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A New Diterpenoid Glucoside from *Aster smithianus*

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Abstract: A new diterpenoid trisaccharide, smithoside A, was isolated from Aster smithianus. Its structure was identified as pimar-15 (16)-β-en-3β，8β, 11α-triol-3-O-β-D-glucopyranosyl (1→3)-[β-glucopyranosyl (1→2)]-β-D-glucopyranoside on the basis of the spectral and chemical methods.

Keywords: Aster smithianus, diterpenoid glucoside, pimarene, smithoside A.

Plants of the genus Aster are widely distributed in China. Most of them possesses medicinal activities, such as antipyretic, detoxicant, expectorant and remediable cough as Chinese herbal medicines. We investigated the chemical constituents of Aster smithianus naturally distributed in Zhang Xian County of Gansu Province. The present report deals with the structural elucidation of a new pimarene-type diterpene trisaccharide 1, isolated from the n-butanol extract of A. smithianus (Compositae).

Smithoside A (**1**), white amorphous powder; m. p. 194 -196°C, $[\alpha]_D^{20}$-28.7 (c 1.0, pyridine). Its IR spectrum showed the absorptions of hydroxyl groups (3374 cm^{-1}), a double bond (1632 cm^{-1}), -CMe2 group (1380 cm-1) and C-O-C bonds (1077 and 1037 cm^{-1}). Its molecular formula was determined as C38H64O18, from the quasi-molecular ion peak at m/z 807 [M-H]- in its negative FAB-MS spectrum, and from 1H and 13C NMR spectral data. Acid hydrolysis of **1** afforded D-glucose. The 1H NMR spectrum of **1** clearly displayed singlets for four methyl groups at δ 1.00, 1.07, 1.17 and 1.59 (s, each 3H), respectively, an ABX pattern for olefinic protons at δ 6.47 (dd, 1H, 10.9, 17,7 Hz), 5.08 (br, 1H, 17.9 Hz) and 4.87 (br, 1H, 11.1 Hz), and three anomeric proton signals at δ 4.92 (d, 1H, 7.6 Hz), 5.39 (d, 1H, 7.7 Hz) and 5.28 (d, 1H, 7.7 Hz), respectively. HMQC showed the corresponding carbon signals at δ 31.6, 17.4, 28.9, 16.1 (4 × Me), 149.2 (CH), 109.1 (CH2), 99.8 (CH), 104.6 (CH) and 104.5 (CH). The above spectral data revealed that compound **1** was a pimarene or isopimarene-type diterpene glucoside1-3. Besides three glucopyranosyl signals, the 13C NMR spectrum of **1** exhibited two carbon signals at δ 73.8 (C) and 66.4 (CH), each of them was attached to the hydroxyl group, and the signal of oxygenated carbon was at δ 83.5 (CH). The assignments of each signal in the

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NMR spectra based on 1H-1H COSY, HMQC and HMBC experiments are shown in **Table 1**. The cross peaks (H-7/C-8, H-9/C-8, H-9/C-11, H-11/C-9, H-3/C-18, 19 and C-3/H-1, 18, 19) in HMBC spectrum showed that two hydroxy groups were located at C-8 and C-11, and that the oxygenated carbon occurred at C-3. If the three rings of pimarene or isopimarene-type diterpenes are in trans form sterochemistry, the methyl at C-20 and the hydroxyl at C-8 were both in β form and H-5 and H-9 both in α form1, 4. Values of J3,2 (11.4 Hz) and J9α,11 (9.9 Hz) suggested α for H-3 and β for H-11. The NOE correlated peaks H-5/H-3, 9 and H-11/H-20 in NOESY spectrum confirmed the above deductions. By comparison of 13C NMR spectral data from C-13 to C-17 of **1** with those of isopimar-15-en-3β， 8β, 19-triol and pimar-15-en-8β, 19-diol2, 5, 6, it was found that 13C NMR spectral data of **1** from C-13 to C-17 paralleled to those of the latter. The correlation peaks H-11/H-15 and H-11/H-16 in NOESY spectrum further demonstrated that the –CH=CH2 group at C-13 would be axial, *i.e.* β.

The cross peaks H-1'/C-3, H-3/C-1', H-1''/C-2', H-2'/C-1'' and H-1'''/C-3' in the HMBC spectrum, and H-3/1', H-1''/H-2' and H-1'''/H-3' in NOESY spectrum, were readily observed. These data indicated that the three glucose units in **1** must be attached to C-3 and the sugar sequence should be two terminal glucoses attached to C-3' and C-2' of the inner glucose, respectively. The chemical shift of C-3 in **1** offer glycosylation downshifted by 5.15 ppm, comparing with that of pimarene-type diterpene. These data were consistent with the above result6. The acetylation of **1** afforded undeacetate (**1a**). The ion peaks at m/z 645 [M-Glc-H]- in the negative FABMS for 1 and at m/z 331 [Glc (AcO)4 + 1]+ in EIMS for acetate (**1a**) of **1** showed that **1** possesses the sugar linkage as in **Figure 1**. The β-configuration of three glucopyranosyl groups was determined on the basis of J1, 2 values (7.6 and 7.7 Hz). Thus smithoside A (**1**) was identified as pimar-15(16)-β-en-3β, 8β, 11α-triol-3-O-β-D-glucopyranosyl(1→3)-[β-glucopyranosyl(1→2)] -β-D-glucopyranoside (**Figure 1**).

Figure 1 The structure of compound **1** and its NOSEY correlations

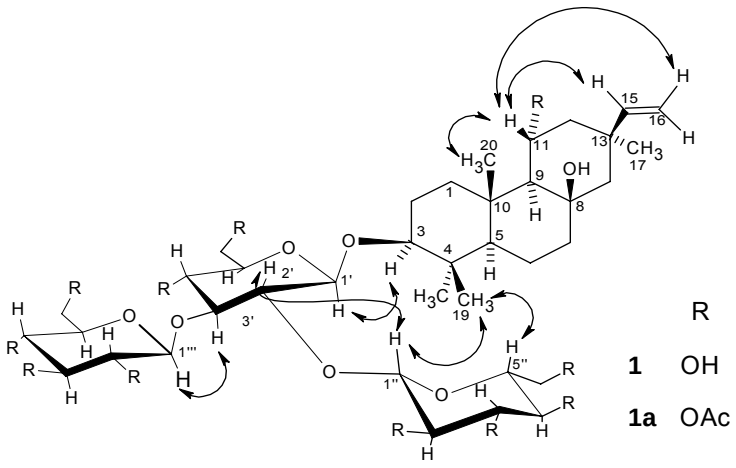

Table 1 NMR spectra data of compound 1 in pyridine-d5 (400 MHz, δ ppm, TMS)

C/ H	δC	δH	C / H	δC	δH
1	40.4	3.27 br (13.0)	18	28.9	1.17 s
		1.23 dd (9.9, 4.9)	19	17.4	1.07 s
2	23.0	2.00 m (11.3)	20	16.1	1.59 s
		2.06 m (13.2, 4.7)	Glc-1'	99.8	4.92 d (7.6)
3	83.5	3.68 dd (11.5, 4.9)	2'	81.1	4.36 dd (7.7, 8.1)
4	39.0		3'	87.3	4.24 dd (8.4, 8.9)
5	56.7	0.83 br (11.7)	4’	70.1	4.02 dd (8,.7, 9.3)
6	17.8	1.89 br (12.3)	5'	77.5	3.76 dd (9.4, 5.7)
		1.26 m	6'	62.6	4.42 d (11.0)
7	43.3	1.44 br (11,2)	6'		4.23 m
		1.82 br (13.3)	1"	104.6	5.39 d (7.7)
8	73.8		2"	76.4	4.11 dd (8.4, 7.7)
9	61.9	0.98 d (9.9)	3"	77.7	4.21 m
10	39.3		4"	71.4	4.28 dd (8.9, 8.4)
11	66.4	4.74 m (9.9)	5"	78.4	3.92 m
12	49.6	2.44 d (11.8)	6"	62.4	4.50 d (11.7)
		1.72 d (11.2)	6"		4.24 m
13	37.2		1"'	104.5	5.28 d (7.7)
14	54.9	1.68 d (13.9)	2"'	75.0	3.96 dd (7.7, 8.3)
		1.37 d (13.6)	3"'	78.3	4.13 dd (8.5, 9.2)
15	149.2	6.47 dd (10.9, 17.7)	4"'	71.4	4.15 dd (8.4, 9.1)
16	109.1	5.08 br (17.9)	5"'	78.3	4.00 m (8.3)
		4.87 br (11.1)	6"'	62.2	4.51 d (11.3)
17	31.6	1.00 s	6"'		4.42 d (11.0)

* values in parentheses are coupling constants in Hz.

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