FLAVONOIDS OF Glycyrrhiza glabra

N. Sh. Kattaev and G. K. Nikonov

UDC 547.972

Continuing a study of the herb Glycyrrhiza glabra (common licorice), we have investigated a fraction of lipophilic flavonoids soluble in benzene, chloroform, and ether which on "deresinification" by existing methods had previously remained unnoticed.

From a methanolic extract of the herb G. glabra L., in addition to the glabranin described previously [1], we have isolated two more substances by chromatography on polyamide with elution by chloroform–acetone (97:3); they gave positive cyanidin reactions with zinc and magnesium in hydrochloric acid and have a very low intensity of the long-wave maximum in the UV spectrum, which showed that they belonged to the group of flavanones or isoflavones.

Flavonoid I, $C_{15}H_{12}O_4$, dark-brown acicular crystals with mp 196-197°C (from methanol), $[\alpha]_D^{25}$ −44° (c 0.284; acetone), M^+ 286, R_f 0.25 [chloroform–acetone (97:3) system, Silufol plates, chromogenic agent a 1% ethanolic solution of $FeCl_3$]. The UV spectrum of the substance showed maxima at 293 and 328 nm (log ε 4.25, 3.68) which permits its assignment to the flavanones. The IR spectrum of (I) showed absorption bands at (cm^{-1}): 1635 (carbonyl of a 5-hydroxy-γ-benzopyrone), 1600, 1580, 1458 (aromatic nucleus), and 3015-3120 (hydroxy groups).

In the NMR spectrum of the flavonoid (I) taken in acetone (on a Geol instrument at 60 MHz, δ scale from the signal of HMDS) a five-proton multiplet was found at 7.13-7.55 ppm (protons of unsubstituted ring B), a singlet at 5.85 ppm (2 H) belonging to the H-6 and H-8 protons, a quartet (1 H) with its center at 5.36 ppm, J_1 = 11 Hz, J_2 = 4 Hz, and a multiplet at 2.72-3.30 ppm (2 H) due, respectively, to the H-2 and H-3 protons (cis and trans) of a dihydropyrone ring. A singlet at 11.5 ppm (1 H) and a broadened signal at 9.20 ppm (1 H) relate to the C_5–OH and C_7–OH protons, respectively.

On the basis of the investigations performed, it was established that this substance is 5,7-dihydroxyflavanone and must be identical with pinocembrin [2].

Flavonoid II, $C_{16}H_{12}O_5$, colorless acicular crystals with mp 241-243°C (from methanol, M^+ 284, R_f 0.18, UV spectrum: λ_{max} 263, 325 nm (log ε 4.16, 3.75), which corresponds to the chromophore of 4',5,7-trihydroxyflavone. In the presence of aluminum chloride a bathochromic shift of the maximum of band II by 12 nm was observed, which disappeared on the addition of citric acid, and in the presence of sodium ethoxide there was an analogous shift by 11 nm, showing the presence in the flavonoid of hydroxy groups in the 4' and 5 positions [3]. IR spectrum, cm^{-1}: 1682 (carbonyl of a 5-hydroxy-γ-benzopyrone), 1628-1588, 1530, 1455 (aromatic nucleus), 2970-3120 (–OCH_3), 3400 (hydroxy groups).

The PMR spectrum of substance (II) (solution in deuteropyridine) had the following signals (ppm): one-proton singlet at 7.79 – the H-2 proton of a pyrone ring; doublets at 7.37 (2 H), J = 8.5 Hz, and 6.91 (2 H), J = 8.5 Hz – the H-2' and H-6' and the H-3' and H-5' protons, respectively; doublets at 6.27 and 6.19, J = 2 Hz (1 H each) – the H-8 and H-6 protons in ring A [14]; and a signal at 11.46-13.20 ppm (1 H) – the proton of the C_5–OH group. A singlet at 3.48 ppm (3 H) was caused by a methoxy group, which may be in position 4' or position 7.

The presence in the mass spectrum of the substance (taken on an MKh-1303 mass spectrometer) of a peak with m/e 167 shows that the methoxy group is in position 7. This is also confirmed by the absence of a bathochromic shift in the UV spectrum taken in the presence of sodium acetate [5].

Order of the Red Banner of Labor Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, p. 93, January-February, 1974. Original article submitted June 19, 1973.

It follows from the facts given that the second substance possesses the structure of 4',5-dihydroxy-7-methoxyisoflavone and is identical with prunetin [6].

This is the first time that pinocembrin and prunetin have been found in the genus Glycyrrhiza .

LITERATURE CITED

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