STRUCTURE OF THE FLAVONOIDS FROM Datisca cannabina. III

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In the present communication we give the properties of two flavonol glycosides that we have isolated previously [1, 2].

Compound (I), with the composition $C_{28}H_{32}O_{14}$, mp 233-235°C (Kofler), $[\alpha]_D^{20}$ −73° (0.4; pyridine), R_f 0.8 (under conditions 2), λ_{max}^{MeOH} 267, 312, 340 nm (inflection) (log ε 4.43, 3.99, 3.92), NaOAc 266 nm.

Acid and enzymatic hydrolysis yielded in equimolar amounts an aglycone $C_{16}H_{12}O_5$, mp 198-199°C, M^+ 284, λ_{max}^{MeOH} 239, 267, 310, 360 nm (diacetate with mp 170-171°C), identified as izalpinin (3,5-dihydroxy-7-methoxyflavone), and D-glucose and L-rhamnose.

In the NMR spectrum of the TMS ether of (I), the carbohydrate protons were represented in the form of three doublets at 5.77 ppm, J = 7 Hz (H-1 of β-D-glucose), 4.18 ppm, J = 2 Hz (H-1 of α-rhamnose), 1.64 ppm, J = 6 Hz (CH_3 of rhamnose), and a multiplet at 3.2-3.7 ppm (10 H).

The acetylation of the glycoside (Ac_2O, pyridine, 20°C, 24 h) gave a heptaacetate with the composition $C_{42}H_{46}O_{21}$, mp 114-115°C. In its NMR spectrum (Fig. 1), the signals of the five protons of the B ring form two multiplets in the 7.45-8.0 ppm region; H-8 and H-6 form doublets at 6.77 and 6.54 ppm. the CH_3O group a singlet at 3.82 ppm, and the seven acetoxy groups singlets from 1.9 to 2.40 ppm. The integration of the signals in the 4.5-5.5 ppm region (8 H) and the 3.2-3.7 ppm region (4 H), in combination with the position of the signal of the rhamnose CH_3 group (doublet at 1.0 ppm) and of its anomeric proton (boradened singlet at 4.4 ppm) permit their assignment to the signals of rutinose [3]. The presence of the signals of an acetoxy group at 2.40 ppm [4] permits the assumption that in the initial compound the 5-OH group is free. Thus, the compound isolated has the structure of 3,5-dihydroxy-7-methoxyflavone 3-O-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside], or izalpin 3-rutinoside, to which we have given the name of cannabin [1].

Compound (II), has the composition $C_{27}H_{30}O_{14}$, mp 155-156°C, $[\alpha]_D^{20}$ −12° (0.33; pyridine), R_f 0.37, λ_{max}^{MeOH} 267, 312, 340 nm (inflection) (log ε 4.25, 3.90, 3.87).

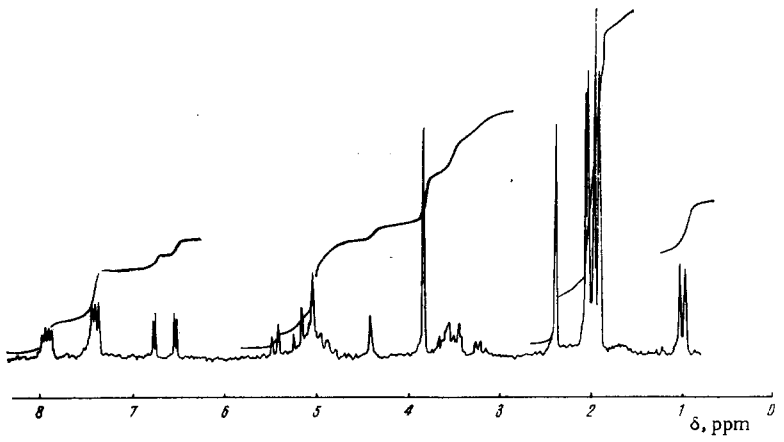

Fig. 1. NMR spectrum of cannabin acetate ($CDCl_3$, internal standard HMDS, Varian HA-100D).

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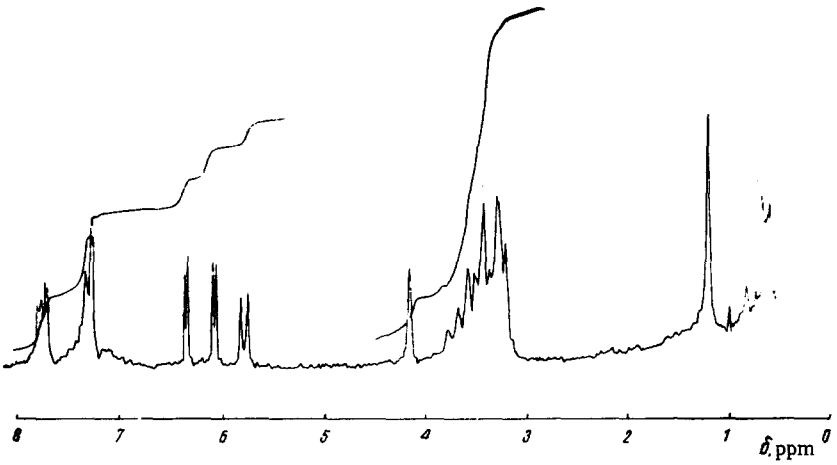

Fig. 2. NMR spectrum of the TMS ether of galanginoside in CCl_4.

Acid hydrolysis gave the same sugars as in (I) and an aglycone $C_{15}H_{10}O_5$ with M^+ 270, mp 218°C, λ_{max} 267, 360 nm, identical with galangin (3,5,7-trihydroxyflavone).

The NMR spectrum of the TMS ether (Fig. 2), in contrast to that of (I), had no singlet of a CH_3O group, but otherwise the spectra coincided. The chemical shifts and the splitting constants of the protons of the sugars enabled them to be assigned to rutinose [5]. The NMR spectrum of the acetate of (II) lacked the signal of the CH_3O group present in the acetate of (I) and, in addition to the 5-OAc group (2.42 ppm) it showed the signal of a second acetoxy group (2.2 ppm); otherwise the spectra were again identical.

The attachment of the rutinose to the 3-OH group was shown by the position of the signal of the anomeric glucose proton (5.79 ppm) [5] and by the UV spectrum (NaOAc: 276 nm). On the basis of the information obtained, it may be concluded that the compound isolated is 3,5,7-dihydroxyflavone 3-O-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside], or galangin 3-rutinoside, which we propose to call galanginoside. This compound has possibly been isolated previously, but its structure was not established [6, 7].

Thus, all the glycosides isolated from the roots of Datisca cannabina – daticin, datinoside, cannabin, and galanginoside – are 3-rutinosides. This agrees with literature information that a highly selective enzyme [6] hydrolyzing only 3-rutinosides of flavonols and not splitting off other sugars or even rutinose in position 7 of flavonoids has been found in the roots of this plant [6].

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