2. É. Kh. Batirov, A. D. Matkarimov, V. M. Malikov, M. R. Yagudaev, and E. Seitmuratov, Khim. Prir. Soedin., 785 (1980).
3. A. Z. Abyshev and H. F. Gashimov, Khim. Prir. Soedin., 401, 403, 845 (1979).
4. H. Pozzi, E. Sanchez, and J. Comi, Tetrahedron, 23, 1129 (1967).
5. J. Reisch, K. Dzendrei, E. Minker, and I. Novak, Tetrahedron. Lett., 4305 (1970).
6. M. E. Perel'son, Yu. N. Sheinker, and A. A. Savina, The Spectra and Structures of Coumarins, Chromones, and Xanthones [in Russian], Moscow (1975).
7. W. Steck and M. Mazurek, Lloydia, 35, 418 (1972).
8. J. Reisch, I. Novak, K. Szendrei, and E. Minker, Pharmazie, 22, 205 (1967).
9. F. E. King, T. J. King, and L. C. Manning, J. Chem. Soc., 563 (1957).
10. M. M. Ballantyne, P. H. McCabe, and R. D. H. Murray, Tetrahedron, 27, 871 (1971).
11. M. M. Ballantyne, R. D. H. Murray, and A. B. Penrose, Tetrahedron Lett., 4155 (1968).
12. R. Braz Filho, A. F. Magalhaes, and D. R. Gottlieb, Phytochemistry, 11, 3307 (1972).

FLAVONOIDS OF *Datisca cannabina*.

V. DATISCANIN — A NEW GLYCOSIDE OF DATISCETIN

G. G. Zapesochnaya, N. A. Tyukavkina, and I. V. Shervashidze

UDC 547.972

The new flavonoid glycoside datiscanin has been isolated from the herbage of *Datisca cannabina* L., and the structure of 2',3,5,7-tetrahydroxyflavone 3-O-β-D-glucopyranoside has been established for it. After datiscin (datiscetin 3-rutinoside), this is the second datiscetin glycoside found in nature.

In the separation of the total flavonoids from the herbage of *Datisca cannabina* L. on polyamide columns [1], fractions of low-polarity glycosides were accumulated, and from these by rechromatography on silica gel a small amount of a new compound which we have called datiscanin (I) has been isolated. A comparison of the physicochemical characteristics of (I) with the properties of the glycoside datiscin (II) known for this plant showed that these compounds had identical UV spectra of PMR spectra differed only in the region of the resonance of the carbohydrate protons (Figs. 1 and 2). In the case of compound (I) in this region there are the signals only of a β-D-glucopyranose residue: δ 5.0 (J = 8 Hz), 3.1-3.8 (6 H). The signals of the aromatic protons were practically identical and were characteristic for the 2'-3,5,7-substitution of the flavone molecule.

The acid hydrolysis of (I) and (II) gave datiscetin (2',3,5,7-tetrahydroxyflavone), which was identified by its spectral characteristics and by comparison with an authentic sample. In contrast to the glycoside (I) and (II), having no long-wave maximum, there is such a maximum in the UV spectrum of the aglycone datiscetin (III) (Fig. 3). A hydrolysate of (I) was found chromatographically (PC, TLC) to contain glucose, while a hydrolysate of (II) contain glucose and rhamnose. Stepwise hydrolysis of (I) performed by Hörhammer's method [2] but at a lower temperature (complete hydrolysis took place at 105-107°C) enabled a product to be obtained which was identical with (I) for which the structure of datiscetin 3-O-β-D-glucopyranoside may be considered to have been demonstrated.

Up to the present time, the only natural glycoside of datiscentin was datiscin (datiscentin 3-rutinoside), which has been detected in *Datisca cannabina*. The new compound datiscanin that we have isolated and studied is the second datiscetin glucoside (datiscentin 3-glucoside).

Datiscanin is difficult to identify chromatographically in the mixture of flavonoids of *D. cannabina* because of the closeness of the R_f values. The presence of datiscanin in the total flavonoid fraction isolated from the herbage of *D. cannabina* was confirmed by high-performance liquid chromatographyusing an added "marker" (Fig. 4).

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. I. M. Sechenov First Moscow Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 176-180, March-April, 1982. Original article submitted June 16, 1981.

 0009-3130/82/1802-0160$07.50

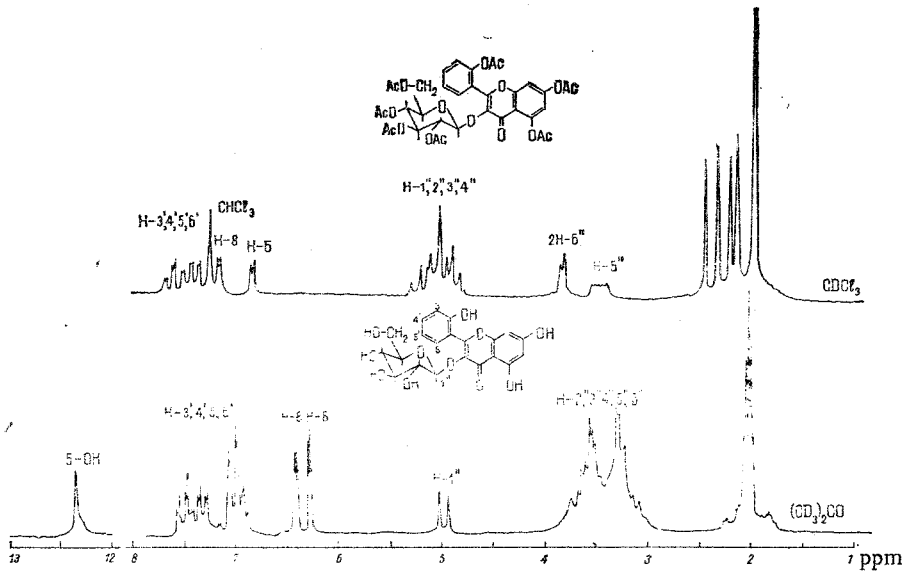

Fig. 1. PMR spectra of datiscanin (I) in deuteroacetone and of datiscanin heptaacetate in deuterochloroform.

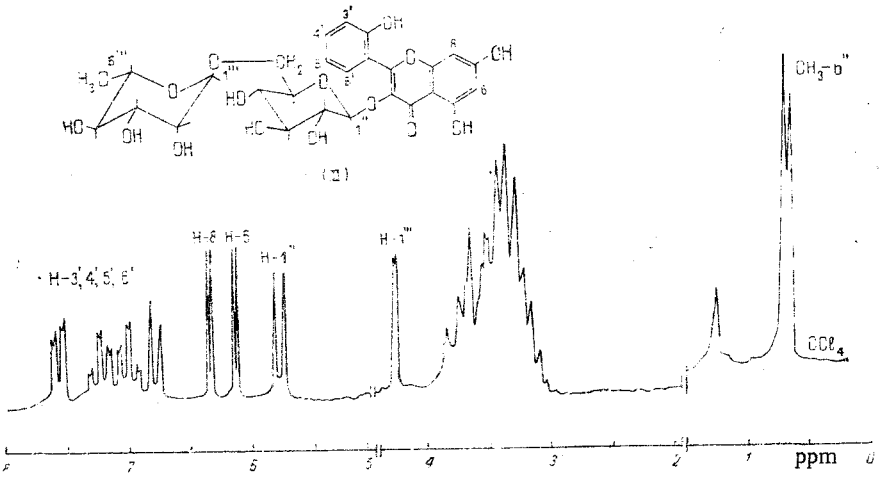

Fig. 2. PMR spectrum of the TMS ether of datiscin (II) in CCl_4.

EXPERIMENTAL

The spectral characteristics were obtained on the following instruments: Varian HA-100D MHz with tetramethylsilane as internal standard (PMR); Varian CH-8 at 70 eV (mass spectra) and Hitachi EPS-3T (UV). Elementary analysis was performed on a Hewlett-Packard 185B automatic CHN analyzer. Melting points were determined on a Kofler block; angles of rotation were obtained on a Polamat A polarimeter at 546 nm and were recalculated from the formula $[\alpha]_{546} = 1.17543 \cdot [\alpha]_D$. Chromatographic monitoring was performed by TLC (Solufol UV254 plates activated at 110°C) in the chloroform–methanol–water (26:14:3) system with observation of the chromatograms in UV light at 250 nm.

The separation of the flavonoids by high-performance liquid chromatography was performed on a Spectra-Physics 8000-04B chromatograph with a UV detector at a wavelength of 330 nm. Column 25 cm × 4.6 mm with the sorbent Lichrosorb 10RP-8. The eluent was methanol–water–acetic acid (45:50:5). The rate of flow was 2 ml/min.

Isolation. The total flavonoids isolated from the herbage of *D. cannabina* [1] were subjected to chromatographic separation on columns of polyamide in the chloroform–methanol–methyl ethyl ketone (12:2:1) system. The least polar fractions of the glycosides from several columns were combined and were then rechromatographed on silica gel. The column was washed with chloroform, with 3% and 5% ethanol in chloroform, and with 7% methanol in chloroform, which eluted compound (I).

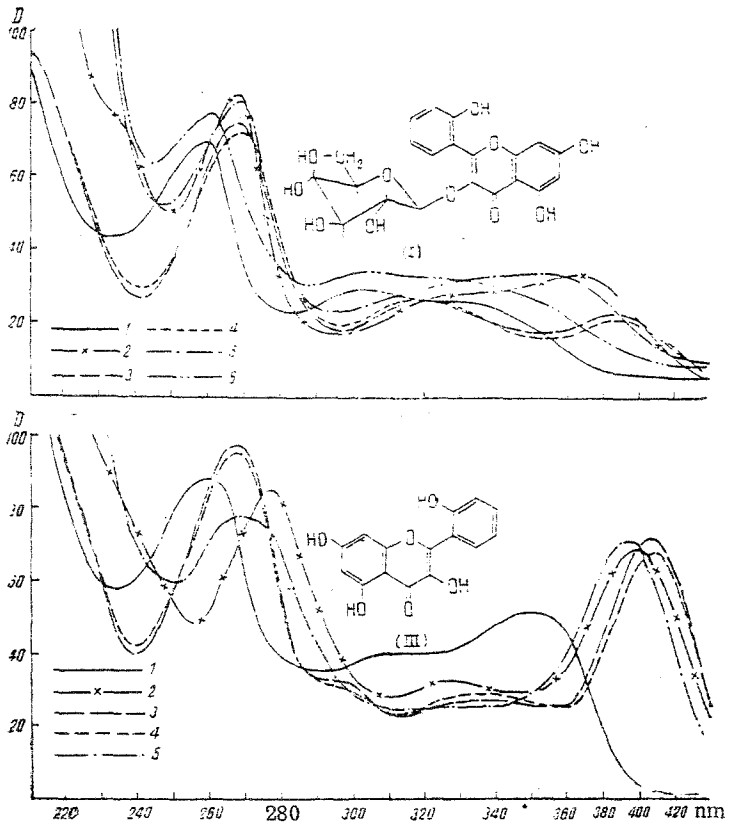

Fig. 3. UV spectra of datiscanin (I) and datiscetin (III): 1) MeOH; 2) NaOMe; 3) $AlCl_3$; 4) $AlCl_3$ + HCl; 5) NaOAc; 6) NaOAC + H_3BO_3.

Datiscanin (I). Light yellow crystals soluble in acetone and alcohols, with the composition $C_{21}H_{20}O_{11}$ $[\alpha]_D^{20}$ −61° (c 0.3 methanol), mp 150-162°C (decomp.). Maxima in the UV spectrum, nm: MeOH − 260, 303, 335 infl.; NaOMe − 268, 325, 368; NaOAc − 259, 350; NaOAc + H_3BO_3 − 261, 303, 335 infl.; $AlCl_3$ and $AlCl_3$ + HCl − 259, 320, 390 (see Fig. 3). PMR spectrum in deuteroacetone (ppm): 12.3 (s, 5-OH), 7.7-7.0 (m, H-3',4',5', 6'); 6.46 (d, 2 Hz, H-8), 6.3 (d, 2 Hz, H-6); 5.0 (d, 8 Hz, H-1"); 3.8-3.1 (m, 6 H of glucose) (see Fig. 1).

Acid Hydrolysis of (I). A mixture of 10 mg of (I) and 4 ml of 2% HCl was heated in the boiling water bath for 1 h. After cooling, the precipitate of datiscetin (III) that had formed was filtered off. Glucose was identified in the evaporated filtrate chromatographically (PC, TLC).

Acetylation of (I). The acetylation of (I) with acetic anhydride in the presence of pyridine (20°C, 24 h) led to the heptaacetate in the form of colorless crystals with mp 93-95°C $[\alpha]_D^{20}$ − 52.6° (c 0.6; acetone). PMR spectrum in $CDCl_3$ (ppm): 7.6-7.2 (m, 4 H); 7.16 (d, H-8); 6.85 (d, H-6); 5.3-4.8 (m, 4 H of glucose); 3.84 (m, 2 H-6"), 3.5 (m, H-5"); 2.46 (s, 3 H); 2.33 (s, 3 H); 2.22 (s, 3 H); 2.15 (s, 3 H); 2.0 (s, 9 H) (see Fig. 1).

Stepwise hydrolysis of (II). With heating, 0.3 g of datiscin (II) was dissolved in 25 ml of cyclohexanol, and then 5 ml of 97% formic acid was added and the mixture was heated at 65-70°C for 10 h. The mixture was washed with hot water (4 × 20 ml), evaporated in vacuum, and chromatographed on silica gel. The column was washed with chloroform and with 5% ethanol in chloroform, and then a mixture of 7% methanol in chloroform eluted 20 mg of compound (I).

CONCLUSION

The new flavonoid datiscanin has been isolated from the herbage of *Datisca cannibina* L. and its structure has been established as 2',3,5,7-tetrahydroxyflavone 3-O-β-D-glucopyranoside. After datiscin (datiscetin 3-rutinoside) this is the second datiscetin glycoside found in nature.

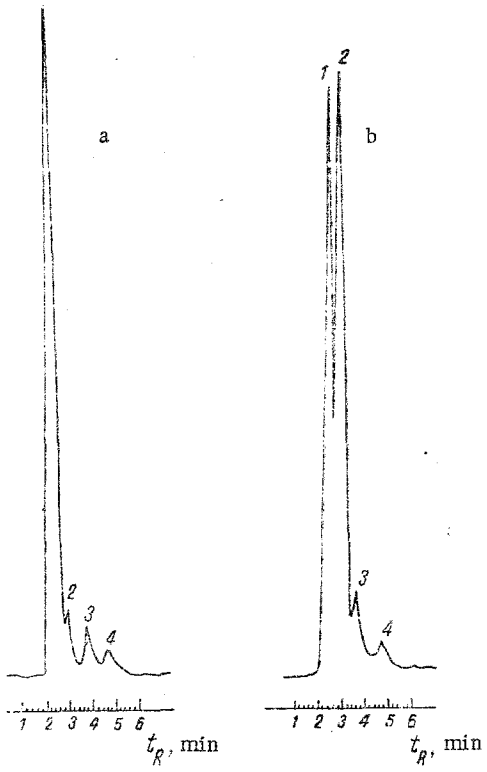

Fig. 4. Separation of the flavonoids of *Datisca cannabina* by liquid chromatography: 1) datiscin; 2) datiscanin (a); after the addition of authentic datiscanin to the initial mixture (b); 3) galanginoside [1]; 4) datinoside [1].

LITERATURE CITED

1. N. A. Tyukavkina, V. G. Gorokhova, G. G. Zapesochnaya, and V. A. Babkin, Khim-farm. Zh., 12, No. 10, 81 (1978).
2. L. Hörhammer, H. J. Gehrmann, and L. Endres, Arch. Pharmacol., 292/64, 113 (1959).

FLAVONOIDS OF *Datisca cannibina*.

VI. PROPERTIES OF DATISCIN

G. G. Zapesochnaya, N. A. Tyukavkina, and S. K. Eremin

UDC 547.972

An authentic individual sample of datiscin has been obtained, its physicochemical constants have been determined, and additional information concerning its structure as 2',3,5,7-tetrahydroxyflavone 3-O-[6"-(O-α-L-rhamnopyranosyl)-β-D-glucopyranoside] has been obtained.

Datiscin (I) was isolated from *Datisca cannabina* as early as 1816 [1]. Until the present time it was the only known glucoside of datiscetin (2',3,5,7-tetrahydroxyflavone) (II), which is present in the same plant [2]. There is contradictory information in the literature relative to the structure of the carbohydrate moiety of (I) [1, 3-8]. Chronologically, the sugar was first identified as glucose [3], then as rhamnose [4], again as glucose [5], and finally as rutinose [6].

In two papers [9, 10], datiscin is characterized as datiscetin 3-rutinoside, although no constants apart from details of the UV spectrum are given. However, in a more recent monograph [11] it is again called datiscetin rhamnoside. In the handbook literature [7, 8],

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. I. M. Sechenov First Moscow Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 180-183, March-April, 1982. Original article submitted June 16, 1981.

0009-3130/82/1802-0163$07.50