Chemistry of Natural Compounds, Vol. 30, No. 6, 1994

GLYCOSIDES OF (+)-SYRINGARESINOL AND 2-METHYLBUT-3-EN-2-YL β-*D*-GLUCOPYRANOSIDE FROM THE LEAVES OF *Nolina microcarpa*

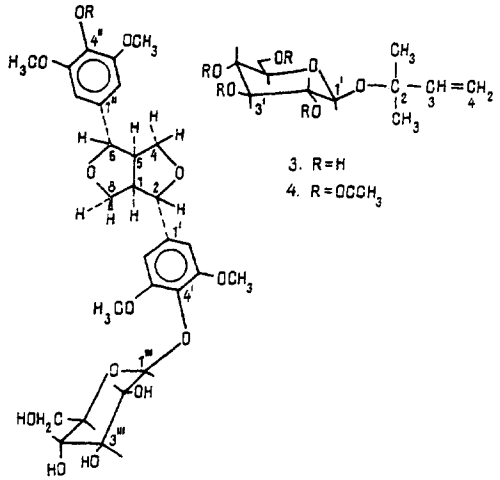
G. V. Shevchuk, A. S. Shashkov, and V. Ya. Chirva

UDC 547.99:543.422

Two furofuranoid lignan glycosides, having the structures of (+)-syringaresinol 4',4''-di-β-D-glucopyranoside (1) and (+)-syringaresinol 4'-β-D-glucopyranoside (2), and also 2-methylbut-3-en-2-yl β-D-glucopyranoside (3), have been isolated from an extract of the leaves of Nolina microcarpa *(fam. Dracaenaceae).*

As a result of the separation of the total extractive substances of the leaves of *Nolina microcarpa* (fam. Draceanaceae), together with compounds of the spirostan and furostan series [1], we have isolated three substances of nonsteroid nature. The present paper is devoted to the proof of the structures of these compounds.

On a thin-layer chromatogram, substances (**1**) and (**2**) were colored violet by vanillin/phosphoric acid, and compound (**3**) blue.



On the basis of an analysis of PMR and ^{13}C NMR spectra, components (**1**) and (**2**) were assigned to the furofuranoid lignan glycosides [2]. In their electron-impact mass spectra the most intense peak in each case, with *m/z* 418, corresponded to M − 2H for (±)-syringaresinol [3, 4].

In the PMR and ^{13}C NMR spectra there were signals corresponding to the protons and carbon atoms of a *D*-glucose residue (Tables 1 and 2). The values of the spin-spin coupling constants (SSCCs) ($J_{1,2}$ = 7.0 Hz) showed the β-configuration of the glycosidic bonds.

On the basis of spectral characteristics and physicochemical constants, the more polar substance (**1**) was identified as the symmetrical diglucoside of (+)-syringaresinol — liriodendrin, isolated from *Liriodendron tulipifera* [3] and *Penstemon deustus* [4].

Simferopol' State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 752-756, November-December, 1994. Original article submitted March 14, 1994.

0009-3130/94/3006-0699$12.50

TABLE 1. Chemical Shifts of the Protons (δ, ppm, 0 — TMS) and Spin-spin Coupling Constants (J, Hz) of (+)-Syringaresinol 4',4''-Di-β-*D*-glucopyranoside and (+)-Syringaresinol 4'-β-*D*-Glucopyranoside (2) (DMSO)

Proton	Compound	
	1	2
H-1	3.08 m	3.01 m
H-5	3.08 m	3.06 m
H-2	4.65 d $J_{1,2}$=4.0	4.60 d $J_{1,2}$=4.0
H-6	4.65 d $J_{5,6}$=4.0	4.66 d $J_{5,6}$=4.0
H-4 eq.	3.81 dd $J_{4e,4a}$=9.0 $J_{4e,5}$=3.5	3.80 dd $J_{4e,4a}$=9.0 $J_{4e,5}$=3.5
H-8 eq.	3.81 dd $J_{8e,8a}$=9.0 $J_{8e,1}$=3.5	3.80 dd $J_{8e,8a}$=9.0 $J_{8e,1}$=3.5
H-4 ax.	4.18 dd $J_{4a,5}$=6.5	4.16 dd $J_{4a,5}$=6.5
H-8 ax.	4.18 dd $J_{8a,1}$=6.5	4.16 dd $J_{8a,1}$=6.5
H-2', H-6'	6.64 s	6.66 s
H-2'', H-6''	6.64 s	6.58 s
OCH_3	3.76 s	3.74 s
OCH_3''	3.76 s	3.72 s
	β-*D*-Glucopyranose residue	
H-1	4.86 d $J_{1,2}$=7.0	4.67 d $J_{1,2}$=7.0
H-2	3.90 dd $J_{2,3}$=9.0	3.85 dd $J_{2,3}$=9.0
H-3	4.20 m	4.24 m
H-4	4.02 t $J_{4,5}$=8.5	4.05 t $J_{4,5}$=8.5
H-5	3.80 m	3.84 m
H-6	4.22 m	4.30 m
H-6	4.44 m	4.48 m

TABLE 2. Chemical Shifts of the ^{13}C Carbon Atoms of (+)-Syringaresinol 4′,4″-Di-β-*D*-glucopyranoside and (+)-Syringaresinol 4′-β-*D*-Glucopyranoside (**2**) (DMSO, ppm, 0 — TMS)

C-Atom	Compound		C-Atom	Compound	
	1	2		1	2
1	53.7	53.7		β-*D*-Glucopyranose	
2	85.2	85.2	1‴	102.8	102.8
4	71.5	71.4	2‴	74.3	74.3
5	53.7	53.8	3‴	76.6	76.6
6	85.2	85.5	4‴	70.0	70.0
8	71.5	71.4	5‴	77.3	77.3
			6‴	61.0	61.0
1′	133.8	133.8			
2′	104.3	104.3			
3′	152.8	152.8			
4′	137.4	137.4			
5′	152.8	152.8			
6′	104.3	104.3			
1″	133.8	133.8			
2″	104.3	103.8			
3″	152.8	148.1			
4″	137.4	131.6			
5″	152.8	148.1			
6″	104.3	103.8			
OCH_3'	56.5	56.5			
OCH_3''	56.5	56.2			

The diequatorial configuration of the phenyl fragments followed from the fact that the benzyl protons resonated at 4.65 ppm, with a SSCC of 4 Hz (Table 1). The chemical shift of the C-2 and C-6 carbon atoms — 85.2 ppm — and that of C-1′ and C-1″ — 133.8 ppm (Tables 2) — coincided with the corresponding values in the diequatorial structure of (+)-syringaresinol [2, 4].

On partial acid hydrolysis, compound (**1**) formed a less polar substance identical with component (**2**). Consequently, compound (**2**) was (+)-syringaresinol 4′-β-*D*-glucopyranoside, this conclusion being in harmony with the NMR spectra (Tables 1 and 2). This is the first time that a substance having the structure of component (**2**) has been isolated from plant raw material.

The epimer of compound (**1**), (−)-syringaresinol 4′,4″-di-β-*D*-glucopyranoside, which was called eleutheroside E, has been isolated previously from *Acanthopanax senticosus* [5]. In addition, eleutheroside E and (−)syringaresinol 4′-β-*D*-glucopyranoside have been isolated from *Viscum album [6]*.

After the acid hydrolysis of component (**3**), glucose was detected in the solution. The treatment of glucoside (**3**) with acetic anhydride in pyridine gave the tetraacetate (**4**). A comparison of the physicochemical constants of substances (**3**) and (**4**) with those for a glucoside from *Ferula loscosii* and its acetate [7] and also an analysis of the spectral characteristics of compound (**3**) enabled it to be identified as 2-methylbut-3-en-2-yl β-*D*-glucopyranoside.

EXPERIMENTAL

General Observations. Thin-layer chromatography was conducted on Silufol plates. For column chromatography we used silica gel with particle sizes of 10-100 μm and 60-100 μm. The following solvent systems were employed: 1) chloroform—methanol (20:1); 2) chloroform—methanol—water (a — 65:10:1; b — 65:15:2; c — 65:22:4); and 3) benzene—methanol (50:1).

IR spectra were taken on a UR-20 instrument in tablets with KBr. Mass spectra were determined on a MKh 1310 instrument at an ionizing voltage of 50-70 V. NMR spectra were obtained on WM-250 and AM-300 instruments (Bruker). The solvents were DMSO and C_5D_5N. 0 — TMS.

Melting points were determined on a Boetius instrument, and optical rotations on a Zeiss polarimeter in a tube 0.5 dm long.

(+)-Syringaresinol 4′,4″-Di-β-*D*-glucopyranoside (1). The individual compound (**1**) (125 mg) was isolated by column chromatography of fractions enriched with this component in system 2b (TLC — in system 2c). The yield was 0.0028% (yields here and below have been calculated on the weight of the freshly gathered plant). $C_{34}H_{46}O_{18}$; mp 262-264°; $[\alpha]_D^{20}$ −16.0 ± 2° (c 0.5; pyridine). IR spectrum (KBr, ν, cm^{-1}): 820, 860, 900, 1240, 1600 (aromatic ring), 3200-3600 (OH). According to the literature [4]: mp 265-266°C $[\alpha]_D^{25}$ −12.1°. Details of the PMR and ^{13}C NMR spectra are given in Tables 1 and 2.

(+)-Syringaresinol 4′-β-*D*-Glucopyranoside (2). Compound (**2**) (80 mg) was obtained by column chromatography in system (**1**). Yield 0.0018%; $C_{28}H_{36}O_{12}$; mp 96-98 °; $[\alpha]_D^{20}$ −24.6 ± 2° (c 0.55; pyridine). IR spectrum (KBr, ν, cm^{-1}): 840, 1230, 1600 (aromatic ring), 3200-3600 (OH). Details of the PMR and ^{13}C NMR spectra are given in Tables 1 and 2.

2-Methylbut-3-en-2-yl β-*D*-Glucopyranoside (3). Column chromatography in system 2a followed by recrystallization from acetone gave 500 mg of glycoside (**3**). Yield 0.11%: $C_{11}H_{20}O_6$; mp 135-136°C (acetone); $[\alpha]_D^{22}$ −21.5 ± 2° (c 1.00; pyridine. According to the literature: [7]: mp 135-136 °, $[\alpha]_D^{20}$ −25°.

PMR spectrum of (**3**) (δ, 0−TMS, C_5D_5N): 1.40 (3H, s, CH_3), 1.48 (3H, s, CH_3), 5.08 (1H, dd, $J_{4a,4b}$ = 1.3 Hz, H-4a), 5.15 (1H, dd, H-4B), 6.18 (1H, dd, $J_{3,4a}$ = 18.0 Hz, $J_{3,4b}$ = 11.0 Hz, H-3), 4.88 (1H, d, $J_{1,2}$ = 7.5 Hz, H-1′), 3.65 (1H, t, $J_{2,3}$ = 7.5 Hz, H-2′). ^{13}C NMR spectrum of 3 (ppm, 0−TMS, C_5D_5N): 26.7, 28.1 ($2CH_3$), 77.8 (C-2), 113.5 (C-4), 145.4 (C-3), 62.9 (C-6′), 71.8 (C-4′), 75.3 (C-2′), 78.1 (C-3′), 78.8 (C-5′), 99.8 (C-1′).

2-Methylbut-3-en-2-yl β-*D*-Glucopyranoside Tetraacetate (4). A solution of 200 mg of compound (**3**) in 4 ml of pyridine was treated with 2 ml of acetic anhydride and the mixture was left in a dark place for 14 h (TLC in system 4). Then it was poured into ice water, and the precipitate was filtered off and dried; after recrystallization 180 mg of the tetraacetate (**4**) was obtained: $C_{19}H_{28}O_{10}$, mp 111-112°C (acetone—hexane), $[\alpha]_D^{24}$ −7.8 ± 2° (c 1.25; chloroform). According to the literature [7]: mp 113-114 °C, $[\alpha]_D^{25}$ −6°.

REFERENCES

1. G. V. Shevchuk, Yu. S. Vollerner, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 672, 678 (1991); G. V. Shevchuk, Yu. S. Vollerner, A. S. Shashkov, M. B. Gorovits, and V. Ya. Chirva, Khim. Prir. Soedin., 801 (1991); G. V. Shevchuk, Yu. S. Vollerner, A. S. Shashkov, M. B. Gorovits, and V. Ya. Chirva, Khim. Prir. Soedin., 218 (1992).
2. P. K. Agrawal and R. S. Thakur, Magn. Reson. Chem., **23**, 389 (1985).
3. E. E. Dickey, J. Org. Chem., **23**, 179 (1958).
4. S. D. Jolad, J. J. Hoffmann, J. R. Cole, M. S. Tempesta, and R. B. Bates, J. Org. Chem., **45**, 1327 (1980).
5. H. Wagner, Y. H. Heur, A. Obermeier, G. Tittel, and S. Bladt, Planta Med., **44**, 193 (1982).
6. H. Wagner, B. Feil, O. Seligmann, and Z. Kalogiera, Planta Med., 102 (1986).
7. M. Pinar and M. Martin-Lomas, Phytochemistry, **16**, 281 (1977).