FLAVONOIDS AND OTHER NATURAL COMPOUNDS FROM Campanula persicifolia. IV

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Continuing an investigation of the polyphenolic compounds of the epigeal part of Campanula persicifolia L. [1] we have obtained another three flavone glycosides (VIII-X) by preparative paper chromatography followed by purification on columns of polyamide sorbent.

Substance (VIII) with the composition $C_{33}H_{40}O_{20}$ consisted of yellowish spherocrystals with mp 216-220°C, $[\alpha]_D^{20}$ −118.3° (c 0.1; MeOH), $\lambda_{max}^{ethanol}$ 241, 270, 344 nm. In 15% CH_3COOH it had R_f 0.39; on the chromatograms it appeared in the form of a dark spot which acquired a yellow-green fluoresence in ammonia vapors. On acid hydrolysis (5% sulfuric acid, 100°C, 1 h), this glycoside was cleaved to form the aglycon luteolin (yield 32.1%) and sugars — D-glucose and L-rhamnose — in ratio of 2:1, which characterized it as a trioside. From its spectral characteristics in the UV region and color reactions, positions 3' and 7 of substitution in the glycoside molecule were assumed.

To determine the positions of attachment of the individual sugars to the aglycon and their sequence, we carried out stepwise acid and enzymatic hydrolysis. Thermostating of the initial glyoside in the presence of emulsin (38°C, 20 min) led to the formation of a less polar substance, the properties of which were identical with those of luteolin 7-rutinoside [2], while glucose was detected in the hydrolysate. On stepwise hydrolysis with 0.5% sulfuric acid and on enzymolysis with pectinase for 1 h, four intermediate products were obtained and an aglycon having in the 15% CH_3COOH system R_f 0.28, 0.19, 0.12, 0.09, and 0.04, respectively.

The structures of the products obtained were established from their UV spectra, the results of acid and enzymatic hydrolysis, and a comparison with authentic samples. As a result, the following luteolin derivatives were identified: the 7-rutinoside, the 3',7-diglucoside, the 7-glucoside, and the 3'-glucoside.

Three luteolin triosides with substitutions at positions 4' and 7 of the aglycon nucleosides had previously been isolated from this plant [3]. Substance (VIII) was a new trioside which we have characterized as luteolin 3'-O-β-D-glucopyranoside 7-O-rutinoside.

Substance (IX) with the composition $C_{27}H_{30}O_{14}$ formed yellow spherocrystals with mp 185-188°C, λ_{max} (in ethanol) 269, 339 nm, and substance (X) with the composition $C_{28}H_{32}O_{15}$ was amorphous, with λ_{max} 253, 268, 350 nm. After the acid hydrolysis of each of them, an aglycon, glucose, and rhamnose in a ratio of 1:1:1 were found in the hydrolysates. The two biosides had the same carbohydrate moiety but different aglycons. In the first case, apigenin was identified and in the second, chrysoeriol. On hydrolysis under mild conditions (1% sulfuric acid, 1 h), their 7-monoglucosides were obtained. Rhamnodiastase split out a specific sugar — rutinose. The results obtained give grounds for assigning to substance (IX) the structure of apigenin 7-O-rutinoside (isorhoifolin) and to substance (X) that of chrysoeriol 7-rutinoside. The amounts of the glycosides identified in the raw material did not exceed 0.05%.

In addition, from the plant we isolated two compounds of nonflavonoid nature. On standing, a concentrated methanolic extract deposited a voluminous precipitate which consisted mainly of two substances. The first compound was obtained after treating the deposit with a mixture of ethanol and chloroform, the removal of the solvent by distillation, and the purification of the residue by recrystallization from various solvents. This gave acicular crystals (with a yield of 0.5%) having mp 280-284°C, $[\alpha]_D^{20}$ +74.7° (c 1.0; chloroform). The remainder of the deposit was dissolved in water with heating, the solution was filtered, and the second compound was crystallized from aqueous methanol until colorless plates had been obtained with mp 225-226°C, $[\alpha]_D^{20}$ ±0° (c 1.0; water). On the basis

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of the results of the investigations performed, ursolic acid [4] and meso-inositol [5] were identified.

LITERATURE CITED

1. L. S. Teslov, Khim. Prir. Soedin., 784 (1986).
2. L. S. Teslov, L. N. Koretskaya, and G. I. Tsareva, Khim. Prir. Soedin., 387 (1983).
3. L. S. Teslov, Khim. Prir. Soedin., 790 (1984).
4. L. S. Teslov, Khim. Prir. Soedin., 582 (1979).
5. L. S. Teslov and K. F. Blinova, Khim. Prir. Soedin., 662 (1972).

FLAVONES AND ROSMARINIC ACID OF Thymus zheguliensis

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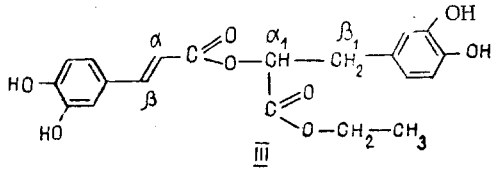
We have investigated the epigeal part of Thymus zheguliensis Klok et Schost. (endemic to the Zhugulev mountains). The air-dry mass of this plant gathered in August, 1980, in the environs of the village of Shiryaevo, Kuibyshev province, was extracted with aqueous ethanol, and the aqueous extracts were evaporated in vacuum to a dry residue which was chromatographed repeatedly on polyamide and silica gel. In this way, three substances of polyphenolic nature (I-III) were isolated. To establish the structures of the substances isolated we used the results of UV and PMR spectroscopy, and also a direct comparison with authentic samples on the basis of chromatographic mobilities and other physicochemical constants [compounds (I) and (II)].

Compound (I) was apigenin (yield 0.01%), forming light yellow crystals with the composition $C_{15}H_{10}O_5$, mp 341-344°C (decomp.); triacetate with mp 180-182°C.

Compound (II) was luteolin (yield 0.02%), forming yellow crystals with the composition $C_{15}H_{10}O_6$, mp 329-331°C (decomp.); tetraacetate with mp 228-230°C. Compound (III) (yield 0.2%) was a light yellow syrupy substance with the composition $C_{20}H_{20}O_8$, giving a tetraacetate in the form of a colorless syrupy substance. PMR spectrum in deuteroacetone, ppm: 7.62 (d, 16 Hz, 1 H_α), 6.60-7.22 (m, 6H-Ar), 6.34 (d, 16 Hz, 1H β), 5.24 (t, 6 Hz, $1H_{\alpha_1}$), 4.20 (q, 2H, $-C\underline{H}_2CH_3$), 3.07 (d, 6 Hz, $2H_{\beta_1}$), 1.28 (t, 6 Hz, $CH_3C\underline{H}_2-$). PMR spectrum of the tetraacetate of (III) in deuterochloroform, ppm: 7.68 (d, 16 Hz, $1H_\alpha$), 7.32 (m, 6H-Ar), 6.44 (d, 16 Hz, $1H_\beta$), 5.35 (t, 6 Hz, $1H_{\alpha_1}$), 4.22 (q, 2H, $-C\underline{H}_2CH_3$), 3.24 (d, 6 Hz, $2H_{\beta_1}$), 2.34 (s, 6H, two aromatic CH_3CO groups), 2.32 (s, 6H, two aromatic CH_3CO groups), 1.24 (t, 6 Hz, $C\underline{H}_3CH_2-$).



III

A comparison of the PMR spectra of compound (III) and its tetraacetate showed that compound (III) was rosmarinic acid esterified with ethanol. In our view, compound (III) was an artefact arising on the prolonged storage of the purified ethanolic extract. This was confirmed by the fact that there was no compound (III) present in acetone extracts and in freshly prepared (by steeping and under the conditions of a boiling extractant) aqueous ethanolic extracts, while, under these conditions rosmarinic acid was detected in both extracts (TLC).

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