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HEARTWOOD CONSTITUENTS OF *BETULA MAXIMOWICZIANA*

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Key Word Index—*Betula maximowicziana*; Betulaceae; heartwood; diarylheptanoids; lignans; X-ray analysis; stereochemistry.

Abstract—In addition to two lignans, (−)-(7*R*, 8*S*, 8′*S*)-lyoniresiol (**3**) and (−)-(7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol (**4**) in their racemic forms, respectively, a biphenyl-type diarylheptanoid (−)-(a‡*S*, 3″*S*, 5″*S*)-alnusdiol (**1**) and a diphenyl ether type diarylheptanoid [(−)-*rel*-(p§*R*, 3*S*, 5*S*)-3′,4″-epoxy-1-(4-hydroxyphenyl)-7-phenylheptane-3,5-diol] named as (−)-*rel*-(p*R*, 3*S*, 5*S*)-maximowicziol A (**2**) were isolated from the heartwood of *Betula maximowicziana*. The absolute configuration of **1** and the relative configuration of **2** are presented on the basis of X-ray and CD analyses for the first time. ©1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Most trees accumulate higher amounts of secondary metabolites in heartwood than in sapwood. These metabolites, which often show antifungal activity, are thought to be produced during heartwood formation [1]. Regarding the chemical constituents of the heartwood of the plants in the genus *Betula*, there is only one report about lupane-type triterpenoids from *B. papyrifera* [2]. For *B. maximowicziana*, there are no reports on the chemical constituents of its heartwood, although the lupane-type triterpenoids, for example betulin and lupeol, have been isolated from the outer bark [3]. Because of the reasons described above, we were interested in the chemical constituents of the heartwood of *B. maximowicziana*. As for the other parts of plants in this genus, triterpenoids [4–8], which are usually major constituents, diarylheptanoids [6–11], lignans [6, 7, 12] and flavonids [6, 7, 11] have been reported. Very recently, an intensive investigation on the chemical constituents in the leaves and bark of *B. maximowicziana* has been carried out, and alnusdiol glucoside and lyoniresinol rhamnoside are reported with triterpenoids and several diarylheptanoids [13].

Herein, we report the isolation and structural determination of the diarylheptanoids (**1** and **2**) and lignans (**3** and **4**) from the heartwood of *B. maximowicziana*. The absolute configuration of **1** and the relative configuration of **2** are also presented based on X-ray and CD spectral analyses.

RESULTS AND DISCUSSION

Compound **1** was obtained as pale brown prisms. The molecular formula $C_{19}H_{22}O_4$ was determined by HR EI mass spectrometry ($[M]^+$ *m/z* 314.1540, requires 314.1518). The ^{13}C NMR spectrum showed only 10 carbon signals (Table 1), which were assigned by DEPT to three aromatic methines, three aromatic quaternary carbons, three methylene carbons and an oxygenated methine carbon, suggesting a symmetrical structure for **1**. The fragment ion *m/z* 211 in the mass spectrum suggested that **1** is a biphenyl-type diarylheptanoid, which has two hydroxyl groups on the biphenyl ring [14]. The partial structure was determined (Fig. 1) by ^1H NMR, ^{13}C NMR, COSY and DEPT experiments. Assignments of the chemical shifts for protonated carbons were carried out on the basis of C-H correlations found in HSQC and C-H long-range correlations found in HMBC. Diagnostically important C-H long-range correlations are shown in Fig. 1. These data suggested a planar structure for **1** similar to alnusdiol, which was previously isolated from *Alnus japonica* [15, 16] and *Casuarina junghuhniana* [17]. Alnusdiol has two chiral carbons at C-3″ and C-5″, in the numbering system employed in this report, and a chiral axis at the biphenyl bond. To determine the absolute structure of **1**, X-ray crys-

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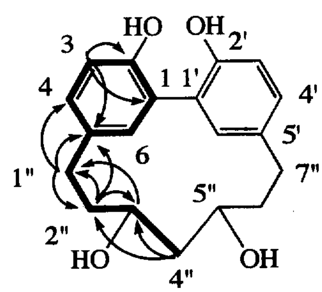
‡ Axial chirality; § planar chirality.

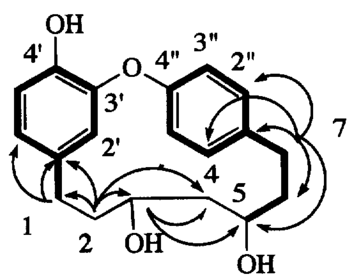
Table 1. ^{13}C NMR spectra data of compounds 1–4 and comparison of ^{13}C NMR assignments of 4 with previously reported compounds (δ in CD_3OD)

C	1	C	2	C	3	4	4*a	4*b
1	127.2	1	28.8	1	139.3	134.8	132.5	134.0
2	152.3	2	37.2	2	106.8	110.5	109.8	110.9
3	117.0	3	69.0	3	148.9	149.1	148.3	148.2
4	130.5	4	48.9	4	134.5	147.5	146.9	148.2
5	132.0	5	66.8	5	148.9	116.1	115.5	116.5
6	135.0	6	42.4	6	106.8	119.7	119.4	119.8
		7	32.2	7	42.3	89.0	87.0	88.4
1′				8	49.0	55.4	55.9	55.1
2′		1′	144.6	9	64.1	65.0	68.2	64.5
3′		2′	115.8					
4′		3′	151.6	1′	130.1	136.9	128.9‡	130.6‡
5′		4′	134.8	2′	107.7	115.8†	114.6	113.8
6′		5′	123.1	3′	148.6	145.2	143.8	144.7
		6′	116.9	4′	138.8	147.5	145.1	147.4
1″	27.5			5′	147.7	129.9	137.9‡	136.2‡
2″	35.8	1″	141.6	6′	126.2	117.9†	114.8	117.6
3″	67.3	2″	132.5 or 131.6	7′	33.6	32.9	34.9‡	32.7
4″	51.8	3″	125.7 or 123.8	8′	40.8	35.8	30.9‡	36.0
5″		4″	157.3	9′	66.7	62.2	68.2	61.5
6″		5″	123.8 or 125.7					
7″		6″	131.6 or 132.5	OMe	56.7 (C3, C5)	56.4 (C3)	55.9	56.3
				OMe	56.6 (C3′)	56.7 (C3′)	55.9	55.9
				OMe	60.1 (C5′)			

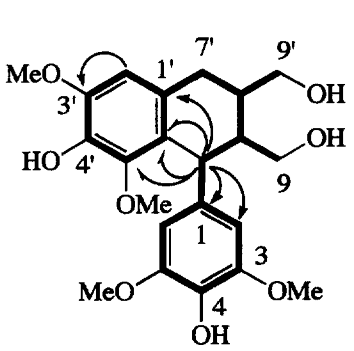
*a Agrawal et al. [24] in $CDCl_3$. *b Miyase et al. [25] in pyridine-d_5.
† Interchangeable.
‡ Data should be corrected.



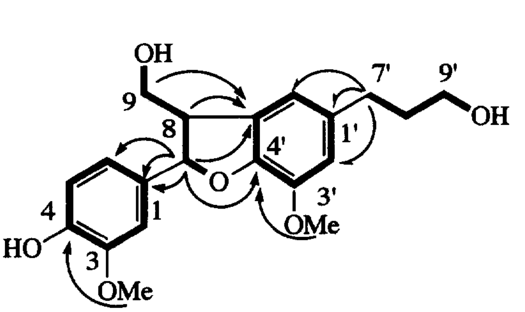
alnusdiol (1)



maximowicziol A (2)

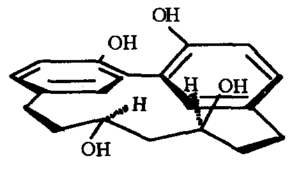


lyoniresinol (3)

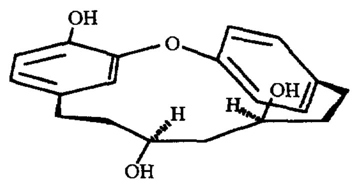


dihydrodehydrodiconiferyl-alcohol (4)

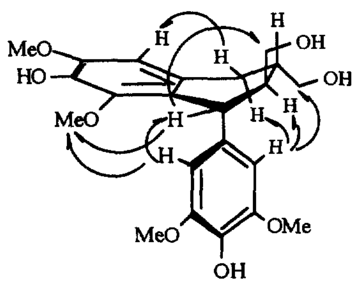
Fig. 1. Planar structures of isolated compounds. Thick lines show partial structures obtained from ^{1}H NMR, ^{13}C NMR, DEPT, COSY and HSQC experiments. Arrows show the diagnostically significant C-H correlation found by HMBC.



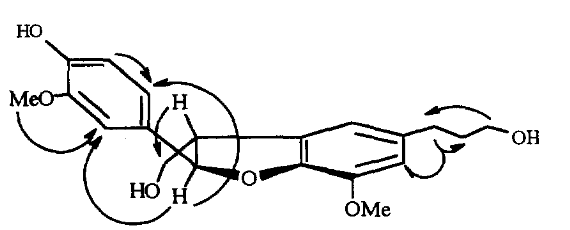
(-)-(a*S*, 3"*S*, 5"*S*)-alnusdiol (1)



(-)-*rel*-(p*R*, 3*S*, 5*S*)-maximowicziol A (2)



(-)-(7*R*, 8*S*, 8'*S*)-lyoniresinol (3)



(-)-(7*R*, 8*S*)-dihydrodehydrodiconiferyl alcohol (4)

Fig. 2. Absolute and relative configurations of isolated compounds. Arrows show diagnostically significant NOEs used to determine conformations.

tallographic analysis was carried out and the relative structure determined as *rel*-(a*S*, 3″*S*, 5″*S*). The dihedral angle between C-1/C-2 and C-1′/C-2′ was 45.3° and that between C-1/C-6 and C-1′/C-6′ was 32.9°. This means that the bond between the two phenyl groups is not extended on the line between the phenyl groups. In addition, the two phenyl rings are distorted and the carbons which comprise the rings are not in a perfect plane. Begley *et al.* [14] reported the absolute configuration of biphenyl-type diarylheptanoids 11*R*-myricanol in their numbering based on an X-ray analysis of a bromo-derivative. Even though they did not mention the chiral configuration at the biphenyl axis, it was apparent that bromomyricanol has a *S* configuration at the axis on the X-ray structure they showed. Since compound **1** showed almost an identical negative Cotton effect at 239 and 296 nm and a shoulder at 254 nm in CD as myricanol, the absolute configuration of **1** at the axis was determined as a *S*. As a result, the absolute configuration of **1** was determined as *S*, 3″*S*, 5″*S* (Fig. 2), for the first time. Alnusdiols isolated from *A. japonica* [16] and *C. junghuhniana* [17] seemed to have the same absolute configuration as **1**, because their optical rotatory activities were identical to that of **1**.

Compound **2** was obtained as clear needles. The molecular formula $C_{19}H_{22}O_4$ was determined by HREI mass spectrometry for ($[M]^+$ m/z 314.1528, requires 314.1518). The ^{13}C NMR spectrum showed 19 carbon signals (Table 1) which were assigned by DEPT to seven aromatic methines, five aromatic quaternary carbons, five methylene carbons and two oxygenated methine carbons. This suggested that compound **2** is an isomer of **1**. Connectivities of carbons (Fig. 1) were obtained by ^1H NMR, ^{13}C NMR, COSY, DEPT and HSQC spectra. Chemical shifts of the aliphatic protons in the heptane structure (1.4 ppm–3.0 ppm) were assigned on the basis of an HSQC experiment and the planar structure determined as **2** by correlations found in the HMBC spectrum. The relative configuration was determined on the basis of X-ray crystallographic analysis as *rel*-(p*R*, 3*S*, 5*S*) (Fig. 2). Six carbon signals of a *para*-substituted phenyl ring were detected separately by ^{13}C NMR. In addition, H-3″ and H-5″, which are at an *ortho*-position on the phenyl ring were also detected separately. The assignments of the two protons were δ 7.04 ppm (*dd* $J = 7.9$, 1.7 Hz, H-3″ or H-5″) and 7.02 ppm (*dd* $J = 7.9$, 1.7 Hz, H-5″ or H-3″), although it was not possible to assign the two chemical shifts completely. Compound **2** is an ansa compound and has a chiral plane, but the configuration of the plane was not determined by the data obtained. The $[\alpha]_D^{23}$ of compound **2** was $-86.3°$. Compound **2** is reported for the first time and named, (−)-*rel*-(p*R*, 3*S*, 5*S*)-maximowicziol A.

The names of compounds **1** and **2** in the CAS system are (−)-(aS, 9S, 11S)-tricylo[12.3.1.12,^{6}]nonadeca-1(18),2,4,6(19),14,16-hexaene-3,9,11,17-tetrol and (−)-*rel*-(pR, 10S, 12S)-2-oxatricyclo[13.2.2.13,^{7}]eicosa-3,5,7,(20),15,17,18-hexaene-4,10,12-triol, respectively. However, because these names do not properly describe the chemical nature of diarylheptanoids and there was no unique numbering system applied to the biphenyl-type and diphenyl ether-type diarylheptanoids, here we propose the names, (−)-(aS, 3″S, 5″S)-5,5′-heptanobiphenyl-2,2′,3″,5″-tetrol for compound **1** and (−)-*rel*-(pR, 3S, 5S)-3′,4″-epoxy-1-(4-hydroxyphenyl)-7-phenylheptane-3,5-diol for compound **2**, with the numbering system used in this report. The numbering system applied to diphenyl ether-type compound **2** is also widely used in acyclic diarylheptanoids. Fuchino *et al.* reported a diphenyl ether-type diarylheptanoid, named (3R)-3,5′-dihydroxy-4′-methoxy-3′4″-oxo-1,7-diphenyl-1-hepten [7]. However, since the name oxo should be used for aldehyde or ketone and not for ether, we propose to use epoxy which can be used to describe the ether bond in diphenyl ether-type diarylheptanoids.

Compound **3** was obtained as clear needles and its M_r 420 was determined by EI mass spectrometry. The planar structure **3** was determined as lyoniresinol by ^{1}H NMR, COSY, DEPT, HSQC and HMBC spectra. Since the NOEs shown in Fig. 2 were observed in an NOESY experiment, the relative configuration at C-7, C-8 and C-8′ were decided as *rel*-(7R, 8S, 8′S). Since, compound **3** exhibited the opposite and smaller optical rotatory activity ($[\alpha]_D = -3.6°$) compared with (7S, 8R, 8′R)-lyoniresinol ($[\alpha]_D = +58°$) isolated from *Cinnamomum cassia* [18], it is suggested that compound **3** was a racemic mixture of (7R, 8S, 8′S)-lyoniresinol and (7S, 8R, 8′R)-lyoniresinol; the former enantiomer was dominant. Because, compound **3** showed the opposite CD spectra to that of the (7S, 8R, 8′R)-isomer dominant racemic lyoniresinol [19] ($[\alpha]_D = +13.3°$, CD = $[\theta]_{285}$ −396, $[\theta]_{244}$ 6732), this assignment was also sustained.

Compound **4** was obtained as oil and its M_r 360 deduced by EI mass spectrometry. From ^{1}H NMR, COSY, DEPT, HSQC and HMBC experiments, the planar structure was determined as dihydrodehydrodiconiferyl alcohol (**4**). Since the coupling constant between H7 and H8 was 6.1 Hz, the relative configuration at C-7, C-8 was decided as *trans* [20]; the NOEs shown in Fig. 2 also supported this conformation. In addition, **4** exhibited an identical CD spectrum at 294, 242 and 224 nm with (7R, 8S)-4-O-methyldihydrodehydrodiconiferyl alcohol [21]; thus, the absolute configuration of **4** was determined as 7R, 8S. Because two peaks were found at R_t 15.4 and 17.3 min by chiral column chromatography (column; TSK-gel enantio-OVM 4.6 × 150 nm, solvent; isopropyl alcohol, flow rate; 1 ml min^{-1}, detection; UV 254 nm), compound **4** was also a racemic mixture and the stereoisomer mentioned above was dominant. Previously reported assignments of the ^{13}C NMR data of **4** were corrected as shown in Table 1.

EXPERIMENTAL

General. Mps: uncorr. Analytical TLC Merck precoated silica gel 60 plates (F254). Solvents used for TLC and CC are abbreviated as follows. Hexane (H), $CHCl_3$ (C), toluene (T), Me_2CO (A), MeOH (M). The main developing solvent system was TAM (toluene–Me_2CO–MeOH, 10:2:1). Compounds on TLC plates were detected under UV light (365 and 254 nm) and by colours produced using the vanillin–H_2SO_4 test. EIMS: direct inlet, 70 eV. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were determined using TMS as int. standard.

Extraction and isolation. Heartwood was obtained from *B. maximowicziana* which was cut in 1963 in Hokkaido, Japan. After removing the old layer of the cut surface, heartwood was chipped, then milled into powder in 1995. The MeOH extract (21.9 g) from the heartwood powder (796.2 g) was extracted successively with $CHCl_3$, EtOAc and MeOH. The wts of each fr. were 10.0, 5.1 and 6.1 g, respectively, and 0.7 g of residue remained. Hexane-sol. substances (1.2 g) were removed from the $CHCl_3$-sol. fr., then among the resultant 8.8 g of $CHCl_3$-sol. fr., 5 g was fractionated into 30 frs by CC on 150 g of silica gel; fr.1 (CM = 20:1, 300 ml), frs 2–24 (CM = 2:1, each 100 ml), and frs 25–30 (CM = 20:5, each 100 ml).

Compound **1** in fr 19 which exhibited a blue colour with vanillin–H_2SO_4 reagent on TLC (R_f 0.27, TAM 10:2:1) was recrystallized from MeOH and 29.6 mg of brown crystals was obtained.

Frs 10–16 were combined after removing white sediments which appeared in frs 11–13 and renamed as frs 10/16. Removing the gelatin-like substance (135.6 mg) obtained in the combined fr. afforded 509.1 mg of substance, which was fractionated into 40 frs on 10 g of silica gel. Frs 10/16-1–10/16-18 (TCA 2:3:2, each 10 ml), frs 10/16-19–frs 10/16-40 (TCAM 4:6:4:1, each 10 ml). Compound **3** (31.1 mg) in frs 10/16-8–10/16-20, which gave a blue colour with vanillin–H_2SO_4 acid reagent (R_f 0.40, TCAM 2:3:2:1), was recrystallized from MeOH containing a small amount of $CHCl_3$.

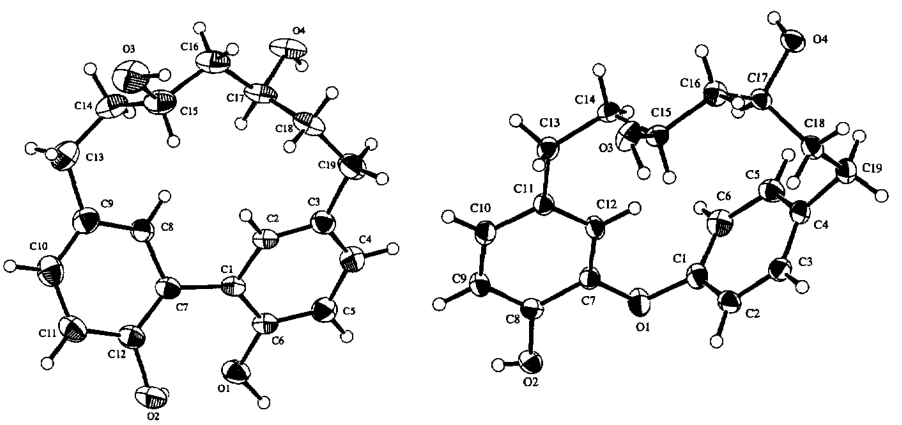
Frs 8 and 9 were combined (fr 8/9, 860 mg) and fractionated into 41 CC frs on 20 g of silica gel. Frs 8/9-1–8/9-23 (TAM 20:2:1, each 13 ml) and frs 8/9-24–8/9-41 (TAM 20:2:5, each 13 ml). A spot which showed at first orange and then grey-blue with vanillin–H_2SO_4 reagent was detected in frs 8/9-16–8/9-21 on TLC (R_f 0.40, TAM 10:2:1). The compound corresponding with this spot was purified by CC on 10 g of silica gel (TA 10:2) twice, and 9.7 mg of compound **4** (oil) was obtained.

Fr 7 (494.8 mg) was fractionated by CC into 24 frs (frs 7-1–7-24) on 10 g of silica gel (TAM 10:2:1, each 10 ml). Clear crystals of compound **2** (23.8 mg) were obtained from fr. 7-7. The compound exhibited a pink colour at first then grey-black purple with vanillin–H_2SO_4 reagent (R_f 0.41, TAM 10:2:2).

X-Ray analysis. Crystallographic data obtained by

Table 2. Crystallographic data of alnusdiol and maximowicziol A

	Alnusdiol (**1**)	Maximowicziol A (**2**)
Molecular formula	$C_{19}H_{22}O_4$	$C_{19}H_{22}O_4$
M_W	314.38	314.38
Crystal system	orthorhombic	orthorhombic
Space group	$P2_1P2_1P2_1$	$P2_1P2_1P2_1$
Cell dimensions		
a	13.142 (5) Å	11.606 (1) Å
b	19.903 (3) Å	13.273 (2) Å
c	12.464 (4) Å	10.344 (1) Å
Volume	3260 (1) Å^3	1593.4 (3) Å^3
Z	8	4
Density	1.281 g cm^{-3}	1.310 g cm^{-3}
Absorption coefficient	7.23 cm^{-1}	7.39 cm^{-1}
F_{000}	1344.00	672.00
Crystal dimensions (mm)	0.30 × 0.20 × 0.15	0.35 × 0.20 × 0.20



Compound 1 **Compound 2**

Fig. 3. ORTEP drawings of compounds **1** and **2** with the numbering system used in X-ray analysis.

X-ray analysis are shown in Table 2. All measurements were made on a Rigaku AFC7R diffractometer with filtered CuKα radiation and a rotating anode generator. The structure was solved by direct methods [22] and expanded using Fourier techniques [23]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Alnusdiol (**1**). (Fig. 3) Data were collected using the ω-2θ scan (2θ max = 120°) technique and a total of 2358 reflections were collected. The final cycle of full-matrix least-squares refinement was based on 2037 observed reflections ($I > 3\sigma(I)$) and 416 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.030$ and $R_W = 0.044$, respectively. Maximum and minimum peaks in final difference Fourier maps were +0.13 e/Å^3 and −0.16 e/Å^3, respectively.

Maximowicziol A (**2**). (Fig. 3). Data were collected using the ω-2θ scan technique (2θ max = 120°) and a total of 1398 reflections were collected. The final cycle of full-matrix least-squares refinement was based on 1270 observed reflections ($I > 3\sigma(I)$) and 209 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.027$ and $R_W = 0.042$, respectively. Maximum and minimum peaks in final difference Fourier maps were +0.11 e/Å^3 and −0.12 e/Å^3, respectively.

The atomic co-ordinates for this work are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory.

(−)-(*a*S,3″S,5″S)-*Alnusdiol* (**1**). Pale brown prisms (MeOH), mp > 300°. $[\alpha]_D^{23}$ −46.0° (*c* 0.85, MeOH). UVλ_{max}^{MeOH} nm: 300, 252sh, 206. CD (MeOH, *c* 1.3 × 10^{-4},): $[\theta]_{296}$ − 65 454, $[\theta]_{267}$ − 11 666, $[\theta]_{239}$ − 109 848, $[\theta]_{225}$ + 115 378. HREIMS: $[M]^+$, 314.1540 ($C_{19}H_{22}O_4$ requires 314.1518). EIMS *m/z* (rel. int.): 316 $[M+H_2]^+$ (35), 315 $[M+H]^+$ (88), 314$[M]^+$ (100), 296 $[M-H_2O]^+$ (14), 255 (32), 213 (50), 212 (73), 211 (93). NMR: Tables 1 and 3.

(−)-rel-(*p*R, 3S, 5S)-*Mamimowicziol A* (**2**). Clear needles (MeOH), mp 220–221°. $[\alpha]_D^{23}$ −86.3° (*c* 0.66,

Table 3. ^{1}H NMR spectral data of compounds **1–4** (δ in CD_3OD)

H	**1**	H	**2**	H	**3**	**4**
3	6.80	1a	2.63 *ddd*	2	6.39 *s*	6.94 *d*
	(8.1)		(16.6, 8.5, 3.1)			(1.8)
4	7.02 *d*	1b	2.45 *ddd*	5		6.75 *d*
	(8.1)		(16.6, 7.6, 3.1)			(8.2)
6	7.02 *s*	2a	1.56 *m*	6	6.39 *s*	6.81 *dd*
		2b	1.47 *m*			(8.2, 1.8)
3′		3	2.85 *m*	7	4.26 *d*	5.48 *d*
4′		4a	1.58 *m*		(5.8)	(6.1)
6′		4b	1.45 *m*	8	1.92 *m*	3.46 *ddd*
		5	2.96 *m*			(7.3, 6.1, 5.8)
1″a	2.88 *ddd*	6a	1.85 *m*	9a	3.45 *m*	3.81 *d*
	(20.1, 3.7, 2.5)	6b	1.55 *m*			(5.8)
1″b	2.88 *ddd*	7a	2.91 *ddd*	9b	3.45 *m*	3.75 *d*
	(20.1, 12.8, 2.5)		(12.8, 3.7, 4.0)			(7.3)
2″a	2.34 *dddd*	7b	2.70 *ddd*			
	(15.9, 12.8, 3.7, 1.5)		(12.8, 12.8, 2.8)	2′		6.72 *s*
2″b	1.75 *dddd*			6′	6.53 *s*	6.72 *s*
	(15.9, 9.5, 2.5, 2.5)	2′	5.40 *br d*	7a	2.65 *dd*	2.62 *t*
3″	3.98 *dddd*		(1.8)		(15.0, 4.6)	(7.6)
	(9.5, 7.9, 4.6, 1.5)	5′	6.68 *d*	7′b	2.53 *dd*	2.62 *t*
4″a	1.91 *dd*		(7.6)		(15.0, 11.6)	(7.6)
	(7.9, 4.6)	6′	6.51 *dd*	8′	1.58 *m*	1.81 *tt*
4″b	1.91 *dd*		(7.6, 1.8)			(7.6, 6.6)
	(7.9, 4.6)			9′a	3.55 *dd*	3.56 *t*
5″		2″	7.30 *d*		(11.0, 5.2)	(6.6)
6″a			(7.9)	9′b	3.45 *m*	3.56 *t*
6″b		3″	7.04 or 7.02			(6.6)
7″a			*dd* (7.9, 2.3)			
7″b		5″	7.02 or 7.04	OMe	3.68 (C3, C5)	3.84 (C3′)
			dd (7.9, 2.3)	OMe	3.33 (C3′)	3.80 (C3)
		6″	7.30 *d*	OMe	3.80 (C5′)	
			(7.9)			

Coupling constant for **1** was obtained by homo-decoupling experiments. Five protons overlapping at δ 1.43–1.61 in **2** were assigned by an HSQC experiment; however, no coupling constants were determined.

MeOH). UVλ_{max}^{MeOH} nm: 278, 238sh, 202. CD (MeOH, c 0.89×10^{-4}):$[\theta]_{289}+1348$, $[\theta]_{272}-3034$, $[\theta]_{263}-2360$, $[\theta]_{244}-23\,910$, $[\theta]_{223}+8652$. HREIMS: $[M]^+$, 314.1528 ($C_{19}H_{22}O_4$ requires 314.1518). EIMS m/z (rel. int.): 316 $[M+H_2]^+$ (22), 315 $[M+H]^+$ (59), 314 $[M]^+$ (66), 297 (67), 296 $[M\text{-}H_2O]^+$ (100), 255 (46), 212 (32), 211 (37). NMR: Tables 1 and 3.

(−)-(7R, 8S, 8′S)-*Lyoniresiol* (**3**) *in a racemic form.* Clear needles (MeOH–$CHCl_3$ 10:1), mp 205.5–206°. $[\alpha]_D^{23}$ −3.6° (c 2.22, MeOH). UVλ_{max}^{MeOH} nm: 280, 235sh, 205. CD (MeOH, c 1.2×10^{-4}):$[\theta]_{285}+692$, $[\theta]_{260}+275$, $[\theta]_{243}-1583$, $[\theta]_{220}+3000$. EIMS m/z (rel. int.): 421 $[M+H]^+$ (63), 420 $[M]^+$ (100), 402 $[M-H_2O]^+$ (14), 371 (24), 205 (39). NMR: Tables 1 and 3.

(−)-(7R, 8S)-*Dihydrodehydrodiconiferyl alcohol* (**4**) *in a racemic form.* Oil. $[\alpha]_D^{23}$ −6.1° (c 0.99, MeOH). UVλ_{max}^{MeOH} nm: 282, 231sh, 204. CD (MeOH, c 1.4×10^{-4}):$[\theta]_{294}-2050$, $[\theta]_{268}+157$, $[\theta]_{242}-7186$, $[\theta]_{224}+4464$. EIMS m/z (rel. int.): 361 $[M+H]^+$ (20). 360 $[M]^+$ (62), 343 (31), 342 $[M-H_2O]^+$ (100), 330 (40), 327 (46), 197 (96). NMR: Tables 1 and 3.

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