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STRUCTURE AND STEREOCHEMISTRY OF FERSORIN AND FERSORIDIN

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From the total extractive substances of the roots of Dzhungarian giant fennel we have isolated two new esters — fersorin and fersoridin. Their structures and stereochemistries have been established on the basis of chemical transformations and spectral characteristics.

From the neutral fraction of the total extractive substances of the roots of Dzhungarian giant fennel gathered in Karaganda province, Republic of Kazakhstan, by column chromatography on KSK silica gel we have isolated two new substances, which we have called fersorin (**1**) and fersoridin (**2**).

Fersorin (**1**) has the composition $C_{24}H_{32}O_5$, M^+ 400. In its UV spectrum a maximum was observed at 262 nm (log ε 4.00), which is characteristic for *p*-hydroxy-substituted benzoyl derivatives.

The IR spectrum of (**1**) was the usual one for esters of sesquiterpene alcohols, showing absorption bands at (cm^{-1}) 1520, 1590, 1620 (aromatic nucleus), 1700, 1720 (ester of a carbonyl group), and 3200-3450 (hydroxy group).

In the PMR spectrum of (**1**) we observed the following proton signals: doublets at 0.80 and 0.92 ppm (3H each, J = 7.5 Hz), singlets at 1.05, 1.77, and 2.25 ppm (3H each), a sextet at 5.27 ppm (1H, $J_1 = J_2 = 10.5$ Hz; $J_3 = 2.5$ Hz), a triplet at 5.50 ppm (1H, $J_1 = J_2 = 7.5$ Hz), and doublets at 7.12 and 8.0 ppm (2H each, J = 9.5 Hz).

When fersorin was subjected to alkaline hydrolysis by heating with a 5% aqueous alcoholic solution of caustic potash, the neutral fraction of the hydrolysate yielded the sesquiterpene alcohol ferutinol, and the acid fraction yielded *p*-hydroxybenzoic acid.

A comparison of the PMR spectra of fersorin and ferutinin [1, 2] showed that the spectrum of (**1**) had an additional signal from the protons of an acetyl group. Judging from the value of the chemical shift (2.25 ppm) it was located in an aromatic nucleus. This was also confirmed by a downfield shift of the H-3′ and H-5′ signals.

On the basis of the facts given above, it was possible to conclude that fersorin is 4′-acetoxy-6-*p*-hydroxybenzoyloxyferutinol and has the relative configuration (**1**) shown in the diagram.

Fersoridin (**2**) has the composition $C_{29}H_{38}O_7$ mp 132-133°C $[\alpha]_D$ −12.8° (*c* 1.0; chloroform). Its spectrum showed a characteristic absorption maximum at 262 nm (log ε 4.02) due to the presence in the molecule of a *p*-hydroxy-substituted benzoyl residue.

The IR spectrum of (**2**) showed absorption bands at 1510, 1610, 1660, 1680 (inflection), 1710, 1725, and 3200-3600 cm^{-1}, which are characteristic for esters with aromatic and aliphatic acids.

The PMR spectrum of (**2**) was characteristic for esters of terpenoid alcohols, the following proton signals being observed: doublets at 0.80 and 0.98 ppm (J = 7.5 Hz, 3H each), singlets at 1.25 and 1.76 ppm (3H each), doublets at 1.87 ppm (J = 1.5 Hz, 3H) and 1.95 ppm (J = 7.0 Hz, 3H), a singlet at 2.22 ppm (3H), a triplet at 4.50 ($J_1 = J_2 = 7.5$ Hz, 1H), a multiplet at 5.50 ppm (2H), a quartet at 6.1 ppm (J = 7.5 and 1.5 Hz, 1H), and doublets at 7.15 and 8.0 ppm (J = 9.5 Hz, 2H each).

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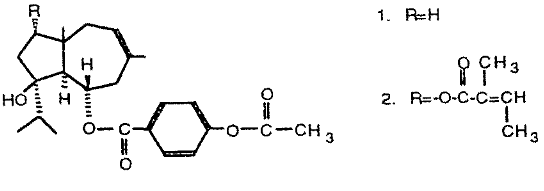
In the mass spectrum of (2), we observed the peaks of ions with *m/z* 481 $(M - 17)^+$, 455 $(M - 43)^+$, 355 $(M - 43 - OO)^+$ [sic], 218, 175, 121 $(C_7H_5O)^+$, and 83 $(C_5H_7O)^+$, which are characteristic for esters of sesquiterpene alcohols with aromatic and aliphatic acids.

When fersoridin was subjected to alkaline hydrolysis, the neutral fraction of the hydrolysate yielded a sesquiterpene alcohol with the composition $C_{15}H_{26}O_3$, mp 155-156°C, which was found to be identical with an authentic sample of akichenol, which we had isolated previously from *Ferula akitschkensis*.

Thus, according to the results of PMR and mass spectroscopy, fersoridin is an ester of akichenol with *p*-hydroxybenzoic, angelic, and acetic acids.

Akichenin, an ester of akichenol with *p*-hydroxybenzoic and angelic acids has been isolated previously from *Ferula akitchkensis* [3]. A comparison of the PMR spectra of fesoridin and akichenin showed that these acid residues had identical positions in fesoridin and akichenin. The difference in the PMR spectra of these substances consisted in the fact that the spectra of fersolin had an additional three-proton singlet from the protons of an acetyl group at 2.2 ppm and a paramagnetic shift of the signals of the protons of the aromatic nucleus by 0.2 ppm. Consequently, the acetic acid residue occupies the $C_{4'}$ position and fersoridin is a natural acetyl derivative of akichenin.

Dhungarian giant fennel is, so far, the only species of the *Ferula* genus where acyl derivatives of terpenoids in which the phenolic group of an aromatic acid is acylated have been found. Most frequently, esters of aromatic acids in which a phenolic hydroxy group has been methylated are found in giant fennels.



EXPERIMENTAL

UV spectra were taken on a Hitachi spectrophotometer, IR spectra on a UR-20 instrument, ^1H NMR spectra on a Tesla BS-567A spectrometer ($CDCl_3$, δ scale, 0 — HMDS) and mass spectra on a MS-25 RF spectrometer (Kratos).

The purity of the substances was checked on Silufol R plates in the hexane–ethyl acetate (3:1) system with a 1% solution of vanillin in conc. sulfuric acid as the revealing agent.

Isolation of Fersoridin. The neutral fraction of the total extractive substances of Dhungarian giant fennel roots (20 g) was transferred to a column of KSK silica gel (3 × 100 cm), and the substances were eluted with hexane–ethyl acetate (9:1), and then with increasing concentrations of the latter. After the solvent had been driven off, fractions 35-51 deposited from a mixture of hexane and ether (1:1) crystals of fesoridin with mp 132-133°C (210 mg).

Isolation of Fersorin. When elution was continued with hexane–ethyl acetate (4:1), fractions 56-62 yielded fersorin (340 mg), R_f 0.33.

Hydrolysis of Fersoridin. A solution of 0.1 g of fersoridin in 20 ml of a 5% aqueous alcoholic solution of caustic potash was heated on the water bath for 2 h. The hydrolysate was diluted with water and treated with ethyl acetate. After the solvent had been driven off, a mixture of petroleum ether and ethyl acetate deposited akichenol, $C_{15}H_{26}O_2$, with mp 155-156°C.

The mother aqueous alcoholic solution was acidified with 10% sulfuric acid and treated with ethyl acetate. This led to the isolation of *p*-hydroxybenzoic acid, $C_7H_6O_3$, with mp 210-212°C.

Hydrolysis of Fersorin. Fersorin (0.15 g) was hydrolyzed as described above. Ferutinol, $C_{15}H_{26}O_2$, with mp 89-90°C and *p*-hydroxybenzoic acid were isolated.

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