Chinese Chemical Letters Vol. 15, No. 4, pp 425-427, 2004
http://www.imm.ac.cn/journal/ccl.html

Two New Diterpene Acetylxylosides from *Aster veitchianus*

Er Wei LI, Kun GAO*, Zhong Jian JIA*

College of Chemistry and Chemical Engineering, National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000

Abstract: Two new acetylxylosides, *ent*-manool-13-*O*-*β*-D-2'-acetylxylopyranoside (**1**) and *ent*-manool-13-*O*-*β*-D-2', 4'-diacetylxylopyranoside (**2**) were isolated from *Aster veitchianus.* Their structures were elucidated by spectroscopic methods.

Keywords: *Aster veitchianus,* Compositae, diterpene, xylosides.

The chemical constituents for *Aster veitchianus* Hutch. *et* Drumm. have not yet been reported so far. In this paper, two new labdane acetylxylosides, ent-manool-13-O-β-D-2'-acetylxylopyranoside (**1**) and ent-manool-13-O-β-D-2', 4'-diacetylxylopyranoside (**2**) were isolated from the whole plants of *Aster veitchianus*. Their structures were deduced by spectroscopic methods.

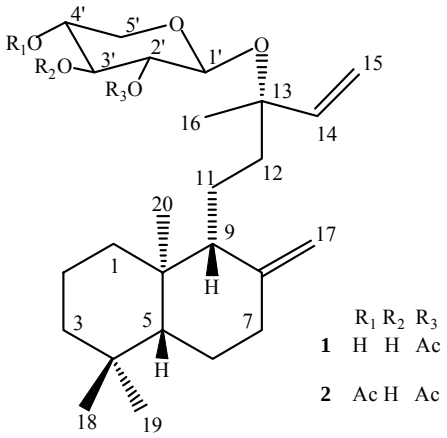
Compound **1,** viscous syrup, $[\alpha]_D^{20}$ -9.0 (c 12.1, $CHCl_3$). HRESI-MS showed $[M+NH_4]^+$ at *m/z* 482.3479 (calcd. for $[C_{27}H_{44}O_6 + NH_4]$ 482.3476), indicating a molecular formula of $C_{27}H_{44}O_6$, which was supported by ^{13}C-NMR and DEPT spectral data (**Table 1**). Meanwhile in the low mass region of MS spectrum a peak at *m/z* 273 was corresponded to the loss of an acetyl pentose ($C_7H_{11}O_6$). The ^{13}C-NMR signals at δ 96.12, 73.34, 74.62, 69.89, 64.55 were very similar to those of the D-xylose moiety of the known diterpene xyloside[1,2]. Furthermore, the signals at δ_C 170.43, 21.61, δ_H 2.10 indicated one of the hydroxyls of D-xylose moiety was acetylated. In ^{1}H-NMR four methyl groups appeared at δ 0.65, 0.79, 0.86 and 1.30 (s, each 3 H), characterisitic methylene signals appeared at δ 4.49, 4.78 (brs, each 1 H) and a vinilic group appeared at δ 5.18, 5.25 and δ 5.72 (dd, each 1 H), indicating that **1** was *ent*-manool with a acetyl D-xylose. The ^{1}H-^{1}H COSY spectrum of **1** showed the correlations of H-5a' (3.19, dd, 1 H) / H-5b' (3.93, dd, 1 H) and H-4' (3.65, m, 1 H); H-3' (3.48, t, 1 H) / H-4' (3.65, m, 1 H) and H-2' (4.70, dd, 1 H); H-2' (4.70, dd, 1 H) / H-1' (4.47, d, 1 H). Compared with the known diterpene xyloside[1], the chemical shift of the H-2' was downfield from δ 3.34 to δ 4.70 and in the HMBC experiment there was the cross peak of δ_C 170.43 / $\delta_{H\text{-}2'}$ 4.70, which indicated the acetyl group located at C-2'. Thus, compound **1** was determined as *ent*-manool-13-*O*-*β*-D-2'-acetylxylopyranoside. The structure of **1** was confirmed by the ^{1}H- and ^{13}C-NMR spectral data, and the HMQC and HMBC experiments.

* E-mail: miaozm@lzu.edu.cn, jiazj@lzu.edu.cn

Table 1 ^{1}H-NMR (400 MHz), ^{13}C-NMR (100 MHz) and DEPT data of compounds **1** and **2** ($CDCl_3$, δ ppm)

H	**1**	**2**	C	**1**	**2**	DEPT
1	1.67~1.74 m	1.67~1.79 m	1	38.90	38.94	CH_2
2	1.36~1.54 m	1.45~1.58 m	2	19.27	19.31	CH_2
3	1.17~1.31 m	1.24~1.36 m	3	42.05	42.08	CH_2
-			4	33.45	33.50	C
5	1.00~1.08 m	1.01~1.08 m	5	55.40	55.45	CH
6	1.17~1.31 m	1.24~1.36 m	6	24.29	24.34	CH_2
7α	2.35 dt (9.6, 3.2)	2.36 dt (9.6, 3.2)	7	38.20	38.23	CH_2
7β	1.93 dt (9.6, 3.2)	1.94 dt (9.6, 3.2)				
-			8	148.21	148.37	C
9	1.36~1.54 m	1.45~1.58 m	9	57.07	57.15	CH
-			10	39.68	39.75	C
11	1.00~1.08 m	1.01~1.08 m	11	17.40	17.44	CH_2
12	1.67~1.74 m	1.67~1.79 m	12	41.04	40.91	CH_2
-			13	80.84	81.31	C
14	5.72 dd (10.5, 17.4)	5.75 dd (10.8, 17.4)	14	141.71	141.50	CH
15a	5.18 dd (1, 17.4)	5.20 dd (1, 17.4)	15	116.02	116.24	CH_2
15b	5.25 dd (1, 10.5)	5.26 dd (1, 10.8)				
16	1.30 s	1.34 s	16	22.88	22.45	CH_3
17a	4.49 br s	4.46 br s	17	106.54	106.44	CH_2
17b	4.78 br s	4.76 br s				
18	0.86 s	0.86 s	18	33.51	33.55	CH_3
19	0.79 s	0.79 s	19	20.98	21.65	CH_3
20	0.65 s	0.66 s	20	14.36	14.41	CH_3
Xyl			Xyl			
1′	4.47 d (5.4)	4.70 d (5.2)	1′	96.12	94.79	CH
2′	4.70 dd (5.4, 8.1)	4.72 dd (6.8, 5.2)	2′	73.34	71.90	CH
3′	3.48 t (8.1)	3.77 br t (6.8)	3′	74.62	69.95	CH
4′	3.65 m	4.81 m	4′	69.89	70.94	CH
5a′	3.19 dd (6.4, 11.7)	3.40 dd (6.4, 12.4)	5′	64.55	60.20	CH_2
5b′	3.93 dd (4.8, 11.7)	4.15 dd (4.4, 12.4)				
Ac			Ac			
			1′	170.43	170.10	C
					170.40	C
2′	2.10 s	2.10 s	2′	21.61	20.91	CH_3
		2.11 s			20.91	CH_3

Compound **2**, viscous syrup, $[\alpha]_D^{20}$ -9.5 (c 5.8, $CHCl_3$). HRESI-MS showed $[M+NH_4]^+$ at *m/z* 524.3584 (calcd. for $[C_{29}H_{46}O_7 + NH_4]$ 524.3582), indicating a molecular formula of $C_{29}H_{46}O_7$, which was confirmed by its ^{13}C-NMR and DEPT spectra data (**Table 1**), and a fragment peak at *m/z* 273, corresponding to the loss of a diacetyl pentose ($C_9H_{13}O_7$) unit. The ^{1}H-NMR spectral data of **2** were very similar to those of **1** (**Table 1**), but the chemical shift of the H-4' was downfield shift from δ 3.65 in **1** to δ 4.81 in **2** and there were cross peaks of δ_C 170.10 / $\delta_{H\text{-}2'}$ 4.72 and δ_C 170.40 / $\delta_{H\text{-}4'}$ 4.81 in the HMBC experiment, which indicated that there were two acetyl groups in **2** and located at C-2' and C-4' respectively. Therefore, compound **2** was *ent*-manool-13-*O*-*β*-D-2', 4'-diacetylxylopyranoside. The result was further confirmed by the analysis of the ^{1}H-^{1}H COSY, HMQC spectra of **2**.



Acknowledgments

This work was supported by the NNSFC (No. 20021001 QT Program and No.29972017).

References

1. A. Urzu, E. Tojo, J. Soto, *Phytochemistry*, **1995**, *38*(2), 555.
2. A. Urzua, L. Mendoza, *Phytochemistry*, **1995**, *39*(6), 1489.

Received 17 April, 2003