COMPONENTS OF PLANTS OF THE FAMILY EMPETRACEAE.

II. FLAVONOIDS OF Empetrum nigrum

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Continuing a study of the chemical composition of the black crowberry <u>Empetrum nigrum</u> L. [1], we have investigated the flavonoids of the plant. For their isolation, the air-dry comminuted epigeal parts (leafy stems) of the crowberry were treated with chloroform to eliminate substances of lipophilic nature and were then extracted exhaustively with boiling 70% ethanol. The aqueous ethanolic extracts were concentrated in vacuum to an aqueous residue, which was purified with chloroform, and the flavonoids were extracted with ethyl acetate. The ethyl acetate fraction was separated on a column of polyamide sorbent in a ratio of 1:30. On elution with water and with aqueous alcohol (containing from 10 to 96% of ethanol), five flavonoid substances (I-V) were isolated.

Substance (I) - $C_{15}H_{10}O_7$, mp 310-312°, λ_{max} 375, 265 nm; yield 0.09%, was identified as quercetin [2].

Substance (II) - $C_{21}H_{20}O_{12}$, mp 236-238°, λ_{max} 360, 255 nm; yield 0.15%, was quercetin 3-O- β -D-galactopyranoside (hyperoside).

Substance (III) - $C_{21}H_{20}O_{12}$, mp 238-240°, λ_{max} 362, 255 nm; yield 0.01%, was identified as quercetin 3-O- β -D-glucopyranoside (isoquercitrin).

Substance (IV) – $C_{20}H_{18}O_{11}$, mp 217-220° (decomp.), λ_{max} 355, 258 nm; yield 0.02%, was quercetin 3-0- α -arabinoside (avicularin) [3].

Substance (V) - yellow crystals readily soluble in boiling ethanol, sparingly soluble in water, mp 262-264°C, yield 0.06%. $\lambda_{\max}^{CH_3OH}$ 259 (303), 364 nm; $\lambda_{\max}^{CH_3ONa}$ 268, (325), 420 nm; $\lambda_{\max}^{CH_3COONa}$ 270, (326), 400 nm; $\lambda_{\max}^{CH_3COONa+H_3BO_3}$ 265, (304), 383 nm; $\lambda_{\max}^{ZrOCl_2}$ 270, 424 nm; $\lambda_{\max}^{ZrOCl_2+citric}$ acid 262, 367 nm. The UV spectrum of the glycosides showed that it belonged to the flavonols.

Acid hydrolysis of the compound with 4% HCl led to a carbohydrate component which was identified as D-galactose [PC in the butan-1-ol-pyridine-water (5:4:3) system]. On the basis of features of the electronic spectra of the glycoside and of the aglycon with diagnostic additives, we came to the conclusion that the D-galactose was attached at C₃ of the aglycon.

An ethanolic solution of the aglycon of substance (V), which had a yellow fluorescnece in UV light, gave a negative test with p-benzoquinone, which showed the absence of a free OH group at C_3 .

The structure of compounds (I-IV) that had been isolated were confirmed by the results of elementary analysis, UV spectroscopy with ionizing and complex-forming reagents, and the results of acid hydrolysis and by their chromatographic behavior and a comparison with authentic samples.

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Tomsk Medical Institute. Translated from Khimiya Prirodynkh Soedinenii, No. 6, pp. 875-876, November-December, 1988. Original article submitted March 10, 1988; revision submitted June 23, 1988.

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