

The molecular weight of the glucofructan determined on a column of Sephadex G-100 was 31,000.

The monosaccharide compositions (2 N H<sub>2</sub>SO<sub>4</sub>, 100°C, 48 h) of the hemicelluloses A and B were represented by the sugars rhamnose, xylose, arabinose, mannose, glucose, and galactose (51.1:3:1:traces:2.4:3.4 and 6.5:1:1.2:1.43:1.8:1.26, respectively, in moles).

Thus, the carbohydrate composition of pomegranate residues has been characterized. The quantitative and qualitative compositions of the polysaccharides isolated have been determined. The pectin substances isolated are distinguished by a high degree of methoxylation.

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#### COUMARINS OF SPECIES OF THE GENUS *Campanula*

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As reported previously [1], fraxetol 7-O-D-glucopyranoside (isofraxoside) has been isolated from the epigeal parts of *Campanula alliariifolia* and *C. letschchumensis* collected in the flowering stage.

Continuing a study of the coumarin compositions of bellflowers of the section *Cordifolia* (Fom.) Fed. [2], from the leaves and flowers of *C. alliariifolia* and *C. ochroleuca* Kem.-Nath (KBASSR [Karabdinno-Balkar Autonomous Soviet Socialist Republic], gorge of R, Cherek-Balkarskii) we have obtained an aqueous-ethanolic extract which, after concentration, was treated successively with petroleum ether, chloroform, and ethyl acetate. The chloroform fraction was evaporated, and the resin was deposited on a column of Al<sub>2</sub>O<sub>3</sub> (Brockman activity grade III) and was eluted with chloroform-methanol (4:1 by volume). The total material obtained was separated on a column of silica gel (type KSK) by repeated fractionation with chloroform-methanol in various proportions [3].

Another two crystalline substances (I and II) belonging to the hydroxycoumarin group were isolated [6].

Substance (I), C<sub>16</sub>H<sub>18</sub>O<sub>10</sub>, light yellow acicular crystals with mp 204°C, [α]<sub>D</sub><sup>20</sup> 86.6°. The UV region of the spectrum of the substance showed one fairly strong maximum at λ<sub>max</sub><sup>CH<sub>3</sub>OH</sup> 350 nm. The IR spectrum contained bands characteristic of the coumarin nucleus [4]. On the basis of its hydrolysis products and physicochemical properties, the substance was identified as fraxoside (8-β-D-glucosyloxy-7-hydroxy-6-methoxycoumarin) [5], isolated previously from *Fraxinus potamophila* Herd. [3].

Substance (II), C<sub>16</sub>H<sub>16</sub>O<sub>5</sub>, formed yellow plates with mp 228-234°C (from aqueous ethanol (1:1)). According to the results of alkaline degradation, UV and IR spectroscopy, and a mixed melting point, and also those of a chromatographic comparison with an authentic sample, the substance was characterized as 7,8-dihydroxy-6-methoxycoumarin (fraxetol) [1, 6] or fraxetin [5].

Fraxoside and isofraxoside have been detected chromatographically in the species *C. alliariifolia* Willd., *C. leskovii* Fed., *C. letschchumensis* Kem.-Nath., and *C. makashwilli* E. Busch. out of the many populations growing in the Western Caucasus, while fraxitol and fraxoside were present only in the species *C. ochroleuca* Kem.-Nath., *C. dolomitica* E. Busch.,

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and *C. kirpicanikovii* Fed., the area of which is formed by the northern slopes of the Central Caucasus [1, 2].

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#### FERUCRIN ISOBUTYRATE AND FERUCRINONE FROM *Ferula foetidissima*

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A substance (I) with the composition  $C_{28}H_{38}O_6$ ,  $M^+$  470, mp 183-195°C has been isolated by chromatography on silica gel in petroleum ether-ethyl acetate from an acetone extract of the fruit of *Ferula foetidissima* Regel. et Schmalh. collected in the Shakhdarinskii range close to the village of Khorog (samples No. 81-9). According to its UV spectrum, (I) is a coumarin derivative with an alkoxy substituent in position 7 ( $\lambda_{\max}^{EtOH}$  216.5; 242; 253; 324 nm; log  $\epsilon$  4.17; 3.47; 3.27; 4.21).

The substance contained a tertiary hydroxy group (3510  $cm^{-1}$  band in the IR spectrum). The PMR spectrum exhibited, in addition to the signals of umbelliferone in the 6.1-7.7 ppm region, the signals of the protons of a terpenoid moiety [1.10, s, 6 H,  $(CH_3)_2C$ ; 1.33, s, 3 H,  $CH_3-\overset{|}{C}$ ; 1.42, s, 3 H,  $CH_3-C-O$ ; and 4.12, u.s., 2 H,  $CH_2-O-Ar$ ] close in position and nature to the signals in the spectrum of ferucrin (II) [1]. However, unlike ferucrin, in the spectrum of which there is the signal of a proton geminal to a hydroxy group (3.15 ppm, m,  $\Sigma J = 15.5$  Hz, 1 H,  $\underline{CH-OH}$ ), in the spectrum of (I) there was the signal of a proton (4.44 ppm, m,  $\Sigma J = 15.5$  Hz, 1 H,  $\underline{HC-acyl}$ ) geminal to an alkoxy group and the characteristic signals of an isopropyl group (1.17 and 1.20 ppm, d,  $J = 7$  Hz, 3 H each  $(\underline{CH_3})_2-CH-COO$ ; 2.52 ppm, m, 1 H,  $(CH_3)_2-\underline{CH}-COO$ ).

Thus, on the basis of these results it may be assumed that (I) was ferucrin isobutyrate. The acylation of ferucrin with isobutyryl chloride gave a substance  $C_{28}H_{38}O_6$ , mp 193-195°C, identical according to its PMR and IR spectra with the isolated compound (I); a mixture of (I) with the synthetic specimen of ferucrin isobutyrate gave no depression of the melting point.

A terpenoid coumarin  $C_{24}H_{30}O_5$ ,  $M^+$  398, mp 221-223°C, was isolated by chromatography under the same conditions from an acetone extract of the fruit of another sample *Ferula foetidissima* collected in the area of the Alai range in the valley of the R. Gar, close to the village of Urdush (No. 81-76). According to its UV, IR, and PMR spectra the substance was identical with ferucrinone (III), obtained previously by the oxidation of deacetylkellerin [2] and of ferucrin [3, 4]. This is the first time that ferucrinone has been isolated from a plant source.

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