

V. Yu. Bagirov, V. I. Sheichenko,
G. V. Aliev, and M. G. Pimenov

UDC 547.615.226.54.011.5

From the total extractive substances of the roots of *Ferula stylosa* two esters have been isolated: chimganin and a new one — stylosin. The structure of stylosin is suggested as the ester of 4-hydroxy-3-methoxybenzoic acid and the monoterpene alcohol fenchol.

From the total extractive substances of the roots of *Ferula stylosa*, by absorption chromatography on neutral alumina, we have isolated esters of an aromatic acid and a monoterpene alcohol having the composition $C_{18}H_{24}O_4$ (I), M^+ with m/e 304, mp 108–109°C, $[\alpha]_D -24^\circ$ (c 0.3; ethanol), and $C_{18}H_{24}O_4$ (II), M^+ with m/e 304, mp 85–86°C, $[\alpha]_D +5^\circ$ (c 0.96; ethanol). On the basis of physicochemical characteristics, compound (II) has been identified as chimganin [1]. Compound (I) proved to be a new one, not previously described in the literature, and we have called it stylosin.

The IR spectrum of compound (I) has absorption bands at (cm^{-1}) 3370 (OH), 1690, 1230 (CO of an ester conjugation), and 1610, 1596, and 1520 (aromatic ring). According to the 1H and ^{13}C NMR spectra the terpene moiety of stylosin does not contain a double bond. Consequently, the terpene moiety of (I) has a bicyclic structure.

The PMR spectrum of (I) (Fig. 1) shows the presence of three tertiary methyl groups (0.82, 1.10, and 1.18 ppm, 3 H, singlets) and the signal of a gem-acyl proton (4.60 ppm, 1 H, doublet, $J = 1.8$ Hz). The presence of an AB quartet was shown by the INDOR method (1.22 and 1.65 ppm, $J = 13.0$ Hz). These facts agree with a fenchol skeleton of the terpenoid moiety of stylosin (the AB quartet represents the signals of a bridge methylene group and of an acyl residue adjacent to a gem-dimethyl group). In this case, the splitting of the $H_{6'endo}$ signal takes place because of long-range interaction with the $H_{2'endo}$ proton [2], from which it follows that the acyl residue is present in the exo position. For a skeleton of the bor-

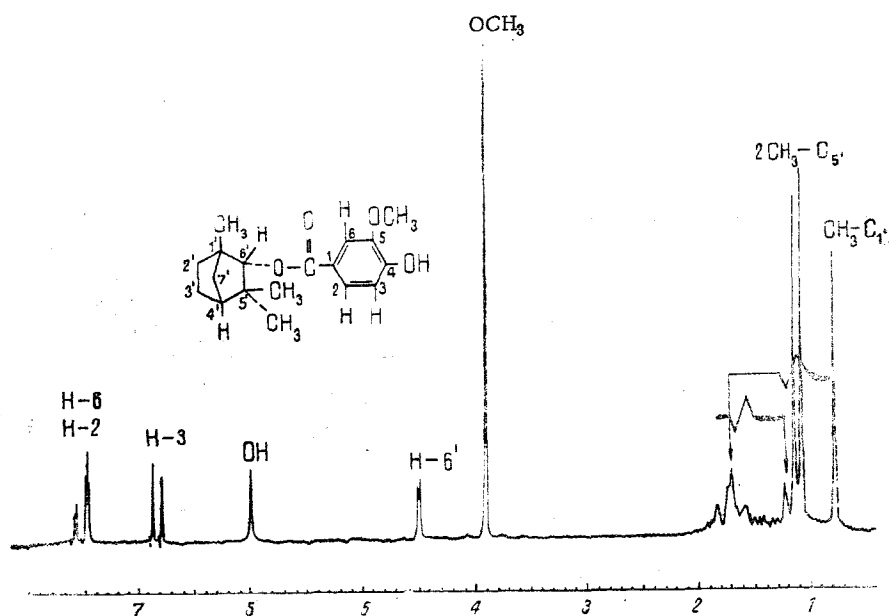


Fig. 1. PMR spectrum of stylosin.

Azerbaijani SSR, Baku, and All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from *Khimiya Prirodnykh Soedinenii*, No. 6, pp. 789–791, November–December 1980. Original article submitted March 11, 1980.

neol type the coupling constant of the gem-acyl proton with the vicinal protons has a considerably greater value [3-5].

Additional parameters were obtained from an analysis of the spectrum at 300 MHz ($J_{4',3'endo} = 4.0$ Hz; ${}^2J_{3'endo,3'exo} = 12.0$ Hz; $J_{3'endo,2'endo} = 12.0$ Hz; $J_{3'endo,2'exo} = 5.8$ Hz). These facts contradict the borneol type of structure and agree with the fenchol type of structure of the terpenoid moiety of stylosin. It must also be noted that in stylosin an extremely large Overhauser effect is observed for the H_6 proton of the benzene ring. Irradiation of the methoxy group with the H_2 field led to an increase in the intensity of the signal of the H_6 proton by 44%, which indicates the predominant orientation of the methyl of the methoxy group in the direction of the H_6 proton. Thus, it may be concluded that stylosin is an ester of 4-hydroxy-3-methoxybenzoic acid and a monoterpenoid alcohol - fenchol.

EXPERIMENTAL

IR spectra (mulls in paraffin oil) were taken on a UR-20 spectrophotometer, NMR spectra (in $CDCl_3$, 0 - TMS, δ scale) on a HA-100D spectrometer, and mass spectra on a CH-8 spectrometer; the melting points of the substances were determined on a Kofler block, specific rotations on a Polamat-A instrument, and R_f values on Silufol-R plates in chloroform. The *Ferula stylosa* roots were collected in May, 1976, in the Dzhambul province of the Kazakh SSR at the town of Khantau.

Isolation of Stylosin (I) and Chimganin (II). The thick resin (4 g) obtained by acetone extraction of the roots of *Ferula stylosa* was dissolved in 20 ml of chloroform and was triturated in a porcelain dish with 50 g of alumina. The dry powder was poured into a column containing neutral alumina (activity grade IV, 1000 g, 4×100 cm) and elution was carried out with hexane and with hexane-chloroform (9:1). Fractions with a volume of 10 ml were collected.

Fractions 26-28, after recrystallization from petroleum ether, yielded a substance with the composition $C_{18}H_{24}O_4$ (I), mp 108-109°C, R_f 0.54. Yield 0.5%. Fractions 30-32, after recrystallization from petroleum ether, yielded a compound with the composition, likewise, $C_{18}H_{24}O_4$ (II), mp 85-86°C, R_f 0.50. Yield 0.3%.

Saponification of Stylosin (I) and Chimganin (II). A solution of 0.2 g of stylosin or chimganin in 30 ml of 5% aqueous ethanolic caustic potash was heated in the water bath ($t = 100^\circ C$) under reflux for 5 h. Then the ethanol was distilled off, and the residue was diluted with water and extracted with chloroform (3×100 ml). The alkaline extract was acidified with 5% sulfuric acid and treated with diethyl ether (3×100 ml). The ether was distilled off and the residue was dissolved in petroleum ether, and the resulting solution on standing deposited crystals of 4-hydroxy-3-methoxybenzoic acid with mp 205-206°C.

SUMMARY

1. Two esters have been isolated from the total extractive substances of the roots of *Ferula stylosa*: chimganin and the new ester stylosin.
2. On the basis of the chemical and spectral characteristics the structure of an ester of 4-hydroxy-3-methoxybenzoic acid and the monoterpene alcohol fenchol is suggested for stylosin.

LITERATURE CITED

1. A. Sh. Kadyrov and G. K. Nikonov, Khim. Prir. Soedin., 59 (1972).
2. F. A. L. Anet. Can. J. Chem., 39, 789 (1961).
3. A. B. Bothner-By, Adv. Magn. Reson., 1, 195 (1965).
4. V. F. Bystrov and A. U. Stepanyants, J. Mol. Spectrosc., 21, 241 (1966).
5. V. F. Bystrov, A. U. Stepanyants, and O. P. Yablonsii, in: Quantum Chemistry and the Radiospectroscopy of Molecules [in Russian], Moscow (1967).