

STRUCTURES OF FERSIN AND FERSININ

N. N. Nazhimitdinova, A. I. Saidkodzhaev,
and V. M. Malikov

UDC 547.992:547.37

*Two new compounds – fersin and fersinin – have been isolated from the neutral fraction of the total extractive substances from the roots of *Ferula soongorica*. Their structures have been established on the basis of chemical transformations and spectral characteristics.*

Continuing an investigation of the components of plants of the genus *Ferula* [1], from the neutral fraction of the total extractive substances of the roots of *Ferula soongorica* Pall ex Spring, gathered in the Karaganda oblast of the Republic of Kazakhstan, we have isolated, by adsorption chromatography on KSK silica gel, esters of organic acids and a monoterpene alcohol with the compositions $C_{19}H_{24}O_4$ (1), M^+ with m/z 346, mp 113-114°C, $[\alpha]_D +16^\circ$ (c 1.0; chloroform) and $C_{20}H_{26}O_5$ (2), M^+ with m/z 346, mp 92-93°C, $[\alpha]_D +19.5^\circ$ (c 1.0; chloroform), which we have called fersin and fersinin, respectively.

In the IR spectrum of (1) we observed absorption bands of an ester carbonyl group (1720, 1700 cm^{-1}), of an aromatic nucleus (1610, 1560, 1510 cm^{-1}), and of an ester bond (1040 cm^{-1}). In the UV spectrum of (1) a maximum was observed at 262 nm ($\log \epsilon$ 4.08), characteristic for *p*-hydroxybenzoyl derivatives, which did not undergo a bathochromic shift when the spectrum was taken with the addition of alkali. This showed substitution of the hydroxy group in the *p*-hydroxybenzoyl residue, as was confirmed subsequently by the PMR spectrum of fersin. The composition and the IR and UV spectra of the substance showed that fersin was an ester of a monoterpene alcohol with aromatic and aliphatic acids.

When fersin was subjected to alkaline hydrolysis by heating it with 5% aqueous alcoholic caustic soda, the neutral part of the hydrolysate yielded a monoterpene alcohol with the composition $C_{10}H_{18}O$, mp 204-205°C, $[\alpha]_D +12^\circ$ (c 1.0; chloroform) with a camphor-like smell which was identified as *d*-borneol by comparison with an authentic sample [2]. *p*-Hydroxybenzoic acid $C_7H_6O_3$ with mp 210-212°C was obtained from the acid part of the hydrolysate.

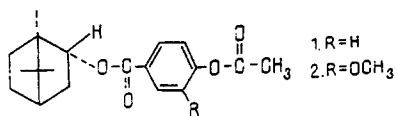
The PMR spectrum of (1) showed the following signals (ppm): singlets at 0.80 (6H) and 0.84 (3H) relating to tertiary methyl groups, a singlet at 2.20 (3H) from an acetoxy group attached to an aromatic nucleus, a multiplet at 5.0 ppm (1H, $W_{1/2} = 18$ Hz) of a hemiacyl proton, and doublets at 7.15 and 7.96 ($J = 9.5$ Hz, 2H each) of the *ortho*-aromatic protons of a *p*-hydroxybenzoic acid residue.

A comparison of the spectra of chimgin [2] and fersin showed that the latter contained an additional signal from an acetoxy group present in the aromatic nucleus. This was confirmed by a paramagnetic shift of the protons at C_3^1 and C_5^1 by 0.33 ppm as compared with those of chimgin [2]. Consequently, fersin is a natural acetate of chimgin, and for it we propose structure (1).

The PMR spectrum of fersinin (2) differed from that of fersin (1) only by the fact that, in place of the signals of a *p*-hydroxybenzoic acid residue, it contained the proton signals of a vanillic acid residue and also a three-proton singlet at 2.22 ppm of the protons of an acetoxy group. The alkaline hydrolysis of (2) yielded *d*-borneol and vanillic acid $C_8H_8O_4$ with mp 205-206°C. The results obtained showed that fersinin had the structure (2).

To confirm the proposed structures of (1) and (2) for fersin and fersinin, we acetylated *d*-chimgin and *d*-chimganin with acetic anhydride in pyridine. The resulting acetates of chimgin and chimganin were identical with fersin and fersinin, respectively.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, FAX (3712) 89 14 75. Translated from *Khimiya Prirodnikh Soedinenii*, No. 4, pp. 504-506, July-August, 1994. Original article submitted December 27, 1993.



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer, UV spectra on a Hitachi EPS-3Y spectrometer (in ethanol), mass spectra on a Kratos MS 25 RF spectrometer, and PMR spectra on a Tesla BS-567A spectrometer in deuteriochloroform. Chemical shifts are given relative to the internal standard HMDS on the δ -scale. For column chromatography we used brand KSK silica gel with a particle size of 160-250 μ .

Isolation of Fersin and Fersinin. The neutral fraction obtained by the alcoholic extraction of ground *Ferula soongorica* roots and the appropriate working up (20 g) was deposited on a column (3 \times 100 cm) of KSK silica gel, and the substances were eluted with hexane-ethyl acetate (9:1, and then increasing concentrations of the latter). Fractions 11-22 yielded fersin C₁₉H₂₄O₄ with mp 113-114°C. On continuing elution with hexane-ethyl acetate (4:1), fersinin C₂₀H₂₆O₅, mp 92-93°C was isolated.

Hydrolysis of Fersin. Fersin (0.2 g) was heated in 50 ml of a 5% aqueous-alcoholic solution of caustic soda in the water bath for 2 h. The hydrolysate was diluted with water and treated with ethyl acetate. After the solvent had been eliminated, the solution deposited crystals of *d*-borneol, C₁₀H₁₈O, with mp 204-205°C.

The mother aqueous alcoholic solution was acidified with 10% sulfuric acid and was treated with ethyl acetate. *p*-Hydroxybenzoic acid C₇H₆O₃ with mp 210-212°C was isolated.

The hydrolysis of fersinin was conducted as described above. *d*-Borneol and vanillic acid, C₈H₈O₄, with mp 205-206°C were isolated.

Acetylation of Chimgin. A solution of 0.15 g of *d*-chimgin H₁₇H₂₂O₄ with mp 154-155°C, isolated from the phenolic fraction of *Ferula soongorica*, in 2 ml of pyridine was treated with 2 ml of acetic anhydride, and the mixture was left at room temperature overnight. After appropriate working up, fersin was isolated from the reaction mixture.

Acetylation of Chimganin. *d*-Chimganin (0.2 g) was acetylated as described above. Fersinin was isolated.

REFERENCES

1. N. N. Nazhimidinova and A. I. Saidkhodzhaev, *Khim. Prir. Soedin.*, 900 (1993).
2. A. Sh. Kadyrov and G. K. Nikonov, *Khim. Prir. Soedin.*, 59 (1972).