FLAVONOIDS OF *Hippophaë rhamnoides* GROWING IN MONGOLIA

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One of us has previously studied the amino-acid composition of the fruit of the wild sea buckthorn (*Hippophaë rhamnoides* L.) growing in Mongolia [1]. In the present communication we give the results of a study of the flavonoids of the dried meal of the flesh of the fruit.

To isolate the flavonoids, the comminuted raw material that had been treated with petroleum ether to free it from lipophilic substances was extracted with methanol. The methanolic extract was concentrated in vacuum to small volume, diluted with a fivefold amount of water, and filtered. The filtrate was evaporated and was chromatographed on a column of polyamide sorbent. Rechromatography of the individual fractions followed by purification on Sephadex LH-20 and preparative paper chromatography in various solvent systems [15% acetic acid, butan-1-ol—acetic acid—water (4:1:5) and (3:1:1)] enabled us to isolate eight individual substances of flavonoid nature.

Substance (I), mp 188-190°C, R_f 0.74 [here and below in the butan-1-ol—acetic acid—water (4:1:5) system]. UV spectrum, λ_{max}, nm: 260, 270 (sh.), 300 (sh.), and 360. Acid hydrolysis gave an aglycone with mp 316-318°C, which was identified as quercetin. Glucose and rhamnose were found in the carbohydrate part of the hydrolysis. On the basis of these facts, and also from the results of IR and UV spectroscopy with complex-forming and ionizing additives, the substance was characterized as 3,3',4',5,7-pentahydroxyflavone 3-O-β-D-rutinoside (rutin) [2].

Substance (II), mp 316-318°C, R_f 0.64 was identified as quercetin.

Substance (III), mp 182-185°C, R_f 0.55. UV spectrum (in methanol), λ_{max}, nm: 256, 270 (sh.), 372. Quercetin and rhamnose were found in the products of the acid hydrolysis of (III). UV spectroscopy showed that the rhamnose was attached to position 7 of the quercetin. On the basis of these facts, the substance can be identified as quercetin 7-O-rhamnoside [2].

Substance (IV) was characterized by means of its physicochemical properties and spectral characteristics as quercetin 3-O-methyl ether.

Substance (V), mp 180-182°C, R_f 0.45. Acid hydrolysis led to isorhamnetin with mp 305-307°C. The carbohydrate components were glucose and rhamnose. IR spectrum, λ_{max}, nm: 255, 265 (sh.), 315, and 356.

The facts given above enabled substance (V) to be identified as isorhamnetin 3-O-rutinoside.

Substance (VI), with mp 246-248°C, R_f 0.60, was identified from its spectral characteristics and acid hydrolysis as isorhamnetin 3-O-β-D-glucoside.

Substances (VII) (mp 305-307°C) and (VIII) (mp 279-280°C) were identified from their IR and UV spectra and also the results of paper chromatography, as isorhamnetin and kaempferol, respectively.

It must be mentioned that quercetin, kaempferol, isorhamnetin, and some of their glycosides have been isolated previously from the leaves of the sea buckthorn growing in the territory of the Kazakh SSR [3, 4].

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LAGOCHILIN 3-MONOACETATE FROM *Lagochilus inebrians*

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Lagochilin and its tetraacetate [1, 2] have been isolated previously from *Lagochilus inebrians* Bge, and three flavonoids have also been detected chromatographically [3].

We have studied the plant collected in August, 1975 in the environs of Samarkand. The air-dry epigeal part (2.8 kg) was extracted with ether. The extract was concentrated to small volume and was then mixed with alumina, and substances were extracted from it successively with hexane and carbon tetrachloride. The carbon tetrachloride fraction was passed through a column of alumina [eluent: chloroform—methanol (100:3)]. The total substances obtained were rechromatographed on a column of type LC 100/250 silica gel (eluent:chloroform). The purified total material was again passed through the column with carbon tetrachloride—methanol (25:1) as eluent.

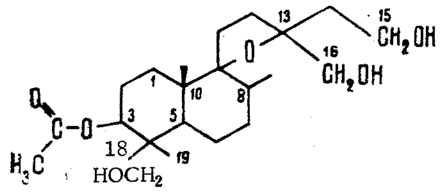
The last fractions yielded a new crystalline substance, not described in the literature, with mp 102-103°C and composition $C_{22}H_{38}O_6$. Its molecular weight was 398 (mass spectrometrically), and its specific rotation $[\alpha]_D^{27}$ +6.3° (c 1; ethanol).

The substance was soluble in ethanol, methanol, ether, chloroform, and benzene and was insoluble in carbon tetrachloride and hexane.

The IR spectrum of the compound had absorption bands characteristic for hydroxy (3370-3500 cm^{-1}) and ester (1743 cm^{-1}) groups.

Hydrolysis of the substance isolated in ethanol with a 5% solution of KOH gave lagochilin and on acetylation with acetic anhydride in pyridine lagochilin tetraacetate was formed. Thus the substance isolated is an acetyl derivative of lagochilin.

The mass spectrum of the compound had peaks with m/e 172, 185, and 198, showing that the acetyl group was present at C-3 or C-18 of the lagochilin molecule. The position of attachment of the acetyl group was established with the aid of PMR spectra. In the PMR spectrum (Varian XL-100, δ scale, HMDS, $CHCl_3$) a three-proton singlet of a single acetyl group was observed at 1.98 ppm and a one-proton quartet at 4.78 ppm which is characteristic for a C-3 proton to which an acetyl group is attached [4]. As was to be expected, the signals of the protons at C-15, C-16, and C-18 appeared in a different region of the spectrum as compared with the signals of the corresponding protons in the PMR spectrum of lagochilin tetraacetate. On the basis of these facts, the structure of lagochilin 3-monoacetate is proposed for the diterpenoid isolated:



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