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FLAVONOIDS OF Senecio subdentatus. III

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UDC 574.972

We have isolated two flavonol glycosides from the herb Senecio subdenatus L. D. B.

Compound 1, $C_{28}H_{32}O_{17}$ mp 210-212°C, R_f 0.31 (BAW, 4:1:2); 0.56 (15% acetic acid), $[\alpha]_D^{20}-85°$ (c 0.5; DMFA), λ_{max} 355, 255 nm (log ε 4.15, 4.28). On hydrolysis with 5% sulfuric acid, it was split into isorhamnetin (yield 52%), galactose, and glucose.

Compound 2, $C_{27}H_{30}O_7$, mp, 215-217°C, [R_f 0.29/0.55, $[\alpha]_D^{20}-92°$ (c 0.3; DMFA), λ_{max} 360, 257 nm (log ε 4.13, 4.31); was hydrolyzed to quercetin (yield 49%), galactose and glucose.

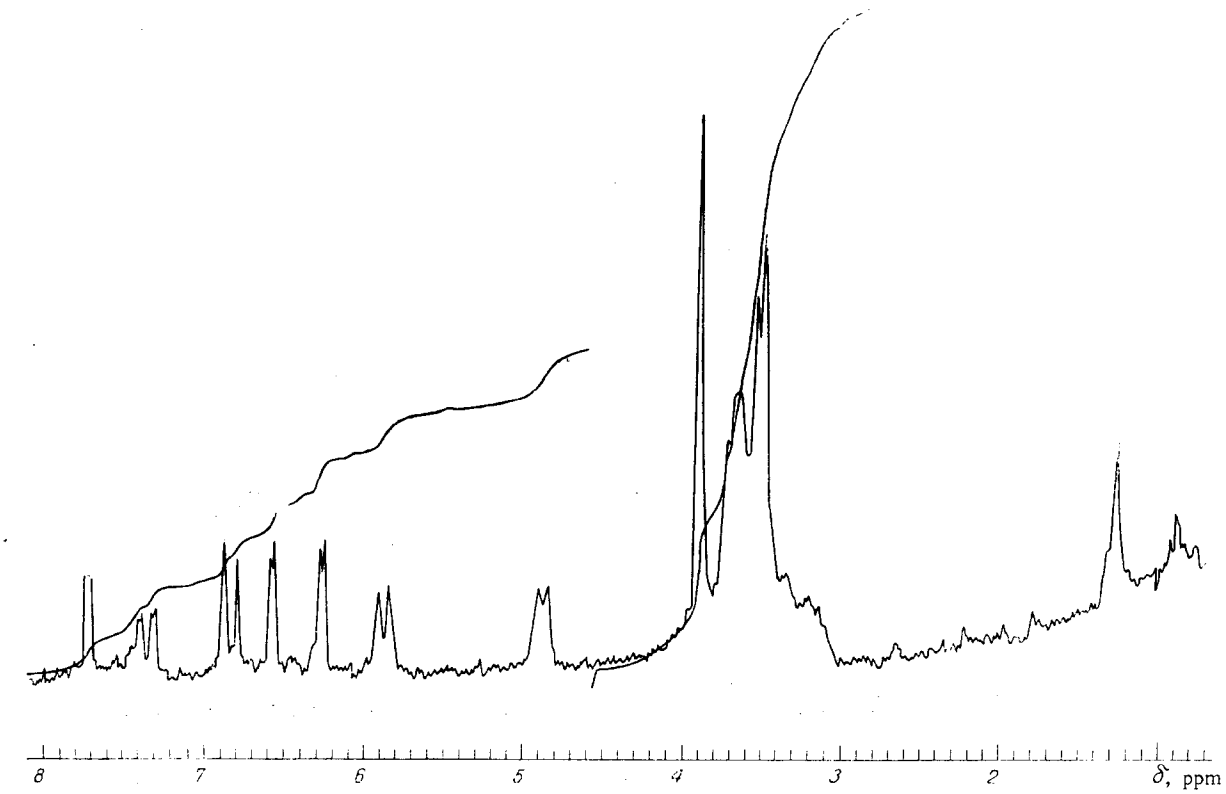

Fig. 1. NMR spectrum of the TMS ether in CCl_4.

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The isorhamnetin and quercetin were identified by their physicochemical constants and by a comparison with markers [1]. The presence of the sugars in the glycosides at C_3 and C_7 was established by a spectral investigation in the UV region.

The products of stepwise acid hydrolysis (0.1% hydrochloric acid) were 7-monosides identical with compounds isolated previously: isorhamnetin 7-O-β-D-glucopyranoside, $C_{22}H_{23}O_{12}$, mp 250-252°C, $[\alpha]_D^{20}-40.5°$, and quercetin 7-O-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$, mp 247-248°C $[\alpha]_D^{20}-52°$ [2]. Alkaline hydrolysis [3] (0.5% KOH) yielded isorhamnetin 3-galactoside, $C_{22}H_{23}O_{12}$, mp 198-200°C, $[\alpha]_D^{20}-120°$ (c 0.1; methanol) and quercetin 3-galactoside, $C_{21}H_{20}O_{12}$, mp 237-239°C, $[\alpha]_D^{20}-128°$ (c 0.12; methanol), respectively. The results of a calculation of molecular rotations according to Klyne [4] showed the β-linkage and the furanose form of the galactose, and this was confirmed by the results of differential spectroscopy in the UV region (890, 1030, 1070 cm^{-1}) and the rapid acid hydrolysis [5]. The NMR spectrum of the TMS ether in CCl_4 showed that the carbohydrates are attached by β-linkages at the C_3 and C_7 of the aglycone: d, 5.80 ppm (1H, J = 7 Hz), d 4.80 ppm (1H, J = 7 Hz) [6] (Fig. 1). On the basis of the results obtained, the flavonoids isolated can be characterized as 3,4',5,7-tetrahydroxy-3'methoxyflavone 3-O-β-D-galactofuranoside-7-O-β-D-glucopyranoside (I) and 3,3'4',5,6-pentahydroxyflavone 3-O-β-D-galacofuranoside-7-O-β-D-glucopyranoside.

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FLAVONOIDS OF THE NEEDLES OF Picea ajanensis

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From a fraction of the methanolis extract of the needles of Picea ajanenis (Yeddo spruce) [1] by preparative chromatography on polyamide sorbent (with chloroform–methanol as the eluent) we have isolated the total flavonoid components. GLC analysis of the TMS ethers in comparison with the authentic samples showed the presence of naringenin (RT 7.12 min, taken as 1.0), aromadendrin (RRT 1.15), kaempferol (RRT 1.86), spigenin (RRT 1.91), and quercetin (RRT 2.56). For identification by the GLC method, we used additions of authentic samples.

The analysis was performed on a Tsvet-4 chromatograph with a flame-ionization detector. The column, 300 × 0.3 cm, was filled with 5% of SE-30 on Chromaton N-AW-HMDS, carrier gas helium, column temperature 284°C, evaporator temperature 350°C.

The naringenin and apigenin, which were present in the fraction in sufficient amount, were obtained by column chromatography on silica gel (with chloroform–methanol as the eluent). Naringenin – mp 249-251°C (CH_3OH), λ_{max} 288 nm (log ε 4.20), mol. wt. 272 (mass spectrometrically).

Apigenin – mp 346-348°C (CH_3OH), λ_{max} 268, 336 nm (log ε 4.39, 4.42), mol. wt. 270 (mass spectrometrically).

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