Indian Journal of Chemistry
Vol.36B, September 1997, pp.840 - 841

Triterpenoid glycoside from *Astragalus adsurgens* Pall

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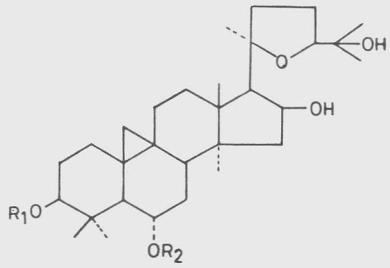
Received 10 March 1997; accepted 19 August 1997

A new triterpenoid glycoside, 3-O-[β-D-glycopyranosyl (1→2)-β- D-xylopyranosyl]-6-O-β- D-xylopyranosyl cycloastragenol **1** has been isolated from *Astragalus adsurgens* Pall along with two known compounds, daucosterol **2** and lupeol **3**. Their structures have been determined on the basis of spectral data (MS, IR, ^{1}HNMR and ^{13}CNMR).

Astragalus adsurgens Pall is a kind of plant peculiar to China, which grows widely in the desert region of northwest. It can be used as windbreak and sandfixation forest, and has a strong adaptability and also is a kind of fine herbage with nutritive value. In the south of Gansu province, its root was also used as a traditional Chinese medicine. In the previous papers, we reported the isolation and the structures of two new triterpenoids[1,2]. In continuation of our studies, we now report the structure elucidation of a new triterpenoid glycoside **1** in addition to two known compounds daucosterol **2** and lupeol **3**.

Compound **1**, $[\alpha]_D^{20}$ +9.5° (c 0.1, MeOH), m.p. 210-12°C, was obtained as colourless crystals and the molecular formula $C_{48}H_{76}O_{18}$ was deduced from elemental analysis and FD-MS at m/z 917 $(M+H)^+$. Its IR spectrum showed the presence of hydroxyl group (3320 cm^{-1}) and cyclopropane (3020 cm^{-1}). In the ^{1}HNMR spectrum, seven methyl signals were observed at δ 0.95-1.89; AB coupling system at 0.38 (1H, d, *J*=3.6 Hz, 19-He) and 0.66 (1H, d, *J*=3.6 Hz, 19-Ha) showed the presence of cyclopropane. Compound **1** on acid hydrolysis gave an aglycone and sugar moiety. The sugar moiety was determined to be D-glucose and D-xylose by TLC and PLC tests. The ^{13}CNMR spectrum of **1** showed forty-six carbon signals,



1a , $R_1 = R_2 = H$
1 , R_1 = glc (1→2)- xyl
R_2 = xyl

thirty carbon signals were accounted for the aglycone moiety, the remaining sixteen carbon signals were attributed to two xylose and one glucose moieties. The aglycone's molecular formula was $C_{30}H_{50}O_5$. Its fragments of EI-MS at m/z 490, 472, 439, 413, 395, 293, 143, 85 indicated its triterpenoid skeleton with tetrahydrofuran side chain. On the basis of spectral data (Table I) and comparison with the data reported in literature, the structure of aglycone was elucidated to be cycloastragenol **1a**[3,4]. FD-MS of **1** exhibited a quasimolecular ion peak at m/z 940 and a molecular ion peak at m/z 917. Thus **1** might be considered to be a triglycoside of cycloastragenol. This was further supported by the fact that the ^{1}HNMR spectrum of the permethylate of **1** showed eleven O-methyl signals at 3.15-3.92.

The comparison of the ^{13}CNMR spectrum of **1** with that of aglycone showed that chemical shifts of 9.1 ppm at C-3 and of 10.2 ppm at C-6 of cycloastragenol were displaced downfield respectively, which may be attributed to the 3-O-D and 6-O-D-xylopyranosyl moieties. The upfield shift of 7.0 ppm at C-1′ of **1** indicated that D-glucose unit was attached to the C-2′ of the 3-O-xylopyranosyl moiety. Another xylose was attached to the C-3 of **1**. This was supported by the data reported in literature[5]. On the basis of the chemical shifts of the anomeric carbon and the coupling constants ($J_{1',2'}$=7.3 Hz, $J_{1''2''}$=7.25 Hz, $J_{1'''2'''}$=7.25 Hz) of the anomeric proton of **1**, the two xylopyranosyl

Table I—^{13}CNMR chemical shifts of **1**, **1a** (δ, ppm)

Carbon	1a	1	Carbon	1a	1
1	32.9	32.8	24	81.6	81.6
2	31.5	31.0	25	71.5	71.5
3	77.8	86.9	26	28.8	28.8
4	42.4	43.3	27	27.5	27.6
5	53.8	53.7	28	21.8	21.8
6	68.2	78.4	29	29.4	29.3
7	38.8	38.7	30	16.6	16.4
8	47.5	47.3	xyl-1′		105.7
9	21.1	21.2	2′		79.6
10	29.9	29.5	3′		78.5
11	26.5	26.4	4′		71.2
12	33.5	33.5	5′		67.0
13	45.5	45.2	glc-1″		105.2
14	46.5	46.3	2″		75.6
15	46.8	46.8	3″		79.2
16	73.2	73.4	4″		71.8
17	58.8	58.3	5″		78.1
18	20.8	20.8	6″		63.1
19	31.2	31.1	xyl-1‴		105.8
20	87.2	87.2	2‴		72.5
21	28.3	28.3	3‴		78.5
22	35.2	35.2	4‴		71.2
23	26.6	26.5	5‴		67.0

moieties and the glycopyranosyl moiety were β-orientated.

Based on the above results, compound **1** was elucidated as 3-O-[β-D-glycopyranosyl(1→2)-β-D-xylopyranosyl]-6-O-β-D-xylopyranosyl cycloastragenol.

Daucosterol **2**, white powder, m.p. 290-93°C; IR(KBr): 3450, 2960, 2950, 2870, 1470, 1380, 1105, 1080, 1020 cm^{-1}; ^{13}CNMR (d_6-pyridine): δ 12.2, 12.3, 19.2, 19.4, 19.6, 20.1, 21.4, 23.6, 24.6, 26.6, 28.7, 29.8, 30.3, 32.3, 34.4, 36.5, 37.0, 37.6, 40.1, 42.6, 46.3, 50.5, 56.4, 57.0, 62.7, 71.6, 75.0, 78.3, 78.6, 102.5, 121.9, 141.4; EI-MS: m/z 414 (M^+, β-sitosteriol); FAB-MS: m/z 576 (M^+).

Lupeol **3**, white crystal, m.p. 210-12°C; IR(KBr): 3340, 3080, 1645, 2941, 2870, 1380 cm^{-1}; EI-MS: m/z 426, 408, 392, 365, 218, 203, 135, 108.

Experimental Section

Melting points were recorded on a Kofter melting point apparatus and were uncorrected. IR spectra were recorded in KBr on a Alpha FT-IR spectrophotometer, ^{1}HNMR and ^{13}CNMR spectra on a Bruker AM-400 instrument and mass spectra on a MAT-44S mass spectrometer.

Isolation. The ethanol extract of the roots of *Astragalus adsurgens* Pall were extracted with MeOH and the solvent was evaporated off to give the MeOH extract. The MeOH extract was dissolved in an *n*-BuOH-H_2O (1:1) and removal of the solvent from the *n*-BuOH phase under reduced pressure yielded the extract (150 g). The extract (50 g) was chromatographed on silica gel and eluted successively with $CHCl_3$-MeOH-H_2O to afford **1** (60 mg), **2** (35 mg), **3** (30 mg).

Compound **1**, FD-MS: m/z 940 $[M+Na+H]^+$, 917 $[M+H]^+$, 916 (M^+); IR(KBr): 3460, 3280, 3030 cm^{-1}; ^{1}HNMR (d_6-pyridine): δ 4.90 (1H, d, *J*=7.3 Hz, 1″-H), 4.36 (1H, d, *J*=7.25 Hz, 1′-H), 4.28 (1H, d, *J*=7.25 Hz, 1‴-H), 0.38, 0.66 (1H each, d, *J*=3.6 Hz, 19-H), 0.95, 1.29, 1.31, 1.34, 1.36, 1.69, 1.89 (3H each, s, 7×CH_3), 4.72 (1H, s, 16α-H), 2.3-2.5 (br, OH).

Per-O-methylation of 1. Compound **1** (9 mg) was methylated by the Hakomori method[6] and the crude product was purified by CC on silica gel with EtOAc-petrol (9:2) to afford 11-O-methyl ether of **1**, m.p. 180-82°C (Found: C, 63.90; H, 9.15. $C_{57}H_{98}O_{18}$ requires C, 63.93; H, 9.16%); IR(KBr): 3030, 2850, 1450, 1070 cm^{-1} (no peak for OH); ^{1}HNMR ($CDCl_3$); δ 0.25, 0.52 (1H each, d, *J*=3.8 Hz, 19-H), 0.95, 0.99, 1.12, 1.16, 1.19, 1.25, 1.30 (3H each, s, 7×CH_3), 3.15-3.90 (3H each, s, 11×OCH_3), 4.92 (1H, d, *J*=7.5 Hz, 1″-H), 4.35 (1H, d, *J*=7 Hz, 1′-H), 4.30 (1H, d, *J*=7 Hz, 1‴-H).

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