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FRUCTOSIDES FROM *CYNOMORIUM SONGARICUM*

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Key Word Index—*Cynomorium songaricum*; Cynomoriaceae; *n*-butyl-α-D-fructofuranoside; *n*-butyl-β-D-fructofuranoside.

Abstract—Two new fructofuranosides, *n*-butyl-α- and β-D-fructofuranoside, were isolated from *Cynomorium songaricum*. Their structures were established on the basis of spectroscopic methods including 2D NMR techniques.

INTRODUCTION

Cynomorium songaricum Rupr. grows in the northwest of China and is used in traditional chinese medicine for the treatment of kidney disorders [1]. We report now on the isolation and structure elucidation of two new D-fructofuranosides from the ethyl acetate extract of this plant. The known *n*-butyl-β-D-fructopyranoside [2] was also isolated and identified.

RESULTS AND DISCUSSION

Compound **1** was assigned the molecular formula $C_{10}H_{20}O_6$ on the basis of elemental analysis and EI mass spectrometry. Its IR spectrum exhibited the characteristic absorption of hydroxyl groups (3510–3180 cm^{-1}). Its EI mass spectrum exhibited a molecular ion peak at *m/z* 236. Fragment peaks at *m/z* 163 $[M - OC_4H_9]^+$, 73 $[OC_4H_9]^+$ and 57 $[C_4H_9]^+$, combined with ^1H NMR (δ0.94, *t*, (*J* = 7.3 Hz); 1.43, *m*; 1.55, *m* and 3.25, *m*) and ^{13}CNMR (δ13.9, 19.1, 32.1 and 60.2) data indicated the presence of a *n*-butoxyl moiety. In the ^{13}CNMR spectrum the remaining six carbon signals (δ60.6, 61.4, 77.0, 81.7, 82.5 and 107.3) were similar to those of the sugar moiety of methyl-α-D-fructofuranoside [3, 4]. Consequently, the structure of **1** was established as *n*-butyl-α-D-fructofuranoside, which was confirmed by the 2D ^1H–^1H cosy, ^1H–^{13}C cosy and ^1H–^{13}C COLOC experiments. (See Tables 1 and 2).

Compound **2** was assigned the molecular formula $C_{10}H_{20}O_6$ on the basis of elemental analysis and EI mass spectrometry. Its IR spectrum showed the characteristic absorption of hydroxyl groups (3510–3160 cm^{-1}). The ^1H and ^{13}CNMR spectral data (see Tables 1 and 2) indicated that **2** was an *n*-butyl six carbon sacchroside also. The ^{13}C NMR spectral data of the sugar moiety of **2** was similar to those of methyl-β-D-fructofuranoside [3, 4], and **2** was thus assigned as *n*-butyl-β-D-fructofuranoside. In the 2D NOESY experiment the cross-peak between H_2-1 and H_2-6, further confirmed a β configuration for **2**.

EXPERIMENTAL

^1H (400 MHz) and ^{13}C NMR (100 MHz): DMSO with TMS as int. standard; IR: KBr; MS: direct inlet, 20 ev; CC: silica gel (160–200 and 200–300 mesh).

Plant material. Cynomorium songaricum was collected in Jiuquan Gansu, China in April 1992 and identified by Prof. Zhao Runeng (Pharmacology Department of Lanzhou Medical College). The voucher specimen (No. 90894) is deposited at the Herbarium in the Department of Pharmacy, Lanzhou Medical College.

Extraction and isolation. Air-dried powdered whole plants of *C. songaricum* (3 kg) were extracted with EtOAc, the extract was concd. and the residue chromatographed on a silica gel column eluted with a gradient of $CHCl_3$ and MeOH. The fraction eluted with $CHCl_3$–MeOH (4:1) was rechromatographed on a silica gel column several times, eluting with $CHCl_3$–MeOH (4:1) to yield **1** (26 mg), **2** (28 mg) and **3** (60 mg).

n-*Butyl-α-D-fructofuranoside* (**1**). Amorphous powder, $[\alpha]_D$ + 96° (MeOH). Analyt: Found: C, 50.85; H, 8.51. $C_{10}H_{20}O_6$ requires: C, 50.74; H, 8.43. IR ν_{max}^{KBr} cm^{-1}: 3510–3180, 2954, 1370, 1120, 1050, 911, 890, 863, 779, 658; EIMS *m/z* (rel. int.): 236 $[M]^+$ (5), 205 (74), 163 (57), 149 (78), 145 (95), 127 (36), 103 (67), 77 (100), 73 (52), 57 (58); ^1H and ^{13}CNMR: see Tables 1 and 2.

n-*Butyl-β-D-fructofuranoside* (**2**). Amorphous powder, $[\alpha]_D$ − 28° (MeOH). Analyt: Found: C, 50.83; H, 8.49, $C_{10}H_{20}O_6$ requires: C, 50.74; H, 8.43. IR ν_{max}^{KBr} cm^{-1}: 3515–3180, 2957, 1369, 1119, 1051, 913, 888, 865, 780, 661; EIMS *m/z* (rel. int.): 236 $[M]^+$ (6), 205 (37), 163 (39),

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Table 1. ^{1}H NMR spectral data of compounds **1–3** (400 MHz, DMSO)

H	**1**	^{1}H–^{1}H COSY correlated with H	**2**	^{1}H–^{1}H COSY correlated with H	**3**	^{1}H–^{1}H COSY correlated with H
n-Butoxyl						
1	3.25 *m*	1,2	3.24 *m*	1,2	3.43 *m*	1,2
2	1.55 *m*	1,2,3	1.54 *m*	1,2,3	1.49 *m*	1,2,3
3	1.45 *m*	2,3,4	1.45 *m*	2,3,4	1.33 *m*	2,3,4
4	0.94 *t* (7.4)	3,4	0.92 *t* (7.4)	3,4	0.86 *t* (7.3)	3,4
Sugar moiety						
1′	3.42 / 3.53 *d* (11.5)	1′	3.38 / 3.44 *d* (11.8)	1′	3.62 / 3.67 *d* (11.3)	1′
3′	3.92 *d* (10.0)	4′	3.90 *d* (10.0)	4′	3.84 *d* (10.0)	4′
4′	3.72 *dd* (3.4; 10.0)	3′,5′	3.47 *dd* (3.5; 10.0)	3′,5′	3.71 *dd* (1.8; 10.0)	3′,5′
5′	3.76 *m*	4′,6′	3.52 *m*	4′,6′	3.77 *m*	4′,6′
6′	3.34 / 3.54 *dd* (2.0; 10.8)	5′,6′	3.33 / 3.52 *dd* (2.0; 10.7)	5′,6′	3.58 / 3.70 *dd* (1.8; 10.4)	5′,6′

Table 2. ^{13}C NMR spectral data of compounds **1–3** (100 MHz, DMSO)

C	**1**	DEPT	^{13}C–^{1}H COLOC correlated with H	**2**	DEPT	^{13}C–^{1}H COLOC correlated with H	**3**	DEPT	^{13}C–^{1}H COLOC correlated with H
n-Butoxyl									
1	60.2	CH_2		59.5	CH_2		59.5	CH_2	
2	32.1	CH_2		32.2	CH_2		31.9	CH_2	
3	19.1	CH_2		19.0	CH_2		19.0	CH_2	
4	13.9	CH_3		14.0	CH_3		13.8	CH_3	
Sugar moiety									
1′	60.6	CH_2	3′	62.4	CH_2		62.4	CH_2	
2′	107.3	C	1,4′,5′	104.1	C	1,4′,5′	100.0	C	1,4′,6′
3′	81.7	CH	1′,5′	76.9	CH	1′,5′	69.1	CH	1′,5′
4′	77.0	CH	5′,6′	75.8	CH	5′,6′	69.7	CH	3′,6′
5′	82.5	CH	3′,6′	82.1	CH	3′,6′	69.3	CH	3′,6′
6′	61.4	CH_2	4′,5′	63.8	CH_2	4′,5′	63.8	CH_2	4′,5′

149 (48), 145 (32), 127 (38), 103 (66), 77 (78), 73 (100), 57 (80); ^{1}H and ^{13}C NMR: see Tables 1 and 2.

n-*Butyl*-β-D-*fructopyranoside* (**3**). Needles, mp. 150–152°, $[\alpha]_D$ − 135° (MeOH). Analyt: Found: C, 50.78; H, 8.47, $C_{10}H_{20}O_6$ requires: C, 50.74; H, 8.43; IR ν_{max}^{KBr} cm^{-1}: 3520–3120, 2950, 1401, 1118, 1062, 912, 890, 864, 780, 649; EIMS *m/z* (rel. int.): 236 $[M]^+$ (9), 205 (45), 163 (20), 149 (63), 145 (34), 127 (24), 103 (62), 77 (56), 73 (100), 57 (80); ^{1}H and ^{13}C NMR: see Tables 1 and 2.

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