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^{13}C NMR ANALYSIS OF SYMPLOCOSIN AND (+)-EPIPINORESINOL GLUCOSIDE

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Key Word Index—*Symplocos lucida*; Symplocaceae; *Forsythia* species; Oleaceae; lignans; epipinoresinol-β-D-glucoside; ^{13}C NMR.

In a previous paper [1] we reported the structure of phillyrin (**5**). This paper deals with ^{13}C NMR analysis of simplocosin (**1**) [(−)-epipinoresinol-β-D-glucoside] from *Simplocos lucida* Sieb. et Zucc. cultivated in Japan [2] and (+)-epipinoresinol-β-D-glucoside (**2**) from *Forsythia* species cultivated in Germany [3].

Table 1 presents ^{13}C NMR data of the lignans and tneir assignments. The chemical shifts of C-1′ and C-1″ are sensitive both to change in substituents on the aromatic rings and to their stereochemistry. The chemical shifts of C-1, 5, C-2, 6 and C-4, 8 are also sensitive to the stereochemistry of the 2,6-diaryl-3,7-dioxabicyclo[3,3,0]octane ring but not to changes in the aryl group [1, 4]. In addition, the C-1 signals of the 3,4-dimethoxyphenyl unit and the 3-methoxy-4-glucosylphenyl unit to the corresponding ones of the 3-methoxy-4-hydroxypheny unit are shifted downfield by *ca* 1.5–3 ppm in DMSO-d_6 when ^{13}C NMR spectra of phillygenin (**3**), phillygenin Me ether (**4**), phillyrin (**5**), (+)-pinoresinol-β-D-glucoside (**6**) and (+)-pinoresinol mono-Me ether-β-D-glucoside (**7**) are carefully studied.

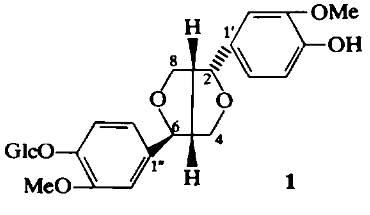
As to epipinoresinol glucoside, the above results make it possible to assign δ values of 132.6 ppm for C-1 of the equatorial aryl group having a free OH, 129.6 ppm for the C-1 of the axial one, 135.4 ppm for C-1 of the equatorial aryl group linked to β-D-glucose and 132.4 ppm for C-1 of the axial one, respectively.

Consequently, the structures are established to be (−)-epipinoresinol-4″-β-D-glucoside as **1** and (+)-epipinoresinol-4′-β-D-glucoside as **2**, respectively.

This paper presents the first example of the important significance of Δ δ value of the C-1′ or C-1″ signal in aryl groups in DMSO-d_6 for ^{13}C NMR analysis of lignan glucosides.

Table 1. ^{13}C NMR chemical shifts of lignan glucosides

	1	**2**	**3**	**4**	**5**	**6**	**7**
C-1	49.4	49.2	49.4	49.3	49.3		
						53.5	53.5
5	54.0	53.6	53.9	53.9	54.0		
4	70.4	70.4	70.4	70.2	70.4		
						70.9	71.0
8	69.0	68.7	68.9	68.8	69.0		
2	81.4	81.1	81.3	81.2	81.3	84.8	
							84.8
6	86.7	86.8	87.1	86.7	86.7	85.1	
1′	129.6	132.4	131.4	131.1	131.2	132.1	133.8
1″	135.4	132.6	132.5	133.9	135.4	135.2	135.2
3′	145.3	145.9	146.1	147.6	146.0	145.9	145.8
3″	145.9		147.6	148.2	147.7	148.9	148.1
4′	147.3		148.6	148.7	148.5		148.7
4″	149.0				149.0		148.9
2′	109.9	110.5	109.5	109.4	109.5	110.4	109.9
2″	110.4	115.2	110.4	109.8	110.5	115.1	110.5
5′	115.2	115.3	115.3	111.6	115.3	118.1	111.6
5″	115.3	117.7	117.7	117.5	116.0	118.6	118.6
6′	117.9	118.5	118.8	118.1	117.7		
6″	118.3				118.2		
MeO	55.7	55.7 55.8	55.6	55.4	55.7	55.6	55.4 55.6
Glc-1	100.2	100.4			100.3	100.1	100.1
2	73.3	73.2			73.3	73.1	73.1
3	76.8	76.7			76.9	76.9	76.8
4	69.8	69.8			69.8	69.6	69.6
5	77.0	76.7			76.9	76.9	76.8
6	60.8	60.7			60.7	60.6	60.6



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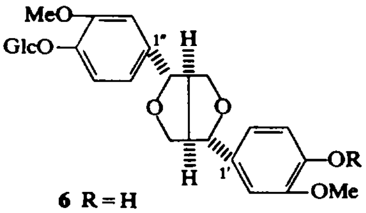
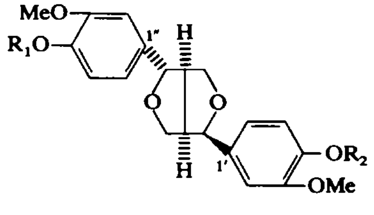


6 R = H
7 R = Me



2 $R_1 = H, R_2 = Glc$
3 $R_1 = H, R_2 = Me$
4 $R_1 = Me, R_2 = Me$
5 $R_1 = Glc, R_2 = Me$

EXPERIMENTAL

The ^{13}C NMR spectra of compounds **3** to **7** were recorded at 15 MHz in DMSO-d_6 with TMS ($\delta = 0$) as int. ref. using micro-cells. FT-NMR conditions were as follows: spectral width, 4 kHz; number of data points, 8192; pulse repeat time, 1.2 sec; number of pulses, 5000–100000; pulse flipping angle, 45°. The ^{13}C NMR spectra of compounds **1** and **2** were recorded at 25.05 MHz in DMSO-d_6 with TMS ($\delta = 0$) as int. ref. using 1.8 mm tubes. FT-NMR conditions were as follows: spectral width, 5 kHz; number of data points, 8192, 4096; pulse repeat time, 1.5, 1.0 sec; number of pulses, 40000–60000; pulse flipping angle, 60°, 70°. Samples of phillyrin (**5**) and (+)-pinoresinol-β-D-glucoside (**6**) were obtained from the fruit of *Forsythia suspensa* Vahl as described in ref. [5].

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BAVACHROMANOL: A NEW CHALCONE FROM THE SEEDS OF *PSORALEA CORYLIFOLIA*

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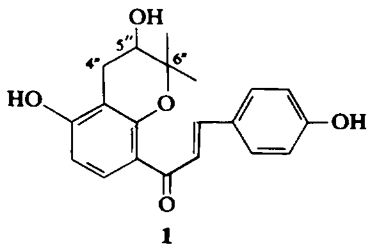
Key Word Index—*Psoralea corylifolia*; Leguminosae; 4,4′,5″-trihydroxy-6″,6″-dimethyldihydropyrano-(2″,3″:2′,3′)-chalcone.

In our earlier communication [1], the isolation of psoralenol, a new isoflavone from the seeds of *Psoralea corylifolia*, was reported. In the present paper we describe the isolation and characterization of bavachromanol, a new chalcone. It was obtained by repeated column chromatography of the ether extract of the defatted seeds over Si gel.

Bavachromanol (**1**) crystallized from EtOAc as light yellow granules. High resolution MS gave its molecular formula as $C_{20}H_{20}O_5$. Its chalcone structure was indicated by its UV bands at 242, 308 and 350 nm. A bathochromic shift of 72 nm of the longer wavelength band along with an increase in the intensity with NaOMe showed the presence of a 4-OH group. The appearance of a long wavelength shoulder with NaOAc showed that 4′-OH may be present. Absence of a bathochromic shift with $AlCl_3$ showed the absence of any chelated OH groups. Its IR (KBr) showed characteristic absorptions at 1638 cm^{-1} due to chalcone carbonyl, at 1378 and 1362 cm^{-1} due to gem dimethyl and at 830 cm^{-1} due to a *para*-substituted benzene ring. The compound formed a triacetate indicating the presence of three OH groups.



1

^1H NMR (Me_2CO-d_6) of the compound gave two sharp singlets at δ 1.43 and 1.49 for gem dimethyl protons. A multiplet at δ 2.81 showed the presence of two benzylic protons. The presence of a methine proton attached to a carbon bearing a secondary hydroxyl group was shown by a triplet at δ 3.92, which in conformity with its assigned character, shifted downfield to δ 5.09 in the ^1H NMR of its triacetate Further, there was an *ortho*-coupled doublet centred at δ 6.92 integrating for two protons at C-3 and C-5 and an A_2B_2 system of a *para*-substituted B-ring, the other doublet for C-2 and C-6 protons merging with a complex multiplet between δ 7.36 and 7.66 integrating for five protons. Another *ortho*-coupled doublet at δ 6.54 integrating for one proton could be assigned to

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