

## FLAVONOIDS OF THE BUDS OF *Populus laurifolia*

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There is no information in the literature on the flavonoid composition of the buds of the laurel poplar *Populus laurifolia* Ledeb., fam. Salicaceae, the natural area of which is Siberia and Central Asia but which is widely cultivated throughout the territory of the former USSR [1]

Air-dry buds of laurel poplar gathered in March, 1992, in the Samara botanical garden were extracted with ethyl alcohol, and the extract obtained was evaporated in vacuum to a dry residue and chromatographed on a column of silica gel L 40/100 with, as eluents, mixtures of hexane and chloroform and of chloroform and ethanol in various ratios. This led to the isolation of twelve flavonoid substances belonging to the flavanones (1, 2), flavanonols (3, 4), flavones (5-7), flavonols (8-10), chalcones (11), and dihydrochalcones (12).

For the identification of the substances isolated we used UV, PMR, and mass spectra, and also direct comparison with authentic specimens of substances (1-3, 5, 6, and 9-11).

**Pinostrobin (1)** (5-hydroxy-7-methoxyflavanone) — white tabular crystals with the composition  $C_{16}H_{14}O_4$  ( $M^+$  270), mp 96-98°C (from hexane—chloroform).

**Pinocembrin (2)** (5,7-dihydroxyflavanone) — light yellow crystals with the composition  $C_{15}H_{12}O_4$  ( $M^+$  256), mp 185-188°C (hexane—chloroform).

The flavanone natures of compounds (1) and (2) were confirmed by their UV spectra ( $\lambda_{max}$  289 nm) [2] and their PMR spectra, each of which contained the characteristic signals of the proton at C-2 in the form of a doublet of doublets with SSCCs of 4 and 12 Hz (chemical shift ~5.5 ppm) and the signals of the protons at C-3 in the form of two doublets of 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.

**Alpinone (3)** (3,5-dihydroxy-7-methoxyflavanone) — white acicular crystals with the composition  $C_{16}H_{14}O_7$  ( $M^+$  286), mp 176-179°C (ethanol).

**Pinobanksin (4)** (3,5,7-trihydroxyflavanone) — white crystals with the composition  $C_{15}H_{12}O_5$  ( $M^+$  272, mp 172-176°C (chlf.—hexane).

Compounds (3) and (4) were the flavanonols analogous to flavanones (1) and (2), respectively, as followed from their UV, NMR, and mass spectra [2, 3]; however, compound (3) differed from substance (4) not only by the methylation of the 7-OH group but also by the configuration of the flavanonol nucleus (at C-2 and C-3). Thus, in the NMR spectrum (deuteroacetone) of alpinone (3) there were two doublet signals with a SSCCs of 17 Hz at 3.25 and 2.92 ppm, which are characteristic for the *trans*- configuration of the H-2 and H-3 protons, and in the NMR spectrum of compound (4) two doublet signals were observed with a SSCC of 11.6 Hz at 5.89 and 5.54 ppm, which showed the *cis*- arrangement of the corresponding protons at C-2 and C-3. The combination of physicochemical constants and spectral characteristics enables compounds (3) and (4) to be identified as alpinone and pinobanksin, respectively [4].

**Chrysin (5)** (5,7-dihydroxyflavone) — yellow crystals with the composition  $C_{15}H_{10}O_4$  ( $M^+$  254) mp 282-285°C (ethanol).

**Tectochrysin (6)** (5-hydroxy-7-methoxyflavone) — yellow acicular crystals with the composition  $C_{16}H_{12}O_4$  ( $M^+$  268), mp 144-147°C (chlf.—hexane).

**Genkwanin (7)** (4',5-dihydroxy-7-methoxyflavone) — yellow crystals with the composition  $C_{16}H_{12}O_5$  ( $M^+$  284), mp 285-287°C (chlf.—hexane),  $\lambda_{max}$  269, 335 nm.

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The presence of a free 5-OH group in compound (7), as also in the cases of flavones (5) and (6), was confirmed by its PMR spectrum (deuteroacetone) in which a one-proton singlet signal was revealed at 12.56 ppm. Flavone (7) differed from tectochrysin (6) by an additional OH group at C-4', as was shown by the NMR spectrum (deuteroacetone) in which two two-proton signals were seen with a SSCC of 9 Hz at 8.00 and 7.12 ppm, belonging to the H-2',6' and H-3',5' protons, and also by the UV spectra, in which sodium methanolate caused a bathochromic shift of the long-wave band with an increase in the intensity of absorption [2]. Structure (7) also agreed with the mass spectrum, which included characteristic peaks of the (A<sub>1</sub>+H) ion with *m/z* 167 (8%) and the B<sub>2</sub> ion with *m/z* 121 (2%) [5].

**Isalpinin (8)** (3,5-dihydroxy-7-methoxyflavone) — light yellow acicular crystals with the composition C<sub>16</sub>H<sub>12</sub>O<sub>5</sub> (M<sup>+</sup> 284), mp 198-199°C (ethanol) λ<sub>max</sub> 267, 360 nm.

**Galangin (9)** (3,5,7-trihydroxyflavone) — light yellow crystals with the composition C<sub>15</sub>H<sub>10</sub>O<sub>5</sub> (M<sup>+</sup> 270), mp 220-223°C (ethanol).

**3,3',4',5'-Tetrahydroxy-7-methoxyflavone (10)** — bright yellow crystals with the composition C<sub>16</sub>H<sub>12</sub>O<sub>7</sub> (M<sup>+</sup> 316), mp 248-250°C (aqueous alcohol).

The PMR spectra of flavonols (9) and (8) differed by the presence in the latter of a three-proton singlet signal at 3.95 ppm belonging to a methoxy group. On the basis of UV spectra and the mass spectrum, containing the peak of the (A<sub>1</sub>+H) ion with *m/z* 167 (15%), it was concluded that the 7-OH group was methylated in compound (8). Methylation of the 7-OH group in compound (10) was shown similarly.

**2',6'-Dihydroxy-4'-methoxychalcone (9)** — bright orange acicular crystals with the composition C<sub>16</sub>H<sub>14</sub>O<sub>4</sub> (M<sup>+</sup> 270) mp 149-151°C (chlf.—MeOH).

**2',6'-Dihydroxy-4'-methoxydihydrochalcone (12)** — light yellow crystals with the composition C<sub>16</sub>H<sub>16</sub>O<sub>4</sub> (M<sup>+</sup> 272) mp 171-174°C (chlf.—hexane).

The chalcone nature of substance (11) followed from its PMR spectrum (deuteroacetone), which contained two characteristic doublets with a SSCC of 16 Hz at 8.27 and 7.80 ppm belonging to the H-β and H-α protons. So far as concerns compound (12), the protons at C-β and C-α were revealed in the PMR spectrum (deuteroacetone) of this substance in the form of two two-proton triplets with a SSCC of 7 Hz at 3.41 and 2.98 ppm, showing the dihydrochalcone nature of (12).

It must be mentioned that this is the first time that compounds (1-12) have been isolated from laurel poplar buds, while, moreover, this is the first description of pinobanksin (4) for plants of the genus *Populus* L. It is striking that, with respect to their flavonoid composition, laurel poplar buds are particularly close to the buds of the black poplar, from which the above-mentioned compounds, with the exception of pinobanksin (4), have been isolated previously [1, 6]. At the same time, it is important to emphasize that the main flavonoids in the buds of the laurel poplar, as in the case of the black poplar [1, 6], and the eastern and balsam poplars [3, 7, 8], are represented by chrysin, pinostrobin, and pinocembrin, pronounced antimicrobial and antifungal properties having been described for the last-mentioned compound [9].

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