PRANDIOL – A NEW DIHYDROFUROCOUMARIN FROM THE ROOTS OF Prangos biebersteinii

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In a study of the chemical composition of a methanolic extract of the roots of Prangos alata Grossh.– Prangos biebersteinii Karjag., in addition to compounds isolated previously [1], we isolated another two substances – (I) and (II) – of the coumarin series.

The composition and constants of substance (I) ($C_9H_6O_3$, mp 229-231°C) and the characteristics of the IR and NMR spectra correspond to a known coumarin – umbelliferone. A mixture with an authentic sample gave no depression of the melting point.

Substance (II), $C_{14}H_{14}O_5$, mp 131-132°C (from benzene), which we have called prandiol, belongs to the group of dihydrofurocoumarins, since it possesses a violet fluorescence in UV light and gives an NMR spectrum (Fig. 1) that is characteristic for 6,7-disubstituted coumarins in which doublets are observed at 6.16 and 7.79 ppm, $J = 10$ Hz (1H each) corresponding to protons 3 and 4 of the coumarin nucleus. Singlets at 7.37 and 6.66 ppm (1H each) are due to the protons in positions 5 and 8, respectively. A triplet at 4.94 ppm (1H) and a doublet at 3.27 ppm (2H), ($J = 8.5$ Hz), show the presence in the molecule of (II) of a methine proton interacting with the protons of an adjacent methylene group attached, in its turn, to an aromatic nucleus [2]. The spectrum of (II) also has the signals of an aliphatic methyl group (1.20 ppm, singlet, 3H) and a methylene group (3.54 ppm, singlet, 2H) on a quaternary carbon atom to which a tertiary hydroxyl is probably attached. The second hydroxy group is apparently present directly at the methylene group.

No signals from hydroxy groups are observed in the spectrum, since they fuse with the signal of the deuteromethanol in which the NMR spectrum of (II) was taken. The facts given permit 5'-(1'',2''-dihydroxyisopropyl)-4',5'-dihydrofuro-2',3':7,6-coumarin to be proposed as the most probable structure for (II). This structure and the presence of the two hydroxy groups in it were confirmed by the results of a study of the IR, NMR, and mass spectra of acetyl derivatives of (II).

The acetylation of (II) with acetic anhydride in pyridine led to the formation of a monoacetate, $C_{16}H_{16}O_6$ (III), with mp 129-130°C (from petroleum ether), M^+ 304, and of a diacetate, $C_{18}H_{18}O_7$ (IV), with mp 103-105°C (from petroleum ether), M^+ 346.

The IR spectrum of (III) has absorption bands at 3460 cm^{-1} (OH group), 1725 cm^{-1} (C = O of an α-pyrone), and 1630 and 1590 cm^{-1} (aromatic nucleus). A broad band of a carbonyl group and a band at 1270 cm^{-1} show the presence of an ester grouping in (III).

In the NMR spectrum (Fig. 1b), the signals from the methylene group in the side chain are observed in a weaker field (4.17 ppm, singlet, 2H) than in the spectrum of (II), which is apparently due to the presence of the acyl residue at this group. Also in favor of this assumption is the fact that the signals from the methine proton in the dihydrofuran ring does not undergo the paramagnetic shift that is generally found on the acylation of a tertiary hydroxyl attached to a quaternary carbon atom.

In the IR spectrum of (IV) absorption bands appear at 1720 cm^{-1} (C = O of an α-pyrone), 1630 and 1580 cm^{-1} (–C = C– in conjugation), and 1750 and 1260 cm^{-1} (ester grouping).

In the NMR spectrum of (IV) (Fig. 1), the same pattern appears in the region of aromatic protons as in the spectrum of (III). In the region of aliphatic protons there are the signals of the following groups:

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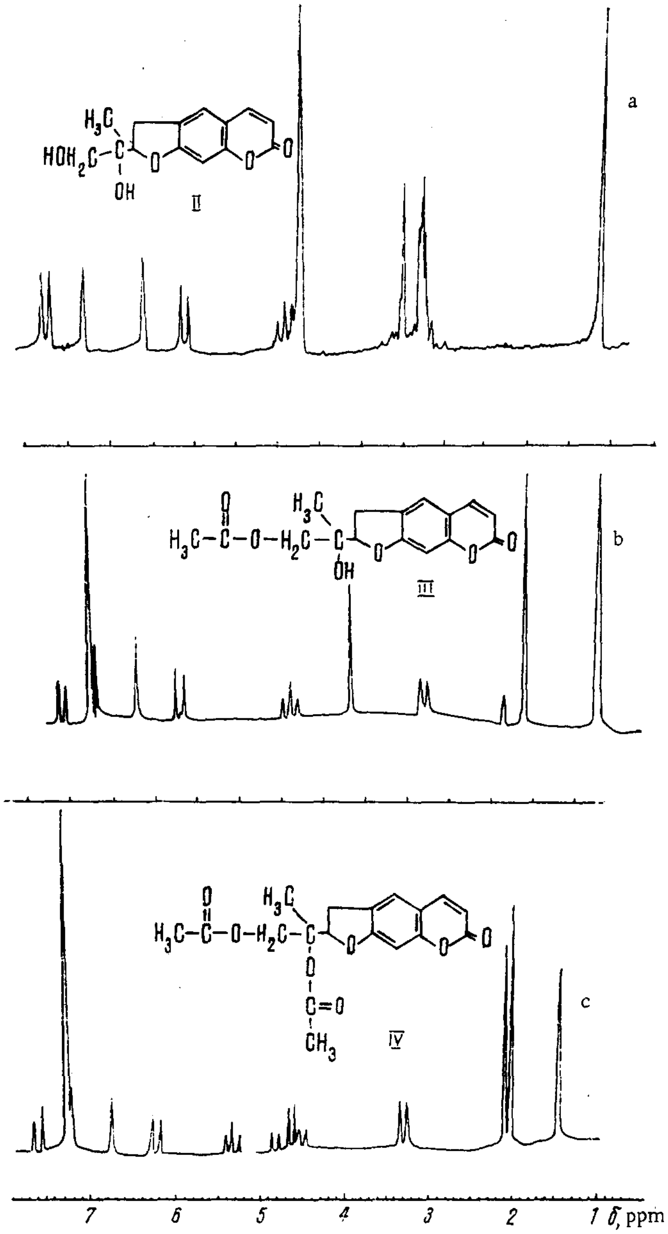

Fig. 1. NMR spectra of prandiol (a), prandiol monoacetate (b), and prandiol diacetate (c).

$-CH_3$ (1.44 ppm, singlet, 3H), $2COCH_3$ (2.0 and 2.06 ppm, singlets, 3H each), and $Ar-CH_2-$ (3.27 ppm, doublet, 2H, J = 8 Hz). The signals from the methine proton in position 5' and from the methylene group in the side chain undergo a paramagnetic shift and appear, respectively, at 5.30 ppm (triplet, 1H) and 4.60 ppm (multiplet, 2H).

Thus, it follows from the combination of facts presented that (III) is a monoacetate and (IV) a diacetate of (II). This agrees completely with the structure proposed for prandiol (II).

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer (in paraffin oil), the NMR spectra on a Varian HA-100D spectrometer [(II) in CD_3OD and (III) and (IV) in $CDCl_3$; 0 – HMDS]. The melting points were determined on a Koffler block.

Isolation of the Coumarins. The comminuted roots of Prangos biebersteinii (200 g) were extracted with methanol three times. The solvent was distilled off under vacuum and the residue (30 g) was chromatographed on a column of neutral alumina (300 g, activity grade IV) with the use as eluents of petroleum ether (fractions 1-3), benzene (fractions 4-8), benzene–chloroform (4 : 1; 2 : 1) (fractions 8-12), chloroform (fractions 13-17), and methanol (fractions 18-22). The volume of each fraction was 100 ml. The quantitative compositions of the fractions were checked by thin-layer chromatography [TLC, Al_2O_3, activity grade IV, ethyl acetate–benzene (1 : 4 and 1 : 2) systems]. From fractions 1-14 components were isolated that had been found previously [1] in a chloroform extract of the plant under investigation.

Isolation of (I) and (II). Fractions 15-22, containing the (I) and (II), after distillation of the solvents, were separated preparatively by the TLC method (Al_2O_3, activity grade IV, ethyl acetate system). This gave substance (I), $C_9H_6O_3$, mp 229-231°C, and substance (II), $C_{14}H_{14}O_5$, mp 131-132°C.

Acetylation of (II). The acetylation of 0.2 g of (II) was performed in acetic anhydride (2 ml) and pyridine (0.5 ml) for 3 h. Then the reaction mixture was worked up by the usual method, and the product was separated preparatively by TLC [Al_2O_3, activity grade II, ethyl acetate–benzene (1 : 4) system]. This gave (III), $C_{16}H_{16}O_6$, mp 129-130°C, and (IV), $C_{18}H_{18}O_7$, mp 103-105°C.

SUMMARY

From a methanolic extract of the roots of Prangos biebersteinii Karjag., in addition to substances found previously, two other components – (I) and (II) – of the coumarin series have been isolated.

The results of a study of their IR, NMR, and mass spectra, and also their chemical properties have enabled (I) to be identified as the known coumarin umbelliferone and the structure of 5'-(1'',2''-dihydroxyisopropyl)-4',5'-dihydrofuro-2',3' : 7,6-coumarin to be proposed for (II), which has been named prandiol.

LITERATURE CITED

1. A. Z. Abyshev, I. V. Brodskii, and P. P. Denisenko, Khim. Prirodn. Soedin., 269 (1973).
2. A. Z. Abyshev and P. P. Denisenko, Khim. Prirodn. Soedin., 114 (1972).