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ISOFLAVONOIDS OF THE BARK AND LEAVES OF *Maackia amurensis*

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It is known that the heartwood of Amur maackia *Maackia amurensis* Rupr. et Maxim (fam. Fabaceae) contains the stilbenes resveratrol, piceatannol, scirpusins, viniferins, and maackinine, and the isoflavones formononetin, genistein, and retusin, and also the isoflavostilbene maackiasin [1-4].

In the present communication we consider the isoflavones of the bark and leaves of Amur maackia gathered in the environs of Khabarovsk in July, 1991 and 1992.

The isoflavones were isolated from the raw material by the following scheme. The dry comminuted leaves and bark were extracted with a tenfold amount of 80% ethanol, the extracts were evaporated unil the solvents had been driven off, the residue was dissolved in distilled water (1:5), the insoluble matter was filtered off, and the filtrate was treated successively with chloroform and ethyl acetate. After the solvent had been eliminated, the residue was chromatographed on silica gel with the addition of 4% of gypsum. The ratio of the mixture to be separated and the sorbent was 1:80.

In the chromatography of the chloroform fraction, the column was eluted with benzene and chloroform—benzene (1:1), and then with chloroform and with chloroform containing up to 5% of ethanol. This led to the isolation of two aglycons of isoflavone nature ((1) and (2)).

The ethyl acetate fraction was separated with, as eluents, chloroform and mixtures of chloroform with increasing concentrations of ethanol. Two isoflavone glycosides ((3) and (4)) were obtained.

The substances isolated were identified from the results of chemical transformations and from their UV, IR, and PMR spectra, and also by direct comparison with authentic specimens.

Formononetin (1). White crystals with the composition $C_{15}H_{10}O_5$, mp 290-293°C (from benzene–chloroform), λ_{max}^{MeOH} 249, 302 nm (shoulder). IR spectrum, cm^{-1}: 3500-3100 (phenolic OH groups), 1665 (γ-pyrone), 2990-2800 cm^{-1} (OCH_3 group). Substance (1) gave no depression of the melting point with formononetin [5].

Genistein (2). White crystals with the composition $C_{15}H_{10}O_5$, mp 290-293°C (from benzene–chloroform). λ_{max}^{MeOH} 260; 330 nm. In the IR spectrum, no bands characteristic for an OCH_3 group were observed in the 2990-2800 cm^{-1} region. Acetylation formed a triacetate — $C_{21}H_{20}O_8$, mp 194-196°C.

On the basis of the results obtained, substance (2) was identified as 4′,5,7-trihydroxyisoflavone, genistein [5].

Ononin (3). Colorless acicular crystals with the composition $C_{22}H_{22}O_9$, mp 212-214°C, λ_{max}^{CH3OH} 257 and 302 nm (weak shoulder) Like substance (1), in the IR region of the spectrum compound (3) had a band characteristic for a methoxy group. Hydrolysis with grape snail enzymes led to the formation of formononetin (1) and D-glucose.

On the basis of the results of a comparison of physical properties and IR and PMR spectra and also of a mixed melting point the substance isolated was identified as 7-(β-D-glucosyloxy)-4′-methoxyisoflavone (ononin) [5].

Genistin (4). Pale yellow tabular crystals with the composition $C_{21}H_{20}O_{10}$, mp 257-259°C, $[\alpha]_D^{23}$ −24° (*c* 0.5; pyridine), λ_{max}^{MeOH} 263, 325 nm. With zirconyl chloride it gave a bathochromic shift of band 1 by 35 nm, which showed the presence of a hydroxy group at C-5 of the isoflavone nucleus. On enzymatic hydrolysis [6], substance (4) was cleaved into D-glucose and the aglycone genistein (3).

From its physicochemical properties, IR spectra, and mixed melting points with authentic specimens [5], substance (4) was identified as 7-(β-D-glucopyranosyloxy)-4′,5-dihydroxyisoflavone (genistin).

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Thus, from the bark and leaves of Amur maackia we have isolated two isoflavones and two isoflavone glycosides, of which formononetin (**1**) and genistein (**2**) are aglycons that have been isolated previously from the wood of this plant, while this is the first time that their glycosides ononin (**3**) and genistin (**4**) have been isolated from it.

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