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PHENOLIC COMPOUNDS OF Lespedeza hedysaroides

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Previous chemical investigations of the epigeal part of Lespedeza hedysaroides have shown the presence of the following flavonoids in it: kaempferol, quercetin, orientin, homoorientin, vitexin, and saponaretin [1].

We have investigated the phenolic composition of the epigeal part of L. hedysaroides (Pall.) Kitag. collected in the water meadows of the R. Khalkhin-Gol. Two-dimensional paper chromatography showed the presence in an ethanolic extract of not less than 14 flavonoid glycosides, five monomeric catechins, and three esters of hydroxycinnamic acids. The aqueous ethanolic extract was concentrated to an aqueous residue, and this was treated with chloroform and the phenolic compounds were extracted with butan-1-ol–ethyl acetate (1:1). The evaporated organic extract was subjected to chromatographic separation on columns of polyamide sorbent. The results of an investigation of the nature of the compounds isolated are given below.

Homoorientin, mp 229-231°C; $[\alpha]_D^{25}$+44.2° (c 0.1; methanol); $\lambda_{max}^{ethanol}$ 268, 355 nm, λ_{max}^{KOH} 266, 410 nm, $\lambda_{max}^{CH_3COONa}$ 278, 326, 394 nm. In the NMR spectrum (Perkin–Elmer R-20-A) of the homoorientin isolated and of its acetate, the presence of a doublet was observed at δ 6.48 ppm corresponding to the H-8 proton, and there was no signal of a H-6 proton. The acetyl derivative had mp 149-150°C.

Bioquercetin (quercetin 3-O-β-robinobioside), mp 194-196°C, $[\alpha]_D^{25}$–48.9° (c 0.2; methanol); $\lambda_{max}^{ethanol}$ 260, 300, 365 nm; λ_{max}^{KOH} 272, 335, 415 nm; $\lambda_{max}^{CH_3COONa}$ 273, 330, 405 nm; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 265, 300, 383 nm; $\lambda_{max}^{AlCl_3}$ 273, 295, 370, 405 nm; $\lambda_{max}^{AlCl_3+HCl}$ 273, 295, 360, 403 nm. The acetyl derivative had mp 127-128°C and $[\alpha]_D^{25}$–117.4° (c 0.1; methanol). Acid hydrolysis (5% HCl, 3 h) gave quercetin, D-galactose, and L-rhamnose. The ratio of $E_{1cm}^{1\%}$ for the glycosides and $E_{1cm}^{1\%}$ for the aglycones, which was 38.8%, is characteristic for a quercetin diglycoside. When the glycoside was incubated with rhamnodiastase, a disaccharide was obtained which was identical with the biose of an authentic sample of robinin. At the present time, the structure of β-robinobiose is a subject of discussion. Thus, for the disaccharide of a quercetin diglycoside from Robinia pseudacacia [mp 201-203°C; $[\alpha]_D^{25}$–27.1° (c 0.1; dimethylformamide] the structure of 6-O-β-L-rhamnopyranosyl-β-D-galactofuranose has been proposed previously [2]. At the present time, for the present time, for the robinobiose of the bioquercetin obtained synthetically [mp 198-201°C; $[\alpha]_D^{25}$–50° (c 0.5; dimethylformamide)] the structure of 6-α-L-rhamnopyranosyl-β-D-galactopyranose has been suggested [3]. The kaempferol galactorhamnoside corresponding to bioquercetin was provisionally considered to be kaempferol 3-β-robinobioside. Orientin, vitexin, and saponaretin were shown to be present by paper-chromatographic comparison with authentic samples.

After the paper-chromatographic separation, the amounts of the main flavonoids were determined by the spectrophotometric method. This showed that the epigeal part contained 0.46% of homoorientin, 0.18% of bioquercetin, and 0.14% of orientin, on the air-dry weight.

We found no flavonoid aglycones or free hydroxycinnamic acids in the epigeal part of this plant.

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THE STRUCTURE OF AKIFERININ

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Continuing a study of esters of Ferula akitschkensis B. Fedtsch ex K.-Pol., by separating the mother liquor after the isolation of akichenin, akiferin, ferutin, and ferutinin on a column of silica gel, we have isolated a substance with the composition $C_{24}H_{34}O_6$ (I) (M^+ 418), with mp 176-177°C, $[\alpha]_D^{20}$ +73.1° (c 0.82; $CHCl_3$). The substance is readily soluble in alcohols, chloroform, and acetone, sparingly soluble in ether and petroleum ether, and insoluble in water. The UV spectrum of (I) showed maxima at 262 and 295 nm (log ε 4.09, 3.76) which are characteristic for a 3,4-dihydroxybenzoyl residue.

The IR spectrum of the substance has absorption bands of an aromatic nucleus (1520, 1590, 1610 cm^{-1}), of an ester group (1235, 1705 cm^{-1}), and of a hydroxy group (3550 cm^{-1}). A comparison with the literature of the physicochemical constants and spectral characteristics that we found for the substance showed that it is new. We have called it akiferinin.

The PMR spectrum of (I) (JNM-4-100 MHz, $CDCl_3$, 0 – HMDS) (Fig. 1) contains the signals of secondary (0.75, 0.85 ppm, d, J=7.5 Hz, 3H each) and tertiary (1.22, 1.44 ppm, s 3H each) methyl groups, of methoxy groups in an aromatic nucleus (3.82, 3.84 ppm, s, 3H each), and of a hemiacyl proton (5.35 ppm, sextet, $J_1=J_2=$ 10 Hz; $J_3=2.5$ Hz). Signals were also observed at 6.85 ppm (d, J=9.5 Hz, 1H), 7.45 ppm (q, $J_1=9.5$; $J_2=2.5$ Hz, 1H), and 7.35 ppm (d, J=2.5 Hz, 1H) due to the protons of a 3,4-dimethoxybenzoic (veratric) acid residue.

When akiferinin was subjected to alkaline hydrolysis, the acidic fraction of the hydrolyzate yielded an acid with the composition $C_9H_{10}O_4$ (II) with mp 192-193°C which was identified as veratric acid [3], and the neutral fraction yielded a sesquiterpene alcohol with the composition $C_{15}H_{26}O_3$ (III) with mp 113-114°C identical with the diol obtained in the hydrolysis of tenuferin, tenuferinin, and tenuferidin [4].

Thus, akiferinin is an ester of the sesquiterpene diol (III) with veratric acid, and structure (I) is proposed for it.

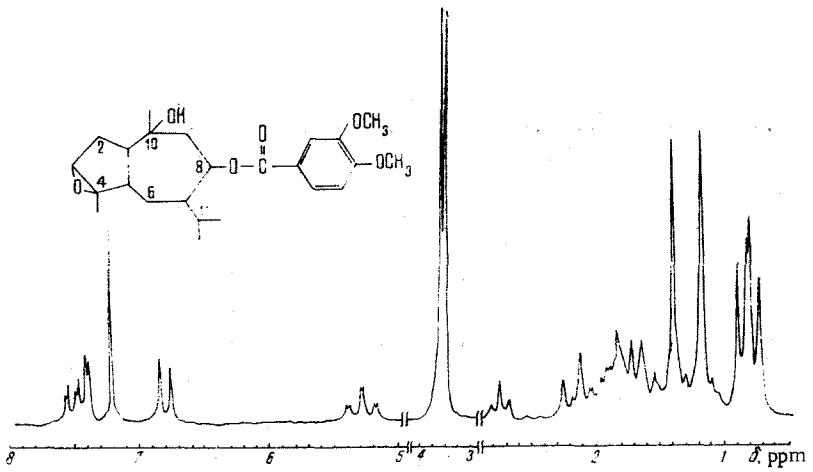

Fig. 1. NMR spectrum of akiferinin.

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