FLAVONOIDS OF THE EPIGEAL PART OF *Glycyrrhiza glabra*

É. Kh. Batirov, F. Kiyamitdinova, and V. M. Malikov

UDC 547.972

The flavonoids pinocembrin, glabranin, and prunetin have been isolated previously from the epigeal part of *Glycyrrhiza glabra* L. [1]. The GLC of an ethanolic extract of the epigeal part collected in the flowering period in Tashkent showed the presence of the spots of not less than nine flavonoids. Chloroform extraction of 2.9 kg of the comminuted raw material gave 205.0 g of extract. This was chromatographed on a column of silica gel in the chloroform—hexane gradient system.

Six individual flavonoids were isolated from the various fractions. Compounds (I) with mp 195-196°C (yield 0.97% on the weight of the dry plant) and (II) with mp 160-169°C (yield 0.31%) were identified as pinocembrin and glabranin, respectively [1].

Compound (III), $C_{15}H_{10}O_5$, mp 217-219°C (from methanol), M^+ 270 (100%). The UV spectrum of (III) exhibited maxima at 268 and 362 nm (log ε 4.20 and 4.01), which permitted it to be assigned to the flavonol group. According to the result of PMR and mass spectroscopy, this compounds contained three hydroxy groups. The presence in the mass spectrum of peaks of ions with m/z 105 and 77 showed that ring B in the molecule of (III) was unsubstituted. From its spectral characteristics and literature information, flavonoid (III) was identified as galangin (3,5,7-trihydroxyflavone) [2, 3].

Compound (IV), $C_{15}H_{12}O_5$, mp 248-250°C, λ_{max} 290, 327* nm (log ε 4.19, 3.62) was assigned to the flavanone derivatives. On the basis of its UV, IR, and PMR spectra, (IV) was identified as naringenin (4',5,7-trihydroxyflavone) [2, 3].

Compound (V), $C_{15}H_{10}O_5$, mp 299-302°C (decomp.), M^+ 270 (100%). Its UV spectrum (λ_{max} 263, 329* nm; log ε 4.42, 3.81) corresponded to a 4',5,7-trihydroxyisoflavone chromophore [2].

The result of a study of its IR, UV, PMR, and mass spectra showed that this compound corresponded to genistein (4',5,7-trihydroxyisoflavone) [2, 3].

Compound (VI), $C_{20}H_{20}O_4$, M^+ 324 (100%), mp 209-211°C (from ethanol), ν_{max}^{KBr} (cm^{-1}): 3130 (OH), 1632 (C=O of a γ-pyrone), 1585 (C=C bond). Its UV spectrum (λ_{max} 297, 335* nm; log ε 3.95, 3.00) was characteristic for flavanone derivatives [2]. The presence in its mass spectrum of the peaks of ions with m/z 105 and 177 showed that ring B contained no substituents.

The acetylation of (VI) formed a diacetate with mp 85-87°C. Consequently, substance (IV) contained two phenolic hydroxy groups which, on the basis of the results of UV spectroscopy with diagnostic reagents, occupied the C-5 and C-7 positions. The PMR spectrum of (VI) showed the signals of the protons of a γ,γ-dimethyldiallyl group attached directly to an aromatic ring, 8 H, of a monosubstituted benzene ring, and of the characteristic H-2 and 2 H-3 protons of a flavanone [2].

According to the CD spectrum, the C-2 asymmetric center in compound (VI) had the S configuration [4]. Thus, substance (VI) was identified as 5,7-dihydroxy-6-(γ,γ-dimethylallyl)-flavanone [5].

This is the first time that the compounds (III)-(VI) have been isolated from *G. glabra*. The high estrogenic activity of Spanish licorice is apparently due to the presence in it of the isoflavonoids genistein and prunetin [6, 7].

LITERATURE CITED

1. N. Sh. Kattaev and G. K. Nikonov, Khim. Prir. Soedin., 805 (1972); 93 (1974).

---

*Inflection.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 111-112, January-February, 1986. Original article submitted June 18, 1985.

0009-3130/86/2201-0107$12.50

2. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
3. Rodd's Chemistry of Carbon Compounds (2nd edn.), S. Coffey (ed.), Elsevier, Amsterdam, Vol. IV, Heterocyclic Compounds, Part E (1977), pp. 189, 214, 279.
4. W. Gaffield, Tetrahedron, 26, 4093 (1970).
5. R. Braz Filho, O. R. Gottlieb, and A. P. Mourao, Phytochemistry, 14, 261 (1975).
6. D. A. Murav'eva, in: Pharmacognosy [in Russian], Moscow (1978), p. 463.
7. V. G. Shimanov, in: The Hormonal Activity of Pasture Plants and Their Influence on the Fertility of Karakul Sheep [in Russian], Tashkent (1972), pp. 39, 157.

AN X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES.

V. CRYSTAL STRUCTURE OF THE LIGROIN* MODIFICATION OF GOSSYPOL

S. A. Talipov, B. T. Ibragimov, B. N. Dadaboev,
T. F. Aripov, and A. S. Sadykov

UDC 548.737+547.972

Adams [1] obtained tabular crystals with mp 214°C from a solution of gossypol (Gp) in ligroin. Even earlier, Clark had obtained the same crystals from a solution of Gp in diethyl ether at the boundary with water, i.e., from the crust in the hydrolysis of Gp acetate [2]. Single crystals of this modification of solid Gp were obtained for our investigations by the slow evaporation of a solution in a mixture of ether and hexane. All this indicates that the ligroin form is free from solvent and can be used to obtain pure Gp. However, for this purpose the temperature of the solution must not be below 18-20°C. At lower temperatures a solution of Gp in a mixture of ether and hexane gives a precipitate of crystals of a different form – an adduct of Gp with ether, the results of an interpretation of the structure of which has been given in [3]. The density of the crystals of the ligroin form amounts to 1.37 g/cm³, which is the highest density of the forms known so far. These features of the crystallization of Gp in this modification can be explained by the results of an x-ray structural analysis.

The crystallographic parameters of the crystals investigated were determined on a Syntex-$P2_1$ automatic diffractometer: $a = 13.467(1)$ Å, $b = 8.794(1)$ Å, $c = 21.376(3)$ Å, $\gamma = 97.23(1)°$, $V = 2511.54\ (0.54)$ Å^3, $z = 4$, sp. gr. $P2_1/c$. The experimental material was obtained on the same diffractometer by the $\theta/2\theta$-scanning method in CuK_α radiation using a graphite monochromator. The calculations were performed with 2714 reflection having $F^2 \geqq 1.96\sigma$. The structure was interpreted by the direct method with the aid of the MULTAN program included in the XTLSM group [4]. Refinement was carried out by the method of least squares, initially in the isotropic approximation ($R = 0.119$) and then in the anisotropic approximation ($R = 0.086$). Fourier difference syntheses revealed all the hydrogen atoms. The final value of the R factor was 0.049, and the corresponding coordinates of the atoms in the structure are given in Table 1.

As in the forms studied previously [3, 5, 6], the Gp molecule has the aldehyde tautomeric form. The angle between the planes of the naphthalene nuclei is 87.5°, which is the largest value for the crystalline forms of Gp so far studied. The isopropyl groupings of the two halves are oriented differently with respect to their closest hydroxy groups O4 and O8 (for the numbering of the atoms, see [5]).

In the crystal structure, the molecules are associated into dimers through O5—H (x, y, z)...O_3(−x, −y, −z) and O_3(x, y, z)...O_5—H (−x, −y, −z) hydrogen bonds 2.864(4) Å long. Infinite walls extended along the b direction are formed from the dimers by O1—H (x, y, z)...

---

*In our investigations, the crystal form of gossypol is indicated by the name of the solvent from which it was obtained.

Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 112-113, January-February, 1986. Original article submitted June 26, 1985.