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CIRCULAR DICHROISM OF FARNESIFEROL A AND SOME OF ITS ANALOGS

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In the proof of the structure of farnesiferol A and its analogs, the determination of the orientation of the substituents at C_9 proved to be the most complex problem [1-6]. Recently, from the shift of the Cotton effect (CE) in the 300 nm region it has been possible to determine the orientation of substituents at C_9 in such diterpenoids as giberellinic acid, cafestol, and kaurene, but no unambiguous results were obtained for derivatives of eperuic acid and, in particular, farnesiferol A [7]. We have considered the interconnection between the nature of the circular dichroism (CD) curves and the stereochemistry at C_9 in farnesiferol A (I), gummosin (II), mogoltadone (III), colladonin (IV), badrakemin (V), and the ketone of badrakemin (VI). In addition to Cotton effects in the 320 and 230 nm regions connected with transitions in the coumarin nucleus, all the compounds considered have a Ce at 200 nm caused by a $\pi \rightarrow \pi^*$ transition in the exomethylene bond. We directed our attention precisely to this CE, since the asymmetric center of interest to us is adjacent to this chromophoric group. As can be seen from the results obtained (Table 1), the orientation of the substituents affects the amplitude of the CE in the 200 nm region. In the case of axial orientation of the C_9-CH_2-R group (I-III), the intensity of the CE is several times greater than for the equatorial orientation (IV-VI). This increase in intensity can probably be explained by the fact that in the axial orientation the aromatic nucleus and the exomethylene group prove to be close to one another in space and partial overlapping of their π orbitals becomes possible.

The CD spectra were recorded ona JASCO-J-20 spectropolarimeter at a concentration of the solution of 0.5 mg/ml with cell thicknesses of 0.05 and 0.01 cm. The solvent was methanol.

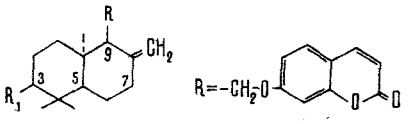

TABLE 1

Substance	R-axial R_1	λ_{max}, nm	$\Delta\varepsilon$	Substance	R equatorial R_1	λ_{max}, nm	$\Delta\varepsilon$
I	α-OH	203	−16,1	IV	α-OH	204	−2,3
II	β-OH	202	−19,3	V	β-OH	205	−5,6
III	-O	202	−18,4	VI	-O	200	−4,7

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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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