FLAVONOIDS OF Betula middendorfii

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By two-dimensional paper chromatography we have found three substances of flavonoid nature in the leaves of Betula middendorfii Trautv. et Mey (Middendorf birch). We isolated these substances from an ethanolic extract purified with chloroform by chromatography on a polyamide sorbent.

Substance (I), $C_{21}H_{20}O_{12}\cdot H_2O$ with mp 228-235°C, $[\alpha]_D$−36.09° (c 1.04; formamide), R_f 0.48 [in a thin layer of Silufol; mobile phase chloroform–methanol (3 : 1) for all the compounds] has been identified on the basis of UV, IR, and NMR spectra and by a direct comparison with an authentic sample as hyperoside.

Substance (II), $C_{21}H_{20}O_{12}\cdot 1/2H_2O$, has mp 235-238°C, $[\alpha]_D$−84° (c 0.51; formamide), R_f 0.32, λ_{max} 258, 360 nm. The acid hydrolysis of (II) gave quercetin and galactose. Substance (II) is a monoside, since the NMR spectrum of the silylated glycoside has the signals of six protons in the 3.16-3.60 ppm region. The car-

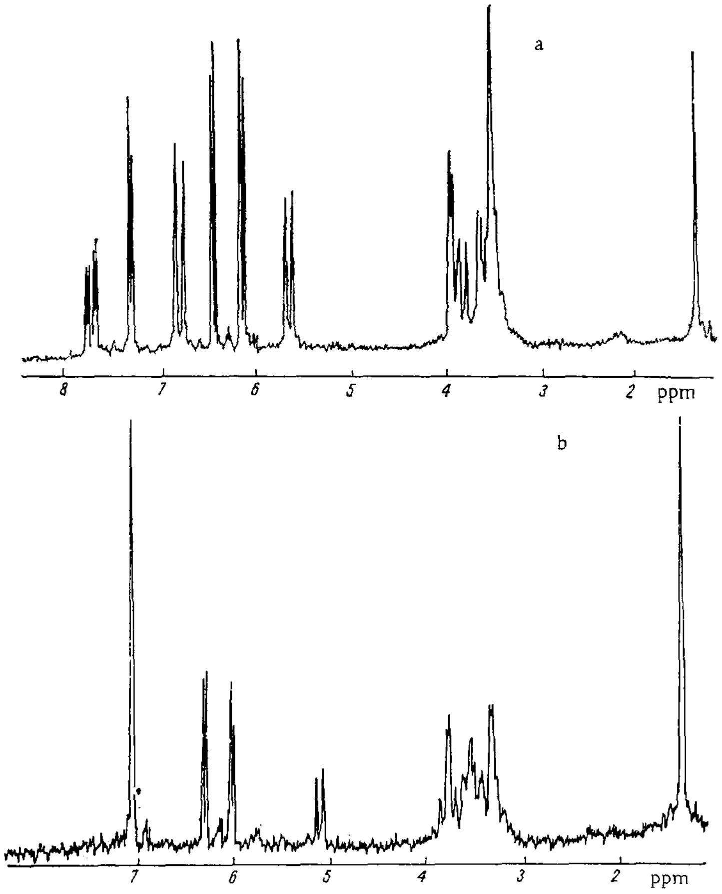

Fig. 1. NMR spectra of silylated isohyperoside (a) and betmidin (b).

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bohydrate substituent is present in position 3, as is shown by the UV spectra of (II): $\lambda_{max}^{CH_3COONa}$ 268, 380, $\lambda_{max}^{Zr(NO_3)_2}$ 275, 430, $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 262, 380, $\lambda_{max}^{CH_3ONa}$ 272, 412, $\lambda_{max}^{CH_3COONa+\text{citric acid}}$ 270, 383 nm. We have called substance (II) isohyperoside. The NMR spectrum of silylated isohyperoside (Fig. 1a) has quadruplets at 7.78 and 7.68 ppm, J = 2.5 Hz and J' = 10 Hz (1 H), corresponding to H-6'; doublets at 7.30 ppm, J = 2.5 Hz (1 H) (H-2'), and 6.78 ppm, J = 10 Hz (H-5'); and two 1-H doublets, each with J = 2.5 Hz, at 6.40 and 6.10 ppm ascribed to the signals of the H-8 and H-6 protons, respectively. A doublet at 5.62 ppm J = 8 Hz (1 H) corresponds to the anomeric proton of β-galactose in position 3 of a flavonol; signals in the 3.16-3.60 ppm region correspond to the six protons of galactose [1]. Isohyperoside can differ from hyperoside only by the size of the oxide ring of the galactose. Thus, isohyperoside is quercetin 3-β-D-galactofuranoside, as has been confirmed by a calculation using Klyne's method [2].

Substance (III), $C_{20}H_{18}O_{12}$, mp 233-234°C, $[\alpha]_D$ −33.01° (c 0.81; formamide), R_f 0.11, λ_{max} 256, 362 nm. The hydrolysis of this substance gave the aglycone myricetin and arabinose. The NMR spectrum of (III) (Fig. 1b) has: the signals of the H-2' and H-6' protons (2 H) in the form of a singlet at 7.01 ppm; doublets at 6.27 ppm (1 H), J = 2.5 Hz (H-8), at 5.98 ppm, J = 2.5 Hz (H-6), and at 5.06 ppm (1 H), J = 8 Hz, corresponding to the anomeric proton of an α-arabinose; the five protons of the arabinose are responsible for signals in the 3.2-3.7 ppm region. In substance (III) the arabinose is present in position 3 (determined by UV spectroscopy). The results of calculation by Klyne's method show that the arabinose possesses the furanose form.

Consequently, substance (III) is myricetin 3-α-L-arabofuranoside. This has not been described in the literature, and we have called it betmidin.

LITERATURE CITED

1. W. Olechnowicz-Stepien et al., Herba Polonica, 1968, No. 3, 179.
2. W. Klyne, Determination of Organic Structures by Physical Methods, Academic Press, New York (1955), p. 98.