TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XXVI. CYCLOARTANES AND STEROLS OF Astragalus schachirudensis

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In continuation of investigations on cycloartane triterpenoids, we have studied Astragalus schachirudensis Bunge (Leguminosae). The epigeal parts of the plant do not contain the desired substances. The comminuted air-dry roots (3.6 kg) collected in June, 1979 in the environs of the village of Chuli (northwest of the town of Firuza, TurkmSSR) were exhaustively extracted with methanol (50 liters). The methanolic extract was evaporated and, after the residue had been treated by the method described in [1], 70 g of combined triterpenoids and sterols was obtained. More than eight substances of triterpenoid and sterol nature were detected in the total extractive substances by TLC in various solvent systems (they are designated 1-8 in order of increasing polarity).

The purified total material (18 g) was chromatographed on a column of type L silica gel (Czechoslovakia). The column was eluted successively with chloroform and the following solvent systems: 1) chloroform–methanol (15:1); 2) chloroform–methanol–water (70:12:1); 3) chloroform–methanol–water (70:23:4). The identical fractions obtained on elution with chloroform were combined and rechromatographed on a column. The column was washed with the benzene–chloroform–ethyl acetate (5:1:1) system. This led to the isolation of 95 mg of substance (1) (0.01%; the yields here and those below are calculated on the air-dry raw material [sic]), mp 131-132°C (from methanol), $[\alpha]_D^{20}$ −38 ± 2° (c 0.6; chloroform), identified as β-sitosterol [2].

Elution of the column by system 1 yielded substance (2) (40 mg, 0.004%), mp 276-279°C (from methanol), $[\alpha]_D^{24}$ −37 ± 2° (c 1.04; pyridine), identical with β-sitosterol β-D-glucopyranoside [2].

Elution by systems 2 and 3 gave fractions containing the individual substances (3-8). To free them from pigments, substances (3) and (4) were rechromatographed on a column with elution by the ethyl acetate–methanol (15:1) system, and substances (5) and (6) by the ethyl acetate–methanol (5:1) system.

Substance (3) (150 mg, 0.016%), mp 229-230°C (from methanol), $[\alpha]_D^{24}$ +21.2 ± 2° (c 1.04; methanol) was identified as cyclosieversioside A [3, 4].

Substance (4) (500 mg, 0.05%), mp 185-188°C (from methanol), $[\alpha]_D^{24}$ +16.6 ± 2° (c 0.84; methanol) was identified as cyclosieversioside B [4, 5].

Substance (5) (200 mg, 0.02%), mp 253-255°C (from methanol), $[\alpha]_D^{24}$ +20.7 ± 2° (c 1.16; methanol), was identical with cyclosieversioside C [3, 4].

Substance (6) (600 mg, 0.02% [sic]), mp 254-257°C (from methanol), $[\alpha]_D^{24}$ +31.3 ± 2° (c 0.96; methanol), was identified as cyclosieversioside D [4, 5].

Substance (7) (30 mg, 0.003%), mp 216-218°C (from methanol), $[\alpha]_D^{20}$ +24 ± 2° [c 0.8; methanol–chloroform (1:1)], was identical with cyclosieversioside E [4, 6].

Substance (8) (80 mg, 0.008%), mp 284-286°C (from methanol), $[\alpha]_D^{20}$ +38 ± 2° (c 0.5; methanol) was identified as cyclosieversioside F [4, 7].

The identification of all the substances was carried out by direct comparison with authentic samples, and also on the basis of PMR and IR spectra.

LITERATURE CITED

1. M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, M. R. Yagudaev and, N. K. Abubakirov, Khim. Prir. Soedin., 572 (1981).

Institute of the Chemistry of Plant Substances, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 136-137, January-February, 1988. Original article submitted June 23, 1987.

0009-3130/88/2401-0123 $12.50

2. L. J. Swift, J. Am. Chem. Soc., 74, 1099 (1952).
3. A. N. Svechnikova, R. U. Umarova, N. D. Abdullaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 629 (1982).
4. N. K. Abubakirov, M. B. Gorovits, and M. I. Isaev, "Progress of cycloartane chemistry," in: Indo-Soviet Symposium on the Chemistry of Natural Products. Abstracts, Vol. 2 (1986), p. 50.
5. R. U. Umarova, A. N. Svechnikova, N. D. Abdullaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 188 (1984).
6. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 204 (1982).
7. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).

COLONOSIDE B – THE MAIN TRITERPENE GLYCOSIDE OF *Codonopsis lanceolata*

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We have investigated the roots of the plant Codonopsis lanceolata (Sieb. et Zucc.) Benth. et Hook., collected in 1979 in Maritime Territory.

The air-dry comminuted roots were extracted first with hexane and then, with heating, from methanol. The methanolic extract was evaporated to dryness (yield 9.8%). The total glycosidic fraction (TGF) was obtained by chromatographing the methanolic extract on Polikhrom-1. The substances were eluted with a water–ethanol system in which the ethanol concentration was gradually increased to 40% (yield 10.7%). According to TLC on KSK silica gel in the chloroform–ethanol–water (15:15:2) system, the TGF contained four compounds giving a crimson red coloration with sulfuric acid. The substances have been called codonosides A, B, and C [sic] in order of increasing polarity. Codonopside B (I) was present in predominating amount.

Substance (I) was obtained by partition chromatography of the TGF on silica gel, the compound being eluted with water-saturated n-butanol: mp 250-256°C (from aqueous n-butanol); $[\alpha]_D^{20}$ −54.4° (c 0.57; aqueous pyridine). IR spectrum, λ_{max}^{KBr}, cm^{-1}: 1614 (COO^-), 1730 (C=O), 3420 (O–H).

The acid hydrolysis of (I) gave echinocystic acid (II) as the aglycone, its structure being established on the basis of chemical transformations and the physicochemical characteristics of the compounds obtained [1]. In its chromatographic behavior the acid (II) was identical with a sample of echinocystic acid kindly provided by I. A. Saltykova (Leningrad State University).

After the aglycon had been separated off, the hydrolysate was neutralized with barium carbonate, and glucuronic acid, glucose, xylose, arabinose, and rhamnose were detected in it by TLC on silica gel.

Silica gel impregnated with a 0.2 M solution of sodium dihydrogen phosphate was used for the TLC of all the compounds.

LITERATURE CITED

1. N. G. Aladyina (Alad'ina), M. A. Nekhayeva (Nekhaeva), and G. B. Elyakova, in: 3rd International Conf. on the Chemistry and Biotechnology of Biologically Active Natural Products, Sofia, Bulgaria (1985), p. 461.

Far-Eastern State University, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 137-138, January-February, 1988. Original article submitted July 20, 1987.

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