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THE STRUCTURE OF A NEW NEOLIGNAN GLYCOSIDE FROM *STAUNTONIA CHINENSIS*

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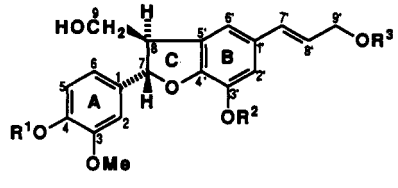
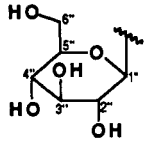
ABSTRACT.—A neolignan glycoside, named yemuoside YM_1 [**1**], was obtained from *Stauntonia chinensis*, and the structure was elucidated on the basis of chemical evidence and spectroscopic studies.

In the course of an investigation of medicinal plants, it was found that the plant *Stauntonia chinensis* DC. (Lardizabalaceae) is effective for analgesia and sedation (1). Consequently, we have undertaken phytochemical research of this plant in the hope of isolating possible active components. In the previous papers (2,3), we reported the isolation and structural elucidation of new lignan glycosides and nortriterpenoid glycosides. As a continuation of this study, we now report the structure of a new neolignan glycoside which was named yemuoside YM_1 [**1**] and determined on the basis of spectroscopic and chemical evidence.

Compound **1** was obtained (see Experimental) as a chromatographically homogeneous and amorphous powder. On treatment with HCl/MeOH and trimethylsilylation, glucose was identified by gc-ms. In the ^{1}H-nmr spectrum of **1**, a doublet at δ 6.53 (1H, J = 16.0 Hz), a doublet of triplets at δ 6.23 (1H), and a doublet of doublets at δ 4.18 (2H, J = 1.5, 5.8 Hz) are characteristic for an $\begin{matrix}Ar\\H\end{matrix}>C=C<\begin{matrix}H\\CH_2O-\end{matrix}$ moiety. There were five aromatic proton signals for two

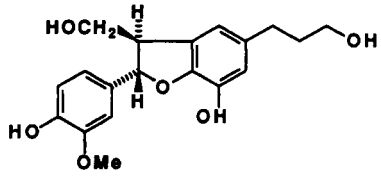


1 R_1=R_3=H, R_2=



4 R_1=Me, R_3=H, R_2=glc

3 R_1=R_3=H, R_2=Me



2

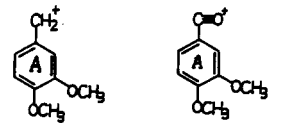
rings: δ 7.15 (1H, J = 1.6 Hz) and 7.05 (1H, J = 1.6 Hz) in one, and 6.95 (1H, J = 2.0 Hz), 6.79 (1H, J = 8.0 Hz), and 6.86 (1H, J = 8.0, 2.0 Hz) in the other. Most of the proton signals of glucose, and H-8 and H-9, fell in the narrow range of δ 3.2–3.8 ppm; hence assignments based solely on conventional 1D spectra are difficult. ^{1}H-^{1}H COSY correlation of a doublet at δ 5.55 (1H, J = 6.0 Hz), a doublet of doublets at δ 3.44 (1H, J = 6.0, 12.0 Hz) and a multiplet at δ 3.73 (2H), as well as HOHAHA experiments, suggested the presence of a 2,3-dihydrobenzofuran system (4). This was further confirmed by comparison of chemical shifts and coupling constants with those of cedrusin [**2**] (5) and dehydrodiconiferylalcohol [**3**] (6).

The fabms of **1** showed a molecular ion at m/z 529 $[M+Na]^+$, indicating a molecular weight of 506. The fragment ion at m/z 345 $[M-Glc+H]^+$ corresponded to the loss of a glucose residue. In the eims of the methylate [**4**], strong peaks appeared at m/z 151 and 165 (6) (Figure 1). This showed that the glucose was not linked to ring A.

The site of glucose linkage was established by ^{13}C-nmr spectroscopy (Table 1) and comparison with known compounds (5, 6, 8). The stereochemistry of the dihydrofuran ring was determined by nOe experiments and the cd spectrum. A positive nOe between H-7 and H-9 indicated the cis arrangement, and the cd curve of **1** exhibited a negative Cotton effect at 275 nm, giving evidence that the configuration in **1** must be 7*S*, 8*R* (7).

The anomeric configuration of the glucose was fully defined by the nmr spectra. In the ^{1}H-nmr spectrum of **1**, the anomeric proton signal at δ 5.04 (1H, d, J = 7.5 Hz) led to the assignment of the β configuration, which was supported by its carbon signals (Table 1).

On the basis of the above evidence, the structure of **1** was elucidated as shown.



m/z 151 m/z 165

FIGURE 1. Characteristic ms fragments of **4**.

TABLE 1. ^{13}C-nmr Chemical Shifts for Compounds **1**–**3**.

Carbon	Compound			Carbon	Compound		
	1[a]	**2**[b]	**3**[c]		**1**[a]	**2**[b]	**3**[c]
C-1	134.06	134.61	132.3	C-5′	131.65	136.56	130.5
C-2	110.82	110.49	110.5	C-6′	118.00	115.69	114.9
C-3	149.20	148.32	147.5	C-7′	132.79	35.62	128.9
C-4	147.86	147.02	146.3	C-8′	127.98	31.91	129.9
C-5	116.41	116.27	115.3	C-9′	63.81	61.94	61.5
C-6	120.10	119.53	118.4	-OMe	56.47	56.28	56.6
C-7	89.80	88.07	87.1	Glc-1″	102.89		
C-8	54.83	55.11	52.9	2″	74.93		
C-9	64.76	64.73	62.9	3″	78.21		
C-1′	131.07	129.67	129.5	4″	71.34		
C-2′	116.27	116.86	110.5	5″	77.78		
C-3′	142.75	141.56	143.6	6″	62.43		
C-4′	149.15	145.98	147.1				

[a]In CD_3OD.
[b]In CD_3COCD_3.
[c]In DMSO-d_6.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The mp was determined on a Boetius micromelting apparatus and was uncorrected. Optical rotation was measured on a Jasco DIP360 polarimeter. Cd was obtained on a Jobin CD-5 polarimeter. ^{1}H-nmr (400 MHz) and ^{13}C-nmr (100 MHz) spectra were recorded on a Jeol GX-400 spectrometer in CD_3OD. Chemical shifts (δ) are expressed in ppm using TMS as an internal standard. The fabms and eims were taken on Hitachi M-80A-M003 and H.P. MS-5988A systems, respectively. The fabms was measured with an accelerating potential of 3.0 kV for an Xe beam source with glycerol matrix. Tlc was performed on Kieselgel G (Merck) using the following solvent systems: $CHCl_3$-MeOH-H_2O (10:5:1) and EtOAc-MeOH-H_2O (8:3:3). Spots were detected by spraying with 10% H_2SO_4 followed by heating.

PLANT MATERIAL.—The plants of *S. chinensis* were collected in Jiangxi province of China in the summer of 1985. A herbarium specimen was identified by Prof. Wan-Zhi Song, Institute of Materia Medica, Chinese Academy of Medical Sciences, and deposited in the Herbarium of this Institute.

EXTRACTION AND ISOLATION.—The dried whole plants (18 kg) were pulverized and extracted wtih 70% EtOH (40 liters × 4, 1.5 h for each extraction) at 80°. The extracts were combined and concentrated in vacuo to give a brown residue (1.98 kg) which was suspended in H_2O (3.5 liters) and extracted with EtOAc (3.0 liters × 5) and then with *n*-BuOH saturated with H_2O (3.0 liters × 5). The *n*-BuOH solution was concentrated to give the *n*-BuOH-soluble fraction (500 g). A portion (55 g) was developed on Kiesel gel by cc with $CHCl_3$-MeOH-H_2O (100:10:1↦10:5:1) to give seven fractions (fractions I to VII).

Fraction IV (6.4 g) was separated by reversed-phase cc on ODS CPO-223L-20 (Kusano) with 15%, 25%, 35%, and 50% MeCN. The 15% MeCN eluate (0.82 g) was purified by preparative hplc on Aquasil SS-352N (Senshuo Science) with $CHCl_3$-MeOH-H_2O (45:10:1) to afford yemuoside YM_1 [**1**] (4.3 mg).

CHARACTERIZATION OF **1**.—White powder, mp 123–127°, $[\alpha]^{23}D$ −30.75 (c = 0.101, MeOH), uv λ max (MeOH) nm 224, 270; ^{1}H-nmr (CD_3OD) δ 3.73 (2H, m, H_2-9), 3.44 (1H, dd, J = 6.0, 12.0 Hz, H-8), 3.82 (3H, s, OMe), 4.18 (2H, dd, J = 1.5, 5.8 Hz, H_2-9′), 5.04 (1H, d, J = 7.5 Hz, H-1″ of glc), 5.55 (1H, d, J = 6.0, H-7), 6.23 (1H, dt, J = 16.0, 6.0 Hz, H-8′), 6.53 (1H, d, J = 16.0 Hz, H-7′), 6.79 (1H, d, J = 8.0 Hz, H-5), 6.86 (1H, dd, J = 8.0, 2.0 Hz, H-6), 6.95 (1H, d, J = 2.0 Hz, H-2), 7.05 (1H, d, J = 1.6 Hz, H-6′), 7.15 (1H, d, J = 1.6 Hz, H-2′); fabms *m/z* $[M + Na]^+$ 529, $[M - \text{glucose} + H]^+$ 345; cd (c = 0.007, MeOH) [θ] (nm) 12141 (270), 0 (245).

SUGAR ANALYSIS BY GC-MS.—Compound **1** (0.1 mg) was heated with 5 drops of anhydrous HCl/MeOH in a sealed micro-tube at 60° for 1.5 h. The reaction mixture was diluted with 10 drops of H_2O, and Ag_2CO_3 (5 mg) was added. The solution was filtered and evaporated to dryness. The residue was heated with 20 μl of pyridine and 20 μl of *N,O*-bis(trimethylsilyl)-trifluoroacetamide in a sealed micro-tube at 80° for 10 min. The reaction mixture was subjected to gc-ms analysis on a Shimadzu GCMS-QP1000: column *Shimadzu* CBP 1-W-12-100 (0.53 mm × 10 m), injection temperature 250°, column temperature 100–200° (10°/min), carrier gas He (30 ml/min), separator temperature 250°, ionization voltage 70 eV, accelerating voltage 1.5 kV.

MONOMETHYLATION OF **1**.—Compound **1** was methylated with CH_2N_2 to give the monomethylate **4**: white powder, eims (rel. int.) *m/z* 382 (50), 309 (18), 165 (25), 151 (58).

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LITERATURE CITED

1. Jiangsu New Medical College, Eds., "Zhong Yao Dai Ci Dian," 1977, Vol. 2, p. 2185.
2. H.B. Wang, D.Q. Yu, X.T. Liang, N. Watanabe, M. Tamai, and S. Omura, *J. Nat. Prod.*, **52**, 342 (1989).
3. H.B. Wang, D.Q. Yu, X.T. Liang, N. Watanabe, M. Tamai, and S. Omura, *Planta Med.*, **55**, 303 (1989).
4. G. Aulin-Erdlmann, Y. Tomita, and S. Forsen, *Acta Chem. Scand.*, **17**, 535 (1963).
5. P.K. Agrawal, S.K. Agrawal, and R.P. Rostogi, *Phytochemistry*, **19**, 1260 (1980).
6. T. Deyama, T. Ikawa, S. Kitagawa, and S. Nishibe, *Chem. Pharm. Bull.*, **35**, 1803 (1987).
7. O.A. Lima, O.R. Gottlieb, and M.T. Magalhaes, *Phytochemistry*, **11**, 2031 (1972).
8. H. Arens, H. Fischer, S. Leyck, A. Romer, and B. Ulbrich, *Planta Med.*, **51**, 52 (1985).

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