FLAVONOIDS OF THE BUDS OF Populus balsamifera

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We have previously reported a preliminary evaluation by the TLC method of the chemical compositions of 12 species of poplar [1]. The results of these investigations have shown that from the practical point of view, in addition to the black poplar, the balsam poplar Populus balsamifera L., family Salicaceae, deserves the greatest attention.

Balsam poplar buds have been studied inadequately in the chemical respect. There is information in the literature on the component composition of the essential oil [2] and also on the presence of prostaglandins [3] and of three flavonoids – chrysin, tectochrysin, and 2',6'-dihydroxy-4'-methoxydihydrochalcone [4].

Buds of the balsam poplar freshly gathered in the Kuibyshev botanical garden in March, 1988, were extracted with hot alcohol and the extract obtained was evaporated in vacuum to a viscous residue, which was chromatographed successively on various sorbents. This led to the isolation of nine flavonoid substances belonging to the flavanones (I, II), the flavones (III-V), the flavonols (VI-VIII) and the chalcones (IX). The results of chemical transformations, and also their UV, PMR, and mass spectra, were used for their identification.

Pinostrobin (I) – white acicular crystals with the composition $C_{16}H_{14}O_4$, mp 96.5-98°C (from chloroform–petroleum ether).

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

The flavanone nature of compounds (I) and (II) followed from their UV spectra (λ_{max} 289, 325 sh.) and PMR spectra, each of which contained the signals of protons at C-2 in the form of a double doublet with SSCCs of 4 and 12 Hz (chemical shift ~ 5.5 ppm) and the signals of protons at C-3 in the form of two double doublets with SSCCs of 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 features and also a comparison of physicochemical constants enabled compounds (I) and (II) to be identified as 5-hydroxy-7-methoxy- and 5,7-dihydroxyflavanones, respectively.

Chrysin (III) – yellow crystals with the composition $C_{15}H_{10}O_4$, mp 282-285°C (ethanol).

Tectochrysin (IV) – yellow acicular crystals with the composition $C_{16}H_{12}O_4$, mp 144-147°C (from chloroform–petroleum ether).

Apigenin (V) – light yellow crystals with the composition $C_{15}H_{10}O_5$, mp 341-343 (aqueous alcohol).

Compounds (III-V) were assigned to the flavones since the PMR spectra of each of these substances contained the singlet signal of a proton at C-3 (in the 6.5-6.8 ppm region). Another common element of their structure was the nature of the substitution of ring A – the presence of substituents at C-5 and C-7. This followed from the PMR spectra in which, for each compound, two doublet signals were observed with a SSCC of 2.5 Hz, belonging to protons at C-6 and C-8 (in a weaker field) in the 6.3-6.8 ppm region. The results of acetylation, together with spectral characteristics, enabled compounds (III), (IV), and (V) to be identified as 5,7-dihydroxy-, 5-hydroxy-7-methoxy- and 4',5,7-trihydroxyflavones, respectively.

Galangin (VI) (3,5,7-trihydroxyflavone) – light yellow crystals with the composition $C_{15}H_{10}O_5$, mp 220-223°C (ethanol).

Kaempferol (VII) (3,4',5,7-tetrahydroxyflavone) – yellow crystals with the composition $C_{15}H_{10}O_6$, mp 285-287°C (aqueous alcohol).

3,3',4',5-Tetrahydroxy-7-methoxyflavone (VIII) – bright yellow crystals with the composition $C_{16}H_{12}O_7$, mp 248-250°C (aqueous alcohol).

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2',6'-Dihydroxy-4'-methoxychalcone (IX) – bright orange-colored acicular crystals with the composition $C_{16}H_{14}O_4$ (M^+ 270), mp 149-151°C (chloroform–MeOH). The chalcone nature of substance (IX) followed from its PMR spectrum, which contained two doublet signals with SSCCs of 16 Hz at 8.26 and 7.78 ppm, belonging to the H-β and H-α protons.

Thus, seven flavonoid compounds have been isolated from balsam buds for the first time, and the presence of two other flavonoids – chrysin and tectochrysin – has been confirmed.

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FLAVONOIDS OF Lathyrus pratensis

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Meadow pea, Lathyrus pratensis L., family Fabaceae, is a perennial herbaceous plant possessing an expectorant, sedative, and anti-inflammatory action. Flavonoids, quinones, phenolic carboxylic acids, cyclitols, and other substances have previously been found in this plant [1].

We have studied the flavonoids of the meadow pea growing in Uzbekistan. The epigeal part of the plant was gathered in the period of mass flowering in the village of Chimgan, Tashkent province, UzSSR. To isolate the total flavonoids, the air-dry herbage was comminuted and was treated with chloroform in order to eliminate substances of lipophilic nature. Then the flavonoids were extracted from the raw material with boiling 70% ethanol. The aqueous alcoholic extract was concentrated to an aqueous residue, which was purified with chloroform. The flavonoids were extracted from the purified aqueous residue with water-saturated butanol. The solvent was distilled off from the extract so obtained, and the residue was separated on a column of silica gel. The eluting liquids used were chloroform and mixtures of chloroform with increasing proportions of ethanol. Monitoring was carried out by thin-layer chromatography on Silufol UV-254 plates [using the chloroform–ethanol (9:1), (8:2), and (7:3) systems]. Four flavonoids were isolated in the individual form.

Flavonoid (I), composition $C_{15}H_{10}O_6$, M^+ 286, mp 326-328°C, $\lambda_{max}^{ethanol}$ 260, 274* (inflection), 356 nm, was identified from its UV, PMR, and mass spectra and comparison with an authentic sample as luteolin.

Flavonoid (II), $C_{21}H_{20}O_{11}$, mp 188-192°C; $\lambda_{max}^{ethanol}$ 271, 290*, 339 nm; $+CH_3COONa$ 272, 357 nm; $+CH_3ONa$ 270, 370 nm; $+AlCl_3$ 277, 349, 383 nm; was a glycoside, as was shown by its chromatographic mobility and its PMR spectrum, which exhibited the signals of an anomeric proton (5.55 ppm, d, J = 6.5 Hz) and other protons of the carbohydrate moiety (3.80-4.57 ppm).

The acid hydrolysis of this flavonoid gave luteolin and D-glucose. UV spectra taken with the addition of diagnostic reagents showed the presence of free phenolic hydroxy groups

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