FLAVONOIDS OF Thermopsis dolichocarpa

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UDC 547.972

Continuing an investigation of the flavonoids of plants of the genus Thermopsis, we have studied the epigeal part of Thermopsis dolichocarpa V. Nikitin, family Fabaceae, gathered in the fruit-bearing period in May, 1987, in the Hissar region of the Tadzhik SSR.

The herbage of Th. dolichocarpa is recommended as an expectorant [1]. The flavonoids luteolin and cynaroside have been detected in this plant previously [2].

The air-dry comminuted raw material (2.6 kg) was exhaustively extracted with 85% ethanol. The extract was evaporated in vacuum, the residue was dissolved in water, and the solution was shaken successively with chloroform and with ethyl acetate. The ethyl acetate extract was evaporated and the residue (33.0 g) was treated with boiling aqueous ethanol. After cooling, the precipitate that had deposited was filtered off and the mother solution was evaporated in vacuum. By chromatography on a silica gel column in a chloroform—methanol gradient system the residue from the mother liquor yielded flavonoids (I-III), while the precipitate gave flavonoids (IV) and (V).

Flavonoids (I) ($C_{15}H_{10}O_6$, M^+ 286, mp 329-330°C) and (II) ($C_{21}H_{20}O_{11}$, M^+ 448, mp 240-242°C) were identified as luteolin and cynaroside, respectively.

Flavonoid (III) ($C_{15}H_{10}O_6$, M^+ 286, mp 272-273°C) was assigned to the isoflavone derivatives on the basis of its UV ($\lambda_{max}^{ethanol}$ 264, 293* inflection) and PMR spectra (signal of the H-2 proton at 8.00 ppm) [3]. IR spectrum: ν_{max}^{KBr} (cm^{-1}): 3420-3270 (OH group), 1660 (C=O of a γ-pyrone), 1622, 1576 (C=C bond). In the PMR spectrum, in addition to the H-2 signal, signals appeared of the protons H-6 (6.48 ppm, d, 2 Hz), H-8 (6.58 ppm, d, 2 Hz), H-5' and H-6' (7.02-7.18 ppm, m) and H-2' (7.62 ppm, br.s).

On the basis of the results of study of the IR, UV, PMR and mass spectra, this flavonoid was identified as orobol (3',4',5,7-tetrahydroxyisoflavone) [4].

Flavonoid (IV) ($C_{21}H_{20}O_{11}$, mp 182-184°C, $\lambda_{max}^{ethanol}$ 263, 292* nm) was a glycoside, and on acid hydrolysis decomposed with the formation of orobol and D-glucose. By the acetylation of flavonoid (IV) with acetic anhydride in pyridine a heptaacetate was obtained with mp 194-195°C. The mass spectrum of the latter contained, in addition to the peak of the molecular ion with m/z 742, intense peaks of the ions of a tetraacetylhexose with m/z 331, 271, and 169. The signal of the anomeric proton of D-glucose residue appeared in the PMR spectrum of compound (IV) at 5.66 ppm in the form of a doublet with SSCC J = 6.5 Hz (β-glucosidic bond). The linkage of the D-glucose residue to the C-7 position in the aglycon was established by a study of UV spectra taken with the addition of diagnostic reagents.

Consequently, compound (IV) was orobol 7-O-β-D-glucopyranoside [5].

Flavonoid (V) ($C_{21}H_{20}O_{10}$, mp 253-255°C, $\lambda_{max}^{ethanol}$ 263, 329* nm) was also assigned to the isoflavone derivatives. In its PMR spectrum (Py-d_5, 0—HMDS) appeared the signal of protons at (ppm) 8.01 (s, H-2), 7.56 (d, 8 Hz, H-2', 6'), 7.16 (d, 8 Hz, H-3', 5'), 6.91 (d, 2.5 Hz, H-8), 6.71 (d, 2.5 Hz, H-6), 5.65 (d, 6.2 Hz, H-1"), 4.60-3.90 ppm (protons of the sugar moiety).

The acid hydrolysis of flavonoid (V) formed genistein (4',5,7-trihydroxyisoflavone) and D-glucose, while its acetylation gave a hexaacetate with mp 189-191°C, M^+ 684.

From spectral characteristics and a direct comparison with an authentic sample, flavonoid (V) was identified as genistin (genistein 7-O-β-D-glucopyranoside) [6].

This is the first time that flavonoids (II-V) have been isolated from Thermopsis dolichocarpa.

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 547-548, July-August, 1990. Original article submitted October 17, 1989.

0009-3130/90/2604-0465$12.50

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FLAVONOIDS OF THE BUDS OF Populus deltoides

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UDC 547.972

There is only one communication in the literature on the flavonoid composition of the eastern or Canadian poplar, Populus deltoides Marsh, family Salicaceae, from the bark of which was isolated 6-C-methyldihydroquercetin and its glycosides [1].

Freshly gathered buds of eastern poplar, obtained in March, 1988, in the Kuibyshev botanical garden, were extracted with aqueous alcohol, and the extract obtained was evaporated in vacuum to a viscous residue, which was chromatographed on a column of silica gel using as eluents mixtures of hexane and chloroform and of ethanol and chloroform in various proportions. This permitted the isolation of ten flavonoid substances, which were assigned to the flavanones (I and II), the flavanonols (III), the flavones (IV-VI), and the flavonols (VII-X).

For the identification of the substances isolated we used UV, PMR, and mass spectroscopies, and also direct comparison with authentic samples [compounds (I), (II), and (IV-X)].

Pinostrobin (I) (5-hydroxy-7-methoxyflavanone) – white acicular crystals with the composition $C_{16}H_{14}O_4$ (M^+ 270), mp 96-98°C (from chloroform–petroleum ether).

Pinocembrin (II) (5,7-dihydroxyflavanone) – light yellow crystals with the composition $C_{15}H_{12}O_4$ (M^+ 256), mp 193-195°C (acetone).

The flavanone natures of compounds (I) and (II) followed from their UV spectra (λ_{max} 289 nm) [2] and their PMR spectra, each of which contained the signals of a proton at C-2 in the form of a doublet of doublets with SSCCs 4 and 12 Hz (chemical shift ~5.5 ppm) and the signals of protons at C-3 in the form of two doublets of doublets with the SSCCs 12 and 17 Hz for the axial proton at 3.2 ppm and 4 and 17 Hz for the equatorial proton at 2.8 ppm.

Analysis of the spectral characteristics, and also a comparison of physicochemical constants permitted the identification of compounds (I) and (II) as 5-hydroxy-7-methoxy- and 5,7-dihydroxyflavanones, respectively.

Alpinone (III) (3,5-dihydroxy-7-methoxyflavanone) – white acicular crystals with the composition $C_{16}H_{14}O_7$ (M^+ 286), mp 176-179 (ethanol). Compound (III) was the flavanonol analogue of pinostrobin (I), as followed from its PMR spectrum (deuteroacetone), which contained, in particular, two doublet signals with SSCCs of 17 Hz at 3.24 and 2.29 ppm belonging to the H-2 and H-3 protons, respectively. The flavanonol nature of compound (III) was also confirmed by its UV spectra (λ_{max} 290 nm) [2], and also by the characteristic peak of the M–17 ion with m/z 269 (68%) in its mass spectrum [1].

D. I. Ul'yanov Kuibyshev Medical Institute. All-Union Scientific-Research Institute of Medicinal Plants Scientific Production Combine, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 548-550, July-August, 1990. Original article submitted November 3, 1989.

0009-3130/90/2604-0466$12.50