TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XIX. CYCLOARTANE COMPOUNDS AND STEROLS FROM Astragalus pamirensis AND A. pterocephalus

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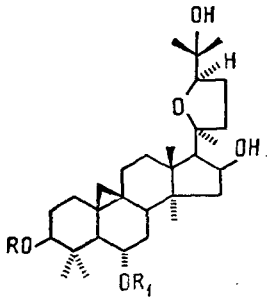
We have continued a study of the methylsteroids of plants of the genus Astragalus (Fabaceae). We have investigated the roots of A. pamirensis Ovcz. et Rassulova, gathered in 1979 in the environs of Lake Kara-Kul' (Eastern Pamir) in the period of the flowering of the plant. The raw material (2.75 kg) was exhaustively extracted with methanol (50 liters). After the solvent had been evaporated off, the concentrated extract was treated with 1 liter of water, and the extractive substances were obtained with ethyl acetate. According to TLC, no cycloartane compounds remained in the aqueous solution. The ethyl acetate extract was evaporated to dryness. The residue (28 g) was chromatographed on a column of silica gel. On elution with the chloroform–methanol (15:1) system, 3 g (0.109%, the yield here and below being calculated on the air-dry raw material) of substance (I) was isolated, with mp 239-241°C (from methanol), $[\alpha]D^{24}$ +50.5 ± 2° (c 1.1; methanol), and this was identified as cyclosiversigenin [1, 2].



I. $R = R_1 = H$
II. $R = \beta$-D-Xylp; $R_1 = H$
III. $R = R_1 = \beta$-D-Xylp
IV. $R = \beta$-D-Xylp; $R_1 = \beta$-D-Glcp

The column was then eluted with the chloroform–methanol–water (70:12:1) system, which gave 1.5 g (0.056%) of a compound (II) of glycosidic nature with mp 263-264°C (from methanol) $[\alpha]D^{24}$ +41.5 ± 2° (c 0.56; methanol). According to GLC, glycoside (II) contained one D-xylose residue. Hydrolysis of the isolated compound with 0.5% methanolic sulfuric acid led to cyclosiversigenin. On the basis of IR and PMR spectrsocopy, and also of a direct comparison in TLC, the substance was identified as cyclosiversigenin 3-O-β-D-xylopyranoside. The monoside (II) had been obtained previously in the hydrolysis of cyclosiversioside F and askendoside D [2, 3]. This is the first time that it has been described as a native glycoside.

The roots (5 kg) of the plant A. pterocephalus Bge., collected in 1983 in Shakhristan (Turkestan range, TadzhSSR), was extracted with ethanol (6 × 16 liters). After evaporation of the solvent, the dry residue (394 g) was then dissolved in 2 liters of ethanol. The precipitate that had deposited was filtered off; it did not contain the desired substances. The mother solution was evaporated to dryness (350 g). Part of the total material so obtained (150 g) was chromatographed on a column of silica gel. Elution was performed with chloroform and then with a chloroform–methanol (15:1) system, giving 0.82 g (0.038% of a substance with mp 131-132°C (from methanol), $[\alpha]D^{20}$ −37.9 ± 2° (c 0.57; chloroform). The compound was identified as β-sitosterol [5].

Continuing the elution of the column with the same solvent system, we isolated 0.103 g (0.0048%) of a product with mp 239-241°C (from methanol), $[\alpha]D^{24}$ +51.0 ± 2° (c 1.20; methanol), which was identified as cyclosiversigenin (1). Further elution of the column with chloroform–methanol–water (70:23:4) system led to the isolation of the following substances:

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0.43 (0.02%) of β-sitosterol β-D-glucopyranoside with mp 276-279°C (from methanol), $[\alpha]_D^{24}$ −36.5 ± 2° (c 1.04, pyridine) [5]; 5 g (0.23%) of cyclosiversioside E (III) with mp 216-218°C (from methanol) $[\alpha]_D^{20}$ +24.5 ± 2° [c 0.81; chloroform–methanol (1:1)] [4, 6]; and 20 g (0.93%) of cyclosiversioside F (IV) with mp 284-286°C (from methanol), $[\alpha]_D^{20}$ +38.1 ± 2° (c 0.57; methanol) [3, 7]. The melting point has been corrected from the values given in [3, 7].

All the compounds were also identified from their PMR and IR spectra and their chromatographic behavior on TLC in comparison with authentic samples.

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DETERMINATION OF CYTISINE IN THE HERBAGE OF Thermopsis alterniflora BY GAS-LIQUID CHROMATOGRAPHY

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Existing methods [1, 2] do not permit the sufficiently rapid and selective determination of the amount of cytisine in various parts of plants of the genus Thermopsis. We have investigated the possibility of using gas-liquid chromatography for the quantitative determination of cytisine in the herbage of Thermopsis alterniflora Regel et. Schmalh.

We used a Chrom-41 chromatograph with nitrogen as the carrier gas in a glass column 1500 mm long packed with Chromaton N super (fraction with a size of 0.16-0.20 mm) impregnated with 3% of the liquid phase OV-17. The temperature of the evaporator and of the flame-ionization detector was 250°C. The working regime of the thermostat was programmed in the interval from 190 to 230°C at a rate of rise of temperature of 2°C/min. Caffeine corresponding to the demands of GF X (State Pharmacopeia, 10th edn.) was selected as the internal standard.

For the quantitative determination of cytosine, the herbage of Thermopsis alterniflora was treated with chloroform in the presence of ammonia for 2 h. An aliquot of the extract was evaporated on the water bath in a current of air, and the dry residue was dissolved in 1 ml of chloroform and 2 ml of an ethanolic solution of the internal standard, 2 μl the solution so obtained being injected into the evaporator of the chromatograph. The amount of cytosine was calculated by the internal-standard method. The calibration graph was linear for ratios of the weights of cytisine and caffeine between 1:3 and 3:1. The sensitivity of the method was determined as 60 μg/ml. The figures obtained were compared with the results obtained by the NTD [Normative Technical Documentation] method. The error of the determination was ±2.5%.

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