THE STRUCTURE OF FERUTININ

A. I. Saidkhodzhaev and G. K. Nikonov

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Continuing a study of the phenols contained in various representatives of the genus Ferula [1-4], from the roots of Ferula tenisecta Eug. Korov. collected in the Tashkent oblast we have isolated a new substance which we have called ferutinin (I).

Ferutinin, $C_{19}H_{24}O_4$, mp 121-122°C, $[\alpha]_D^{22} \pm 66.1°$ (c 1.36; ethanol) dissolves readily in chloroform, carbon tetrachloride, ether, and ethanol, and sparingly in petroleum ether, and is insoluble in water. It has a neutral character, and it gives a positive reaction with ferric chloride which shows the presence of a phenolic hydroxyl in its molecule. It dissolves in the cold in a solution of caustic potash, and on being heated with the latter it undergoes cleavage, which shows the presence of an ester grouping in (I).

The UV spectrum of (I) has a maximum at 261 nm (log ε 4.16), which is characteristic for an aromatic nucleus, and in the IR spectrum (Fig. 1) there are absorption bands at (cm^{-1}) 3200-3600 (hydroxy group), 2840-2980 (methyl and methylene groups), 1690 (carbonyl of an aromatic acid), 1610, 1595, and 1515 (aromatic nucleus). A bathochromic shift of the UV maximum in the presence of alkali (307 nm) shows that it contains a free phenolic group. The mass spectrum of (I) shows in addition to the peak of the molecular ion (M^+ 316) fragments with m/e 177, 159, and 151.

In the NMR spectrum of (I) there are two two-proton doublets at 6.81 and 7.81 ppm (J = 9 Hz) due to ortho protons of an aromatic nucleus, a broadened signal with its center at 8.58 ppm corresponding to a phenolic hydroxy group, a triplet with secondary splitting due to a geminal proton at an ester grouping at 5.22 ppm ($J_1 = 7$ Hz, $J_2 = 3$ Hz) and broadened one-proton signals due to an olefinic proton and to an alcoholic hydroxyl at 5.50 and 2.65 ppm, respectively.

The alkaline hydrolysis of (I) gave an alcohol with the composition $C_{12}H_{20}O_2$, mp 82-83°C, and an aromatic hydroxy acid $C_7H_6O_3$, with mp 212-213°C. A comparison of physicochemical constants and IR spectra and mixed melting points showed that the alcohol obtained was ferutinol [2] and the acid was p-hydroxybenzoic acid.

Consequently, ferutinin is an ester of ferutinol and p-hydroxybenzoic acid.

A substance of this type, which has been called ferungin (II), has recently been isolated from Ferula prangifolia Eug. Korov. [4]. However, in contrast to the case of ferungin, the IR spectrum of (I) clearly shows two maxima at 3000-3400 cm^{-1} and 3500-3550 cm^{-1} which are characteristic for phenolic and alcoholic hydroxy groups, while ferungin has only one broad band at 3200-3550 cm^{-1}. The NMR spectrum of I has a broadened one-proton singlet at 8.58 ppm due to the proton of a phenolic hydroxy group, while in the NMR spectrum of II this signal does not appear distinctly. These facts permit the conclusion that (I) and (II), although they are esters of the same acid and ferutinol, are different from one another and may be characterized as isomers. In the molecule of (II), the phenolic and tertiary hydroxyls apparently form

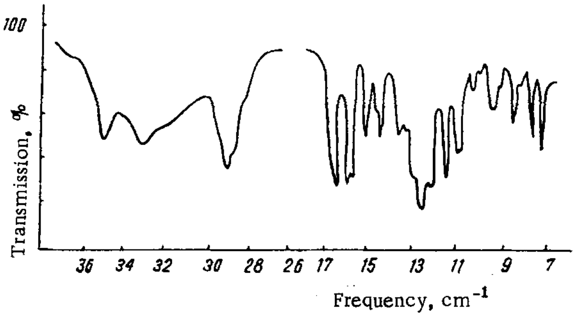

Fig. 1. IR spectrum of ferutinin.

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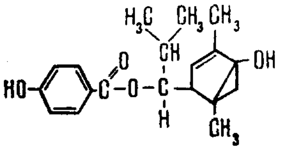
an intramolecular hydrogen bond, which is possible, as a Dreiding model shows, if the aromatic and cyclohexene nuclei are located in parallel planes and one above the other. Thus, ferutinin has the following structure:



EXPERIMENTAL

The conditions for recording the UV, IR, mass, and NMR spectra have been described previously [2].

Isolation of Ferutinin. The dried comminuted roots (1 kg) were treated three times with 6-liter portions of methanol. The extract was concentrated to 2 liters, diluted with water (2 : 1), and extracted with ether (4 × 0.4 liter). Evaporation of the solvent yielded 135 g of crude extract.

Part of the extract (25 g) was deposited on a column (h = 20 cm, d = 9 cm) filled with silica gel (particle dimensions 250 μ). When the column was eluted with benzene–petroleum ether (7 : 3), ferutinin (5.2 g) was isolated with mp 121-122°C (petroleum ether).

Hydrolysis of Ferutinin. A. Ferutinol was isolated as described previously [2].

B. The mother solution after the isolation of the ferutinol was acidified with 5% sulfuric acid and treated with ether. The residue after the solvent had been eliminated was recrystallized from water. Crystals with mp 212-213°C deposited. A mixture with p-hydroxybenzoic acid gave no depression of the melting point.

SUMMARY

From Ferula tenuisecta Eug. Kor. a new substance with the composition $C_{19}H_{24}O_4$ (mp 121-122°C) has been isolated, and it has been named ferutinin. On the basis of UV, IR, mass, and NMR spectra and the products of alkaline hydrolysis it has been established that ferutinin is an ester of p-hydroxybenzoic acid and ferutinol.

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