STRUCTURE OF THE FLAVONOIDS FROM Datisca cannabina. II

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Continuing a chemical study of the combined flavonoids isolated from the roots of Datisca cannabina L. [1], we have used preparative TLC and also the column variant of thin-layer chromatography [2] on Woelm polyamide, for this purpose. As the mobile phase we used chloroform–methanol–methyl ethyl ketone (12:2:1). Four flavonoid glycosides and five aglycones were obtained. In the present paper we give the properties of three of these compounds.

Compound (I), with the composition $C_{16}H_{12}O_6$, mp 235-236°C, R_f 0.3, UV spectrum (MeOH + HCl): 259, 350 nm. Triacetate, $C_{22}H_{18}O_{19}$, mp 127-128°C.

The NMR spectrum of the trimethylsilyl ether (100 MHz, CCl_4, internal standard HMDS) had the signals of four protons of the B ring (multiplet, 6.7-7.4 ppm), two doublets of H-8 and H-6 (6.35 and 6.13 ppm, J = 2.5 Hz), and the singlet of a methoxy group at 3.73 ppm. In dimethyl sulfoxide, compound (I) gave the signal of a 5-OH group at 12.34 ppm.

The mass spectrum (JMS-01SG-2, 75 eV, 180°C) showed the peak of the molecular ion, M^+ 300 (100%). The presence of a strong M−17 peak (m/e 283; 88.5%), which is characteristic for 2'-hydroxyflavonols [3], and of fragments from the A and B rings (m/e 167, 28.6%, and m/e 121, 11.9%) due to decomposition of the type of a retro-Diels–Alder reaction [4], show that the CH_3O group is located in ring A, i.e., only position 7 is possible for it.

Thus, the compound studied is 2',3,5-trihydroxy-7-methoxyflavone. This compound has been synthesized previously [5], but we are the first to have isolated it from natural sources, and we propose to call it datin.

Compound (II), with the composition $C_{28}H_{32}O_{15}$, mp 188-189°C, $[\alpha]_D^{20}$ −10° (0.64; pyridine), R_f 0.65, λ_{max}^{MeOH} 262, 300, 335 (inflection) (log ε 4.4, 3.97, 3.9); with NaOAc 260 nm; with $AlCl_3$/HCl 269, 380 nm.

Acid hydrolysis gave equimolar amounts of D-glucose, R-rhamnose, and an aglycone $C_{16}H_{12}O_6$ with mp 238-239°C, M^+ 300, identical with datin (I). In the NMR spectrum of the TMS ether of (II) (Fig. 1), the signals of the flavone nucleus and of the CH_3 group scarcely differed from the corresponding signals in the TMS ether of (I), and the carbohydrate part of the molecule was represented by three doublets at 5.79 ppm (J = 7 Hz), 4.16 ppm (J = Hz), and 0.64 ppm (J = Hz) and a multiplet in the 3.2-3.8 ppm region (10 H). In the NMR spectrum of the acetate of the glycoside (in $CDCl_3$) the positions of the signals of the carbohydrate protons (8 H in the 4.5-5.5 ppm region, 4 H in a 3.2-3.7 ppm region, doublet at 1.0 ppm of the CH_3 group of rhamnose and the signal of its H-1 at 4.4 ppm) enabled them to be assigned to rutinose, and the signal of an acetoxy group at 2.40 ppm permitted the assumption that in the initial compound (II) there is a free 5-OH group [7]. Consequently, the compound isolated has the structure of 2',3,5-trihydroxy-7-methoxyflavone 3-O-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside] or datin 3-rutinoside. This compound has not been described in the literature, and we propose for it the name of datinoside.

Compound (III) consisted of bright yellow crystals with mp > 350°C (previously assumed by us to be a chalcone [1]). Its UV spectrum (in MeOH and in the presence of $AlCl_3$/HCl) had maxima at 267 and 410 nm, but they changed on acidification: 259, 307, and 349 nm.

The NMR spectrum of the TMS ether was completely identical with the spectrum of the corresponding derivative of (I), and their mass spectra were also identical. The acidification of (III) and recrystallization also gave (I).

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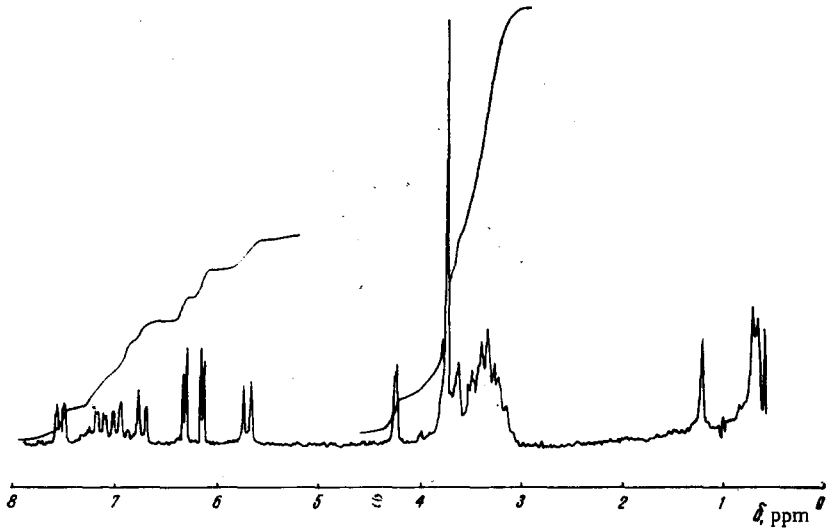

Fig. 1. NMR spectrum of the TMS ether of datinoside (CCl_4, internal standard HMDS, Varian HA-100 D).

When (III) was burnt, an incombustible residue remained. The results of emission analysis on a ISP-28 spectrograph (with the spectrum of iron for comparison) showed that (III) contained calcium and magnesium ions.

A process for obtaining the amorphous salt Al(morin)$_3$ by heating 2',3,4',5,7-pentahydroxyflavone (morin) with $AlCl_3$ in pyridine has been described [8]. The methylation of this salt with diazomethane gave 4',5,7-trimethoxymorin and, as Hyashia [8] assumed, an internally complex salt is formed through bonds between positions 2' and 3.

Datin also has a 2',3-dihydroxy grouping which possibly takes part in the formation of the salt which we have isolated and which we have called datinate-CM (datinate of Ca and Mg). The study of its structure is continuing.

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