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LIGNANS OF *ARAUCARIA ANGUSTIFOLIA* AND ^{13}C NMR ANALYSIS OF SOME PHENYLTETRALIN LIGNANS

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Key Word Index—*Araucaria angustifolia*; Araucariaceae; lignans; secoisolariciresinol monomethyl ether; lariciresinol-4-methyl ether; ^{13}C NMR; galbulin; galcatin; isogalcatin; cyclogalgravin.

Abstract—Secoisolariciresinol monomethyl ether and lariciresinol-4-methyl ether were isolated from the knots of dead trees of *Araucaria angustifolia*. On the basis of spectral evidence, the position of the OH group was located in these compounds. The ^{13}C NMR spectra of the phenyltetralin lignans galbulin, galcatin, isogalcatin and cyclogalgravin have also been recorded and the signals assigned, based on the methyl shifts of cyclogalgravin.

INTRODUCTION

Continuing our investigations on the constituents of the knots of *Araucaria angustifolia* O. Ktze [1], we have now isolated pinoresinol **1a** and its monoMe ether **1c**, previously reported from the same source by Anderegg and Rowe [2]* and two new monophenolic lignans, secoisolariciresinol monoMe ether **2a** and lariciresinol-4-Me ether **3c**†. The determination of the position of the phenolic OH groups of **2a** and **3c**, deduced by comparison of their *O*-Me derivatives with known products and by application of spectroscopic techniques, together with some comments on the effects of acetylation on the ^{13}C NMR shifts of **1a** and **1c** and the ^{13}C NMR analysis of some phenyltetralin lignans, forms the basis of this report.

RESULTS AND DISCUSSION

MS fragmentation pattern, M^+, and ^1H NMR spectrum of **2a** indicate a secoisolariciresinol lignan-type skeleton. The base peak at *m/e* 151 and the peak at *m/e* 137, together with the OMe proton signals (δ 3.80 (6H) and 3.85 (3H)), suggested the presence of a dimethoxy group and a methoxyhydroxybenzyl group. On acetylation, **2a** yielded a triacetyl derivative **2b**, whose ^1H NMR signals confirm the above observations and further show, on the basis of the doublet at δ 6.87 (J = 7 Hz), that a guaiacyl unit is present in **2a**. Further confirmation of the structure of the secoisolariciresinol monoMe ether was obtained by analysis of its ^{13}C NMR spectrum. The carbon shifts of **2a**, its triacetyl derivative **2b**, the *O*-Me ether **2c** and its diacetyl derivative **2d** (Table 1) show the expected effects in comparison with the previously reported ones for secoisolariciresinol and its tetraacetate [1].

Table 1. ^{13}C NMR data for secoisolariciresinol monoMe ether and its derivatives*

Carbon	2a	2b†	2c	2d‡
1	133.0	131.9	132.9	131.9
2	111.0§	111.1§	111.0§	111.0§
3	148.6	148.7	148.7	148.7
4	147.0	147.3	147.0	147.2
5	112.0§	111.9§	112.0§	111.8§
6	120.8	120.9	120.8	120.7
7	35.8	34.9	35.7	34.8
8	43.8	39.7	43.8	39.6
9	60.4	64.2	60.3	64.2
1′	132.2	138.5	132.9	131.9
2′	111.4	112.8	111.0§	111.0§
3′	146.3	150.8	148.7	148.7
4′	143.6	138.0	147.0	147.2
5′	114.0	122.4	112.0§	111.8§
6′	121.4	120.9	120.8	120.7
7′	35.8	35.4	35.7	34.8
8′	43.8	39.7	43.8	39.6
9′	60.4	64.2	60.3	64.2
OMe	55.7	55.7; 55.8	55.7	55.7

* The spectra were obtained at 25.2 MHz in the Fourier transform mode in $CDCl_3$ solns. Chemical shifts are expressed on the TMS scale according to the following equation $\delta^{TMS} = \delta^{CDCl_3} + 76.9$ ppm.

† The acetyl CO and Me shifts are 170.7; 168.8; 21.0; 20.7 and 20.6 ppm, respectively.

‡ The acetyl CO and Me shifts are 170.6 and 20.9 ppm, respectively.

§ Signals may be reversed.

The second monophenolic compound, which yielded the diMe ether of lariciresinol by treatment with diazomethane, was analysed by ^{13}C NMR spectroscopy. We have previously shown that the shifts of C-4 and C-4′, carrying the phenolic OH groups in lariciresinol **3a**, or in its triacetate, are different [1], and by comparison of their δ values with related carbons of the monoMe ether now isolated, its diacetyl derivative, secoisolariciresinol monoMe ether triacetate **2b** and pinoresinol diacetate **1b**, it could be suggested that the OH or OAc groups are

* This reference, in which the isolation of **1a**, **1b**, pinoresinol diMe ether, hinokiresinol, isolariciresinol and secoisolariciresinol from the knots of *A. angustifolia* is described, was not cited in [1] since our main interest was the ^{13}C NMR spectral analysis of this group of natural products.

† The nomenclature and numbering are those used in our previous publication [1].

Table 2. ^{13}C NMR data for lariciresinol and its derivatives*

Carbon	3a†	3c	3d‡	3e	3f§	3g‖	3a¶
1	131.6	132.7	132.2	132.0	138.8	132.3	132.3
2	111.6	111.0	111.1	110.9	112.6	111.2	112.7
3	146.9	148.6	148.7	146.4	150.7	148.3	147.4
4	143.9	147.1	147.3	143.8	138.0	147.3	144.5
5	114.6**	111.8	111.6	114.2	122.6	111.8	114.9**
6	120.6	120.3	120.1	120.9	120.4	120.2	120.9
7	32.3	33.0	33.0	33.2	33.4	33.1	32.5
8	42.1	42.2	42.1	42.3	42.1	42.3	42.5
9	72.1	72.6	72.6	72.7	72.6	72.6	72.1
1′	133.7	134.5	141.3	135.2	134.6	134.7	135.1
2′	108.7	108.2	109.4	108.8	108.7	108.8	109.6
3′	146.9	146.4	150.7	148.8	148.8	148.8	147.4
4′	145.1	144.7	138.7	148.2	148.3	148.3	145.4
5′	114.4**	114.0	122.3	111.0	110.8	110.9	114.7**
6′	118.1	118.4	117.5	117.8	117.9	117.9	118.3
7′	82.3	82.6	82.7	82.6	82.8	82.9	82.3
8′	52.2	52.4	48.8	52.4	48.9	48.8	52.8
9′	59.1	60.5	62.5	60.8	62.5	62.6	59.2
OMe	55.1	55.7	55.7	55.8	55.8	55.8	55.2

* The spectra were obtained at 25.2 MHz in the Fourier transform mode in $CDCl_3$ solns. Chemical shifts are expressed on the TMS scale according to the following equation $\delta^{TMS} = \delta^{CDCl_3} + 76.9$ ppm.

† Taken from ref. [1].

‡ The acetyl CO and Me shifts are 170.5; 168.7; 20.7 and 20.5 ppm, respectively.

§ The acetyl CO and the Me shifts are 170.6; 168.8; 20.8 and 20.6 ppm, respectively.

‖ The acetyl CO and the Me shifts are 170.6 and 20.8 ppm, respectively.

¶ In d_6-Me_2CO–D_2O (9:1) soln. Chemical shifts are expressed on the TMS scale according to $\delta^{TMS} = \delta^{d_6\text{-}Me_2CO} + 29.2$ ppm.

** Signals may be reversed.

located at C-4′ and C-9′, as in **3c** and **3d**. Further confirmation of the position of the phenolic OH function in **3c** was obtained by preparation of the alternative structure **3e** by careful methylation of **3a**. The shifts showed by C-4 of **3e** and its diacetyl derivative **3f** are the expected ones, in agreement with the above results. The carbon shifts of compounds **3c–3f**, together with the shifts of the acetate of lariciresinol diMe ether **3g**, not previously reported, are listed in Table 2.

An analysis of the shifts of C-1 and C-1′ of lariciresinol **3a** and its derivatives—mainly the diacetates **3d** and **3f**—indicates that our previous assignments at 133.7 and 131.6 ppm, respectively [1], based on a comparison with the shifts of related carbons of the guaiacyl units of secoisolariciresinol and the neolignan licarin A, were not correct. As shown in Table 2, by reversal of these two assignments a more consistent set of shifts is obtained. Further support for the new assignment is obtained by comparison of C-1′ shift of **3a** (Table 2) with related carbons of the benzofurans **4a** (134.5 ppm) and **4b** (134.3 ppm) [3]. Although the stereochemistry of **4a** and **4b** is not indicated in reference [3], they probably represent better models than the previously selected one for C-1′.

That the phenolic OH in **3c** is located at C-4′ was confirmed by comparative ^1H NMR and MS analysis of **3c** and **3e**, and their corresponding diacetyl and *O*-Me derivatives **3d**, **3f** and **3g**, respectively. As was previously observed in sanshodiol **5** [4], acetylation of the OH at C-4′ induces small, but significant changes on the benzylic proton signal at C-7′ of **3c** (deshielding of *ca* 5 Hz and decrease of *J* value), while the comparable proton signal of **3e** is unaffected in the transformation (**3e** → **3f**).

In agreement with these results, the MS of the diacetate **3d** shows as its base peak the ion *m/e* 151, assigned by accurate mass measurements to the ions **6a** and **7a**, arising via benzylic (a) and path b cleavages, **8** [5], with ketene elimination, respectively. The benzylic cleavage of **3g** also gives rise to a base peak at *m/e* 151, as expected from the presence of a dimethoxybenzyl moiety, while in **3b** and **3f**, the same benzylic cleavage with loss of ketene produces base peaks at *m/e* 137, **6b**. Further, in **3f** and **3g** the fragment at *m/e* 165, **7b**, arising by path b is also detected.

The observed effects of acetylation on the ^1H NMR signal of the benzylic protons adjacent to the guaiacyl units of 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane lignans, such as pluviatilol and xanthoxylol [4, 6], prompted us to compare the ^{13}C NMR shifts of those carbons of pinoresinol **1a**, its monoMe ether **1c** and the acetyl derivatives **1b** and **1d**, hoping to detect features that could be used to supplement previous studies [6, 7] for the structure elucidation of other members of this group of natural products. However, as in the case of the monoMe ethers of lariciresinol **3c** and **3e**, acetylation of the phenolic OH produces the known effects on the aromatic carbons of **1a** and **1c**, while the benzylic ones are practically unaffected. The carbon shifts of compounds **1a–1d**, assigned on the basis of previous results [6, 7], on ^{13}C–^1H long-range couplings and on specific proton decoupling data, are listed in Table 3.

Following our ^{13}C NMR spectral studies on lignans [8], the analysis of the natural phenyltetralins with identical relative configurations at C-7, C-8 and C-8′, galbulin **9a**, galcatin **9b** and isogalcatin **9c** [9]*, together with cyclogalgravin **10**, easily obtained by acid treatment of tetrahydrofuran lignan galgravin [10], was carried out. Table 4 lists the carbon shifts of compounds **9a**, **9b** and **9c**, assigned on the basis of their multiplicity in the

* The designation 8.8′, 7.2′-neolignan has also been suggested for the members of this group of natural products.

Table 3. ^{13}C NMR data for pinoresinol and its derivatives*

Carbon	1a	1b†	1c	1d‡
1′	132.0	139.8	132.6	140.0
2′	108.8	109.6	108.4	109.7
3′	146.8	150.9	146.5	151.0
4′	145.2	138.9	145.0	138.9
5′	114.4	122.5	114.1	122.5
6′	118.5	117.7	118.7	117.7
1	53.7	54.2	54.0	54.3
2	85.7	85.3	85.6	85.4
4	71.3	71.8	71.5	71.7
5	53.7	54.2	54.0	54.0
6	85.7	85.3	85.6	85.6
8	71.3	71.8	71.5	71.7
1″	132.0	139.8	133.3	133.2
2″	108.8	109.6	109.0	109.1
3″	146.8	150.9	148.9	149.0
4″	145.2	138.9	148.4	148.4
5″	114.4	122.5	110.8	110.9
6″	118.5	117.7	118.0	118.1
OMe	55.6	55.8	55.8	55.8

* The spectra were obtained at 25.2 MHz in the Fourier transform mode in $CDCl_3$ solns. Chemical shifts are expressed on TMS scale according to the following equation $\delta^{TMS} = \delta^{CDCl_3} + 76.9$ ppm.

† The acetyl CO and Me shifts are 168.8 and 20.5 ppm, respectively.

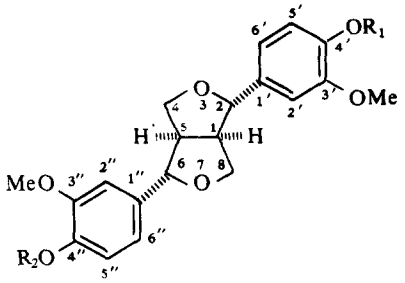
‡ The acetyl CO and Me shifts are 168.8 and 20.5 ppm, respectively.

Table 4. ^{13}C NMR data for compounds **9a–9c** and **10***

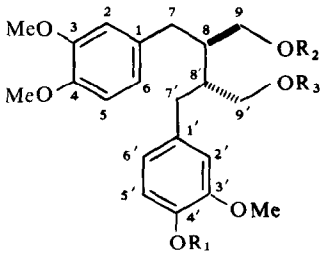
Carbon	9a	9b	9c	10
1	138.9	138.9	140.4	138.5
2	110.5	110.7	107.5	108.8
3	146.7	147.3	145.6	147.1
4	146.7	147.3	145.6	147.1
5	112.0	112.0	109.1	110.8
6	121.8	121.6	122.6	119.4
7	54.3	54.1	54.2	50.8
8	43.8	43.6	44.0	41.9
9	17.2	16.9	17.1	18.6
1′	128.9	129.8	129.0	126.9†
2′	112.7	109.4	112.7	112.7
3′	148.7	144.3	147.5	148.4
4′	148.1	144.3	147.3	147.3
5′	110.5	107.5	110.5	110.8
6′	132.3	133.4	132.1	127.1†
7′	39.0	39.4	39.0	120.9
8′	35.6	35.5	35.4	137.9
9′	20.0	20.3	20.0	22.1
OMe	55.8; 54.3	55.8; 54.5	55.8; 54.2	55.7
$-OCH_2O-$		100.3	100.7	

* The spectra were obtained at 25.2 MHz in the Fourier transform mode in $CDCl_3$ solns. Chemical shifts are expressed on the TMS scale according to the following equation $\delta^{TMS} = \delta^{CDCl_3} + 76.9$ ppm.

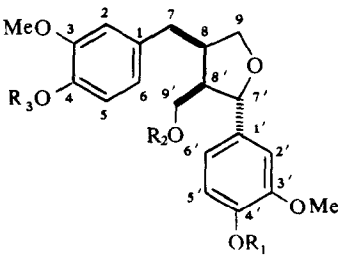
† Signals may be reversed.



1a $R_1 = R_2 = H$
1b $R_1 = R_2 = -OC-Me$
1c $R_1 = H$; $R_2 = Me$
1d $R_1 = -OC-Me$; $R_2 = Me$

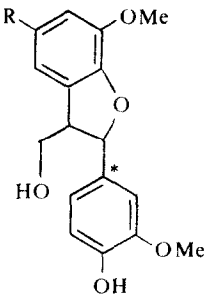


2a $R_1 = R_2 = R_3 = H$
2b $R_1 = R_2 = R_3 = -OC-Me$
2c $R_1 = Me$; $R_2 = R_3 = H$
2d $R_1 = Me$; $R_2 = R_3 = -OC-Me$

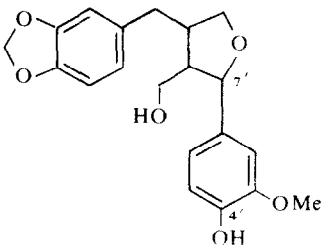


3a $R_1 = R_2 = R_3 = H$
3b $R_1 = R_2 = R_3 = -OC-Me$
3c $R_1 = R_2 = H$; $R_3 = Me$
3d $R_1 = R_2 = -OC-Me$; $R_3 = Me$
3e $R_2 = R_3 = H$; $R_1 = Me$
3f $R_2 = R_3 = -OC-Me$; $R_1 = Me$
3g $R_1 = R_3 = Me$; $R_2 = -OC-Me$

single-frequency off-resonance decoupled (sford) spectra, on the δ values recorded for isolariciresinol diMe ether **11** [1], on the effects produced by the replacement of two OMe groups of an aromatic system by a $-OCH_2O-$ moiety and on comparison of the signals of the 3 compounds with each other. As expected, and according to the known effects of an OH group on the α, β and γ carbons, C-9, C-9′, C-8 and C-8′ are shielded while C-7 and C-7′ are deshielded in **9a**, **9b** and **9c** in comparison to related sites of **11**. The replacement of the 3′,4′-dimethoxy groups of **9a** and **9c** by the methylenedioxy unit of **9b**, produces the expected changes on the ring A carbon shifts, i.e. shielding of C-3′, C-4′, C-2′ and C-5′ and deshielding of C-1′ and C-6′ by magnitudes similar to those previously observed [11]. A comparison of the essentially identical ring C shifts of **9a** and **9b** with the corresponding ones of



4a R = $-CH_2-CH_2-CH_2OH$
4b R = $-CH=CH-CH_2OH$



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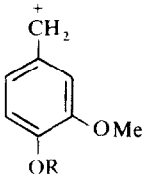
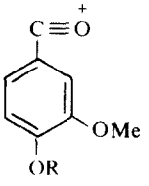
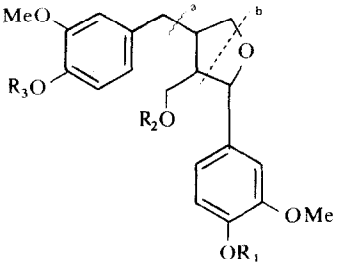


6a R = Me
6b R = H



7a R = H
7b R = Me



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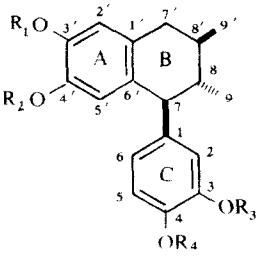
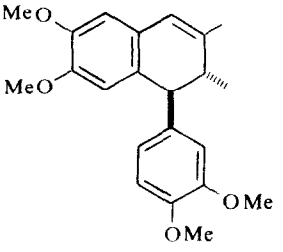


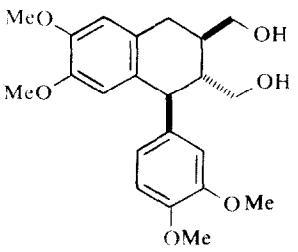
9a $R_1 = R_2 = R_3 = R_4 = Me$
9b $R_1 + R_2 = CH_2$; $R_3 = R_4 = Me$
9c $R_1 = R_2 = Me$; $R_3 + R_4 = CH_2$

the piperonyl unit of **9c** shows again the expected changes, shielding of C-3, C-4, C-2 and C-5 and deshielding of C-1 and C-6, allowing the assignment of most of the aromatic shifts of **9a**, **9b** and **9c**. Comparison of the aromatic shifts of **9a** with those found for isolariciresinol diMe ether **11** shows significant differences for the shifts at 131.7 and 137.6 ppm assigned to C-1 and C-6′, respectively [1]. It then seems reasonable, on the basis of the present results, to reverse the previous assignment.

The carbon shifts of cyclogalgravin **10**, based on a comparison with those of **9a**, on the analysis of the sford spectrum and on the effects produced by the introduction of a double bond on the endocyclic homoallylic positions [12], are listed in Table 4. Distinction of some close resonances like those of C-6 and C-7′, and C-1 and C-8′ was made by specific proton decoupling and ^{13}C–^{1}H long-range couplings, while the signals at 126.9 and 127.1 ppm remain for C-1′ and C-6′ or vice versa. The analysis of the Me shifts, compared with those of **9a**, **9b** and **9c**, reveals some information about the conformation of **10**. Galbulin, **9a**, and its relatives **9b** and **9c**, possess the same relative configuration of the substituents on ring B and it would be expected to prefer a half-chair conformation with the phenyl and both methyls at pseudoequatorial positions, as was shown by ^{1}H NMR spectroscopy [13]. On the assumption that a neighbouring double bond does not affect the chemical shift of a Me group [14], it could be expected that the flattening of ring B, because of the introduction of the double bond between C-7′ and C-8′ in **10**, will induce a shielding effect on the Me groups as a consequence of the decrease in the dihedral angle between them. In cyclogalgravin **10**, however, the Me groups are deshielded compared with those of **9a**, **9b** and **9c**, indicating a preferred conformation previously suggested for 1,2-dihydronaphthalenes by ^{1}H NMR spectroscopy [15], in which C-9 and ring C are at



10



11

pseudoaxial positions. In agreement with these observations, in the ^{1}H NMR spectrum of **10**, the signal at δ 3.67, assigned to the methine at C-7, appears as a doublet with a J value of 4 Hz, compatible with a dihedral angle of *ca* 70° between the methines at C-7 and C-8.

EXPERIMENTAL

The remaining fractions of the chromatography on a Si gel column of the C_6H_6 extract of *Araucaria angustifolia* knots [1] were purified on Si gel H (Merck) columns, eluted with $CHCl_3$ containing 1–10% MeOH, furnishing pinoresinol (**1a**), its monoMe ether (**1b**), secoisolariciresinol monoMe ether (**2c**) and lariciresinol-4-methyl ether (**3c**), the monoMe ethers being eluted before their respective diphenols. The acetates and Me ethers were prepared by standard methods, except for compound **3e**. The MS of secoisolariciresinol and lariciresinol derivatives were obtained by direct inlet using similar conditions (140°, 20 eV and 140°, 70 eV, respectively).

Pinoresinol, **1a**, 0.56 g, mp 118–120°, $[\alpha]_D^{25}$ +64° (*c* 1.0, $CHCl_3$), M^+ 358. Pinoresinol diacetate, **1b**, mp 162–164°, $[\alpha]_D^{25}$ +48° (*c* 1.0, $CHCl_3$), M^+ 442.

Pinoresinol monoMe ether, **1c**, 0.24 g, viscous oil, $[\alpha]_D^{25}$ +56° (*c* 1.0, $CHCl_3$), M^+ 372. Pinoresinol monoMe ether acetate, **1d**, mp 122–124° (from Et_2O–Me_2CO), $[\alpha]_D^{25}$ +52° (*c* 1.0, $CHCl_3$), M^+ 414; ^{1}H NMR ($CDCl_3$): δ 2.3 (3H, *s*, OC-Me), 3–3.25 (2H, *m*, C-1 and C-5), 3.85 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 3.9 (3H, *s*, OMe), 4 (2H, *d*, J = 4 Hz, C-4 and C-8), 4.15–4.45 (2H, *m*, C-4 and C-8), 4.75 (1H, *bd*, J ~ 4 Hz, C-6), 4.85 (1H, *bd*, J ~ 3.5 Hz, C-2), 6.75–7.15 (6H, *m*, aromatic protons).

Secoisolariciresinol monoMe ether, **2a**, 0.235 g, viscous oil, $[\alpha]_D^{25}$ −34° (*c* 1.0, $CHCl_3$), MS (high resolution) found: 376.1808, calc. for $C_{21}H_{28}O_6$: 376.1886; MS *m/e* (rel. int.): 376 [M^+] (5), 189 (5), 177 (6), 151 (100), 137 (60); ^{1}H NMR ($CDCl_3$): δ 1.7–2.15 (2H, *m*, C-8 and C-8′), 2.75 (4H, *br d*, C-7 and C-7′), 3.55–3.75 (*m*, C-9 and C-9′), 3.8 (6H, *s*, 2 × OMe), 3.85 (3H, *s*, OMe), 6.5–6.9 (6H, *m*, aromatic protons).

Secoisolariciresinol monoMe ether triacetate, **2b**, viscous oil, $[\alpha]_D^{25}$ −35° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 502 [M^+] (20), 460 (20), 203 (15), 189 (15), 177 (8), 151 (100), 137 (50); ^{1}H NMR ($CDCl_3$): δ 1.7–2.15 (*m*, C-8 and C-8′), 2.05 (6H, *s*, 2 × OC-Me), 2.3 (3H, *s*, OC-Me), 2.7 (4H, *br d*, C-7 and C-7′), 3.75 (3H, *s*, OMe), 3.8 (3H, *s*, OMe), 3.83 (3H, *s*, OMe), 4.07 (2H, *d*, J ~ 4 Hz, C-9 or C-9′), 4.17 (2H, *d*, J ~ 4 Hz, C-9′ or C-9), 6.4–6.7 (*m*, aromatic protons), 6.87 (1H, *d*, J ~ 8 Hz, C-5′).

Secoisolariciresinol diMe ether, **2c**, mp 121–123°, $[\alpha]_D^{25}$ −33° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 390 [M^+] (36), 372 (7), 221 (9), 203 (34), 177 (33), 151 (100); ^{1}H NMR ($CDCl_3$): δ 1.7–2.15 (2H, *m*, C-8, C-8′), 2.75 (4H, *br d*, C-7 and C-7′), 3.5 (2H, *br d*, C-9 or C-9′), 3.7 (2H, *br d*, C-9′ or C-9), 3.8 (6H, *s*, 2 × OMe), 3.83 (6H, *s*, 2 × OMe), 6.6–6.9 (6H, *m*, aromatic protons). This compound prepared from secoisolariciresinol was identical in all respects to the diMe ether obtained from **2a**.

Secoisolariciresinol diMe ether diacetate, **2d**, viscous oil, $[\alpha]_{max}^{25}$ −28° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 474 [M^+] (20), 203 (15), 177 (10), 151 (100); ^{1}H NMR ($CDCl_3$): δ 1.9–2.15 (*m*, C-8 and C-8′), 2.07 (6H, *s*, 2 × OC-Me), 2.67 (4H, *br d*, C-7 and C-7′), 3.8 (6H, *s*, 2 × OMe), 3.83 (6H, *s*, 2 × OMe), 4.1 (2H, *d*, J ~ 4 Hz, C-9 or C-9′), 4.16 (2H, *d*, J ~ 4 Hz, C-9′ or C-9), 6.4–6.8 (6H, *m*, aromatic protons).

Lariciresinol-4-monoMe ether, **3c**, 0.495, viscous oil, $[\alpha]_D^{25}$ +10° (*c* 1.0, $CHCl_3$); MS (high resolution) found: 374.1706, calc. for $C_{21}H_{26}O_6$: 374.1729; ^{1}H NMR ($CDCl_3$): δ 2.3–3 (4H, *m*, C-7, C-8 and C-8′), 3.7–4.1 (*ca* 4H, *m*, C-9 and C-9′), 3.87 (9H, *s*, 3 × OMe), 4.8 (1H, *d*, J = 6 Hz, C-7′), 6.7–6.95 (6H, *m*, aromatic protons).

Lariciresinol-4-monoMe ether diacetate, **3d**, viscous oil, $[\alpha]_D^{25}$ +5° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 458 [M^+] (45), 416 (32), 356 (10), 339 (28), 219 (14), 205 (27), 178 (18), 164 (8), 151 (100), 137 (21); ^{1}H NMR ($CDCl_3$): δ 2.03 (3H, *s*, OC-Me), 2.3 (3H, *s*, OC-Me), 2.4–2.8 (4H, *m*, C-7, C-8 and C-8′), 3.5–4.1 (*ca* 2H, *m*, C-9), 3.83 (3H, *s*, OMe), 3.88 (6H, *s*, 2 × OMe), 4.1–4.4 (2H, *m*, C-9′), 4.9 (1H, *d*, J = 5 Hz, C-7′), 6.65–6.95 (6H, *m*, aromatic protons). MS (high resolution) ion **6a**, found: 151.0749, calc. for $C_9H_{11}O_2$: 151.0759; ion **7a**, found: 151.0390, calc. for $C_8H_7O_3$: 151.0395.

Lariciresinol-4′-monoMe ether, **3e**. Lariciresinol, **3a** (0.3 g) in MeOH was treated with CH_2N_2–Et_2O, at 10°. When the dimethylated product was detected on TLC, excess reagent was evaporated and the residue chromatographed on a Si gel H (Merck) column. Elution with $CHCl_3$ containing 1% MeOH yielded the following compounds: **3h** (35 mg), **3e** (75 mg), a mixture of **3c** and **3e** (132 mg) and **3a** (48 mg).

Lariciresinol-4′-monoMe ether, a viscous oil, showed $[\alpha]_D^{25}$ +8° (*c* 1.0, $CHCl_3$); MS (high resolution) found: 374.1747, calc. for $C_{21}H_{26}O_6$: 374.1729; ^{1}H NMR ($CDCl_3$): δ 2.4–2.9 (4H, *m*, C-7, C-8 and C-8′), 3.65–4.1 (*ca* 4H, *m*, C-9 and C-9′), 3.83 (9H, *s*, 3 × OMe), 4.81 (1H, *d*, J = 6 Hz, C-7′), 6.65–6.95 (6H, *m*, aromatic protons). The diMe ethers obtained from **3c** and **3e** were identical to each other and identical in all respects to the diMe ether prepared from lariciresinol.

Lariciresinol-4′-monoMe ether diacetate, **3f**, viscous oil, $[\alpha]_D^{25}$ +5° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 458 [M^+] (60), 416 (20), 356 (22), 233 (20), 219 (48), 205 (12), 192 (28), 190 (20), 166 (29), 165 (80), 164 (10), 151 (58), 137 (100); ^{1}H NMR ($CDCl_3$): δ 2.03 (3H, *s*, OC-Me), 2.3 (3H, *s*, OC-Me), 2.4–2.9 (4H, *m*, C-7, C-8 and C-8′), 3.5–4.1 (*ca* 2H, *m*, C-9), 3.83, 3.87, 3.88 (9H, all *s*, 3 × OMe), 4.1–4.4 (2H, *m*, C-9′), 4.8 (1H, *d*, J = 6 Hz, C-7′), 6.6–7 (6H, *m*, aromatic protons).

Lariciresinol diMe ether acetate, **3g**, viscous oil, $[\alpha]_D^{25}$ +16° (*c* 1.0, $CHCl_3$); MS *m/e* (rel. int.): 430 [M^+] (90), 339 (12), 233 (18), 219 (23), 205 (11), 189 (13), 178 (12), 166 (14), 165 (50), 151 (100), 137 (8); ^{1}H NMR ($CDCl_3$): δ 2 (3H, *s*, OC-Me), 2.4–2.8 (4H, *m*, C-7, C-8, C-8′), 3.5–4.1 (*ca* 2H, *m*, C-9), 3.87 (12H, *s*, 4 × OMe), 4.1–4.4 (*ca* 2H, *m*, C-9′), 4.8 (1H, *d*, J = 6 Hz, C-7′), 6.65–6.9 (6H, *m*, aromatic protons).

Lariciresinol triacetate, **3b**; MS *m/e* (rel. int.): 486 [M^+] (28), 444 (20), 402 (23), 384 (31), 367 (32), 342 (33), 325 (21), 219 (27), 205 (43), 190 (20), 164 (14), 151 (40), 137 (100) [1].

Ciclogalgravin, **10**, mp 89–90°, MS *m/e* M^+ 354, ^{1}H NMR ($CDCl_3$): δ 1.1 (3H, *d*, J = 8 Hz, C-9), 1.8 (3H, *d*, J = 1.5 Hz, C-9′), 2.15–2.65 (1H, *m*, C-8), 3.67 (*ca* 1H, *d*, J = 4 Hz), 3.77 (6H, *s*, 2 × OMe), 3.8 (3H, *s*, OMe), 3.87 (3H, *s*, OMe), 6.13 (1H, *bd*, J ~ 1.5 Hz), 6.5–6.85 (6H, *m*, aromatic protons).

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