Chinese Chemical Letters Vol. 16, No. 4, pp 491-493, 2005
http://www.imm.ac.cn/journal/ccl.html

Two New Eudesmanoildes from *Sonchus transcaspicus*

Yi Feng HAN, Xin LI, Kun GAO*, Zhong Jian JIA*

State Key Laboratory of Applied Organic Chemistry, Institute of Organic Chemistry,
Lanzhou University, Lanzhou 730000

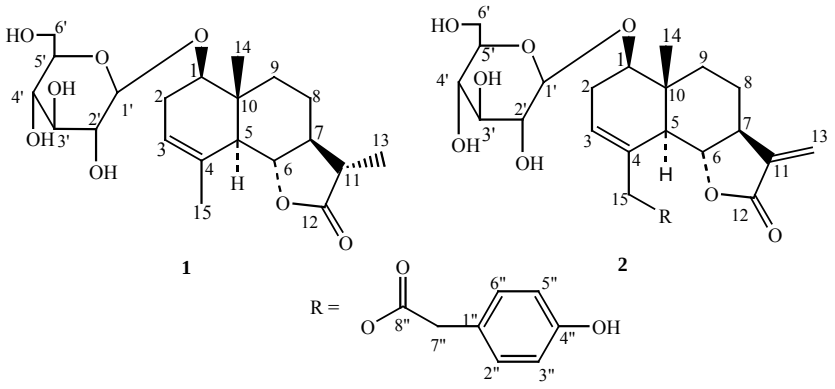
Abstract: Two new sesquiterpene lactone glycosides were isolated from the whole plant of *Sonchus transcaspicus*. Their structures were elucidated as 1β-*O*-β-D-glucopyranosy-5α, 6β H-eudesma-3-en-12, 6α-olide and 1β-*O*-β-D-glucopyranosy-15-*O*-(*p*-hydroxylphenylacetate)-5α, 6β H-eudesma-3, 11(13)-dien-12, 6α-olide by spectral methods (HRMS, 1D and 2D NMR).

Keywords: *Sonchus transcaspicus*, Compositae, eudesmanolide, sesquiterpene lactone glycosides.

Most plants of the *Sonchus* species have long been used as folk medicine in China, because they are efficacious for the treatment of fever, inflammation, stasis, *etc*, apart from functions such as detoxication, mobilization of blood circulation[1]. The chemical constituents of the *Sonchus transcaspicus* were not reported until now. Here we report the structural elucidation of two new sesqiuterpene lactone glycosides.

Compound **1**, colorless gum, $[\alpha]_D^{20}$ +9.0 (*c* 0.4, Me_2CO). HRMS of **1** revealed $[M+Na]^+$ at *m/z* 435.1995, corresponding to the molecular formula $C_{21}H_{32}O_8$ (calcd 435.1989). In its NMR spectra (**Table 1**), typical signals for a β-D-glucopyranoside were readily recognized, which was confirmed by PC after acid hydrolysis of **1** [*Rf* =0.70, EtOAc-Pyridine-H_2O (2:1:5); **1** (5 mg) in aqueous H_2SO_4 (2 mol/L, 3 mL) and toluene (3

Figure 1 The structures of compounds **1** and **2**



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

mL) was gently heated under reflux for 3h]. The ^{1}H and ^{13}C NMR spectra of **1** indicated the presence of one >C=CH- group, two >CH(-O-)- units, one CH_3-CH< unit and an ester carbonyl group. Further ^{1}H-^{1}H COSY experiment revealed two partial structures of compound **1**: -CH(-O-)-CH_2-CH= and -CH_2-CH_2-CH-CH(-O-)-CH<. The C-C interconnectivity of all the fragments was established through cross peaks in HMBC experiment (see **Figure 2**). The remaining signals of the aglycone were similar to those of the known eudesmanoilde, 11α, 13-dihydrosantamarin[2]. The attachment of glucose to the hydroxyl at C-1 is deduced from the long range coupling between H-1' and C-1 in the HMBC spectrum. The large coupling constants of H-1 with H-2 ($J_{1\alpha,\,2\beta}$ = 9.6 Hz), H-6 with H-5 ($J_{6\beta,\,5\alpha}$ = 11.1 Hz) and H-6 with H-7 ($J_{6\beta,\,7\alpha}$ = 11.1 Hz) showed that the H-1 was α-orientation and the lactone group at C-6 and C-7 was *trans*-fused. The signal at δ_C 12.5 (C-13) in the ^{13}C NMR spectrum (**Table 1**) was a typical value in eudesmanolides with α-Me groups at C-11[3], which had been further confirmed by the cross peaks of H-13 with H-7α and H-9α in the NOESY spectrum. The structure of the eudesmanoilde glucoside was thus assigned to be **1**.

Compound **2,** yellow gum, $[\alpha]_D^{20}$ +81.0 (*c* 0.5, MeOH). The FABMS displayed a quasi-molecular ion peak at *m/z* 583 $[M+Na]^+$, 567 $[M+Li]^+$, and a prominent fragment ion peak at *m/z* 421 $[M+Na-162]^+$ due to the loss of sugar moiety. In combination with the NMR spectra (**Table 1**), the molecular formula of **2** was determined to be $C_{29}H_{36}O_{11}$. Its IR spectrum revealed the absorptions of hydroxyl group (3410.5 cm^{-1}), α-methylene-γ-lactone group (1757.6, 1615.6 cm^{-1}) and a benzyl group (1600.1, 1517.1, 1449.2 cm^{-1}). The ^{13}C and DEPT NMR spectra of **2** clearly exhibited 29 carbon signals (1×CH_3, 7×CH_2, 14×CH, 5×C, 2×CO). The ^{1}H and ^{13}C NMR of **2** indicated the presence of *p*-hydroxylphenylacetate moiety[4]. The remaining partial NMR signals of **2** were similar to those of **1** except that the methyl γ-lactone group (δ_H 2.43dq, δ_C 39.2, CH; δ_C 179.6, δ_H 1.06d, δ_C 12.5, CH_3) in **1** was replaced by methylene-γ-lactone group (δ_C 139.5, C; δ_C 170.6, δ_H 5.88, 5.45, brs, δ_C 117.4, CH_2). Its HMBC spectrum show the cross-peaks from H-15 (δ_H 4.42, dd) and H-7" (δ_H 3.46, brs) to the ester carbon (δ_C 171.4), which indicated that *p*-hydroxylphenylacetate was located at the C-15. So the structure of **2** was identified as 1β-*O*-β-D-glucopyranosy-15-*O*-(*p*-hydroxylphenyl-acetate)-5α, 6βH-eudesma -3, 11(13)-dien-12, 6α-olide.

Figure 2 The important HMBC (H to C) correlations of **1** and **2**

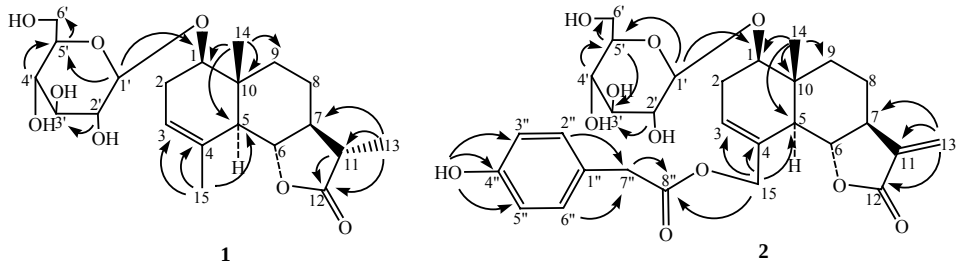


Table 1 ^{1}H (300MHz), ^{13}C NMR (75MHz) and DEPT data of **1** and **2** (DMSO, TMS, δ ppm)

NO	δ_H (α/β, *J* in Hz)	δ_C (DEPT)	δ_H (α/β, *J* in Hz)	δ_C (DEPT)
	1		**2**	
1	3.67 (dd, 6.3, 9.6)	78.8 (CH)	3.69 (dd, 6.6, 9.3)	78.8 (CH)
2	2.38 (dd, 6.3, 17.5)/1.91 (dd, 9.6, 17.5)	29.2 (CH_2)	2.49 (dd, 6.6, 17.5,)/1.90 (dd, 9.3, 17.5)	29.6 (CH_2)
3	5.34 (brs)	121.5 (CH)	5.67 (brs)	127.9 (CH)
4		133.3 (C)		131.9 (C)
5	2.21 (d, 11.1)	50.3 (CH)	2.40 (d, 11.4)	49.2 (CH)
6	4.05 (t, 11.1)	80.8 (CH)	3.46 (t, 11.4)	80.7 (CH)
7	1.52 (dddd, 11.1, 4, 13, 7.5)	53.0 (CH)	2.40 (dddd, 11.4, 4, 13, 2.7)	50.3 (CH)
8	1.55 (ddd, 4, 13, 3)/1.48 (dd, 4, 13)	22.3 (CH_2)	1.90(ddd, 4, 13, 3)/1.36 (dd, 4, 13)	21.2 (CH_2)
9	1.22 (dd, 4, 13)/1.91 (ddd, 4, 13, 3)	34.5 (CH_2)	1.90 (dd, 4, 13)/1.36(ddd, 4, 13, 3)	34.5 (CH_2)
10		40.1 (C)		40.3 (C)
11	2.43 (dq, 7.5, 6.6)	39.2 (CH)		139.5 (C)
12		179.6 (C)		170.6 (C)
13	1.06 (d, 6.6)	12.5 (CH_3)	5.88, 5.45 (brs)	117.4 (CH_2)
14	0.84 (s)	12.2 (CH_3)	0.68 (s)	12.4 (CH_3)
15	1.71 (s)	23.4 (CH_3)	4.42 (dd, 12.0, 6.3)	67.4 (CH_2)
1'	4.16 (d, 7.8)	100.1 (CH)	4.16 (d, 7.5)	100.5 (CH)
2'	2.89 (dd, 8.2, 7.8)	73.8 (CH)	2.89 (dd, 8.2, 7.5)	74.2 (CH)
3'	3.04 (dd, 8.8, 8.2)	77.2 (CH)	3.05 (dd, 8.8, 8.2)	77.5 (CH)
4'	3.40 (dd, 8.7, 8.8)	70.6 (CH)	3.39 (dd, 8.7, 8.8)	70.9 (CH)
5'	4.35 (ddd, 8.7, 2, 5.7)	77.2 (CH)	4.40 (ddd, 8.7, 2, 5.7)	77.5 (CH)
6'	3.65 (dd, 2, 11.8)/3.40 (dd, 5.7, 11.8)	61.6 (CH_2)	3.67 (dd, 2, 11.8)/3.46 (dd, 5.7, 11.8)	61.9 (CH_2)
1"				125.1 (C)
2"			6.94 (d, 8.1)	131.0 (CH)
3"			6.59 (d, 8.1)	115.8 (CH)
4"				156.7 (C)
5"			6.59 (d, 8.1)	115.8 (CH)
6"			6.94 (d, 8.1)	131.0 (CH)
7"			3.46 (brs)	40.6 (CH_2)
8"				171.4(C)
OH			9.27(brs)	

Acknowledgments

This work was supported by the NNSFC (No. 20372029 and No. 20021001- QT Program).

References

1. Jiangsu New Medical College, *A Dictionary of the Traditional Chinese Medicines*, Shanghai Science and technology Press, Shanghai, **1976**, p.1286.
2. J. F. Sanz, G. Casieuano, J. A. Marco, *Phytochemistry*, **1990**, *29*(2), 541.
3. G. P. Moss, P. S. Pregosin, E. W. Randall, *J. Chem. Soc. Perkin Ⅰ*, **1974**, 1525.
4. T. Miyase, S. Fukushima, *Chem. Pharm. Bull*., **1987**, *35*, 2869.

Received 7 April, 2004