A CHEMICAL STUDY OF PLANTS OF THE MONGOLIAN FLORA LARISIDE — A NEW SCOPOLETIN GLYCOSIDE FROM *Salsola laricifolia*

S. Narantuyaa, D. Batsurén,
É. Kh. Batirov, and V. M. Malikov

UDC 547.9:582.89

A new coumarin glycoside lariside — $C_{21}H_{26}O_{13}$, mp 155-156°C (from methanol) — has been isolated from the epigeal part of *Salsola laricifolia* Turcz. et Litw. On the basis of acid hydrolysis and spectral characteristics the structure of lariside has been established as 7-[O-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranosyloxy]-6-methoxy-2H-1-benzopyran-2-one.

We have previously isolated six coumarins, including scopoletin 7-O-β-D-glucopyranoside (scopolin (I)) from the epigeal part of *Salsola laricifolia* Turcz. et Litw [1]. Continuing the investigation, from ethyl acetate and butanol fractions of an ethanolic extract we have isolated a new glycoside with the composition $C_{21}H_{26}O_{13}$, which we have called lariside (II). In the present paper we give a proof of the structure of this glycoside.

The presence in the PMR spectrum of (II) of two one-proton doublets at 6.34 and 7.70 ppm with a spin-spin coupling constant of 9.5 Hz permitted lariside to be assigned to the coumarin derivatives.

The UV spectrum of (II) was characteristic for 6,7-di-O-substituted coumarins and was similar to that of scopolin. Its mobility on TLC and the presence in its PMR spectrum of the signals of the protons of a carbohydrate moiety in the 3.90-5.60 ppm range permitted us to assume the glycosidic nature of lariside.

The acid hydrolysis of (II) led to the formation of scopoletin and of the monosaccharides D-glucose and D-apiose. D-Apiose was identified by paper chromatography with a sample obtained by the hydrolysis of umbelliferone β-D-apiosyl-(1 → 6)-β-D-glucopyranoside, which has been isolated from several species of *Phlojodicarpus* [2]. Information on the structure of the carbohydrate moiety of glycoside II) was obtained as the result of an analysis of the characteristics of the ^{13}C NMR spectra of scopolin, apiin (apigenin 7-O-[O-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside]), and lariside [3, 4]. The spectrum of lariside, unlike the spectrum of scopolin, contains the signals of the carbon atoms of the terminal apiofuranosyl ring at (ppm) 108.4 (C-1"), 77.1 (C-2"), 79.4 (C-3"), 74.0 (C-4"), and 64.5 (C-5"). The signal of the C-1' anomeric carbon atom in the spectrum of scopolin resonates at 99.6 ppm [5]. On passing from scopolin to lariside, the signal of the C-1' carbon undergoes a diamagnetic shift by 1.5 ppm [$\Delta\delta(C\text{-}1')_I$, 99.6 − $\delta(C\text{-}1')_{II}$ 98.1 = 1.5 ppm], while the C-2' resonance signal shifts downfield by 1.9 ppm. Thus, the value of the shifts of the C-1' and C-2' signals is evidence in favor of the attachment of the apiofuranosyl residue to the hydroxyl in the C-2 position of the glucose residue in the molecule of (II) [4, 6].

In the PMR spectrum of lariside taken in deuteropyridine, the anomeric protons of the glucose and apiose residues resonate at 5.60 and 4.78 ppm in the form of a doublet with the SSCC J = 7.5 Hz and a broadened singlet with the half-width $W_{1/2}$ = 3.5 Hz, respectively. Below we give the chemical shifts of the ^{13}C nuclei of scopolin (I) and of lariside (II) (δ, ppm relative to TMS; asterisks mark signals that are superposed). (See display, following page.) This indicates the β configuration of the glycosidic centers of the above-mentioned carbohydrates [7].

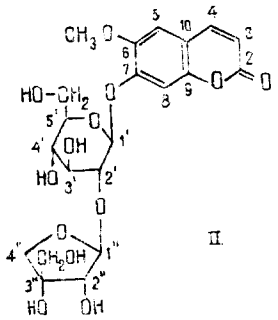
The chemical shifts of the signals of the ^{13}C nuclei of the sugar moiety of lariside agree well with those of apiin, since the two glycosides have similar carbohydrate moieties.

Institute of Chemistry, Academy of Sciences of the Mongolian Peoples' Republic, Ultan-Bator. Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 288-291, May-June, 1986. Original article submitted December 20, 1985.

0009-3130/86/2203-0267$12.50

C-atom	*I*	*II*	C-atom	*I*	*II*
2	161,4	160,6	1^{I}	99,6	98,1
3	113,2	112,4	2^{I}	73,0	74,9
4	144 0	144,3	3^{I}	77,0	77,1*
5	109,7	109,6	4^{I}	69,6	70,0
6	145,9	146,0	5^{I}	76,7	76,1
7	149,9	149,0	6^{I}	60,6	60,7
8	103,0	103,0	1^{II}		108,4
9	148,	149,8	2^{II}		77,1*
10	112,2	113,4	3^{II}		79,4
CH_3O	56, 0	56,1	4^{II}		74,0
			5^{II}		64,5

Thus, the structure of lariside is 7-[O-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranosyloxy]-6-methoxy-2H-1-benzopyran-2-one (II).



II

Glycosides containing D-apiose residues are found fairly frequently in nature. In addition to lariside, the coumarin glycosides diospyroside [3] and umbelliferone β-D-apiofuranosyl(1 → 6)-β-D-glucopyranoside [2, 8], each containing a D-apiose residue, have been found previously.

EXPERIMENTAL

General Remarks. Thin-layer chromatography was performed on Silufol UV-254 plates in the solvent system chloroform–methanol (8:2), and paper chromatography on Leningrad slow chromatographic paper in the solvent system butan-1-ol–pyridine–water (6:4:3). Silica gel L 100/160 (Chemapol, Czechoslovakia) was used for column chromatography. UV spectra were taken on a PS-3T spectrophotometer in methanol, and IR spectra on a UR-20 instrument in paraffin oil. PMR spectra were recorded on a JNM-C-60-HL spectrometer in deuteropyridine (0, HMDS) and ^{13}C NMR spectra on a Bruker WP-200S instrument in DMSO-d_6 with TMS as internal standard.

Isolation of Coumarins. The air-dry comminuted epigeal part of *Salsola laricifolia* (17kg), collected in the fruit-bearing period (South Gobi aimak, Mongolian Peoples' Republic) was extracted with ethanol four times at room temperature. The concentrated extract obtained after the ethanol had been distilled off was diluted with water in a ratio of 1:1 and was extracted successively with hexane, chloroform, ethyl acetate, and butanol. After the solvents had been distilled off, 70.9 g of hexane fraction, 66.6 g of chloroform fraction, 37.5 g of ethyl acetate fraction, and 47.5 g of butanol fraction were obtained. The chloroform faction was chromatographed on a column of silica gel (400 g). On elution with benzene, 0.26 g of fraxidin and 1.5 g of isofraxidin were isolated. Elution with chloroform–methanol yielded the coumarins fraxetin (5.0 g), isofraxidin 7-O-β-D-glucoside (3.0 g), and fraxidin 8-O-β-D-glucoside (0.11 g).

The ethyl acetate and butanol fractions were combined and chromatographed on a column of silica gel (1360 g) using chloroform–methanol systems. At a (9:1) composition of the mixture, 0.12 g of scopoletin 7-O-β-D-glucopyranoside was obtained, and the same mixture in a ratio of (85:15) eluted 0.07 g of lariside.

Lariside (II). $C_{21}H_{26}O_{13}$, mp 155-156°C (from methanol), λ_{max} 229, 250*, 260*, 290, and 340 nm (log ε 3.96, 3.49, 3.38, 3.62, and 3.83); ν_{max} (cm^{-1}): 3210 (OH groups), 1730 (α-pyrone

C=O), 1630, 1590 (arom. C=O) bonds). PMR spectrum (Py-d_5, δ scale, ppm): 3.60 (s, OCH_3) 3.90-4.62 (protons of the sugar moiety); 4.78 (br.s, $W_{1/2}$ = 3.5 Hz, H-1"); 5.60 (d, 7.5 Hz, H-1'); 6.06-6.58 (OH groups); 6.34 (d, 9.5 Hz, H-3); 7.00 (s, H-8); 7.34 (s, H-5); 7.70 (d, 9.5 Hz, H-4).

Acid Hydrolysis of Lariside (II). A solution of 10 mg of glycoside (II) in 3 ml of a 3% solution of hydrochloric acid was heated in the water bath for 4 h. The reaction product was extracted with ethyl acetate. After the ethyl acetate had been washed with water and evaporated to dryness, a compound was obtained with mp 203-204°C (from benzene) which was identical with an authentic sample of scopoletin.

The aqueous solution was neutralized with anion-exchange resin, filtered, and evaporated. D-Glucose and D-apiose were identified in the residue in the paper chromatography in the presence of authentic samples.

SUMMARY

A new glycoside of the coumarin series — lariside — has been isolated from the epigeal part of *Salsola laricifolia*; it has the structure of 7-[O-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranosyloxyl-6-methoxy-2H-1-benzopyran-2-one.

LITERATURE CITED

1. S. Narantuyaa, D. Batsurén, É. Kh. Batirov, and B. M. Malikov, Khim. Prir. Soedin., 243 (1986).
2. D. Gantimur, Coumarins of Plants of the Genus *Phlojodicarpus* [in Russian], Author's abstract of Candidate's dissertation, Irkutsk (1985), p. 17.
3. D. Forgacs, J.-F. Desconclois, J.-L. Pousset, and A. Rabaron, Tetrahedron Lett., No. 48, 4783 (1978).
4. K. R. Markham, B. Ternai, R. Stanley, H. Geiger, and T. J. Mabry, Tetrahedron, 34, 1389 (1978).
5. H. Tsukamoto, S. Hisada, and S. Nishibe, Chem. Pharm. Bull., 33, No. 1, 396 (1985).
6. P. K. Agrawal and P. Rastogi, Heterocycles, 16, No. 12, 2181 (1981).
7. K. Kudo, T. Nohara, T. Komori, T. Kawasaki, H.-R. Schulten, Planta Medica, 40, No. 3, 250 (1980).
8. P. Satyanarayana, P. Subrahmanyam, P. Kasai, and O. Tanaka, Phytochemistry, 24, No. 8, 1862 (1985).