standard sample (β-glycyrrhetinic acid).

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STEROID SAPONINS AND SAPOGENINS OF *Allium*.

XIII. TUROSIDE A 6-O-BENZOATE FROM *Allium turcomanicum*

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We have continued the study of the total extractive substances obtained previously [1] from the bulbs of *Allium turcomanicum* Rgl. By chromatographing the extract on a column of SiO_2 [elution with chloroform–methanol (7:1)] we isolated 0.24% (calculated on the air-dry raw material) of a glycoside (I), $C_{57}H_{86}O_{25}$ with mp 242-245°C (methanol–chloroform); $[\alpha]_D^{23}$ −108.7±2° [c 0.92; chloroform–methanol (10:1)]; ν_{max}^{KBr}, cm^{-1}: 3500-3300 (OH); 1720, 1280 (ester group); 1605, 1590, 725 (benzene ring); 990, 930 > 900, 860 (spiroketal chain of the 25S series) [2, 3].

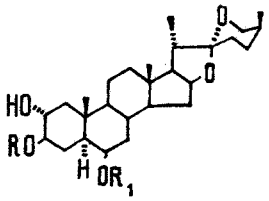
In a hydrolyzate of compound (I) by the GLC method [4, 5] we detected galactose, glucose, and xylose in a ratio of 1:2:1.

The acid hydrolysis of 200 mg of the glycoside (I) with 5% methanolic HCl at the boil for 5 h led to 48 mg of a mixture of genins (II) and (III). They were separated chromatographically on SiO_2. When the column was eluted with the chloroform–methanol (50:1) system, 12 mg of compound (II) was isolated [mp 137-138°C (ether–hexane); $[\alpha]_D^{23}$ −60.8±3° (c 0.67; chloroform)], which was identified as neoapigenin 6-O-benzoate [6]. On continuing elution with chloroform–methanol (20:1) we isolated 18 mg of a genin (III) [mp 266-267°C (methanol); $[\alpha]_D^{23}$ −70.5±3° (c 0.92; chloroform–methanol (10:1))], identified as neoapigenin [7].

Compound (I) (200 mg) was dissolved in 50 ml of 2% KOH solution and the mixture was left at 0°C for 16 h, after which it was poured into water, the methanol was distilled off, and the product was extracted with butanol. This gave 70 mg of the glycoside (IV) which, by its physicochemical constants [mp 281-283°C (methanol), $[\alpha]_D^{23}$ −62.3±3° (c 0.76; chloroform–methanol (10:1))] and by a comparison of IR spectra and R_f values on TLC [SiO_2, chloroform–methanol–water (65:35:8)] was identified as turoside A [1].

The aqueous residue was acidified (HCl) and treated with chloroform. Benzoic acid was found in the extract with the aid of TLC [SiO_2, ethanol–ammonia–water (10:1.4:1.2)].

From an analysis of the PMR spectrum (HMDS, δ, ppm, C_5D_5N) of compound (I) it follows that it contains only one benzoate group, the protons of which appear at 7.94 ppm (2 H, doublet with fine splitting of the protons in the ortho position to the ester group)[8]) and at 7.27 ppm (3 H, multiplet – the remaining protons of the benzoate group, the signal of which



I. R = lycotetraose, $R_1 = C_6H_5CO$;
II. R = H, $R_1 = C_6H_5CO$
III. R = R_1 = H;
IV. R = lycotetraose, R_1 = H;

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is partially masked by the signal of the deuteropyridine).

The facts given show that the aglycone of glycoside (I) is neoapigen 6-O-benzoate, and the carbohydrate moiety is identical with the carbohydrate component of turoside A — lycotetraose [9]. Compound (I) is turoside A 6-O-benzoate.

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CARDENOLIDES OF *Erysimum repandum*

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We have investigated the seeds of *Erysimum repandum* L. grown in the experimental field of the Institute of the Introduction of Plants and of Plant Resources, Sofia. This species of erysimum is widely distributed in Bulgaria [1] and has been identified botanically in the same institute. The presence of cardiac glycosides in it has been reported previously [2-5]. The isolation of erysimin, erysimoside, and cheirotoxin from *Erysimum repandum* and their identification by paper chromatography is also known. In view of the results of our investigations (see below) the presence of cheirotoxin appears disputable. From the seeds of this plant we have isolated two cardiac glycosides and have identified them as periplorhamnoside and glucoperiplorhamnoside [6]. The chemical composition of this plant has been little studied.

Making use of a typical scheme of treating plant material containing cardiac glycosides — namely, comminution, defatting with petroleum ether, extraction with 70% ethanol, purification of the glycosides with lead hydroxide in 40% ethanol and alumina in aqueous solution — we obtained the purified combined glycosides with a biological activity of 0.349±0.006 mg/kg weight of a pigeon (determined by L. Ya. Topchii). We also obtained a fatty oil in an amount of 35% of the weight of the seeds.

On separating the glycosides by adsorption chromatography on alumina (activity grade III) using chloroform—ethanol (98:2-30:7) as eluent we isolated seven cardenolides in the individual crystalline state. Five of them were identified by their physicochemical properties and by direct comparisons with authentic samples, including comparison of their IR spectra, as periplogenin [7, 9], strophanthidin [8, 9], periplorhamnoside [10, 11], glucoperiplorhamnoside [6, 12], and glucostrophalloside [13]. The other two glycosides, provisionally denoted Er 9 and Er 10, are still being studied. Their properties: Er 9, mp 250-254/278-280°C; $[\alpha]_D^{21}$ −12.4±4° (c 0.25; methanol); Er 10, mp 267-270°C; α_D^{20} −5.8±2° (c 0.42; methanol).

The presence in the plant of a strophalloside monoglycoside was also established by paper chromatography in various solvent systems [14].

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