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# OIL AND CARBOHYDRATES OF THE FRUIT OF *Bunium persicum*

D. A. Rakhimov, G. A. Stepanenko, Kh. Ubaev, A. I. Glushenkova, and E. S. Kondratenko

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Continuing an investigation of plants of the family Umbelliferae we have studied the oil and carbohydrates of the seeds of *Bunium persicum* (Boiss.) K.-Pol. (local name, zira) collected in the village of Dugaba, Dzhizak province. In the literature, only the fatty acid composition of the oils is given for the seeds of the species of the genus *Bunium* studied and there is no information on their carbohydrate composition.

The seeds were ground and the oil was extracted by steeping in hexane at room temperature. The oil content of the seeds was 4.6%. The extracted meal was dried and used for the subsequent extraction of various groups of carbohydrates: mono- and oligosaccharides, water-soluble polysacchrides (WSPSs), pectin substances (PcSs), and hemicelluloses (HCs) by the method of Arifkhodzhaev et al. [3]. The polysaccharides were hydrolyzed with 2 N $H_2SO_4$ at 100°C for 10-24 h and the sugars of the hydrolysate were investigated by PC and GLC [4].

The sum of the lipids was separated according to polarity by column chromatography on silica gel: triacylglycerols (TAGs), 96%; components of the essential oil, 2%; free fatty acids (FFAs), 0.3%; sterols, chlorophyll, and an unidentified component, 1.7% (as percentages of the mass of the extract).

The fatty acid composition of the TAGs and the FFAs determined by the GLC method were as follows:

| | Acid | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 12:0 | 14:0 | 15:0 | 16:0 | 18:0 | 18:1Δ6 | 18:1Δ9 | 18:2 |
| TAGs | 0.7 | 3.4 | — | 6.3 | 3.4 | 46.2 | 12.4 | 27.6 |
| FFAs | — | 2.1 | 1.1 | 14.5 | 7.5 | 45.8 | 18.8 | 10.2 |

In the oil of the seeds of *B. persicum*, as in the majority of plants of this family, petroselinic acid forms the bulk of the monounsaturated acids both in the TAGs and in FFAs.

The mono- and oligosaccharides (yield of an ethanolic extract 3.7% on the air-dry seeds) contained glucose, fructose, mannitol, sucrose, and raffinose.

The total WSPSs were obtained with a yield of 0.7%. They consisted of an amorphous powder giving a negative starch reaction with iodine and possessing no reducing capacity. In the products of its hydrolysis we detected rhamnose (Rha), arabinose (Ara), xylose (Xyl), mannose (Man), glucose (Glc), and galactose (Gal) in a ratio of 3.2:7.7:1:17.1:18.1:16, together with a very small amount of galacturonic acid. As the sugars in the WSPSs, hexoses were quantitatively predominant.

The pectin substances (yield 4.2%) had the form of a white amorphous powder. In the products of acid hydrolysis we detected mainly galacturonic acid and the neutral sugars Rha, Ara, Xyl, Man, Glc, and Gal in a ratio of 8.5:14.4:1:18.4:8.0:17.1.

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The alkali-soluble polysaccharides of the HCs A and B (yields 7.7 and 7.2%, respectively) were present in considerably larger amounts than in the WSPSs and PCSs. In the HCs A we found Rha, Ara, Xyl, Man, Glc, and Gal in a ratio of 17:2.5:1:41.1:3.4:1, and in the HC B the same sugars in a ratio of 6.7:4.2:1:30.7:9.7:7.5. The HCs A and B differed in their contents of the individual monosaccharides.

The predominating component in the polysaccharide fractions was mannose. The latter is rarely found in the free state in nature. Direct hydrolysis of the seeds by the method of Stepanenko and Baksova [5] (2 N $H_2SO_4$, 100°C, 5 h) gave D-mannose with a yield of 1.5% (on the air-dry seeds).

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# COMPONENTS OF *Haplophyllum dauricum*


É. Kh. Batirov, D. Batsurén, and V. M. Malikov



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Continuing a study of the epigeal part and roots of *Haplophyllum dauricum* (L.) G. Don [1], we have isolated another five individual substances, four of which have been identified on the basis of spectral characteristics and by direct comparison with samples isolated by us from other species of *Haplophyllum*.

Compounds (I), mp 285-286°C (acetate with mp 231-233°C) and (II), mp 202-204°C, were shown to be identical with the lignan diphyllin [2] and the coumarin scopoletin, respectively.

Substances (III), mp 212-214°C, and (IV), mp 225-228°C, proved to be identical with the flavonol glycosides haplosides B and D [3, 4].

Compound (V) (dauroside C), with the composition $C_{24}H_{30}O_{14}$, mp 93-95°C, according to its UV spectrum, ($\lambda_{max}^{ethanol}$ 229, 251 infl., 259 infl., 288, 343 nm; log ε 4.11, 3.65, 3.57, 3.67, 3.74), was assigned to the 6,7-di-O-substituted coumarins. IR spectrum, $\nu_{max}^{KBr}$, $cm^{-1}$: 3520-3290 (OH groups); 1717-1702 (C=O of α-pyrone and ester groups); 1616, 1565 (aromatic C=C bonds); 1105-1026 (C–O vibrations). The PMR spectrum of dauroside C (Py-$d_5$) showed the signals of the H-3 and H-4 protons (6.09 and 7.49 ppm, d, 1 H each, J = 9.5 Hz), H-5 (7.47 ppm, 1 H, s), and H-8 (6.82 ppm, 1 H, s) and of $CH_3O$– (3.51 ppm, 3 H, s), $CH_3COO$– (1.81 ppm, 3 H, s), and $CH_3$– (1.43 ppm, 3 H, d, 5 Hz) groups.

In the 3.70-4.63 ppm region were observed the signals of ten protons of the sugar moiety, the signals of the anomeric protons of which were found at 5.24 ppm (1 H, br.s) and 5.44 ppm. Apparently, the signal of gem-acyl proton is superposed on the signal of one of the anomeric protons as a result of which the signal at 5.44 ppm appears in the form of a two-proton multiplet.

The IR and PMR spectra permitted the assumption that dauroside C was an acylated coumarin glycoside. The hydrolysis of compound (V) with 5% sulfuric acid led to scopoletin, D-glucose, and L-rhamnose. The acetylation of (V) with acetic anhydride in pyridine gave a hexaacetate $C_{34}H_{40}O_{19}$ (VI), $M^+$ 752. Consequently, the coumarin glycoside (V) is a bioside. In the mass spectrum of (VI), together with others, there were strong peaks of ions with m/z 273 (100%), 213 (8), 153 (38), and 111 (22), showing that in (V) the rhamnose is the terminal sugar residue [1].


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