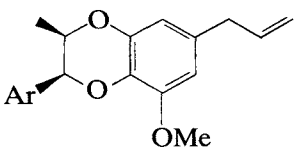
established by analogy with the compounds in Section 5.1.1 and as described for derivatives of benzofuran in Section 3.1.

5.2. Benzodioxane type

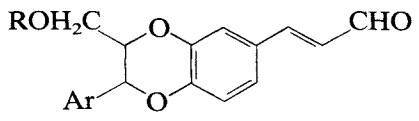
When C-7 and C-8 of one C_6–C_3 unit are linked with the aryl ring carbon atoms of the other C_6–C_3 unit through two oxygen atoms, a benzodioxane type of skeleton is generated. This may be substituted with either a methyl or a hydroxymethyl substituent. In the former case, where C-9 is a methyl carbon, it can be *cis* or *trans* to the C-7 aryl substituent. The chemical shifts of C-7, C-8 and C-9 are of diagnostic importance for depicting the stereochemistry, as they are shielded by 3–5 ppm in the *cis* compounds[75a,78] as in **232** and **233** compared with the *trans* isomers **230** and



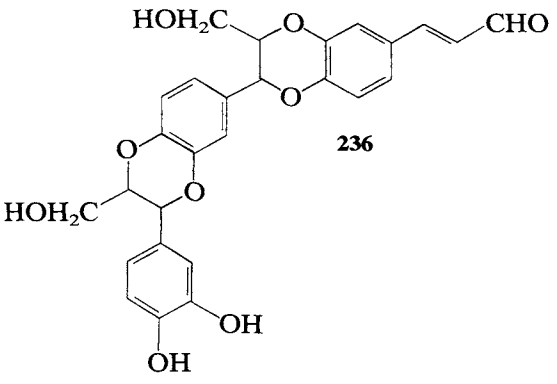
230 Ar = Tp
231 Ar = Pi



232 Ar = Tp
233 Ar = Ve



234 Ar = Ca, R = H
235 Ar = CaAc, R = Ac



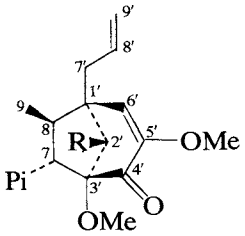
236

231. Where C-9 is part of a CH_2OH group, both C-7 and C-8 absorb in the range of 75–78 ppm; the downfield signal is due to C-8 and the other to C-7.

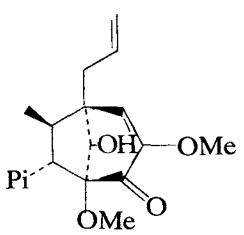
5.3. Bicyclo[3.2.1]octane type

In these cases the aromatic ring of one of the C_6–C_3 units is involved in cyclization with C-7 and C-8 of the other C_6–C_3 unit in such a way that it leads to the formation of a cyclopentane ring system. This could be one of the following two types, depending on the location of the side-chain on the modified cyclohexane ring system:

5.3.1. Guianin type. Here the side-chain is located at the ring junction, and the chemical shift of the C-1′ quaternary carbon is diagnostic for this category (see below). The shift of the methoxy-substituted C-3′ was reported to be dependent on the relative dispositions of the rings, absorbing at 90.5 ± 0.3 ppm in the series in which C-2′ is α-oriented and at 64.9 ppm, an unusually higher field, when C-2′ is β-oriented.[80a]



237 R = OH
238 R = OAc



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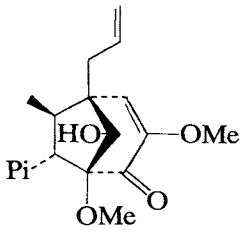
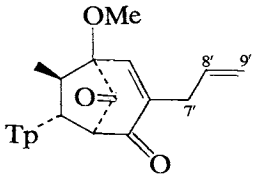


240

5.3.2. Macrophyllin type. The side-chain in this class is not located at the ring junction but is substituted on the olefinic bond, thus giving rise to the signal due to C-1′ at 140.3±0.3 ppm as a singlet.[81] The C-6′ signal



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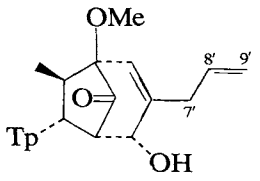

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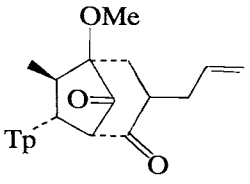
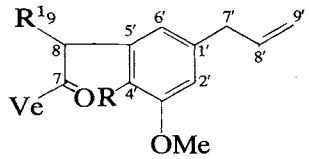


243

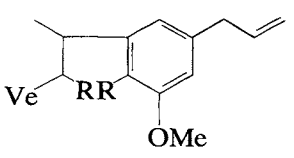
appears around 126 ppm in the absence of a 2′-carbonyl, as in **242**, while the presence of the 2′-carbonyl shifts this signal 15–20 ppm downfield owing to the conjugation effect.

5.4. Carinatane type

These are formed by the coupling of C-8 of one C_6–C_3 unit with the aryl carbon of the other C_6–C_3 unit, resulting in the formation of an open-chain system. This may also be regarded as the product formed as a



244 R = OH, $R^1 = CH_3$
245 R = OH, $R^1 = CH_2OH$

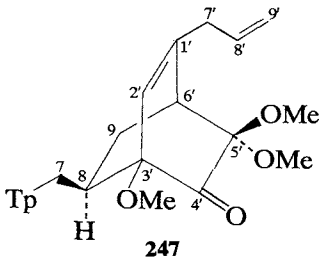


246 R = OH

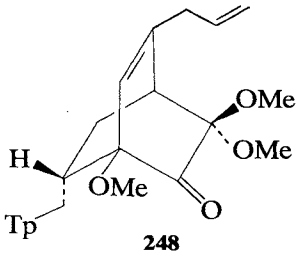
result of benzofuran ring opening of the benzofuran type of lignans, hence C-7 may bear a hydroxy or an oxo function. Its chemical shift differentiates between the 7-hydroxy (78.9 ppm) and 7-oxo (199.4±0.3 ppm) types.[83a,d]

5.5. Heterotropanone type

C-8 and C-9 of one of the C_6–C_3 units couples with the modified aromatic ring of the other C_6–C_3 unit to produce a [2.2.2]octane skeleton. The signals at



247

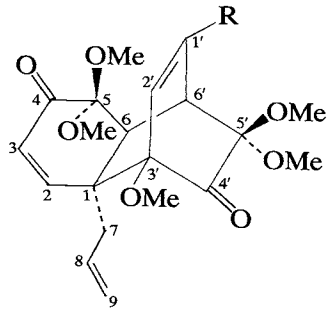


248

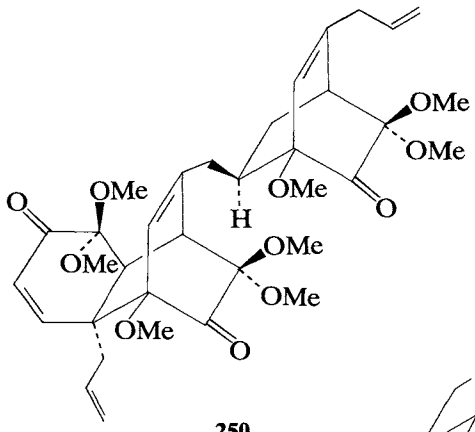
94.5±0.3 and 201.4+0.4 ppm, assignable to the dimethoxylated C-3′ and 4′-carbonyl functionalities, respectively, distinguish this category from other categories of lignans and neolignans.[25a,b]

5.6. Asatone type

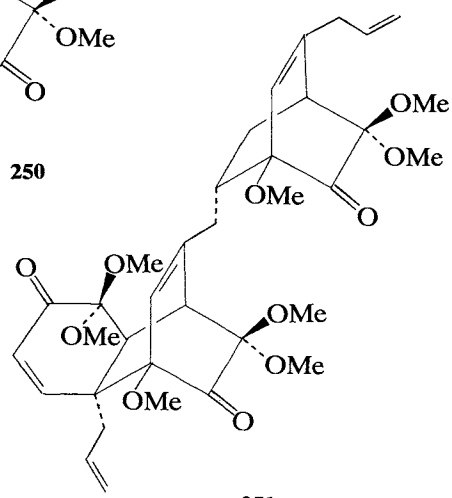
This type belongs to a unique skeleton in which the aromatic rings of both of the C_6–C_3 units become modified and couple together to generate a tricyclic skeleton of the **249** type containing two keto functions. The α,β-unsaturated carbonyl absorbs at approximately 188.0±0.7 ppm, while the signal of the



249a R = CH_2—CH = CH_2
249b R = CH = CH—CH_3



250



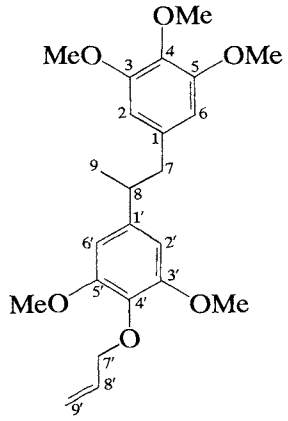
251

other carbonyl group is at 201.4±0.2 ppm. The reported data for these compounds[83b] have been analysed and tabulated.[25b]

5.7. Other types

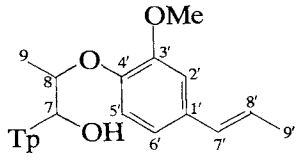
Various other types of skeletons, not widely distributed, are included in this group and can be categorized into the following sub-groups:

5.7.1. Aurein type. This is an unusual type of lignan in which C-8 of one of the C_6–C_3 unit forms a bond with the aryl ring of the other C_6–O–C_3 unit. The chemical shifts of C-7, C-8 and C-9 are of diagnostic importance for the characterization of this category as they absorb at 45.2, 41.9 and 20.8 ppm, respectively.[26]



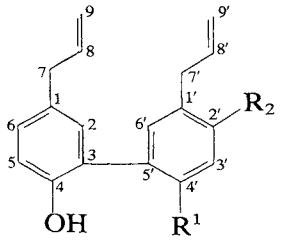
252

5.7.2. Surinamensin type. The C-8 of one of the C_6–C_3 units is linked with an aryl carbon of the other C_6–C_3 unit through an ether linkage, forming an open-chain system.[76] The oxygenated C-8 absorbs at 78.0 ppm and the hydroxylated C-7 at 83.6 ppm in **253**.

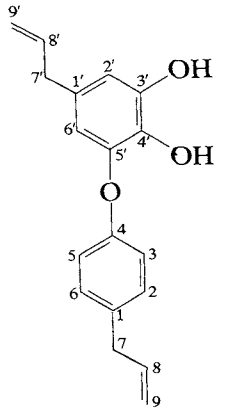


253

5.7.3. Biphenyl type. Carbon–carbon coupling between the aromatic rings of the two C_6–C_3 units produces such a type of neolignan. The substitution pattern of the aromatic rings determines the chemical shift of the aryl carbons involved in the biphenyl linkage formation.[82a,b] Representatives of this series are magnolol (**254**) and honokiol (**255**).

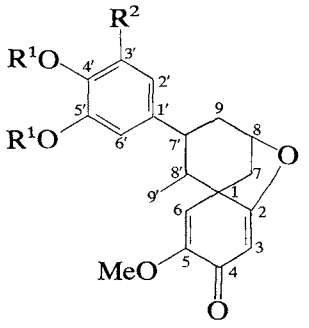


254 R^1 = OH, R^2 = H
255 R^1 = H, R^2 = OH



255a

5.7.4. Biphenyl ether type. The aromatic rings of the two C_6–C_3 units are linked via an ethereal bond to generate such neolignans. Only one example, obovatol (**255a**), has been recently reported.[82b]



255b R^1+R^1 = CH_2, R^2 = H
256 R^1 = Me, R^2 = OMe

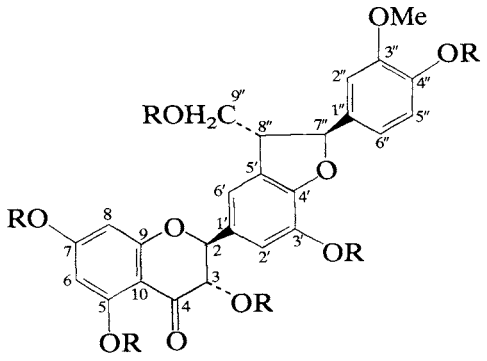
5.7.5. Spiro[5.5]undecanoid type. The modification of one of the aryl rings to cyclohexadienone and its involvement in cyclization with the side-chain of the other C_6–C_3 unit generate such a skeleton, present in futoenone (**255b**) and denudatone (**256**). The signals of C-8 at 81.9 ppm and of the carbonyl (C-4) at 183.1 ppm facilitate their characterization.[81b]

6. MISCELLANEOUS LIGNANS

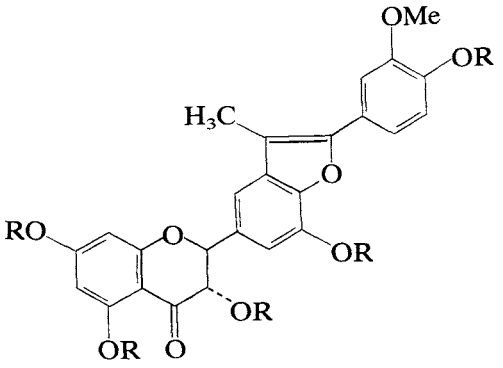
The flavonolignans, xanthonolignan and coumarinolignans constitute this category. The ^{13}C signals due to the non-lignan moiety could be assigned by comparison with the standard values for flavonoids,[94] coumarins[95] and xanthones (e.g. Ref. 96). These may possess three types of linkages; (a) through an oxygen and an aromatic ring carbon to form a furan ring; (b) through two oxygens to form a dioxane ring system; and (c) other types.

6.1. Flavonolignan

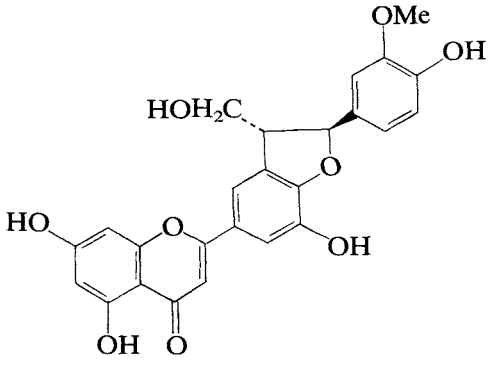
These may exhibit all three types of linkages, and are therefore categorized as above.



257 R = H
258 R = $COCH_3$



259 R = H
260 R = $COCH_3$

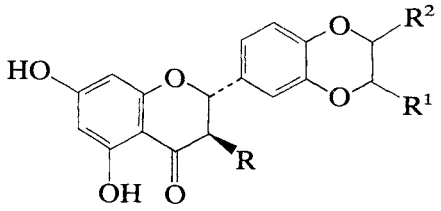


261

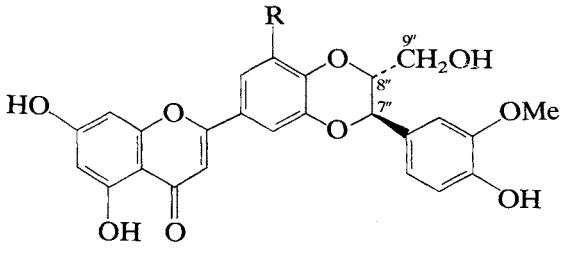
6.1.1. Furan type. The stereochemical assignments for silychristin (**257**) could be achieved on the basis of the ^{13}C shielding data which could be compared with the lignans described in Section 3, and are supported by mild dehydrogenation results.[86b] Analogously, the resemblance of the chemical shift for C-7″, C-8″ and C-9″ in isohydnocarpin (**261**) and **257** leads to the prediction of similar stereochemical assignments.[87]

6.1.2. Dioxane type. In these cases, C-7″, C-8″ and C-9″ resonate at 75.7 ± 0.4, 78.0 ± 0.4 and 59.5 ± 0.3 ppm, respectively, and indicate an equatorial orientation of both of the substituents possessing a *trans* relationship.

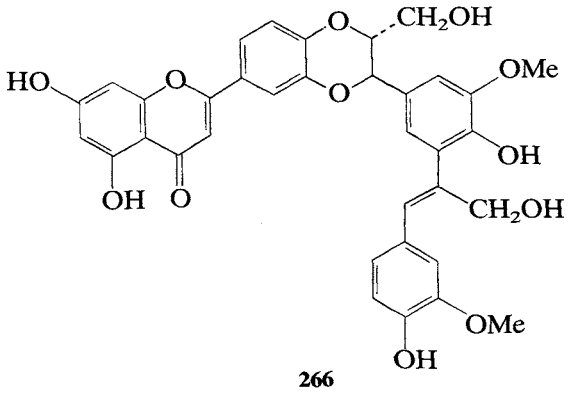
6.1.3. Other types. There is only one compound of its specific type, neohydnocarpin (**267**), belonging to this category which has been analysed by ^{13}C NMR spectroscopy. The signals of C-7″, C-8″ and C-9″ were observed at 40.9, 35.2 and 69.2 ppm, respectively.



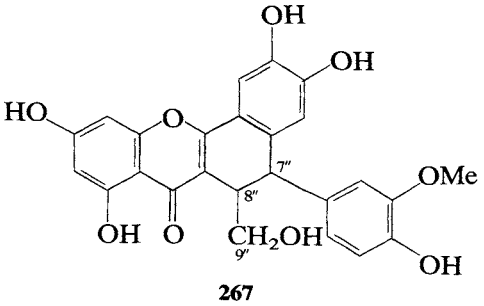
262 R = OH, R^1 = Gu, R^2 = CH_2OH
263 R = H, R^1 = Gu, R^2 = CH_2OH
270 R = OH, R^1 = CH_2OH, R^2 = Gu



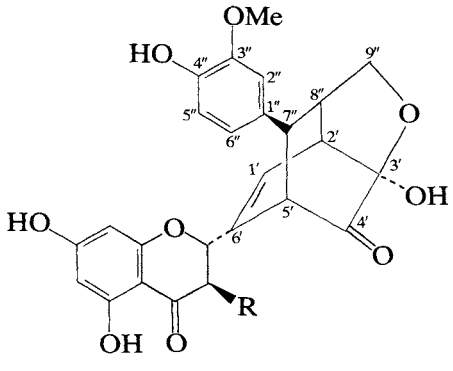
264 R = H
265 R = OCH_3



266



267



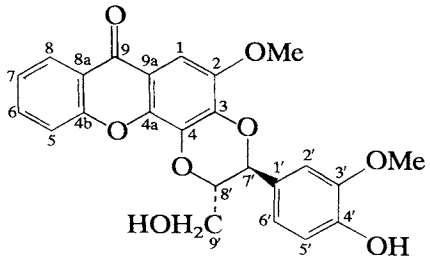
268 R = H
269 R = OH

The aromatic ring B of the flavonoid nucleus becomes modified and couples with a C_6–C_3 unit to produce a new structural type such as in silymonin (**268**) and silandrin (**269**). In these cases, the ^{13}C signal resonances due to C-7″, C-8″ and C-9″ are observed at 53.2 ± 0.1, 46.0 ± 0.1 and 72.7 ppm, respectively.

Thus, from the above discussion, it is evident that the chemical shifts for C-7″, C-8″ and C-9″ are informative enough for the characterization of various structural variants.

6.2. Xanthonolignan

When isolated, these were found to be of the (b) type, i.e. a xanthone and a C_6–C_3 unit are linked through a dioxane ring system. These exhibited similar spectral behaviour for C-7′, C-8′ and C-9′ as described for C-7″, C-8″ and C-9″ in flavonolignans of this type (see Section 6.1.2). So far, ^{13}C shielding data have been reported[90] for kielcorin, (**271**).



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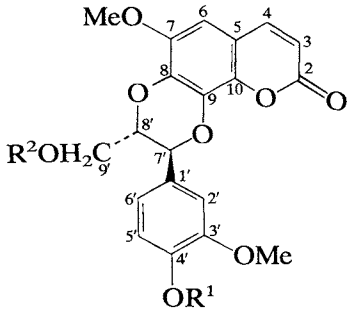
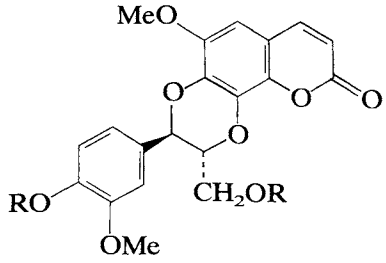
6.3. Coumarinolignan

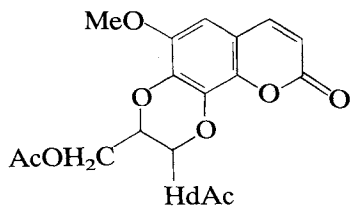
Several compounds belonging to this class have been reported, and ^{13}C NMR spectral analysis has proved



272 $R^1 = R^2 = H$
273 $R^1 = C_2H_5$, $R^2 = H$
274 $R^1 = R^2 = COCH_3$



275 R = H
276 $R = COCH_3$



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to be very useful in determining their structures. All of these so far reported are of the (b) type, i.e. the dioxane type, and exhibit analogous shielding behaviour to flavonolignans and xanthonolignans.

In miscellaneous dioxane-type lignans, the C-7′ and C-8′ of the lignan moiety give rise to the signals in the 75–78 ppm region. C-8′, bearing a CH_2OH group, resonates approximately 1.5 ppm downfield of C-7′, bearing an aryl substituent.

7. DERIVATIZATION-INDUCED SHIFTS

This section deals with the shifts associated with derivatization of the hydroxy group. For convenience, the subject is discussed under the following subheadings:

7.1. Glycosidation-induced shifts.
7.2. Acetylation-induced shifts.
7.3. Methylation-induced shifts.

7.1. Glycosylation-induced shifts

In O-glycosides, C-1 of the monosaccharide is linked via a hemiacetal bond to the aglycone moiety, which produces a shift in the C-1 resonance to lower field. Apart from a much smaller shift for the C-2 resonance, the remainder of the sugar spectrum is largely unaffected. The signal assignments of the sugar carbons can be made by comparison and best fit matching with the reported data for monosaccharides[97] and methyl glycosides.[98]

The effect on the signals of the lignan nucleus itself is more diagnostic than the glycosylation effect on the sugar carbon signals. In general terms, the carbon at the site of glycosylation is shifted to higher field, whereas *ortho*- and *para*-carbons shift downfield.[94,95] Usually, shifts of *ipso*- and *ortho*-carbon atoms are in the range of only 0.7–2 ppm. Significantly, the most reliable indication of glycosylation appears to be the downfield shift of the *para*-carbon signal, which is invariably larger than the other shifts and generally in the range 1.7–4 ppm.

Furanose sugars are readily distinguished from their pyranose isomers owing to the difference in their chemical shifts. The signals for C-1, C-2 and C-4 are shifted downfield (4–14 ppm) and C-5 is upfield (4–7 ppm) in the furanose form compared with their respective pyranose isomer.[97–99]

The chemical shift of the anomeric carbon atom is strongly dependent on the anomeric configuration and can be of use in elucidating this configuration. The

best method for determining the anomeric configuration of pyranose is from the one-bond coupling for the anomeric carbon [^1J(CH)].[100] The ^1J value for the other carbons (C-2 to C-6) of the sugar varies in range 143–148 Hz, whereas the anomeric carbon exhibits a larger value of 160–175 Hz. The difference in couplings for the two anomeric configurations is generally about 10 Hz, with the value for the equatorial ^{13}C–H coupling being larger. For example, in methyl-β-D-glucopyranoside, ^1J(CH) for C-1 is 160 Hz, whereas for methyl-α-D-glucopyranoside it is 170 Hz. The one-bond coupling is solvent dependent,[101] so comparison has to be made in the same solvent.

The above discussion deals with the lignan glycosides having a sugar linked with a phenolic hydroxy group. However, there are several lignan glycosides in which the sugar is linked to an alcoholic hydroxy group. The effect on the sugar moiety due to the aglycone is similar to that described above; however, the shift changes of the aglycone nucleus due to glycosylation, i.e. a downfield shift of the α-carbon and an upfield shift of the β-carbon atoms, are of diagnostic importance in recognizing the site of glycosylation. Thus, a comparison of the chemical shifts of the lignan glycoside with the appropriate sugar and lignan, together with the consideration of the glycosylation-induced shifts, provides a reliable method for structure elucidation.

7.2. Acetylation-induced shifts

Acetylation of free phenolic hydroxy groups[102] produces marked changes in ^{13}C NMR spectrum of the compounds, and can be used to detect the location of hydroxy groups on the aromatic rings. On acetylation the signal of the hydroxylated carbon moves upfield by 5.3–6.5 ppm, the *ortho*- and *para*-carbon signals are moved downfield by 4.1–8.2 ppm and the *meta*-carbon signals are only slightly affected. If the *ortho* position is substituted by a methoxy group as in the guaicyl unit, the methoxy-substituted aryl carbon exhibits a higher downfield shift (6.3–8.2 ppm) than that for the unsubstituted aryl carbon, which shifts by only 4.0–5.0 ppm. Where a 4-hydroxy group has two *ortho*-substituents as in the 3,5-dimethoxy-4-hydroxyphenyl ring, the *ortho* effect (4–5 ppm) is identical for both *ortho* positions.

Acetylation of an alcoholic hydroxy group[103] causes deshielding of the α-carbon (0.7–4.0 ppm) with subsequent shielding of the β-carbon atoms (3–5 ppm). In cases where the α-effect is small, the β-upfield shift helps in unambiguously determining the site of acetylation.

Acetylation introduces two more signals, due to the acetyl carbonyl and the methyl group, into the spectrum of the original compound, but these do not interfere with the assignments owing to their narrow ranges, 168–172 and 18–21 ppm, respectively.

7.3. Methylation-induced shifts

Methylation of a free phenolic hydroxy group shifts the hydroxylated carbon downfield by 1.0–4.7 ppm, and the signal of the *ortho*-carbon upfield by 0.8–3.6 ppm. The methylation of an alcoholic hydroxy group produces a downfield shift of the hydroxylated carbon by 8.8–12.9 ppm and an upfield shift of 3.0–3.5 ppm for the β-carbon atoms.

The methoxy signals are in the range 55–63 ppm and the chemical shift provides information about their behaviour. Aromatic methoxy signals having at least one unsubstituted *ortho* position appear at 55–56.8 ppm, whereas this absorption is at 59.5–63 ppm for these methoxyl groups with both *ortho* positions substituted.[104] The alcoholic methoxy group usually appears in a narrow range (58.6–58.8 ppm) between the two types of aromatic methoxy group.

Thus the chemical shifts of the methoxy carbons give sufficient information for the assignment of the methoxy groups in the molecule. Based on the fact that a signal at 55.9 ppm possess at least one free *ortho* position, the structure of a new arylnaphthalide lignan,[60c] identified as orosunol (**171d**), has been revised to **171b**, as the ^{13}C NMR spectrum has signals at 59.5 and 55.9 ppm, instead of two signals around 60 ppm which would be expected in the case of structure **171d**.

8. LIST OF ^{13}C CHEMICAL SHIFTS

The ^{13}C chemical shifts of all lignan and neolignan derivatives available from the literature (until 1982) are listed in Table 1. In order to avoid excessive data, the shifts for the sugar carbon atoms are not included, and Table 1 is restricted to the carbon atoms of the lignan and neolignan nuclei only, except for miscellaneous lignans where the shifts for the nonlignan moiety are also incorporated. The chemical shifts of all other atoms can be taken from the original papers or requested from the present authors. The numbering is uniform (C-1 to C-9 for the first C_6–C_3 unit and C-1′ to C-9′ for the second C_6–C_3 unit), and is given on every key molecule where it is different from the systematic numbering.

The tabulated ^{13}C chemical shift data (Table 1) are divided into several sub-headings according to the classification shown above. Trivial names are given in the second column and the solvent (A = $CDCl_3$, B = DMSO-d_6, C = CD_3OD, D = CD_3COCD_3, E = D_2O + CD_3COCD_3F = D_2O, G = C_5D_5N) is shown in the third column.

Structures are given for all the compounds, and also the various symbols (see footnotes to Table 1) used for the representation of the substitution pattern on the aromatic ring. For a given entry, references containing data for the particular compound are quoted in the last column.

Acknowledgements

We are grateful to Dr Akhtar Husain for his constant encouragment. P.K.A. thanks Professor Dr H. J. Schneider, Universität des Saarlandes, Saarbrücken, FRG, for helpful discussions and to Alexander-von-Humboldt Stiftung for a stipend. We are also grateful to Mr Bikram Singh for his consistent help.

Table 1. ^{13}C chemical shifts (ppm) of lignan and neolignan derivatives[a]

Substance		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3, OCH_2O or others	$OCOCH_3$	Ref.
1.1. Derivatives of butane:																						
1 *meso*-Dihydroguaiarctic acid dimethyl ether	A	134.5	112.4	148.8	147.2	111.2	121.0	38.9	39.2	16.3	134.5	112.4	148.8	147.2	111.2	121.0	38.9	39.2	16.3	55.8, 55.9	—	22a
2 Secoisolariciresinol	A	132.4	111.7	146.6	143.7	114.3	121.5	35.8	43.7	60.5	132.4	111.7	146.6	143.7	114.3	121.5	35.8	43.7	60.5	55.7	—	20
3 Secoisolariciresinol tetraacetate	A	137.9	112.7	150.8	138.4	120.8	122.4	35.2	39.5	64.1	137.9	112.7	150.8	138.4	120.8	122.4	35.2	39.5	64.1	55.7	170.7, 20.8, 168.8, 20.6	20
4 Secoisolariciresinol 4′-methyl ether	A	132.2	111.4	146.3	143.6	114.0	121.4	35.8	43.8	60.4	133.0	111.0	148.6	147.0	112.0	120.8	35.8	43.8	60.4	55.7	—	21
5 Secoisolariciresinol 4′-methyl ether triacetate	A	138.5	112.8	150.8	138.0	122.8	120.9	35.4	39.7	64.2	138.5	112.8	150.8	138.0	122.4	120.9	35.4	39.7	64.2	55.7, 55.8	170.7, 21.0, 168.8, 20.7	21
6 Secoisolariciresinol 4,4′-dimethyl ether	A	132.9	110.0	148.7	147.0	112.0	120.8	35.7	43.8	60.3	132.9	110.0	148.7	147.0	112.0	120.8	35.7	43.8	60.3	55.7	—	21
7 Secoisolariciresionol-4,4′-dimethyl ether diacetate	A	131.9	110.0	148.7	147.2	111.8	120.7	34.8	39.6	64.2	131.9	111.0	148.7	147.2	111.8	120.7	34.8	39.6	64.2	55.7	170.6, 20.9	21
8 Phyllanthin	A	133.7	111.2	148.8	147.2	112.4	121.2	35.0	40.8	72.7	133.7	111.2	148.8	147.2	112.8	121.2	35.0	40.8	72.7	55.7, 55.9, 58.7	—	22a
9 Dihydrocubebin	A	134.3	107.9	147.3	145.5	109.2	121.7	35.7	44.1	59.8	134.3	107.9	147.3	145.5	109.2	121.7	35.7	44.1	59.8	100.6	—	23a
10 Dihydrocubebin dimethyl ether	A	135.2	108.2	147.8	145.9	109.6	122.2	34.9	41.1	72.7	135.2	108.2	147.8	145.9	109.6	122.2	34.9	41.1	72.7	58.8, 100.9	—	23a
11 Dihydrocubebin diacetate	A	133.2	108.0	147.5	145.7	109.0	121.7	34.8	39.9	64.2	133.2	108.0	147.5	145.7	109.0	121.7	34.8	39.9	64.2	100.7	170.8, 20.9	23a
12 Acoradin	A	124.2	112.7	143.3	147.8	98.2	151.9	45.5	43.5	19.3	124.2	112.7	143.3	147.8	98.2	151.9	45.5	43.5	19.3	56.3, 56.6, 56.9	—	24
13 Heterotropan	A	122.1	112.4	142.3	147.2	97.7	151.6	34.0	42.5	15.1	122.1	112.4	142.3	147.2	97.1	151.6	34.0	42.5	15.1	56.1, 56.3, 56.7	—	25a,b
1.2. Derivatives of butanolide:																						
14 Matairesinol	A	129.4	110.8	146.4	144.2	113.9	121.2	38.3	40.9	71.3	129.5	111.3	146.5	144.3	114.3	121.9	34.5	46.5	178.6	55.7	—	20
14 Matairesinol	A	129.6	111.0	146.6	144.2	114.3	120.9	37.7	40.7	71.7	129.3	111.6	146.5	144.2	114.1	121.7	34.2	46.1	178.1	55.5	—	29
15 Matairesinol diacetate	A	136.8	112.7	151.1	138.5	120.6	122.8	38.1	40.8	71.0	136.5	113.3	151.1	138.5	121.3	122.6	34.4	46.2	178.2	55.7	168.8, 20.5	29
16 HPMF {*trans*-(±)3,4-bis [(3-hydroxyphenyl)methyl]-dihydro-2(3*H*)-furanone}	A	—	116.3	—	113.9	130.0	121.7	—	—	—	—	115.7	—	114.0	130.0	121.1	—	—	—	—	—	27
17 Pluviatolide	A	131.1	109.2	147.5	146.4	107.9	122.0	38.1	41.2	71.0	129.5	110.9	146.1	144.2	114.3	121.0	34.6	46.3	178.2	55.7, 100.8	—	26
18 Pluviatolide acetate	A	131.1	109.3	147.7	146.3	108.1	122.1	38.5	41.0	71.0	136.7	112.5	151.0	138.4	120.4	122.7	34.4	46.5	178.0	55.7, 100.9	168.7, 20.6	26
19 Hinokinin	A	131.0	109.0	147.4	146.0	107.8	121.8	37.9	41.0	70.7	131.2	108.4	147.4	145.8	107.8	121.1	34.4	46.1	177.9	100.6	—	26
19a (−)-Hinokinin	A	131.2	109.3	147.7	146.2	108.7	122.1	38.3	41.2	71.1	131.4	108.2	147.7	146.3		121.4	34.8	46.4	178.2	100.9		23a
19b Yatein	A	133.2	106.2	153.2	136.8	153.2	106.2	35.2	46.4	178.5	131.6	108.8	147.9	146.4	108.2	121.5	35.2	46.4	178.5	56.1, 60.8, 101.0		28c
20 (See Scheme)	A	133.6	105.5	153.2	136.7	153.2	105.5	38.8	40.9	71.2	129.4	111.6	146.7	144.6	114.1	121.9	34.4	46.5	178.7	60.7, 55.9	—	29
21 (See Scheme)	A	133.7	105.7	153.5	136.9	153.5	105.7	38.9	41.1	71.2	130.3	112.5	149.2	148.1	111.2	121.4	34.6	46.6	178.7	60.9, 55.9, 56.1	—	29
22 (See Scheme)	A	133.6	105.7	153.5	137.0	153.5	105.7	38.9	41.1	71.2	136.7	113.4	151.3	138.8	121.4	122.7	34.6	46.4	178.5	60.9, 55.9, 56.1	168.9, 20.6	29
23 Methylarctigenin	A	130.9	112.9	149.6	148.5	112.1	120.9	38.4	41.3	71.2	130.7	113.3	149.6	148.5	112.3	121.7	34.8	46.7	178.5	56.2	—	29
24 Di-*O*-methylthujaplicatin methyl ether	A	130.1	111.7	148.8	147.7	111.2	120.2	38.1	41.0	71.1	133.1	106.2	152.9	136.8	152.9	106.2	35.0	46.4	178.1	55.8, 56.0, 60.7	—	29
25 (−)-Arctigenin	A	129.5	111.2	147.8	146.7	111.7	120.5	38.1	40.9	71.3	130.4	111.4	146.6	144.5	114.1	122.0	34.6	46.5	178.7	55.8, 55.9	—	28a
25a (+)-Arctigenin	A	130.8	114.5	148.1	147.1	111.8	120.8	34.6	41.1	71.4	129.6	112.3	149.3	144.9	112.0	122.1	38.2	46.7	179.0	55.9	—	32b
26 7-Allohydroxymataresinol dimethyl ether§	A	134.4	109.0	148.9	147.9	112.4	118.3	73.9	43.5	68.2	130.0	111.1	149.2			121.4	34.7	46.2	179.1	55.8	—	28a
27 7-Alloacetoxymataresinol dimethyl ether[b]	A	129.5	109.7	149.1	148.0	111.2	118.2	75.4	44.0	67.9	130.0	112.4	149.0	148.0		121.4	34.3	44.0	178.0	55.9	169.8, 20.9	28a

28 7-Hydroxymatairesinol[b]	A	133.6	108.3	146.9	145.8	114.0	118.0	75.4	45.2	68.5	129.5	112.0	144.6	146.8	114.5	122.6	35.2	43.8	178.9	55.9	—	30
28 7-Hydroxymatairesinol[b]	A	133.5	108.3	146.9	145.5	114.0	118.8	75.2	45.2	68.6	129.5	111.9	146.8	144.4	114.0	122.6	35.0	43.6	179.4	55.8	—	28a
29 7-Acetoxymatairesinol diacetate	A	136.1	110.7	151.4	139.9	122.8	118.5	75.4	43.4	67.7	136.1	113.7	151.1	138.8	121.7	123.2	34.9	43.5	178.0	55.8	168.7, 168.9, 169.7, 20.5, 20.5, 20.9	30
30 7-Hydroxymatairesinol dimentyl ether[b]	A	134.1	109.1	149.0	149.1	111.2	118.3	75.4	43.9	68.4	130.2	109.1	149.0	149.4	112.9	121.8	35.0	45.2	179.2	55.9	—	28a
31 7-Acetoxymatairesinol dimethyl ether[b]	A	129.6	109.7	149.1	148.1	111.2	118.9	76.1	43.4	67.9	129.6	109.7	149.2		112.7	121.7	34.8	44.0	178.2	55.9	169.8, 21.1	28a
32 Parabenzlactone	A	135.3	106.1	146.2	147.6	108.2	119.3	75.4	43.7	68.4	131.1	108.1	147.5	148.0	109.8	122.7	35.1	45.1	178.7	100.8, 101.6	—	28a
33 Parabenzlactone acetate	A	130.7	106.6	146.6		108.2	120.1	76.3	43.5	68.0	131.0	108.2	147.8	148.1	109.8	122.0	35.1	43.9	178.0	101.0, 101.4	169.8, 20.9	28a
34 Isoarctigenin monoacetate	A	130.9	111.5	147.9	149.2	112.8	120.9	32.7	40.0	69.5	138.5	112.0	151.3	137.7	120.4	122.9	30.8	45.4	177.8	55.9	169.1, 20.7	28a
35 7-Acetoxyisoarctigenin monoacetate[b]	A	130.1	109.5	149.8	149.8	113.6	120.5	72.1	43.3	66.7	139.1	112.2	151.7	137.5	118.1	123.2	30.7	43.5	177.1	56.3	168.9, 20.6, 169.8, 21.0	28a
36 Trachelogenin	A	131.1	111.6	146.6	149.2	112.8	120.9	31.6	43.8	70.2	126.2	112.3	145.1	147.9	114.4	123.2	42.0	76.5	178.6	55.9	—	28a
37 Trachelogenin acetate	A	130.3	111.6	148.0	149.2	111.8	120.5	33.5	42.7	71.8	132.7	111.6	151.2	139.5	114.9	122.9	43.2	80.2	174.9	55.9	168.9, 170.3, 20.5	28a
38 7-Hydroxytrachelogenin[b]	A	133.9	109.0	145.2	148.6	112.9	117.6	70.0	48.1	79.2	126.2	111.4	146.8	149.2	114.4	123.2	42.9	79.2	178.7	56.1	—	28a
39 7-Acetoxytrachelogenin diacetate[b]	A	130.4	109.9	149.2	151.2	114.5	122.8	73.1	45.5	67.8	131.9	111.2	151.2	139.5	119.1	122.8	41.5	80.4	174.0	55.9	168.9, 169.3, 170.3, 20.7, 20.9	28a
40 7′-Hydroxyisomethyl-*trachelogenin*	A	130.1	110.7	147.9	149.2	111.4	120.6	31.8	47.5	70.1	130.9	110.7	148.7	149.6	111.7	111.9	76.9	75.4	177.8	55.9	—	28a
41 Isomethyl arctigenin	A	125.5	111.2	148.9	149.1	111.4	122.2	39.1	78.1	74.1	126.6	111.2	149.1	148.9	113.4	122.5	37.8	78.6	—	55.9	—	28a
42 Di-*O*-methylthujastandin	A	132.9	111.3	148.1	150.2	113.6	122.3	37.6	77.0	74.2	135.4	111.7	149.3	150.6	114.7	123.3	37.1	79.0	181.3	55.8, 55.9	—	28a
43 Kaerophyllin	A	125.7	108.4	149.2	146.6	111.4	121.9	37.5	39.6	69.5	126.9	109.1	150.8	148.0	113.0	123.0	137.4	131.5	172.5	56.0, 101.1	—	31
43a (−)-Hibalactone	A	126.1	108.5	148.4	146.6	108.8	122.1	37.6	39.9	69.5	128.2	108.7	149.2	148.0	109.2	125.9	137.2	131.5	172.5	101.8, 104.0	—	28b
43b Nemerosin	A	127.1	108.4	148.0	146.6	109.0	121.9	37.8	39.4	69.7	129.4	107.4	153.4	157.4	153.4	107.4	137.6	131.3	172.3	56.3, 60.9, 101.1	—	28b
1.3. Derivatives of tetrahydrofuran.																						
1.3.1. 7,7′-Monoepoxy lignan:																						
44 Galbacin	A	136.1	106.4	147.5	146.7	107.7	119.5	88.1	50.9	13.7	136.1	106.4	147.5	146.7	107.7	119.5	88.1	50.9	13.7	100.7	—	32a
45 Galgravin	A	134.6	109.6	148.7	148.2	110.8	118.4	87.1	44.3	12.9	134.6	109.6	148.7	148.2	110.8	118.4	87.1	44.3	12.9	55.8	—	32a
46 Nectandrin	A	134.9	109.3	145.1	145.1	110.7	118.6	87.2	44.3	12.9	134.9	109.4	145.1	145.1	110.1	119.3	87.2	44.3	12.9	55.9	—	33
47 Veraguensin	A	133.6	110.5	148.7	148.3	110.8	118.1	87.1	45.9	14.9	133.2	109.7	148.3	147.8	110.5	118.4	82.8	47.8	14.9	55.7	—	32a
48 Tetrahydrofuroguaicin B dimethyl ether	A	132.8	109.5	148.2	147.4	110.6	118.2	82.4	41.2	11.6	132.8	109.5	148.2	147.4	110.6	118.2	82.4	41.2	11.6	55.6	—	32a
49 Neo-olivil tetraacetate	A	139.4	110.0	151.2	140.0	127.7	118.0	82.6	50.4	63.4	139.4	110.0	151.2	140.0	127.7	118.0	82.6	50.4	63.4	56.4	168.6, 170.4, 20.6	34
50 See Scheme	A	138.9	126.1	128.4	127.5	128.4	126.1	81.2	48.1	60.8	138.9	126.1	128.4	127.5	128.4	126.1	81.2	48.1	60.8	—	—	35a
51 See Scheme	A	137.6	127.4	127.8	127.8	127.8	127.4	81.5	52.5	169.5	137.6	127.4	127.8	127.8	127.8	127.4	81.5	52.5	169.5	60.3, 13.6	—	35a
51a See Scheme	A	137.4	126.8	128.4	128.1	128.4	127.0	82.8	54.6	171.2	137.4	126.8	128.5	128.1	128.5	127.0	83.8	55.2	172.1	60.8, 61.3, 13.5, 14.1	—	35a
52 Di-*O*-methylferaguaiacin	A	124.7	108.7	148.4	147.5	110.9	117.9	146.4	117.4	9.6	124.7	108.7	148.4	147.5	110.9	117.9	146.4	117.4	9.6	55.5	—	32a
1.3.2. 7,9′-Monoepoxy lignan:																						
53 Lariciresinol	A+C	133.7	108.7	145.1	146.8	114.4	118.1	82.3	52.2	59.1	131.6	111.6	145.1	146.9	114.6	120.6	32.3	42.1	72.1	55.1	—	20
54 Lariciresinol triacetate	A	138.7	109.5	150.9	141.4	122.5	117.6	82.7	49.0	62.6	138.0	112.6	150.9	138.7	122.6	120.4	33.4	42.1	72.7	55.8	168.9, 170.7, 20.6	20
55 Lariciresinol dimethyl ether	A+C	132.9	108.9	148.9	148.8	111.3	117.9	82.7	52.5	60.7	135.4	111.0	148.2	147.3	111.9	120.4	33.2	42.4	72.9	55.9	—	20
55a Lariciresinol dimethyl ether monoacetate	A	134.7	108.8	148.8	148.3	110.9	117.9	82.9	48.8	62.6	132.3	111.2	148.3	147.3	111.8	120.2	33.1	42.3	72.6	55.8	170.6, 20.8	21

(cont'd)

Table 1. (*continued*)

Substrate		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3, OCH_2O or others	$OCOCH_3$	Ref.
55b Lariciresinol 4′-mono-methyl ether	A	134.5	108.2	146.4	144.7	114.0	118.4	82.6	52.4	60.5	132.7	111.0	148.6	147.1	111.8	120.3	33.0	42.2	72.6	55.7	—	21
55c Lariciresinol 4′-methyl ether 4,9-diacetate	A	141.3	109.4	150.7	138.7	122.3	117.5	82.7	48.8	62.5	132.2	111.1	148.7	147.3	111.6	120.1	33.0	42.2	72.6	55.7	168.7, 170.5, 20.5, 20.7	21
55d Lariciresinol 4-mono-methyl ether	A	135.2	108.8	148.2	148.2	111.0	117.8	82.6	52.4	60.8	132.0	110.9	146.4	143.8	114.2	120.9	33.2	42.3	72.7	55.8	—	21
55e Diacetate of **55d**	A	134.6	108.7	148.8	148.3	110.8	117.9	82.8	48.9	62.5	138.8	112.6	150.7	138.0	122.6	120.4	33.4	42.1	72.6	55.8	168.8, 170.6, 20.6, 20.8	21
55f (−)-Olivil	D	110.4–123.0				129.4–147.1		83.7	61.2	60.0	110.4–123.0		129.4–147.1				39.9	81.5	77.0	57.8	—	56
56 See Scheme	A	134.5	107.2	146.9	147.3	107.6	120.0	84.0	61.4	60.4	136.2	107.4	147.0	147.6	108.4	120.9	73.2	84.2	75.7	100.8	—	42
57 Acetate of **56**	A	133.7	106.6	147.3	147.8	107.9	120.0	83.4	53.4	61.0	129.4	107.8	147.6	147.8	108.3	122.4	75.2	90.0	73.9	100.9, 101.2	170.5, 169.4, 169.2, 20.7, 21.0, 22.2	42
1.3.3. 9,9′-Monoepoxy lignan:																						
58 See Scheme	E	132.9	113.2	148.3	145.7	115.6	121.9	39.8	47.1	73.5	132.9	113.2	148.3	145.7	115.6	121.9	39.8	47.1	73.5	—	—	19
59 See Scheme	E	139.8	106.0	152.9	127.7	152.9	106.0	39.8	47.1	73.5	139.8	106.0	152.9	127.7	152.9	106.0	39.8	47.1	73.8	—	—	19
60 *cis*-Burseran	A							33.9	43.6	72.0							33.4	43.8	71.9	—	—	36a
61 *trans*-Burseran	A							39.9	43.6	73.2							39.2	46.3	73.2	—	—	36a
62 See Scheme	A	133.9	107.9	147.5	145.7	108.8	121.3	39.2	46.5	73.2	133.9	107.9	145.7	147.5	108.8	121.3	39.2	46.5	73.2	100.7	—	23a
63 Isoliovil acetate	A	137.7	111.3	151.2	139.8	123.0	120.9	76.6	48.2	69.9	137.8	119.4	123.0	139.8	151.3	113.1	33.7	50.0	102.9	56.0	169.2, 20.7	30
1.4.1. Derivatives of 3,7-dioxabicyclo(3.3.0)octane																						
64 See Scheme	E	133.8	128.3	116.1	157.7	116.1	128.3	86.7	55.0	64.5	133.8	128.3	116.1	157.7	116.1	128.3	86.7	55.0	64.5	—	—	19
65 Pinoresinol	A	132.0	108.8	146.8	145.2	114.4	118.5	85.7	53.7	71.3	132.0	108.8	146.8	145.2	114.4	118.5	85.7	53.7	71.3	55.6	—	21
65 (±)-Pinoresinol	A	133.0	108.5	145.4	146.8	108.8	119.0	85.9	54.2	71.7	133.0	108.5	145.4	146.8	108.8	119.0	85.9	54.2	71.7	56.0	—	51
66 Pinoresinol diacetate	A	139.8	109.6	150.9	138.9	122.5	117.7	85.3	54.2	71.8	139.8	109.6	150.9	138.9	122.5	117.7	85.3	54.2	71.8	55.8	168.8, 20.5	21
66 Pinoresinol diacetate	A	139.2	110.0	151.4	140.2	122.9	118.0	85.6	54.4	72.0	139.2	110.0	151.4	140.2	122.9	118.0	85.6	54.4	72.0	56.0	169.2, 20.7	35a
66 (±)-Pinoresinol diacetate	A	139.2	110.0	151.3	140.2	122.7	111.9	85.5	54.4	72.0	139.2	110.0	151.3	140.2	122.7	111.9	85.5	54.4	72.0	55.9	169.0, 20.6	51
67 Pinoresinol 4-methyl ether	A	133.3	109.0	148.9	148.4	110.8	118.0	85.6	54.0	71.5	132.6	108.4	146.5	145.0	114.1	118.7	85.6	54.0	71.5	55.8	—	21
68 Pinoresinol 4-methyl ether acetate	A	133.2	109.1	149.0	148.4	110.9	118.1	85.6	54.0	71.7	140.0	109.7	151.0	138.9	122.5	117.7	85.4	54.3	71.7	55.8	168.8, 20.5	21
69 Pinoresinol dimethyl ether	A	134.0	109.7	149.5	148.8	111.4	118.4	85.8	54.3	71.7	134.0	109.7	149.5	148.8	111.4	118.4	85.8	54.3	71.7	55.6, 55.9	—	37
70 (±)-Eudesmin	A	134.0	109.1	148.8	149.5	111.4	118.4	85.8	54.3	71.7	134.0	109.1	148.8	149.5	111.4	118.4	85.8	54.3	71.7	55.6, 55.9	—	41, 51, 54
71 (±)-Sesamin	A	134.9	106.3	146.8	147.7	107.9	119.1	85.6	54.2	71.5	134.9	106.3	146.8	147.7	108.0	119.1	85.6	54.2	71.5	100.9	—	41
71 (±)-Sesamin	A	134.9	106.3	146.9	147.7	108.0	119.1	85.6	54.2	71.6	134.9	106.3	146.9	147.7	108.0	119.1	85.6	54.2	71.6	100.9	—	51
72 Methylpiperitol	A	134.9	106.3	146.9	147.7	107.9	119.1	85.6	54.2	71.6	133.4	109.1	148.4	149.0	110.9	118.1	85.7	54.1	71.6	55.8, 100.9	—	39
73 Yangambin	A	136.6	102.8	153.3	137.5	153.3	102.8	85.9	54.4	71.9	136.6	102.8	153.3	137.5	153.3	102.8	85.9	54.4	71.9	56.2, 60.8	—	39
74 See Scheme	E	133.1	104.5	148.8	136.1	148.8	104.5	86.7	55.0	64.5	133.1	104.5	148.8	136.1	148.8	104.5	86.7	55.0	64.5	—	—	19
74 (+)-Syringaresinol	B	132.1	102.7	147.1	134.3	147.1	102.7	86.1	54.3	71.8	132.1	102.7	147.1	134.3	147.1	102.7	86.1	54.3	71.8	—	—	46b
75 Aschantin	A	134.9	106.4	146.4	147.8	108.1	119.2	85.7	54.3	71.6	136.7	102.8	153.3	137.4	153.3	102.8	85.9	54.3	71.9	56.1, 60.8, 101.0	—	39
76 9-Hydroxysesamin	A	135.4	106.3	147.2	148.1	108.1	119.2	83.0	62.1	101.0	136.1	107.1	147.3	148.1	108.2	120.0	88.1	53.2	72.3	101.1	—	42
77 9-Hydroxysesamin acetate	A	135.1	106.1	147.2	148.1	108.1	119.2	83.3	61.1	101.1	135.5	106.6	147.3	148.1	108.3	119.8	89.0	52.6	72.5	101.1	170.3, 21.3	42
78 9,9′-Dihydroxypinoresinol	B	134.2	110.8	145.8	147.5	114.9	118.9	84.2	60.9	100.2	134.2	110.8	145.8	147.5	114.9	118.9	84.2	60.9	100.2	55.5	—	51
79 9,9′-Dihydroxypinoresinol tetraacetate	B	139.3	110.9	151.4	141.1	122.8	118.3	85.0	58.5	101.1	139.3	110.9	151.4	141.1	122.8	118.3	85.0	58.5	101.1	55.8	169.1, 170.1, 20.3, 20.9	51
80 9,9′-Dimethoxypinoresinol	B	133.4	110.5	146.3	147.8	115.2	119.3	84.8	59.2	107.1	133.4	110.5	146.3	147.8	115.2	119.3	84.8	59.2	107.1	54.3, 55.4	—	51
81 9,9′-Dimethoxypinoresinol diacetate	B	139.1	111.1	151.1	141.5	122.8	118.5	84.2	59.1	107.5	139.1	111.1	151.1	141.5	122.8	118.5	84.2	59.1	107.5	54.5, 55.9	168.4, 20.3	51
82 9,9′-Dihydroxysesamin	A	136.5	107.3	147.2	147.9	107.9	119.0	85.3	60.4	101.2	136.5	107.3	147.9	147.9	107.9	119.0	85.3	60.4	101.2	101.0	—	42

82	9,9′-Dihydroxysesamin[b]	A	136.5	107.3	147.2	147.9	107.9	119.0	85.3	60.4	101.2	136.5	107.3	147.2	147.9	107.9	119.0	85.3	60.4	101.2	101.0	—	51
83	9,9′-Dihydroxysesamin diacetate[b]	A	134.7	106.3	147.6	148.2	108.2	119.8	85.9	58.5	100.3	134.7	106.3	147.6	148.2	108.2	119.8	85.9	58.5	100.3	101.0	169.7, 21.2	42
83	9,9′-Dihydroxysesamin diacetate[b]	A	134.7	106.4	147.6	148.2	108.1	119.8	85.9	58.5	100.3	134.7	106.4	147.6	148.2	108.2	119.8	85.9	58.5	100.3	101.2	169.8, 21.2	51
84	9,9′-Dihydroxyeudesmin[b]	A	135.9	110.4	148.2	148.9	111.5	118.6	84.2	60.9	100.4	135.9	110.4	148.2	148.9	111.5	118.6	84.2	60.9	100.4	55.4, 55.6	—	51
85	9,9′-Dihydroxyeudesmin diacetate[b]	A	133.8	109.7	148.5	148.9	111.6	118.5	85.1	58.2	100.4	133.8	109.7	148.5	148.9	111.6	118.5	85.1	58.2	100.4	55.3, 55.6	169.4, 21.0	51
86	9,9′-Dihydroxyeudesmin dimethyl ether[b]	A	135.0	110.1	148.5	149.1	111.6	118.9	84.7	59.2	107.1	135.0	110.1	148.5	149.1	111.6	118.9	84.7	59.2	107.1	54.3, 55.3, 55.6	—	51
87	Paulownin	A	129.4	108.2	147.9	148.2	108.6	120.1	87.5	91.7	71.6	134.8	106.9	147.9	148.2	107.5	119.8	85.9	60.6	75.0	101.1, 101.2	—	43
87	Paulownin	A	129.4	108.2	147.3	148.2	108.6	120.1	87.5	91.7	71.6	134.8	106.9	147.3	148.2	107.5	119.8	85.9	60.6	75.0	101.1, 101.2	—	23
88	Paulownin acetate	A	130.1	108.1	147.2	147.9	108.7	122.2	86.7	97.1	69.8	133.9	106.7	147.4	147.9	107.8	119.7	85.7	58.9	75.1	100.9, 101.0	169.2, 20.9	23
89	Isoarboreol	A	135.0	108.2	147.9	148.3	108.3	120.1	102.7	95.0	76.8	135.0	106.8	147.9	148.3	107.2	119.6	90.1	60.3	68.6	101.3, 101.5	—	37
90	6″-Bromoisoarboreol	A	133.8	106.8	147.1	147.5	107.8	119.5	101.5	94.1	76.3	134.8	107.5	147.4	147.6	112.0	111.6	87.7	59.6	69.0	100.9, 101.6	—	42
91	Gummadiol	A	129.7	106.2	147.2	147.7	107.5	119.2	83.4	66.0	101.0	135.1	108.1	147.7	148.0	108.4	120.1	88.0	92.0	75.1	101.0, 101.2	—	38, 42
92	Gummadiol diacetate	A	129.9	106.3	147.1	147.9	107.6	119.5	83.7	64.7	100.2	133.9	108.1	147.3	147.5	109.3	123.4	88.8	94.6	75.8	101.0	169.0, 169.7, 20.7, 21.2	38, 42
93	Kigeliol	A	129.3	107.6	147.7	147.9	108.3	120.3	86.9	87.6	76.4	129.3	107.6	147.7	147.9	108.3	120.3	86.9	87.6	76.4	101.2	—	50
94	Wodeshiol	A	129.5	107.5	147.9	147.9	108.3	120.2	86.9	87.5	76.4	129.5	107.5	147.9	147.9	108.3	120.2	86.9	87.6	76.4	101.1	—	40
94	Wodeshiol	A	130.9	107.6	147.1	147.3	108.3	120.6	87.2	87.7	75.9	130.9	107.6	147.1	147.3	108.3	120.6	87.2	87.7	75.9	100.9	—	23
95	Wodeshiol acetate	A	130.0	108.1	147.5	147.8	109.2	123.0	86.8	92.3	74.3	130.0	108.1	147.5	147.8	109.2	123.0	86.8	92.3	74.3	100.2	169.0, 20.9	23
96	Prinsepiol	B	128.4	112.2	145.8	146.8	114.5	120.1	86.9	87.5	74.5	128.4	112.2	145.8	146.8	114.5	120.1	86.9	87.5	74.5	55.5	—	53
97	(+)-Pinoresinol-4-β-D-glucoside	B	135.2	110.4	145.9	148.9	110.4	120.3	85.1	53.5	70.9	132.1	110.4	145.9	148.9	115.1	118.1	84.8	53.5	70.9	55.6	—	44
98	Pinoresinol-4-glucoside peracetate	A	137.8	110.7	145.7	151.3	118.8	120.3	85.6	54.3	72.0	140.2	110.0	150.9	139.2	122.1	117.9	85.6	54.5	72.0	56.0, 56.2	169.1, 169.4, 170.3, 170.6, 20.7	43
99	(+)-Pinoresinol-4′-(methyl ether)-4-*O*-β-glucoside	B	135.2	110.5	148.9	148.9	110.5	118.6	84.8	53.5	71.0	133.8	109.9	145.8	148.1	111.6	118.6	84.8	53.5	71.0	55.4, 55.6	—	44
100	Liriodendrin	F	133.7	104.6	153.4	138.8	153.4	104.6	86.5	54.0	70.1	133.7	104.6	153.4	138.8	153.4	104.6	86.5	54.0	70.1	57.1	—	45
100	Liriodendrin	B	133.9	104.3	152.7	137.2	152.7	104.3	85.1	53.6	71.3	133.9	104.3	152.7	137.2	152.7	104.3	85.1	53.6	71.3	56.4	—	46a
101	(+)-8-Acetoxypinoresinol-4-β-glucoside	B	130.3	110.7	146.3	148.2	114.6	119.0	86.1	97.0	73.8	131.2	113.0	147.5	148.2	115.3	121.1	84.5	58.2	69.7	55.6, 55.8	168.8, 20.6	43
102	(+)-8-Acetoxypinoresinol-4′-(methyl ether)-4-*O*-β-glucoside	B	130.2	110.1	146.2	148.3	114.6	118.5	86.0	96.9	73.7	131.7	111.6	148.1	148.7	112.9	121.0	84.3	58.2	60.7	55.4, 55.7	168.7, 20.5	43
103	(+)-8-Hydroxypinoresinol-4-*O*-β-glucoside	B	131.1	110.7	145.9	147.4	114.6	118.8	86.9	91.2	74.7	132.3	112.5	147.4	148.3	115.1	119.7	85.4	60.8	70.3	55.6	—	43
104	(+)-8-Hydroxypinoresinol-4′-(methyl ether)-4-*O*-β-glucoside	B	131.1	110.2	145.9	148.7	112.5	118.4	86.9	91.2	74.7	133.9	111.6	148.3	148.7	114.6	119.7	85.1	60.8	70.3	55.7, 55.9	—	43
105	(+)-8-Hydroxypinoresinol-4′-(methyl ether)-4-*O*-β-glucoside	A	133.1	109.9	146.2	151.1	111.4	119.0	87.5	91.9	74.9	132.2	111.2	149.3	148.9	111.4	120.3	71.7	60.3	85.8	55.9, 56.2	169.4, 170.3, 170.6	43
106	(+)-8-Acetoxypinoresinol-4′-(methyl ether)-4-*O*-β-glucoside tetraacetate	A	133.1	109.6	146.0	148.9	113.8	119.7	86.8	97.2	74.9	132.4	111.0	148.9	150.3	118.6	120.5	72.5	58.7	85.6	55.9, 56.1	20.5, 20.7, 169.3, 170.1, 170.4	43
107	(+)-8-Acetoxypinoresinol-4-A*O*-β-glucoside pentaacetate		133.1	110.1	146.1	150.3	118.2	120.6	86.7	97.1	74.9	139.1	113.7	151.3	139.4	119.7	122.9	72.5	58.9	85.4	55.9, 56.1	20.5, 169.0, 169.3, 170.2, 170.5	43

(cont'd)

Table 1. (*continued*)

Substance		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3, OCH_2O or others	$OCOCH_3$	Ref.
108 See Scheme	A+B	131.4	107.8	147.2	147.3	108.5	121.5	82.3	94.9	68.6	131.4	107.8	147.2	108.5	121.5	82.3	94.9	68.6	—	100.9	—	23
109 (+)-Epieudesmin	A	133.8	108.9	148.5	148.7	110.9	118.3	87.5	54.4	69.6	130.8	109.0	147.8	149.0	110.9	117.6	82.0	50.1	70.9	55.8	—	39, 54
110 Phillygenin 4-*O*-methyl ether	A	133.1	109.1	146.8	145.4	111.2	119.2	87.8	54.5	71.1	131.0	108.6	148.9	148.1	114.3	117.8	82.1	50.2	69.7	55.9	—	48a
111 Horsfieldin	A	130.4	108.5	144.8	146.5	114.4	119.5	87.7	54.6	71.1	135.3	106.5	148.0	147.2	108.2	118.5	82.1	50.2	69.7	56.0, 101.0	—	46c
112 (+)-Episesamin	A	135.6	106.6	147.4	148.2	108.3	119.6	87.7	54.8	69.7	132.6	106.7	146.8	147.9	108.3	118.9	82.1	50.3	71.0	101.1	—	39
112a Asarinin	A	135.3	108.1	147.2	147.6	106.3	119.5	87.6	54.6	69.6	132.3	106.5	146.5	147.9	108.1	118.7	82.0	50.1	70.9	101.0	—	46c
113 Gmelinol	A	130.7	110.5	148.3	149.4	111.5	119.2	88.8	57.4	68.4	128.1	109.2	148.3	149.1	111.4	117.7	81.2	90.8	75.9	55.6	—	37
114 Neogmelinol	A	132.9	109.7	149.2	149.5	111.3	118.7	85.2	62.7	69.7	129.7	108.8	148.7	149.0	111.4	117.5	88.7	93.9	76.8	56.0	—	37
115 Arboreol	A	133.7	106.7	148.0	148.3	108.2	119.6	102.8	94.8	76.8	135.3	107.1	148.0	148.3	108.2	120.7	90.0	60.2	68.5	101.3, 101.4	—	37
116 Methylarboreol	A	130.0	107.2	147.6	148.3	108.1	120.0	105.2	95.6	76.6	135.2	107.4	147.9	148.1	108.2	120.5	90.0	60.4	68.5	101.2, 101.3, 49.0	—	37
117 Ethylarboreol	A	130.6	107.1	147.5	148.2	108.2	120.0	105.0	95.5	76.6	135.2	107.2	147.8	148.0	108.2	120.3	90.0	60.5	68.5	101.1, 101.3, 15.3, 57.4	—	37
118 Epiaschantin	A	135.2	106.6	147.3	148.0	108.2	119.5	87.7	54.6	71.1	134.1	102.8	153.3	137.1	153.3	102.8	82.2	50.1	69.8	56.2, 60.9, 101.1	—	47
119 Epimagnolin	A	133.7	109.3	148.8	149.3	111.2	118.5	87.6	54.5	71.1	134.2	102.8	153.3	137.1	153.3	102.8	82.2	50.1	69.7	56.2, 56.0, 60.9	—	47
120 Phillygenin	A	133.1	109.1	148.9	148.1	111.2	119.2	87.8	54.5	71.1	131.0	108.6	146.8	145.4	114.3	117.8	82.1	50.2	69.7	55.9	—	48a, 54
120 Phillygenin	A	132.8				110.9		87.5	54.4	70.9	130.7				114.0		81.9	50.1	59.5		—	48b
121 Sylvatesmin	A	132.6	108.4	146.5	145.1	114.0	118.7	87.3	54.0	69.1	130.7	108.9	147.7	148.6	110.9	117.4	81.6	49.7	70.6	55.5	—	48c
122 Sylvatesmin acetate	A	138.9	109.7	150.9	140.1	117.7	122.3	87.0	54.2	69.4	130.7	108.6	147.8	148.6	111.0	117.5	81.7	49.8	70.9	55.6	168.8, 20.4	48c
123 Phillygenin acetate	A	140.3	110.0	151.3	139.2	122.7	118.1	87.4	54.6	71.1	131.0	109.1	148.9	148.1	111.2	117.8	82.1	50.2	69.8	55.9	169.1, 20.7	48a
124 (+)-Epipinoresinol-4-β-D-glucoside	A	132.4	110.5	145.9	145.9	115.2	118.5	81.1	49.2	68.7	132.6	110.5	145.9	145.9	115.3	117.7	86.8	53.6	70.4	55.7, 55.8	—	44
125 Phillyrin	B	131.2	109.5	146.0	147.7	115.3	118.2	81.3	49.3	69.0	135.4	110.5	148.5	149.0	116.0	117.7	86.7	54.0	70.4	55.7	—	44
126 Dieudesmin		131.4	109.6	147.0	148.7	110.9	118.4	83.9	49.5	68.7	131.4	109.6	147.0	148.7	110.9	118.4	83.9	49.5	68.7	55.8	—	41
127 Gmelanone	A	127.4	108.3	147.7	148.6	108.6	119.6	81.4	77.2	204.7	130.6	106.9	147.9	148.6	107.1	120.2	85.2	50.0	67.5	101.2, 101.4	—	37
1.4.2. Derivatives of 3,7-dioxabicyclo[3.3.0]octan-8-one:																						
128 See Scheme	A	131.2	107.9	146.8	145.5	114.5	118.1	83.5	50.0	188.0	132.4	108.2	147.0	146.2	114.8	118.5	72.8	53.4	84.6	56.1	—	35a
129 Hydroxysesamin γ-lactone	A	132.8	105.6	147.1	148.2	108.2	118.6	84.3	49.9	176.4	134.2	105.8	147.8	148.2	108.4	118.9	83.2	53.2	72.6	101.0, 101.3	—	42
130 Gummadiol γ-lactone	B	128.9	106.6	146.8	147.2	107.9	119.7	82.6	58.8	174.9	134.6	107.6	146.9	147.4	108.0	121.2	85.6	86.2	77.2	101.0	—	42
1.4.3. Derivatives of 3,7-dioxabicyclo[3.3.0]octan-4,8-dione:																						
131 9,9′-Dihydroxysesamin dilactone	A	131.7	105.6	148.3	148.4	108.6	119.0	81.9	48.2	174.9	131.7	105.6	148.3	148.4	108.6	119.0	81.9	48.2	74.9	101.5	—	42
132 9,9′-Dihydroxypinoresinol dilactone	B	129.0	110.6	147.4	147.9	115.5	119.1	82.1	48.1	175.4	129.0	110.6	147.4	147.9	115.5	119.1	82.1	48.1	175.4	55.8	—	51
133 9,9′-Dihydroxyeudesmin dilactone	B	130.5	110.0	146.3	149.4	111.7	118.8	81.7	48.1	175.3	130.5	110.0	146.3	149.4	111.7	118.8	81.7	48.1	175.3	55.6, 55.7	—	51
134 9,9′-Dihydroxypinoresinol diacetate dilactone	B	137.2	110.8	151.3	139.8	123.3	118.3	81.2	47.9	175.1	137.2	110.8	151.3	139.8	123.3	118.3	81.2	47.9	175.1	56.0	168.4, 20.3	51
2. Cyclolignans.																						
2.1. Derivatives of tetrahydronaphthalene:																						
135 Galbulin	A	132.5	112.3	149.0	147.0	110.8	122.0	54.4	43.9	17.2	129.1	110.8	147.2	147.4	113.0	139.1	39.1	35.6	20.0	55.9, 55.8	—	22
136 Galcatin	A	133.4	112.0	147.3	147.3	110.7	121.6	54.1	43.6	16.9	129.8	109.4	144.3	144.3	107.5	138.9	39.4	35.5	20.3	54.5, 55.8, 100.3	—	21
136a Isogalcatin	A	132.1	112.7	147.5	147.3	110.5	122.6	54.2	44.0	17.1	132.1	107.5	145.6	145.6	109.1	140.4	39.0	35.4	20.0	54.2, 55.8, 100.8	—	21
137 (+)-Isolariciresinol	A	132.6	112.0	145.2	143.5	114.5	121.9	47.4	47.5	62.1	127.2	110.6	147.1	144.1	115.8	136.8	32.8	39.5	65.7	55.6	—	20
138 (+)-Isolariciresinol tetraacetate	A	138.4	113.1	151.0	142.7	122.7	121.5	47.2	43.5	63.0	134.0	111.7	149.2	137.9	123.6	131.0	33.1	35.2	66.2	55.9	170.8, 170.6, 169.0, 168.8 20.8	20

139 (+)-Isolariciresinol 4,4'-dimethyl ether	A	131.7	112.8	148.9	146.9	110.8	121.7	48.0	48.2	62.6	128.1	110.7	147.3	147.0	111.9	137.6	33.2	39.9	66.2	55.7	—	20
140 (+)-Isolariciresinol 4,4'-dimethyl etherdiacetate	A	131.0	112.5	148.9	147.1	111.0	121.6	47.3	43.7	63.4	127.5	110.7	147.6	147.1	111.9	136.6	32.7	35.4	66.4	55.8	170.8, 170.7, 20.9	20
141 (+)-Isolariciresinol 4-monomethyl ether	A	132.8	112.5	149.1	145.8	111.5	122.1	47.7	48.0	62.4	127.7	111.0	147.6	144.0	116.3	138.4	33.2	39.9	66.0	56.0	—	20
142 (+)-Isolariciresinol 4-monomethyl ether-triacetate	A	131.7	111.9	149.1	147.8	111.1	121.7	47.0	43.4	63.1	133.8	111.7	149.1	137.8	123.5	135.9	33.1	35.3	66.3	56.4	171.4, 171.2, 169.5, 21.4, 21.1	20
143 (+)-Isolariciresinol 4'-monomethyl ether	A	131.9	112.6	146.4	144.1	114.3	121.6	47.0	47.0	61.3	128.3	110.6	147.0	146.5	111.8	136.5	32.4	38.9	65.0	55.1	—	20
144 (+)-Isolariciresinol 4'-monomethyl ether-triacetate	A	138.4	113.1	150.9	143.4	122.7	121.5	47.6	43.8	63.4	127.7	110.8	147.4	147.3	112.6	130.4	32.7	35.5	66.4	55.9	170.9, 170.7, 168.4, 20.9	20
145 Isolariciresinol tetra-methyl ether	A	132.1	112.4	148.9	147.4	111.0	121.8	47.3	44.9	71.4	128.9	111.1	147.2	147.5	112.9	138.1	33.1	36.4	75.4	55.8, 58.9	—	22
146 Lyonyresinol	B	137.6	106.0	147.4	133.3	147.4	106.0		46.6	62.3	128.5	106.6	146.3	137.1	146.8	124.9	32.2	—	64.6	55.6, 56.1, 56.1, 58.9	—	55
147 Lyonyresinol tetraacetate	A	144.9	105.0	151.9	127.3	151.9	105.0	43.0	44.4	63.1	135.2	106.9	151.3	131.7	150.9	124.3	33.6	35.5	66.3	56.0, 56.2, 60.1	—	55
148 Nirtetralin	A	132.0	112.1	148.6	146.8	110.9	119.9	45.3	41.4	73.6	135.6	102.9	147.5	139.8	141.9	124.8	33.4	37.0	76.1	55.8, 55.9, 59.0, 58.9, 100.6	—	22
149 Hypophyllanthin	A	131.8	112.0	148.6	147.1	110.8	120.5	45.4	41.9	71.9	115.1	106.7	147.2	133.4	142.1	138.1	33.3	36.7	75.5	55.8, 55.9, 56.4, 58.9, 101.1	—	22
150 Lintetralin	A	131.9	109.4	145.9	147.8	107.7	122.7	47.3	45.1	71.2	129.0	111.2	147.1	147.3	113.1	139.7	33.2	36.3	75.3	55.8, 55.9, 58.9, 100.8	—	22
151 (+)-Cycloolivil	A	117.4–122.9				129.4–142.1		44.8	47.6	60.5	117.4–122.9				129.4–142.1		40.1	73.4	69.4	56.0	—	56
152 (+)-Isolariciresinol-9α-β-xylopyranoside penta-acetate	A	138.6	113.1	151.3	143.0	122.7	121.7	46.8	44.1	67.1	134.3	111.9	149.3	137.9	123.5	131.5	33.1	34.6	65.9	56.1	171.1, 20.7, 168.9, 169.7, 169.9	57
153 Lyoniside	B	137.4	106.0	147.4	133.3	147.4	106.0		44.5	69.0	128.5	106.6	146.4	137.1	146.7	124.9	32.5	38.8	65.6	55.6, 56.0, 58.9	—	55
154 Lyoniside hexaacetate	A	145.1	105.0	151.9	127.0	131.9	105.0	42.5	45.0	68.2	135.4	106.8	151.4	131.7	150.8	124.3	33.5	35.3	66.2	56.0, 56.3, 60.0	—	55
155 9-β-Xylopyranosyl-(−)-5-methoxyisolariciresinol	B	135.5	106.4	147.3	133.5	147.5	106.4	46.7	43.4	67.9	126.9	111.5	145.3	143.8	115.9	131.7	32.2	38.3	65.5	55.3, 55.8	—	55
155a Cyclogalgravin	A	138.5	108.8	147.1	147.1	110.8	119.4	50.8	41.9	18.6	126.9	112.7	148.4	147.3	110.8	127.1	120.9	137.9	22.1	55.7	—	21
2.2. Derivatives of tetrahydronaphthalene lactone:																						
156 Deoxypodophyllotoxin	A	136.0	108.1	152.3	136.9	152.3	108.1	44.5	46.5	172.7	128.1	108.1	146.8	146.5	110.3	130.5	33.1	32.7	72.0	56.2, 60.6, 101.0	—	58
157 Podophyllotoxin	A	135.4	108.1	152.1	136.6	152.2	108.1	44.0	45.0	174.6	133.1	106.2	147.2	147.2	109.3	130.6	72.1	40.0	71.3	56.0, 60.5, 101.1	—	58
158 Podophyllotoxin acetate	A	134.6	108.0	152.0	137.0	152.0	108.0	43.6	45.6	173.2	128.1	106.8	147.3	147.8	109.4	132.1	73.4	38.6	71.1	56.0, 60.5, 101.4	171.0, 20.9	58
159 Epipodophyllotoxin	A	134.9	108.1	152.3	136.9	152.3	108.1	43.8	40.4	174.9	131.7	108.9	148.2	147.2	110.2	131.7	66.5	38.3	67.6	56.1, 60.6, 101.3	—	58
160 Epipodophyllotoxin acetate	A	134.1	107.7	152.2	137.1	152.2	107.7	43.5	41.2	173.8	127.3	109.2	148.4	147.0	110.1	132.4	67.8	36.4	67.1	56.1, 60.6, 101.5	170.0, 20.8	58
161 Picropodophyllotoxin	A	139.1	105.6	153.2	136.6	153.3	106.3	43.8	45.4	178.0	132.8	104.8	146.6	146.5	108.5	130.3	68.3	42.6	69.7	56.4, 60.3, 101.2	—	58
162 Picropodophyllotoxin acetate	A	138.8	106.3	153.3	136.6	153.0	106.3	44.4	45.4	176.7	126.2	109.8	147.2	148.4	108.3	131.3	72.4	29.8	70.5	56.0, 60.7, 102.0	170.0, 20.8	58
163 Picropodophyllone	A	131.9	107.5	152.8	137.4	152.8	107.5	44.5	46.5	172.7	128.0	105.5	147.8	152.9	110.2	141.3	188.0	43.3	66.8	56.1, 60.6, 102.2	—	58
164 α-Conidendrin	C	134.8	112.7	148.6	146.0	115.8	121.8	48.2	42.5	72.9	126.6	111.9	147.2	145.2	116.5	132.4	29.6	50.2	179.2	56.2	—	30
165 α-Conidendrin diacetate	A	140.8	111.9	151.5	139.0	123.1	120.6	49.7	47.3	71.5	133.6	113.0	149.9	138.3	123.6	130.6	29.6	41.5	176.4	55.9	168.9, 20.5	60
165 α-Conidendrin diacetate	A	140.9	112.0	151.8	139.3	123.3	120.7	47.6	41.7	71.7	133.8	113.1	150.0	138.6	123.8	130.6	29.7	50.0	176.6	56.0	169.0, 20.7	30
166 β-Conidendrin diacetate	A	138.6	113.1	151.4	139.0	123.2	120.9	46.6	41.2	71.2	133.9	112.1	149.9	138.0	121.9	131.4	28.4	38.6	179.1	55.8	168.9, 20.7	59, 60
2.2a. Derivatives of tetrahydronaphthalene acetal:																						
167 See Scheme	A	142.6	112.0	151.2	138.6	122.8	120.6	49.1	49.5	70.9	134.9	112.8	149.5	138.0	123.5	131.3	31.9	47.6	109.9	55.7, 56.4	168.8, 20.5	59, 60
168 See Scheme	A	140.1	113.4	151.2	138.0	121.0	121.4	47.5	45.8	70.6	136.0	111.7	149.3	137.8	123.0	133.1	31.6	44.9	110.6	55.8, 54.4	168.9, 20.6	59
169 See Scheme	A	140.4	113.7	151.4	139.9	121.7	121.3	47.6	46.0	70.8	136.1	111.8	149.6	138.1	123.1	133.4	31.7	45.1	109.6	56.0, 56.2, 62.7, 15.3	169.1, 169.2, 20.7	59
170 (+)-Africanal	D		126.1–147.1		112.0–121.3			48.5	45.1	70.3	126.1–147.1				112.0–121.3		37.3	79.0	103.3	56.1		56

(*cont'd*)

Table 1. (*continued*)

Substance		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3, OCH_2O or others	$OCOCH_3$	Ref.
2.3. Derivatives of naphthalene lactone:																						
171 Diphyllin	A	145.0	105.8	146.7	146.9	107.7	123.7	118.7	121.7	169.6	129.7	101.0	149.8	150.6	111.0	129.7	123.5	129.0	66.6	55.6, 55.2, 101.0	—	23a
171a Helioxanthin	B	131.4	109.7	146.6	147.0	116.7	120.7	125.7	128.5	170.4	130.5	107.8	120.9	140.0	141.2	126.8	122.8	130.1	69.3	101.1, 101.4	—	60c
171b Orosunol	B	131.2	115.0	147.4	148.9	116.5	120.6	121.6	130.9	168.4	129.1	112.7	121.3	143.2	145.2	122.1	146.3	125.3	69.7	55.9, 59.5, 101.2	—	60c
171c Demethylorosunol[b]	B	131.2	114.5	145.1	148.8	116.5	120.7	121.6	130.8	168.4	126.4	112.7	121.4	143.3	144.0	122.2	147.3	125.5	69.9	59.5, 101.2	—	60c
172 Cleistanthin A	A	144.2	106.1	147.5	147.5	108.2	123.7	119.2	126.9	169.9	130.7	130.8	150.3	151.9	110.8	135.9	128.4	129.2	67.4	55.8, 56.2, 58.0 60.1, 101.2	— —	23a
173 Cleistanthin A acetate	A	144.1	106.1	147.5	147.5	108.2	123.6		126.0	169.7	130.7	100.8	150.4	151.9	110.7	135.6	126.1	128.4	66.9	55.8, 56.2, 58.5, 59.9, 101.2	—	23a
174 Cleistanthin A methyl ether	A	144.4	106.3	147.5	147.5	108.1	123.6	119.2	127.0	169.7	131.0	105.1	150.2	151.9	110.7	136.4	128.4	130.8	67.3	55.8, 56.1, 58.7, 60.7, 61.2, 101.2	—	23a
174a Cleistanthin D	A	144.6	106.1	147.5	147.5	108.1	123.5	119.4	123.6	169.8	130.7	104.9	150.2	151.9	110.7	136.1	128.5	127.1	67.6	55.7, 56.1, 57.4, 57.8, 61.3, 101.2		23a
3. Isolignan and benzofuran types of neolignan.																						
3.1. Derivatives of dihydrobenzofuran:																						
175 Licarin A	A	131.6	108.6	146.1	145.3	113.8	119.3	93.3	45.2	17.2	131.7	112.9	132.8	146.3	143.6	109.0	130.5	122.8	18.0	55.5	—	26
176 (±)-Dehydrodiisoeugenol	A	133.2	110.0	146.7	146.4	116.0	122.0	94.4	46.6	17.7	134.0	114.0	134.0	147.6	143.4	112.0	132.0	125.6	18.0	56.0	—	33
176 (±)-Dehydroiisoeugenol	A	132.1	108.9	146.6	145.8	114.1	119.9	93.8	45.6	17.6	132.2	113.3	133.3	146.7	144.2	109.3	130.9	123.4	18.3	55.9	—	61
177 (+)-Dehydrodiisoeugenol	A	132.4	110.0	149.5	119.5	111.5	119.2	93.6	45.7	17.8	135.5	113.6	133.1	146.9	144.3	110.1	131.2	123.3	18.3	56.1	—	60b
178 Licarin B	A	134.0	106.3	147.5	147.2	107.7	119.7	93.0	45.5	17.6	131.8	113.0	132.7	146.2	143.7	109.2	130.6	122.9	18.1	55.7, 100.7	—	26
179 See Scheme	E	133.8	128.1	116.2	158.1	116.2	128.1	88.3	54.6	64.5	129.4	123.7	109.8	160.5	129.9	128.1	130.9	128.0	63.3	—	—	19
180 Dehydrodiconiferyl alcohol	E	134.3	110.7	148.6	147.3	115.8	119.5	88.3	54.6	64.5	130.4	111.8	145.1	148.9	132.0	116.2	130.9	128.0	63.3	—	—	19, 62
181 Cedrusin	D	134.6	110.5	148.2	147.0	116.3	119.5	88.1	55.1	64.7	129.7	115.7	141.5	146.0	136.2	116.9	35.6	31.9	61.9	56.3	—	63
182 Dihydrodehydrodiconiferyl alcohol	A	132.5	109.8	148.3	146.9	115.5	119.4	87.0	55.9	68.2	128.9	114.6	143.8	145.1	137.9	114.8	34.9	30.9	68.2	55.9	—	63
182 Dihydrodehydrodiconiferyl alcohol	E	134.5	110.8	148.5	147.1	115.8	119.4	88.3	54.6	64.5	129.9	113.9	136.4	144.8	129.9	117.7	35.3	32.4	61.7		—	19
183 Cedrusin tetraacetate	A	139.6	109.4	151.1	139.2	122.7	117.3	87.8	51.1	65.5	127.8	122.2	134.7	148.7	133.6	121.9	31.5	30.3	63.6	55.9	168.1, 168.7, 170.8, 170.8, 20.7, 20.8, 20.9	63
184 Dihydrodehydrodiconiferyl alcohol triacetate	A	139.5	109.8	150.9	139.3	122.6	118.0	87.6	50.7	65.4	126.8	112.5	143.9	145.9	134.9	16.1	32.0	30.5	63.1	55.8, 56.0	168.6, 170.4, 170.8, 20.6, 20.8, 20.9	63
185 Cedrusin-4-glucoside	C	137.9	111.5	146.8	150.1	116.8	118.9	87.6	56.5	64.6	129.1	117.2	141.2	145.9	136.5	116.8	35.1	32.2	62.1	56.5	—	63
186 Cedrusin-4-glucoside peracetate	A	137.4	109.8	150.7	145.5	120.1	117.4	87.8	51.1	65.5	127.9	121.9	134.7	148.8	133.6	122.3	31.5	30.3	63.6	56.1	168.2, 169.1, 169.9, 170.3, 170.4, 170.9, 20.7, 20.9, 21.0	63
187 Dihydrodehydrodiconiferyl alcohol-4-glucoside hexaacetate	A	137.3	110.2	150.7	145.8	120.1	118.5	87.8	50.7	65.4	126.8	112.4	143.9	145.9	134.9	116.1	32.1	30.6	63.7	55.1, 56.0	169.2–170.9, 20.8–21.0	63
188a Dehydrodiconiferyl alcohol-4-glucoside	A	137.5	110.9	150.4	147.1	117.5	119.5	88.4	54.7	64.5	129.7	111.7	145.0	148.7	132.2	116.1	131.6	127.3	63.5	56.4	—	64
188b Dihydrocarnatin	A	132.7	109.5	149.1	144.0	115.6	119.2	93.6	45.7	17.5	133.2	110.8	133.5	149.1	133.5	111.9	40.2	137.9	115.5	55.9	—	83a
188c Balanophonin	A	129.1	108.6	146.5	145.6	114.3	119.1	88.8	52.9	63.7	127.8	112.3	144.4	151.2	132.0	118.0	152.9	126.0	193.2	55.9, 56.0	—	75b

188d Dihydrocarinatinol	A	127.7	109.3	149.0	147.0	116.1	118.7	87.8	53.8	63.9	133.7	111.0	144.3	149.2	133.8	112.6	40.1	137.8	115.7	55.9	—	83d
189 Americanin D	A	130.2	113.1	145.2	145.2	115.3	116.6	87.5	52.9	63.0	127.4	117.0	141.3	150.2	132.3	116.6	125.5	154.0	193.8	—	—	84
190 Leptolepisol	A	134.7	110.5	149.0	146.2	116.1	119.5	89.1	55.4	65.1	138.4	112.6	148.3	144.8	129.1	116.4	75.5	56.8	64.4	56.4, 56.6	—	69
191 See Scheme	A							87.9	53.6	64.0										56.0	—	68
192 See Scheme	A							87.9	53.6													68
193 Herpetotriol	C	134.3	110.4	148.8	147.3	116.3	119.5	89.2	55.2	64.8	130.1	115.5	148.9	145.2	136.3	116.0	89.1	55.2	64.6	56.7, 56.3	—	65
194 Herpetriol	C	134.5	110.4			116.0	119.6	88.9	55.3	64.8	130.0	116.0			135.6	116.0				56.3, 56.5		66
195 Herpetetrol	C	133.8	110.5	149.2	147.5	116.3	119.7	89.1	55.2	64.8	130.0	115.7	148.6	145.1	135.3	116.3				56.3, 56.7		66
3.2. Derivatives of benzofuran:																						
195a Ratanhiaphenol II	A	124.6	128.4	115.7	155.1	115.7	128.4	155.5	109.8	9.3	132.9	116.2	131.5	151.3	110.7	122.3	131.5	124.2	18.3	—	—	67
195b Carinatin	A	133.0	107.6	148.9	144.7	111.1	119.9	154.2	110.2	9.6	135.2	110.0	141.5	148.9	124.3	111.0	40.6	138.0	115.6	55.9, 56.0, 56.1	—	83a
4. Benzocyclooctadiene lignan.																						
4.1. R-Biphenyl configuration.																						
4.1.1. (+)-Deoxyschizandrin group:																						
196 (+)-Deoxyschizandrin	A	139.1	107.3	153.0	140.3	151.6	122.4	35.7	40.9	21.8	133.9	110.6	151.7	139.9	151.5	123.5	33.8	39.2	12.7	55.7, 60.3, 60.7	—	70
197 (+)-Gomisin K_2	A	139.4	107.4	152.9	139.9	151.5	122.3	35.6	40.9	21.8	134.7	113.1	147.6	137.7	150.4	122.6	33.8	38.8	12.6	55.9, 60.1, 60.5, 61.0	—	71
198 (+)-Gomisin K_2 acetate	A	139.1	107.4	153.3	139.9	151.4	121.9	35.6	40.8	21.8	134.2	120.4	142.5	142.8	151.7	129.0	33.8	38.6	12.5	56.0, 60.3, 60.6, 60.8, 60.9	169.1, 20.8	71
199 (+)-Gomisin K_3	A	139.8	107.3	153.2	139.9	151.3	121.3	35.8	40.9	21.7	134.3	107.9	150.6	134.0	146.9	117.0	33.8	39.2	12.8	55.9, 56.0, 61.0, 61.1	—	71
200 (+)-Gomisin K_3 acetate	A	140.2	107.5	153.2	139.6	151.3	120.9	35.5	40.6	21.6	134.0	113.1	151.5	139.4	142.3	123.5	33.8	39.2	13.0	55.9, 56.1, 56.2, 60.7, 60.9	168.4, 20.5	71
201 Deoxy-(+)-gomisin K_3	A	139.3	107.7	152.6	140.1	151.0	126.5	35.7	40.5	21.6	128.5	114.7	147.2	146.4	114.0	130.3	33.4	38.8	12.8	55.9, 56.0, 60.5, 61.1	—	71
4.1.2. Schizandrin group with a hydroxy group at C-8:																						
202 Gomisin A	A	132.1	110.4	152.3	140.8	152.1	124.2	40.6	71.7	30.1	132.5	105.9	147.9	135.0	143.3	121.9	33.8	42.1	15.8	56.0, 59.6, 60.6, 61.0, 100.8	—	70
203 Schizandrin	A	131.8	110.5	152.3	140.8	151.9	124.2	40.9	71.8	29.7	133.8	110.1	152.0	140.3	153.6	122.8	34.4	41.8	15.9	56.0, 60.5, 60.9	—	70
204 Gomisin H	A	132.5	110.6	152.6	140.8	152.6	123.2	41.1	72.0	29.7	134.3	107.3	150.7	134.0	146.9	116.5	34.5	41.8	15.9	55.8, 56.0, 61.0, 61.1	—	70
4.2. S-Biphenyl configuration.																						
4.2.1. Gomisin J group:																						
205 Gomisin N	A	134.1	110.7	151.6	140.2	151.7	123.4	39.2	33.6	12.9	137.8	102.9	148.7	134.6	141.1	121.4	35.6	40.8	21.5	55.9, 59.6, 60.5, 61.0, 100.7	—	70
205a Wuweizisu C	A							38.9	33.7	12.6							35.4	40.8	21.7	59.6	—	74
206 (−)-Gomisin K_1	A	134.1	110.8	157.7	140.3	157.6	123.4	39.6	33.8	12.8	140.0	110.0	148.8	137.5	150.3	121.6	35.3	40.9	21.7	56.0, 60.1, 60.5, 60.9, 61.0	—	70
207 (−)-Gomisin K_1 acetate	A	133.9	110.7	152.0	140.3	151.5	122.0	39.1	33.7	12.6	139.5	117.5	143.7	142.4	151.6	128.0	35.1	40.9	21.7	56.6, 60.3, 60.6, 60.8, 61.0	169.0, 20.8	70
208 Dimethylgomisin J	A	133.5	110.3	151.3	140.3	151.3	123.3	39.1	33.7	12.7	138.8	107.0	152.7	139.6	151.5	122.2	35.5	40.7	21.8	55.7, 60.4, 60.8	—	70
209 Gomisin J	A	134.9	113.3	147.6	137.8	150.3	122.5	38.9	33.8	12.6	140.2	110.2	148.8	137.5	150.5	121.5	35.3	41.0	21.7	60.1, 61.0	—	70
4.2.2 Gomisin O group with a hydroxy group at C-7:																						
210 Angeloyl gomisin O	A	132.8	111.3	151.9	141.7	151.9	123.8	80.8	37.0	15.8	135.1	102.2	148.8	134.6	142.0	121.7	37.9	37.2	17.8	56.0, 59.3, 60.4, 60.9, 100.7	—	72c
210a Gomisin O	A	137.0	110.2	152.1	141.7	151.9	122.2	81.4	40.1	16.6	135.5	102.5	149.2	134.6	141.5	120.7	38.1	37.2	17.5	56.0, 59.5, 60.3, 60.8, 100.7	—	70
210b Gomisin R	A	136.0	105.6	148.2	136.4	141.6	121.5	81.1	40.1	16.5	135.7	102.7	149.3	134.5	141.6	120.4	37.9	37.1	17.5	59.5, 59.6, 100.8, 101.2	—	72d
211 Epigomisin O	A	136.5	106.4	152.3	140.8	151.2	121.3	73.4	42.6	7.8	137.9	102.8	149.2	134.6	140.9	119.6	34.7	39.3	22.0	56.0, 59.6, 60.6, 61.0	—	70
211a Deangeloyl isogomisin O	A	135.2	105.5	148.1	136.4	141.6	121.6	81.1	40.2	15.6	137.2	107.1	153.6	140.1	151.9	121.3	37.3	36.6	18.7	55.9, 59.6, 60.7, 60.9, 101.7	—	72c
211b Benzoyl isogomisin O	A	130.8	106.5	148.0	137.0	141.7	122.8	81.2	36.4	14.3	136.9	107.1	153.2	140.1	151.8	122.8	37.9	37.2	19.2	56.0, 59.7, 60.2, 60.7, 101.3	—	72c

(cont'd)

Table 1. (*continued*)

Substance		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3, OCH_2O or others	$OCOCH_3$	Ref.
4.2.3. Gomisin B group with two hydroxy groups at C-7 and C-8:																						
212 Deangeloylgomisin B	A	133.6	110.3	152.1	141.5	151.9	122.1	86.0	73.6	28.5	135.0	103.2	149.8	135.5	140.7	119.6	36.3	41.6	18.8	56.0, 59.6, 60.7, 60.8, 101.0	—	70
212a Deangeloylschisantherin D	A	132.6	106.0	140.8	136.3	140.8	120.3	85.8	73.6	28.6	135.6	103.4	149.8	134.9	141.5	119.5	36.1	41.6	18.6	59.6, 59.7, 101.1, 101.3	—	72d
213 Deangeloylgomisin F	A	132.2	106.0	148.1	136.5	141.5	120.6	85.9	73.6	28.7	136.7	107.7	154.2	140.5	151.4	120.5	36.4	41.6	18.9	55.9, 59.7, 60.6, 61.0, 101.3	—	70
214 Gomisin P	A	135.4	106.4	152.4	140.8	150.9	122.2	75.0	76.2	16.0	136.9	102.7	149.1	134.9	141.1	119.5	36.9	46.6	18.8	56.0, 59.8, 60.5, 60.9, 100.8	—	70
215 (−)-Gomisin Q	A	133.3	110.2	152.0	140.6	152.0	120.6	86.1	73.8	28.6	136.6	107.6	154.2	141.6	151.3	121.2	36.5	41.7	19.0	56.0, 60.6, 60.9, 61.0, 60.7	—	72
4.2.4. Derivatives of benzocyclooctadiene lactone:																						
216 See Scheme	A	132.0	112.2	148.9	147.3	114.3	132.5	32.1	46.9	176.5	131.0	111.9	148.8	147.3	114.1	132.5	34.2	50.1	70.1	56.0	—	73
4.2.5 (and 4.1.3). With a keto function at C-7 and/or C-7′:																						
216A See Scheme	A	137.0	101.1	154.6	142.4	152.8	117.9	209.6	52.4	8.5	131.7	104.2	149.8	141.0	141.2	122.6	201.7	47.2	15.5	56.1, 59.9, 61.1, 61.3, 102.2	—	73b
216b See Scheme	A	137.3	105.7	153.6	141.3	152.9	120.3	79.4	47.8	10.2	131.0	104.0	149.2	141.3	140.9	125.8	200.5	44.2	16.0	56.0, 59.8, 61.0, 102.0		73b
216c See Scheme	A	131.8	108.4	153.4	146.3	151.7	122.1	201.9	47.2	15.3	135.6	97.1	150.1	137.0	142.1	117.8	209.2	52.5	8.4	55.9, 59.8, 60.5, 61.0, 101.7		73b
216d See Scheme	A	130.9	108.2	152.8	146.4	151.7	125.1	200.3	44.0	15.8	135.7	101.5	149.5	136.2	142.2	119.5	79.5	48.1	10.3	55.9, 59.8, 60.5, 61.0, 101.5		73b
216e See Scheme	A	134.3	106.9	152.7	141.3	151.7	120.5	73.1	43.2	8.0	134.3	97.2	149.6	136.7	140.9	115.7	209.4	48.9	14.1	55.9, 59.9, 60.8, 61.1, 101.5		73b
216f Kadsurin	A	133.3	110.4	151.6	139.7	151.0	123.4	200.3	44.0	14.8	134.9	102.5	148.4	136.0	141.4	120.6	82.3	41.9	19.6	56.0, 59.7, 60.3, 60.7, 101.2	170.1, 20.7	73b
216g See Scheme	A	137.0	101.0	154.5	142.3	152.5	118.1	209.6	52.4	8.6	131.7	108.2	153.4	146.5	151.7	122.3	201.9	47.1	15.5	56.0, 56.1, 60.5,		73b
5. Neolignan.																						
5.1. Hydrobenzofuranoid type.																						
5.1.1. Angularly methoxylated hydrobenzofuranoid type:																						
217 Mirandin A	A	135.5	102.6	152.8	137.2	152.8	102.6	94.3	46.9	16.1	142.5	131.6	80.9	172.6	104.6	186.8	33.2	134.8	116.9	56.1, 60.7±0.1, 50.3	—	26
218 Mirandin B	A	132.7	103.5	153.3	138.4	153.3	103.5	91.2	49.8	6.9	142.8	130.9	77.6	174.3	102.7	186.8	33.5	134.8	117.1	56.1, 60.7±0.1, 51.1	—	26
5.1.2. Angularly allylated hydrobenzofuranoid type:																						
219 Ferriearin	A	133.9	100.2	148.6	133.9	143.1	105.5	81.8	44.5	10.8	52.5	99.7	192.6	125.7	150.9	31.0	40.4	133.9	117.6	56.4, 101.2	—	77
220 Burchellin	A	131.5	106.5	148.1	148.1	107.8	120.5	90.9	49.5	8.3	153.3	107.8	50.9	181.4	101.8	182.8	36.6	130.9	120.0	101.2, 51.8	—	26
221 See Scheme	A	129.8	109.1	149.6	149.2	110.9	119.3	91.0	49.3	8.5	153.3	107.8	51.0	181.3	101.9	182.6	36.7	130.7	119.9	55.2, 55.9	—	26
222 See Scheme	A	130.1	109.2	149.5	149.2	110.9	119.2	91.5	49.6	8.5	152.7	107.2	49.8	183.9	166.0	189.7	36.7	130.7	119.8	55.3, 55.9, 60.4	—	26
223 See Scheme	A	130.2	106.0	147.7	147.1	108.1	118.7	87.2	44.6	12.0	152.7	109.0	53.9	181.2	101.8	182.4	43.9	131.5	120.0	101.0, 55.2	—	26
224 See Scheme	A	134.6	99.7	148.9	131.0	143.4	105.0	87.1	44.5	11.9	152.6	108.9	53.8	181.0	101.8	182.3	43.8	131.5	120.0	56.7, 101.4, 55.1	—	26
225 See Scheme	A	130.7	102.4	153.2	132.1	153.2	102.4	87.2	44.5	12.0	152.6	108.9	53.9	181.1	102.0	182.4	43.9	131.5	120.1	56.1, 60.7, 55.2	—	26
226 See Scheme	A	129.8	106.2	147.8	147.8	108.2	118.7	87.4	42.8	11.6	48.7	167.0	166.6	192.3	77.3	32.2	39.8	132.7	119.8	55.9, 101.1	—	77
227 Porosin	A	128.3	108.6	148.8	148.5	110.9	117.8	87.2	42.5	11.6	76.8	32.0	50.2	183.4	100.1	196.6	39.0	131.5	119.7	55.9, 58.7	—	26
228 See Scheme	A	129.9	109.2	149.6	149.2	110.9	119.4	91.1	49.4	8.5	51.0	181.4	101.9	182.7	153.0	107.9	36.7	130.8	119.9	55.9, 55.2	—	81
229a See Scheme	A	133.1	103.4	153.3	131.5	153.3	103.4	91.1	49.4	8.5	51.0	181.4	101.9	182.7	153.0	107.9	36.7	130.8	119.9	56.1, 60.7	—	81
229b See Scheme	A	136.1	102.3	149.7	130.2	143.4	109.1	62.1	82.2	18.9	48.3	169.6	127.4	192.7	77.2	37.8	39.1	133.7	118.8	57.1, 59.3, 60.3, 101.7	—	80b

5.1.3. Linearly allylated and methoxylated hydrobenzofuranoid type:																					
229c See Scheme	A	131.4	106.1	148.1	148.1	108.2	120.0	93.7	42.6	16.1	80.8	134.1	140.2	172.0	99.5	199.3	45.0	130.7	119.0	100.3, 53.5	—	26
229d See Scheme	A	133.2	103.0	153.4	138.5	153.4	103.0	93.7	42.6	16.3	80.6	134.1	140.0	171.0	99.6	199.2	44.8	130.8	118.8	56.1, 60.7±0.1, 53.4	—	26
5.2. Benzodioxane type:																					
230 Eusiderin	A	131.9	104.1	153.0	138.0	153.0	104.1	80.6	73.7	17.0	132.1	104.3	148.1	130.9	143.8	109.1	39.7	136.9	115.3	55.7, 55.8, 60.4	—	26
230 Eusiderin	A	132.4	104.4	153.4	138.3	153.4	104.4	81.0	74.0	17.3	132.2	104.5	148.4	131.1	143.8	109.4	39.9	137.1	115.6	56.3, 60.7	—	75a
231 See Scheme	A	130.7	107.1	147.9	147.9	108.2	121.3	80.6	74.1	17.2	132.2	104.5	148.4	131.1	144.2	109.4	40.0	137.2	115.6	56.1, 101.1	—	75a
232 See Scheme	A	129.6	103.2	153.5	137.8	153.5	103.2	77.1	73.2	12.6	132.5	105.1	148.1	132.3	143.4	109.8	40.0	137.5	115.9	56.2, 60.9, 56.1	—	78
233 See Scheme	A	129.5	111.2	149.1	148.9	109.5	118.7	77.1	73.2	12.7	132.5	104.9	149.2	132.3	143.5	109.8	40.1	137.5	115.9	56.0, 56.1	—	78
234 Americanin A	B	127.2	115.0	145.3	145.9	115.5	118.9	76.1	78.1	60.1	127.6	122.6	117.3	146.5	143.5	116.8	126.8	153.0	194.0	—	—	79
235 Americanin A triacetate	A	134.2	123.0	142.5	142.1	123.9	126.0	75.4	74.3	62.0	128.1	123.0	117.5	145.8	142.7	116.9	127.2	152.6	193.9	—	168.0, 169.8, 20.2	79
236 Americanin B		129.4	116.1	143.2	144.0	116.7	120.4	75.2	78.2	60.0	127.5	116.7	143.7	146.1	117.3	123.0	126.9	152.9	193.9		—	84
5.3. Bicyclo[3.2.1]octane type.																					
5.3.1. Guianin type:																					
237 See Scheme	A	131.4	107.6	147.4	146.3	110.8	120.3	57.0	48.6	13.9	51.4	78.2	90.8	194.6	151.4	123.8	36.6	134,4	117.9	54.5, 55.4, 100.8	—	80a
238 See Scheme	A	131.0	107.7	147.5	146.5	110.6	119.5	57.5	49.4	13.9	50.8	77.6	90.2	193.6	152.1	124.1	37.1	133.9	118.6	54.8, 55.5, 100.9	169.1, 21.0	80a
239 See Scheme	A	132.2	107.9	147.5	146.4	109.6	119.4	55.6	46.3	13.4	48.1	84.5	90.2	195.8	151.2	123.0	38.1	132.4	117.9	53.5, 55.4, 100.8	—	80a
240 See Scheme	A	133.3	108.2	148.0	147.8	108.7	121.4	53.1	47.4	17.4	51.8	80.9	64.9	185.8	153.0	126.8	34.,6	134.3	118.2	55.3, 100.9	—	80a
5.3.2. Macrophyllin type:																					
241 See Scheme	A	137.2	104.6	153.8	137.2	153.8	104.6	45.4	49.5	13.9	140.6	202.2	69.9	194.3	89.4	147.3	32.8	134.1	118.0	54.0, 56.3, 60.8	—	81
242 Macrophyllin B	A	140.3	104.7	153.7		153.7	104.7	45.4	46.0	11.9	140.3	76.3	58.9		85.5	126.6	36.4	135.1	117.3	56.3, 60.8, 52.9	—	81
243 See Scheme	A	136.7	104.5	153.9	136.7	153.9	104.5	45.3	46.6	15.6	140.1	189.3	66.4		94.5	143.6	34.1	133.8	118.5	56.3, 60.9, 51.0	—	81
5.4. Carinatane type:																					
244 (−)-Carinatone	A	127.6	109.5	148.8	146.6	120.0	123.2	199.6	39.8	17.9	129.7	110.2	140.4	153.0	131.9	111.2	39.9	137.6	115.6	55.9	—	83a
245 Carinatinol	A	122.2	110.1	148.7	146.7	120.4	123.5	199.3	48.2	63.9	129.3	110.1	140.9	153.2	131.9	110.9	39.8	137.3	115.7	55.8, 55.9	—	83d
246 (−)-Carinatanol	A	129.0	109.4	148.5	146.7	119.5	120.4	78.9	42.0	17.1	131.6	109.7	142.1	148.9	135.7	110.7	40.1	137.8	115.6	55.8	—	83a
5.5 Heterotropanone type:																					
247 Heterotropanone	A	135.0	106.1	152.8	144.8	152.8	106.1	37.4	39.7	27.1	135.0	41.2	94.2	201.7	86.1	118.8	39.5	133.9	117.2	49.2, 50.7, 53.7, 56.0, 60.6	—	25a,b
248 Isoheterotropane	A	136.1	105.8	152.8	146.2	152.8	105.8	36.2	41.7	26.2	136.1	41.4	94.7	201.0	86.5	120.2	39.6	133.7	117.3	49.0, 50.7, 52.9, 56.0, 60.6	—	25a,b
5.6. Asatone type:																					
249a Asatone	A	49.8	121.7	150.2	188.7	93.2	43.9	41.3	135.2	118.2	144.9	116.6	92.1	201.4	98.7	44.5	39.0	116.9	133.4	50.1, 50.2, 54.8, 55.5	—	25b, 83b
249b Isoasatone	A	50.2	122.1	150.2	187.7	93.3	43.2	41.5	135.0	117.3	141.2	116.0	91.8	201.2	98.5	39.6	128.7	128.2	18.4	50.2, 50.5, 50.8, 54.8, 55.4		25b
250 Heterotropatrione	A	49.5	121.1	150.2	187.9	93.2	43.9	41.1	133.8	116.7	144.0	115.8	91.8	201.3	98.3	44.6	36.7	33.0	28.0	48.9–55.4	—	25b
251 Isoheterotropatrione	A	49.8	120.6	150.5	187.5	93.4	44.1	41.7	134.2	117.0	145.8	117.0	91.6	201.6	98.2	44.1	35.6	36.9	27.1	49.4–55.4	—	25b
5.7. Other types:																					
252 Aurein	A	135.8	105.7	152.6	135.6	152.6	105.7	45.2	41.9	20.8	141.9	103.8	152.2	134.5	152.2	103.8	73.7	134.2	116.9	55.6, 55.7, 60.4	—	26
253 Surinamensin	A	137.6	104.2	152.9	135.5	152.9	104.2	83.6	78.0	17.0	133.3	109.1	150.5	146.4	118.6	118.7	130.2	124.6	18.2	55.6, 56.0, 60.7	—	76
254 Magnolol	A	133.3	131.4	124.5	151.0	116.8	129.8	39.4	137.6	115.8	133.3	131.4	124.5	151.0	116.8	129.8	39.4	137.6	115.8	—	—	82a,b
255 Honokiol	A	132.4	131.1	127.8	150.7	116.8	129.6	39.4	137.8	115.6	126.5	153.9	116.5	130.3	128.6	128.8	35.0	136.1	115.6	—	—	82a,b
255a Obovatol	A	133.3	129.8	117.8	155.2	117.8	129.8	39.5	137.4	115.8	132.5	111.1	144.0	135.0	144.9	111.5	39.4	137.2	115.7	—	—	82b
255b Futoenone	A	50.3	180.1	101.4	183.1	153.4	109.0	43.7	81.9	38.0	137.3	107.7	148.0	146.4	108.3	121.1	46.2	45.5	14.5	55.2, 101.0	—	81b
256 Denudatone	A	50.4	180.1	101.4	183.1	153.3	109.0	43.6	81.9	37.9	139.1	104.8	153.3	139.1	153.3	104.8	46.9	45.3	14.6	55.2, 56.2, 60.8	—	81b

(cont'd)

Table 1. (*continued*)

Substance		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1″	C-2″	C-3″	C-4″	C-5″	C-6″	C-7″	C-8″	C-9″	OCH_3	Ref.
6. Miscellaneous lignans.																											
6.1. Flavonolignan:																											
257 Silychristin	B	83.5	72.1	197.3	163.6	96.6	167.0	95.2	162.6	100.5	129.0	115.3	147.6	147.4	129.9	115.8	132.6	110.2	147.4	140.4	115.1	118.7	87.3	53.7	63.2	—	86a
257 Silychristin	B	83.3	71.6		163.3	95.9	166.7	95.0	162.5	100.4	129.0	115.3	147.5	147.0	129.9	115.6	132.4	110.4	146.3	140.6	115.3	118.6	86.9	53.3	62.9	—	84, 85
258 Silychristin acetate	A	80.9	73.2	185.1	151.8	111.4	156.4	109.0	166.4	110.7	128.6	122.7	139.7	151.9	139.9	123.0	139.4	109.6	151.5	139.7	121.3	117.6	88.3	51.0	65.2	—	86a
259 Anhydrosilychristin		83.5	71.9	197.6	163.3	96.1	166.8	95.0	162.5	100.5	122.0	109.8	150.9	141.6	122.0	110.0	132.5	110.4	147.8	147.1	115.9	119.7	141.7	109.5	9.3	—	86a
260 Anhydrosilychristin acetate		81.4	73.6	185.9	151.4	111.3	156.4	109.1	162.5	110.7	129.4	116.1	140.1	152.1	130.3	119.9	134.9	109.3	151.3	140.1	123.1	117.2	145.2	112.0	9.4	—	86a
261 Isohydnocarpin	B	164.7	103.8	181.7	157.4	99.0	161.6	94.0	164.1	103.8	123.6	116.6	130.7	141.6	145.2	114.4	132.0	110.4	147.8	147.7	115.7	119.2	87.9	52.8	62.9	55.8	87
262 Silybin	B	82.0	71.0	196.6	162.5	95.5	165.9	94.5	161.6	99.8	129.3	114.7	142.5	142.9	115.8	120.1	126.7	111.0	146.8	142.5	115.8	120.9	75.3	77.6	59.8	55.2	88
263 Silandrin	B	78.1	41.9	195.5	163.4	95.9	166.6	95.0	162.5	101.8	131.6	114.9	143.1	143.6	115.4	119.1	127.4	112.2	147.6	147.1	116.5	120.4	75.7	77.8	60.2	55.9	88
264 Hydnocarpin	B	164.2	103.8	181.6	157.3	98.5	161.4	93.9	162.8	103.8	123.6	119.3	116.7	147.2	143.6	114.6	127.0	110.9	147.7	147.0	115.4	120.6	76.4	78.1	59.6	55.8	87
265 Methoxyhydnocarpin	B	164.3	103.8	181.7	157.3	98.9	161.4	94.0	163.0	103.8	122.3	104.1	149.0	136.0	144.3	108.1	127.0	112.0	147.7	147.2	115.4	120.6	75.7	78.3	59.9	55.8 56.0	87
266 Hydnowightin	B	164.1	103.9	180.4	157.7	98.8	161.5	93.8	156.9	103.9	127.1	112.1	145.3	147.3	115.5	113.4	127.1	113.2	147.8	147.2	132.5	119.2	76.1	77.8	59.8	55.6	87
267 Neohydnocarpin	B	164.5	104.8	180.8	157.3	97.1	161.3	96.8	161.3	104.8	120.3	113.7	147.2	148.2	119.2	133.9	132.4	112.3	147.9	147.6	115.7	127.2	40.9	35.2	69.2	56.1	87
268 Silymonin	B	77.5	39.6	195.1	163.4	96.0	166.6	94.1	162.4	101.8	133.0	47.5	96.9	201.5	44.3	123.6	140.3	113.0	147.3	145.3	115.2	120.5	53.1	46.1	72.7	55.8	88
269 Silydianin	B	81.6	70.8	196.4	163.3	96.1	166.8	95.0	161.9	100.2	132.9	48.9	96.6	201.8	44.0	124.0	139.4	112.4	147.0	144.9	114.8	120.8	53.3	46.0	72.7	55.4	88
270 Isosilybin	B	82.4	71.4	197.4	163.1	95.9	166.6	94.9	162.2	100.3	130.1	116.2	142.7	143.7	116.2	120.7	127.2	111.5	147.4	146.8	115.1	120.8	77.9	75.7	60.0	55.6	89

		C-1	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7	C-8	C-8a	C-9	C-9a	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3	Ref.
6.2. Xanthonolignan:																									
271 Kielcorin	B	96.4	145.6	139.4	132.3	141.1	155.1	117.9	134.5	124.1	125.7	120.6	174.5	113.7	126.5	112.0	147.6	147.2	115.3	120.7	76.4	77.8	59.8	55.6	90a

		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′	C-9′	OCH_3	$OCOCH_3$	Ref.
6.3. Coumarinolignan:																						
272 Cleomiscosin A	G	160.8	113.6	144.5	101.1	146.3	138.4	133.0	139.3	111.9	127.5	112.3	150.0	149.0	116.6	121.7	77.5	79.9	60.7	55.8, 56.2	—	91
273 Cleomiscosin A monoethyl ether	G	160.7	113.3	144.5	101.0	146.3	138.2	132.0	139.2	112.2	129.1	111.6	150.1	149.6	113.8	121.0	77.3	79.7	60.6	55.7, 56.1, 64.4, 14.9	—	91
274 Cleomiscosin A diacetate	A	160.4	114.4	143.5	100.5	145.8	136.9	133.5	140.8	111.9	131.7	111.5	151.7	138.8	123.3	119.9	76.7	75.1	62.4	56.0, 56.3	168.5, 170.2, 20.6	91, 92
275 Cleomiscosin B	G	160.7	113.8	144.4	101.2	146.2	138.1	133.2	139.4	111.8	127.5	112.3	150.1	149.1	116.5	121.7	77.1	80.2	61.1	55.9, 56.1	—	92
276 Cleomiscosin B diacetate	A	160.4	114.3	143.5	100.8	145.7	136.3	132.1	140.7	111.8	133.5	111.3	151.6	138.8	123.2	119.8	76.0	75.6	62.4	56.0, 56.4	168.6, 170.2, 20.6	92
277 Aqillochin diacetate	A	160.2	114.1	143.5	101.1	145.8	136.9	131.6	145.7	111.8	133.1	104.5	152.7	138.7	152.7	104.5	77.0	75.0	62.3	56.2	168.2, 170.1, 21.0, 21.2	93

[a] Symbols for aryl groups and sugars used in structural formulae in text for the compounds listed in Table 1:

Ang	Angeloyl
Benz	Benzoyl
Ca	*Ca*techyl (3,4-dihydroxyphenyl)
CaAc	*Ca*techyl *Ac*etate (3,4-diacetoxyphenyl)
Hd	4-*H*ydroxy-3,5-*d*imethoxyphenyl
Hy	4-*H*ydroxyphenyl
Gu	*Gu*aicyl (4-hydroxy-3-methoxyphenyl)
GuAc	*Gu*aicyl *Ac*etate (4-acetoxy-3-methoxyphenyl)
Mp	3-Methoxy-4,5-methylenedioxyphenyl
Ph	*Ph*enyl
Pi	*Pi*peronyl (3,4-methylenedioxyphenyl)
Tp	Tri-o-methylpyrogallyl
Ve	*Ve*ratryl (3,4-dimethoxyphenyl)
Glu	*Glu*cose
$Glu(OAc)_4$	2,3,4,6-tetracetylglucose
Xyl	*Xyl*ose
$Xyl(OAc)_3$	2,3,4-triacetylxylose

[b] See numbering scheme (different from original reports).

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