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THE STRUCTURES OF TWO LIGNAN GLYCOSIDES FROM *STAUNTONIA CHINENSIS*

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ABSTRACT.—Two new lignan glycosides were isolated from *Stauntonia chinensis*. Their structures were elucidated as (−)-olivil-9-*O*-β-D-apiofuranosyl(1↦6)-β-D-glucopyranoside (designated as yemuoside YM_2) [**1**] and (−)-cyclo-olivil-9′-*O*-β-D-apiofuranosyl(1↦6)-β-D-glucopyranoside (designated as yemuoside YM_6) [**2**] on the basis of spectroscopic and chemical evidence.

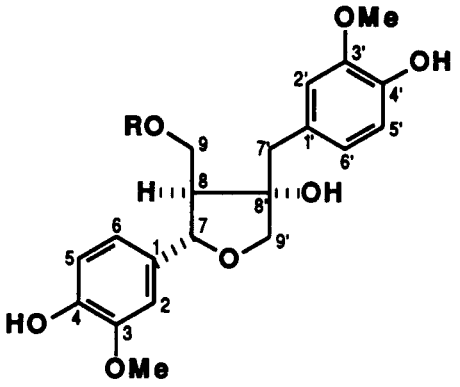
In the previous paper (1), we reported the isolation and structural determination of nortriterpenoid glycosides isolated from *Stauntonia chinensis* DC. (Lardizabalaceae), collected in South China. As a continuation of this study, we now report the isolation and structural elucidation of two new lignan glycosides, yemuosides YM_2 [**1**] and YM_6 [**2**].

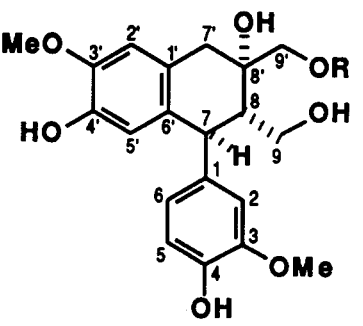
RESULTS AND DISCUSSION

The extraction and separation were carried out as described in the Experimental section.

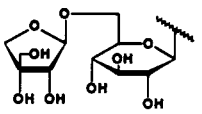
Compound **1** was obtained as an amorphous powder, $[\alpha]^{23}D$ −48.7° ($c = 0.08$, MeOH), which showed absorption maxima at 224 and 273 nm in the uv spectrum and gave peaks at *m/z* $[M+K]^+$ 709, $[M+Na]^+$ 693, $[M-Api+Na]^+$ 561, and $[M-Glc-Api+Na]^+$ 399 in the secondary ion mass spectrum (sims). The ^{1}H-nmr spectrum of **1** showed signals at δ 3.86 and 3.87 (each 3H, s) due to two aromatic methoxyl groups and δ 6.70–7.15 (m) due to six aromatic protons. Compound **2** was obtained as an amorphous powder, $[\alpha]^{23}D$ −21.2° ($c = 0.10$, MeOH), which showed absorption maxima at 230 and 281 nm in the uv spectrum and gave peaks at *m/z* $[M+Na]^+$ 693, $[M-Api+Na]^+$ 561, and $[M-Glc-Api+Na]^+$ 399 in sims. The ^{1}H-nmr spectrum of **2** showed signals at δ 3.84 and 3.85 (each 3H, s) due to two aromatic methoxyl groups and δ 6.22–6.84 (m) due to five aromatic protons. On the basis of spectroscopic investigations, the skeletons of **1** and **2** were elucidated as olivil and cyclo-olivil, respectively. Hydrolysis of **1** and **2** with the tlc-HCl vapor method (2,3) gave, respectively, the aglycones olivil [**3**] and cyclo-olivil [**4**] which were identified through direct comparison (tlc) with the authentic samples.

With the aglycones of **1** and **2** ascertained, inspection of ^{13}C-nmr data revealed that **1** and **2** contained identical sugar residues (Table 1). In the ^{13}C-nmr spectrum, only eleven sugar carbons were observed. In the ^{1}H-nmr spectrum, a pair of vicinal methine protons (5.02 and 3.88, each 1H, d, $J = 2.5$ Hz) and two isolated methylene groups [ca. δ 3.74, 3.92 (2H, ABq, $J = 9.5$ Hz) and 3.54 (2H, s)] suggested a pentose branched at C-3′. A ^{1}H-^{13}C COSY spectrum permitted assignment of the carbons of the pentose residue (Table 1), and the data matched those previously reported for apiose (4–7). Positive nOe between the branching methylene (C-5′) and methine (C-2′), the magnitude of $J_{1,2}$, and the ^{13}C-nmr data confirmed this sugar was β-D-apiose. The remaining sugar carbon signals were appropriate for a 6-linked β-D-glucosyl unit and matched data reported for **5** from *Ligstrum japonicum* Thunb. (Oleaceae) (4). Acid hydrolysis of **1** and **2** gave apiose and glucose.





1 R=
3 R=H



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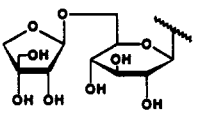
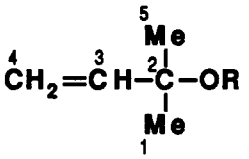
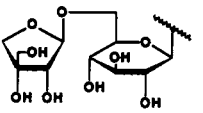
4 R=H





5 R=



As shown in Table 1, the glycosylation shifts of corresponding carbons in going to **1** from **3** and going to **2** from **4** were, respectively, +7.51 (C-9) and +7.24 (C-9′), which suggested that **1** and **2** have a 9-*O*-glycosidic linkage and a 9′-*O*-glycosidic linkage, respectively.

From the above results, **1** and **2** were identified as (−)-olivil-9-*O*-β-D-apiofuranosyl-(1↦6)-β-D-glucopyranoside and (−)-cyclo-olivil-9′-*O*-β-D-apiofuranosyl(1↦6)-β-D-glucopyranoside, respectively.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All mp's were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. The following instruments were used: optical rotations, Jasco DIP360 polarimeter; uv, Hitachi 220 spectrophotometer; hplc, Waters 6000A with a uv detector; sims, Hitachi M-80; nmr, Jeol GX-400 with TMS as an internal reference. For cc, Kieselgel (70–230 mesh, Merck) was used; tlc was performed on Kieselgel G (Merck) using the following systems: for glycosides, (a) $CHCl_3$-MeOH-H_2O (10:5:1); (b) EtOAc-MeOH-H_2O (3:1:1); for aglycones, (c) $CHCl_3$-MeOH (10:1); for sugars, (d) EtOAc-H_2O-MeOH-HOAc (13:3:3:4). Detection: for aglycones and glycosides, spraying with 10% H_2SO_4 followed by heating; for sugar, aniline phthalate reagent.

EXTRACTION AND ISOLATION.—The dried whole plants (18 kg) of *S. chinensis* were collected in Jiangxi province of China in the summer of 1985. The specimen was identified by Prof. Wan-Zhi Song, the Institute of Materia Medica, Chinese Academy of Medical Sciences and deposited in the Herbarium of this institute. The plants were pulverized and extracted with 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 cc with $CHCl_3$-MeOH-H_2O (100:10:1↦10:5:1) to give seven fractions.

The fourth fraction (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 (827 mg) was purified by preparative hplc on

TABLE 1. ^{13}C Nmr Chemical Shifts (in CD_3OD).

Carbon[a]	1	3	Δδ (1–3)	2	4	Δδ (2–4)	5[b]
1	130.40	130.40	0.00	133.38	133.7	−0.32	28.0(1)
1′	134.96	135.35	−0.39	138.31	138.4	−0.09	
2	115.41	115.21	+0.20	114.45	114.3	+0.15	77.7(2)
2′	111.57	111.54	+0.03	112.98	113.3	−0.32	
3	149.00	149.00	0.00	149.07	149.2	−0.13	145.0(3)
3′	148.56	148.54	+0.02	147.50	147.6	−0.10	
4	147.24	147.16	+0.08	146.09	146.2	−0.11	113.5(4)
4′	146.14	146.13	+0.01	145.22	145.5	−0.28	
5	115.85	115.79	+0.06	117.31	117.4	−0.09	26.6(5)
5′	115.80	115.67	+0.13	116.27	116.2	+0.07	
6	124.06	123.86	+0.20	123.38	123.7	−0.32	
6′	120.78	120.75	+0.03	126.52	126.6	−0.08	
7	85.38	85.82	−0.44	44.87	45.0	−0.13	
7′	40.70	40.62	+0.08	39.97	40.1	−0.13	
8	60.26	61.92	−1.66	46.54	47.9	−0.36	
8′	82.41	82.59	−0.18	74.44	74.9	−0.46	
9	68.29	60.78	+7.51	69.60	69.5	+0.10	
9′	77.78	77.95	−0.17	68.24	61.0	+7.24	
OCH_3	56.48	56.33	+0.15	56.53	56.6	−0.07	
	56.42	56.33	+0.09	56.38	56.6	−0.22	
Glc-1	104.69			105.25			99.5
2	75.20			75.06			75.0
3	78.00			78.05			78.5
4	71.72			71.63			71.8
5	77.08			76.97			76.9
6	68.56			68.52			68.9
Api-1′	110.97			110.93			111.0
2′	78.00			77.90			77.5
3′	80.54			80.57			80.4
4′	74.99			75.02			74.9
5′	65.03			65.67			65.5

[a]Glc = glucose, Api = apiose.
[b]In C_5D_5N; from Kudo *et al.* (4).

YMC-D-ODS-5 and Nucleosil$_5$ C_{18} with 12–14% MeCN to afford yemuoside YM_6 [**2**] (7.5 mg) and yemuoside YM_2 [**1**] (6.1 mg).

CHARACTERIZATION OF **1**.—Amorphous powder, mp 124–126°; uv λ max (MeOH) nm 224, 273; ^1H nmr (CD_3OD) δ 2.46 (1H, m, H-8), 2.93, 3.03 (2H, ABq, J = 14.0 Hz, H-7′), 3.63, 3.86 (2H, ABq, J = 9.1 Hz, H-9′), 3.54 (2H, s, H-5 of apiose), 3.74 and 3.94 (2H, ABq, J = 9.5 Hz, H-4 of apiose), 3.86 (3H, s, -OMe), 3.87 (3H, s, -OMe), 3.88 (1H, d, J = 2.5 Hz, H-2 of apiose), 3.76 (1H, dd, J = 11.0, 6.0 Hz, H-9a), 4.11 (1H, dd, J = 11.0, 5.5 Hz, H-9b), 4.29 (1H, d, J = 7.8 Hz, H-1 of glucose), 4.79 (1H, d, J = 7.8 Hz, H-7), 5.02 (1H, d, J = 2.5 Hz, H-1 of apiose), 6.73 (1H, d, J = 8.0 Hz, H-5), 6.76 (1H, dd, J = 8.1, 1.9 Hz, H-6), 6.77 (1H, d, J = 8.0 Hz, H-5′), 6.92 (1H, dd, J = 8.0, 1.9 Hz, H-6′), 6.94 (1H, d, J = 1.9 Hz, H-2), 7.12 (1H, d, J = 1.9 Hz, H-2′); ^{13}C nmr see Table 1; sims *m/z* $[M+K]^+$ 709, $[M+Na]^+$ 693, $[M-Api+Na]^+$ 561, $[M-Glc-Api+Na]^+$ 399.

CHARACTERIZATION OF **2**.—Amorphous powder, mp 143–145°; uv λ max (MeOH) nm 230, 281; ^1H nmr (CD_3OD) δ 2.32 (1H, m, H-8), 2.64 and 3.29 (2H, ABq, J = 16.0 Hz, H-7′), 3.54 (2H, s, H-5 of apiose), 3.55 and 3.78 (2H, ABq, J = 11.0 Hz, H-9′), 3.84 (3H, s, -OMe), 3.85 (3H, s, -OMe), 3.46 (1H, dd, J = 12.0, 2.5 Hz, H-9a), 3.77 (1H, dd, J = 12.0, 4.1 Hz, H-9b), 3.77 and 3.94 (2H, ABq, J = 9.5 Hz, H-4 of apiose), 3.85 (1H, d, J = 2.5 Hz, H-2 of apiose), 3.96 (1H, d, J = 10.0 Hz, H-7), 4.04 (1H, d, J = 8.0 Hz, H-1 of glucose), 5.02 (1H, d, J = 2.5 Hz, H-1 of apiose), 6.22 (1H, s, H-2′), 6.67 (1H, s, H-5′), 6.71 (1H, dd, J = 7.8, 1.9 Hz, H-6), 6.80 (1H, d, J = 7.8 Hz, H-5), 6.84 (1H, d, J = 1.5 Hz, H-2); ^{13}C nmr see Table 1; sims *m/z* $[M+Na]^+$ 693, $[M-Api+Na]^+$ 561, $[M-Glc-Api+Na]^+$ 399.

HYDROLYSIS OF **1** AND **2**.—The thin-layer plate with spots of samples was placed in an atmosphere of concentrated HCl vapor maintained at 60° for 20 min and then air-dried to remove residual HCl (2,3). Development with solvent system d and comparison with standard sugars showed glucose and apiose in both **1** and **2**, while development with solvent c and comparison with standard sample showed olivil in **1** and cyclo-olivil in **2**.

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LITERATURE CITED

1. H.B. Wang, D.Q. Yu, X.T. Liang, N. Wantanabe, M. Tamai, and S. Omura, *Planta Med.*, in press.
2. T. Kartnig and O. Wegschaider, *J. Chromatogr.*, **61**, 375 (1971).
3. P.P. Zhao, B.M. Li, and L.Y. He, *Acta Pharm. Sin.*, **22**, 70 (1987).
4. K. Kudo, T. Nohara, T. Komori, T. Kawasaki, and H.R. Schulten, *Planta Med.*, **40**, 250 (1980).
5. P. Forgacs, J.F. Desconclois, J.L. Pousset, and A. Rabaron, *Tetrahedron Lett.*, 4783 (1978).
6. Y. Asheervadan, P.S. Rao, and R.D.H. Murray, *Fitoterapia*, **57**, 231 (1986).
7. B.C. VanWagenen, J. Huddleston, and J.H. Cardellina, *J. Nat. Prod.*, **51**, 136 (1988).

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