FLAVONOIDS OF THE LEAVES OF *Hibiscus cannabinus*

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UDC 547.972

The flowers and leaves of *Hibiscus cannabinus* (kenaf), family Malvaceae, have been studied for flavonoids by Indian scientists [1-5]. The flavonoid compositions of Soviet varieties of kenaf have not hitherto been studied.

The leaves of kenaf of variety 1574, collected in September, 1974, in the fields of the Politotdel communal farm, Verkhnechirchikskii region, Tashkent oblast, contained 1.5% of total flavonoids on the weight of the air-dry plant. The total flavonoids consisted of four substances, three of them being kaempferol glycosides and the fourth an arabinoside of an undetermined aglycone. The main component was glycoside I, with a yield of 0.5% on the weight of the air-dry plant. The other substances were isolated in minute amounts. Glycoside I was obtained by the extraction with hot 70% methanol of 3 kg of leaves previously defatted with chloroform. The flavonoids were exhaustively extracted with ethyl acetate from the aqueous mother liquor remaining after the methanol had been distilled off. The concentrated ethyl acetate extract soon deposited elongated light yellow needles with mp 202-203°C (from aqueous acetone and aqueous methanol), $C_{27}H_{30}O_{14}\cdot 2H_2O$, R_f 0.69 (BAW, 4:1:5; paper chromatography) and 0.37 (chloroform–methanol, 9:1; TLC, silica gel), $[\alpha]_D^{22}$ −180.4° (c 0.2; dimethylformamide). UV spectrum: λ_{max} 342, 263 nm (C_2H_5OH); 342, 264 nm (C_2H_5OH/CH_3COONa); 342, 264 nm ($C_2H_5OH/CH_3COONa/H_3BO_3$); 395, 339, 264 nm ($AlCl_3$).

In UV light on a paper chromatogram, compound (I) gave a dark brown spot which acquired a bright yellow fluorescence after treatment with a butanolic solution of aluminum chloride. The hydrolysis of (I) with a 7% methanolic solution of hydrochloric acid for 7 h led to the formation of the aglycone, which was identical with kaempferol, and a sugar — L-rhamnose. The ratio of kaempferol and rhamnose (1:2) was determined gravimetrically.

One molecule of rhamnose is attached in position C_3 of the kaempferol, as is confirmed by the reaction with zirconyl oxide and citric acid. The absence of a shift of the shortwave band in the UV spectrum of (I) after the addition of fused sodium acetate shows the position of the second molecule of rhamnose at C_7 of kaempferol.

The hydrolysis of (I) with a 0.2% methanolic solution of hydrochloric acid for 15 min gave kaempferol 7-monorhamnoside (II). Substance (II) forms bright yellow crystals, $C_{21}H_{20}O_{10}\cdot H_2O$, mp 220-222°C, R_f 0.88 (BAW, 4:1:5; paper chromatography), 0.81 (chloroform–methanol, 9:1; TLC, silica gel), $[\alpha]_D$ −157.6° (c 0.63; dimethylformamide). In UV light on a paper chromatogram, a spot of (II) fluoresced bright yellow.

It was impossible to split off the rhamnose from the C_7 position with 0.5% methanolic caustic soda under the conditions described by Litvinenko and Makarov [6]. On more prolonged heating, the molecule of (I) decomposed.

The IR spectrum of (I) has absorption bands of hydroxy groups (3450-2280 cm^{-1}), a carbonyl group (1657 cm^{-1}), CH in a methyl group (2930 cm^{-1}), deformation vibrations of an axial CH group (895 cm^{-1}, β anomer), of an equatorial CH group (844 cm^{-1}, α anomer), and of a $-CH_3$ group in a deoxypyranoside (975 cm^{-1}), the pulsation vibrations of a pyranose (776 cm^{-1}) and of a furanose (746 cm^{-1}), and the asymmetric vibrations of a pyranose ring (920 cm^{-1}) [7-9].

Calculations of the molecular rotations of (I) and (II) by Klyne's method in Kovalev and Litvinenko's modification [9], and also analysis of their IR spectra and differential IR spectra, permit the assumption for (I) of the structure of kaempferol 3-β-L-rhamnopyranoside-7-α-L-rhamnofuranoside.

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PHENOLIC ACIDS FROM *Trifolium alpestre, T. medium,* AND *T. pratense*

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UDC 547.972

Studying the chemical composition of plants of the genus *Trifolium* growing in the Northern Caucasus, we have previously established that clover is rich in phenolic compounds.

From the epigeal parts of *Trifolium alpestre* L., *T. medium* L., and *T. pratense* L. we obtained 40% ethanolic extracts. Paper chromatography in the 2% acetic acid system revealed three spots of substances with R_f 0.30, 0.58, and 0.63 which were assigned on the basis of their qualitative reactions to the phenolic carboxylic acids.

The following individual substances were obtained by physicochemical methods.

Substance (I). $C_9H_8O_3$, mp 210-212°C, λ_{max} 300 nm — p-coumaric acid.

Substance (II). $C_{16}H_{18}O_9$, mp 203-205°C, $[\alpha]_D^{20}$ −36.2° (c 0.1; methanol), λ_{max} 325, 240 nm — chlorogenic acid.

Substance (III). $C_{16}H_{18}O_8$, mp 243-242°C, $[\alpha]_D^{20}$ −52.3° (c 0.1; methanol) — 3-p-coumaroylquinic acid.

The substances obtained were identified by a study of their physicochemical properties and comparison with authentic samples provided by L. I. Dranik (KhNIKhFI [Khar'kov Scientific-Research Institute of Pharmaceutical Chemistry], Khar'kov). The phenolic acids from the plants mentioned have not been studied previously.

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, p. 258, March-April, 1976. Original article submitted April 30, 1975.