GLABRANIN – A NEW FLAVANONE FROM *Glycyrrhiza glabra*

N. Sh. Kattaev and G. K. Nikonov

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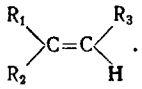
There is much information in the literature on the presence in the herb Glycyrrhiza glabra L. (common liquorice) of substances with estrogenic properties [1-6]. More than ten flavonoids and phenolic and other compounds have been isolated from this plant [7]; however, the nature and composition of the estrogenic components has not been investigated. We have investigated the phenolic substances with UV absorption maxima in the 280-nm region. One of the substances, with mp 135-137°C, of undetermined composition possesses the activity mentioned [3].

The liquorice plant collected in the Sverdlov region of the Bukhara [Bokhara] oblast was treated with 2 N caustic soda solution, and the extract was neutralized. The precipitate was dissolved in ether and the solution was washed with ammonia solution and evaporated to dryness. The residue was chromatographed on Kapron, the column being eluted with chloroform–acetone (9 : 1). A colorless crystalline substance with the composition $C_{20}H_{20}O_4$, mp 154-155°C (from methanol), M^+ 324, was obtained, which we have called glabranin. This substance is readily soluble in chloroform and acetone and is insoluble in water, and it gives a positive cyanidin reaction and a dark-brown coloration with alcoholic ferric chloride. Its UV spectrum has a maximum at 297 nm (log ε 351) which permits the substance to be assigned to the flavan group.

The IR spectrum of the substance (Fig. 1) shows bands at 1620, 1520, and 1540 cm^{-1} (aromatic nucleus), 1645 cm^{-1} (carbonyl of a γ-pyrone with a hydroxy group at C_5), 3355-3370 cm^{-1} (hydroxy groups) and 1350 and 1390 cm^{-1} (gem-dimethyl group on a double bond). Bands at 810, 830, and 859 cm^{-1} and at 710 and 768 cm^{-1} correspond to 1,2,3,4,5-penta-substituted and 1-monosubstituted benzene rings, and a band at 810 cm^{-1} is due to the grouping



In the NMR spectrum (taken at 100 MHz in $CDCl_4$ [8], δ scale from the signal of HMDS) there is a five-proton singlet at 7.20 ppm (protons of an unsubstituted ring C), a one-proton singlet at 5.98 ppm (H-6), and broadened signals at 11.90 and 7.8 ppm (C_5-OH and C_7-OH protons). A quartet (1H) with its center at

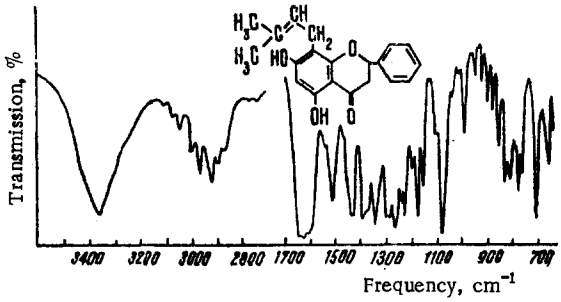


Fig. 1. IR spectrum of glabranin (in KBr).

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5.35 ppm J_1 = 11 Hz, J_2 = 5 Hz, and bands at 2.78, 2.85, and 2.97 ppm (2H) are due, respectively, to the H_1 and H_2 (cis and trans) protons of a pyrone ring. A six-proton singlet at 1.65 ppm, a multiplet at 5.0-5.35 ppm, and a doublet at 3.20 ppm, J = 7.5 Hz (2H) relate to a grouping $Ar-CH_2-CH=C(CH_3)_2$.

Consequently, glabranin is 8-(3'3'-dimethylallyl)-5,7-dihydroxyflavanone and has the structure shown in Fig. 1.

LITERATURE CITED

1. C. H. Costello and E. V. Lynn, J. Amer. Pharm. Assoc., 3 (1950).
2. V. S. Goryachev, Tr. VSSS N.-i. In-ta Karakulevodstva, 14 (1964).
3. I. A. Murav'ev and N. F. Kononikhina, Questions of Spa Treatment, Pharmacy and Pharmacology [in Russian], Pyatigorsk (1967), p. 332.
4. V. S. Goryachev, Questions of the Physiology and Biochemistry of Karakul Sheep [in Russian] (1968).
5. I. A. Murav'ev and N. F. Kononikhina, Abstracts of Lectures at a Symposium on the Study of Utilization of Liquorice in Folk Medicine of the USSR [in Russian], Ashkhabad (1969), p. 84.
6. E. Krause, Monatshefts für Veterinarmedizin, 25, 4 148 (1970).
7. V. I. Litvinenko and T. P. Nadezhina, Rast. Res., 8, No. 1, 35 (1972).
8. T. J. Mabry, J. Kagan, and H. Rösler, Nuclear Magnetic Resonance Analysis of Flavonoids, University of Texas (1964).