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STRUCTURE OF SHAIROL FROM *Ferula lapidosa*

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In continuation of research on terpenoids from plants of the genus *Ferula* L., a crystalline sesquiterpene alcohol of formula $C_{15}H_{26}O$, mp 83–85°C, $[\alpha]_D^{21}$ –24.5° (*c* 1.2, MeOH) was isolated from the total neutral components of *F. lapidosa* Eug. Korov. [1–3] roots by column chromatography over silica gel using a hexane:EtOAc gradient.

A comparison of the physicochemical constants and spectral data (IR, UV, and ^{13}C NMR) showed that this compound was identical to the sesquiterpene alcohol shairol, which was isolated earlier from *F. ferulaeoides* (Steud.) Korov. and *F. pyramidata* Kar. et Kir. [4–7]. PMR, ^{13}C NMR, and DEPT experiments found that the molecule contained four CH_3, five CH_2, three CH groups, and three quaternary C atoms, two of which were situated on a double bond. The positions of the functional groups were established using 2D experiments (COSY, NOESY, HETCOR). Shairol was isolated from *F. lapidosa* Eug. Korov. for the first time. An x-ray crystal structure analysis (XSA) was performed in order to establish unequivocally the structure and stereochemistry of shairol because these issues were not addressed in the prior study [7].

Figure 1 shows the molecular structure of shairol that was found from the XSA.

The five-membered ring with the C1=C5 endocyclic double bond [1.322(5) Å] adopted a flattened 3α-envelope conformation. The condensed cycloheptene ring had the half-chair conformation characteristic of such rings with atoms C1, C5, C6, C8, and C10 lying in the same plane within ±0.042 Åand atoms C7 and C9 deviating from this plane to different sides by 0.751(2) and 0.778(2) Å, respectively.

The C10 methyl and the C7 hydroxypropyl groups in shairol had β-equatorial orientations; the C4 methyl, the β-axial orientation. The hydroxyls in the crystal formed an intermolecular O–H…O H-bond [with parameters 2.816(6), 2.00 Å, 175°] between molecules transformed by 3_1 symmetry. As a result, chains were formed along the crystallographic *c* axis.

Thus, shairol, which was isolated for the first time from *F. lapidosa* Eug. Korov., was 11-hydroxy-4,7,10α(H)-guai-1(5)-ene [8].

IR spectra were recorded in KBr pellets on a Perkin–Elmer model 2000 Fourier-IR spectrometer. UV spectra were measured on a Perkin–Elmer Lambda-16 spectrophotometer. PMR spectra were taken in CCl_4 and CCl_4 (C_6D_6 + DMSO) solutions on a Varian Unity spectrometer at operating frequency 400 MHz. The internal standard was HMDS on the δ-scale.

Isolation of Shairol. The alcohol extract of dried and ground *F. lapidosa* roots (2 kg) was condensed, diluted with H_2O (1:2), and worked up with Et_2O. The Et_2O extract was worked up several times with alkali solution (1%), washed with H_2O, and dried. The solvent was evaporated to afford total neutral components (266 g), a portion (47 g) of which was chromatographed over a column of silica gel (105 × 4.5 cm, 600 g) with elution by hexane and then hexane:EtOAc (25:1). Fractions (100 mL) were collected. Fractions 72–78 were combined. The solvent was distilled off. The solid was crystallized from hexane to afford a compound (4.5 g), mp 84–85°C, $[\alpha]_D^{21}$ –24.5° (*c* 1.2, MeOH).

X-ray Crystal Structure. Crystals were grown from EtOH solution by slow evaporation at room temperature. Transparent crystals were elongated prisms, $a = 13.110(1)$, $b = 13.110(1)$, $c = 7.1785(6)$ Å, $\gamma = 120°$, $V = 1068.4(2)$ Å^3, $\rho_{calc} = 1.037$ g/cm^3, space group $P3_1$, $Z = 3$. Unit-cell constants were determined and refined on a CCD Xcalibur Ruby diffractometer (Oxford Diffraction) using Cu Kα-radiation (300 K, graphite monochromator). A three-dimensional dataset of reflections ($3.9 \le \theta° \le 71.3$) was obtained on the same diffractometer. Absorption corrections were applied by a semi-empirical method using the SADABS program [9].

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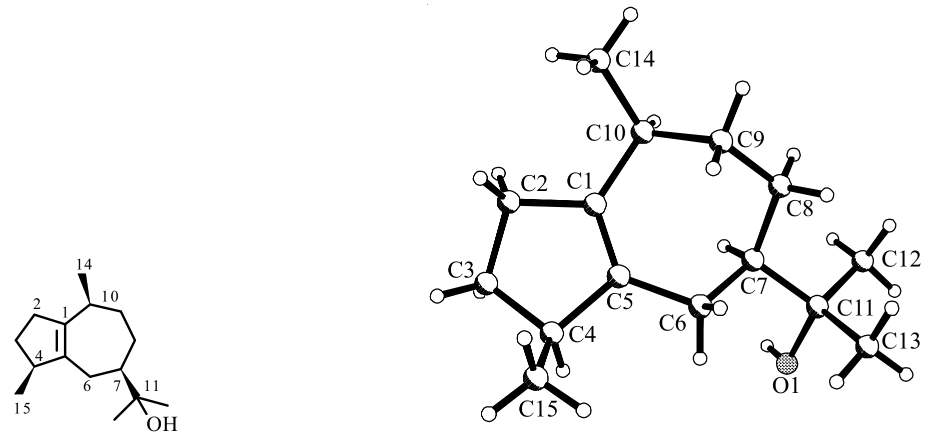

Fig. 1. Molecular structure of shairol.

The structure was solved by direct methods using the SHELXS-97 programs. The structure was refined using the SHELXL-97 program [10]. All nonhydrogen atoms were refined by anisotropic full-matrix least-squares methods (over F^2). Coordinates of hydroxyl H atoms were determined from a difference electron-density synthesis and refined isotropically. The other H atoms were found geometrically and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$, where n = 1.2 and U_{eq} was the equivalent isotropic thermal parameter of the corresponding C atom. The final agreement factors (R_1) were 0.052 ($wR_2 = 0.135$) for 1233 reflections with $I > 2\sigma(I)$ and 0.075 ($wR_2 = 0.149$) over all 1773 reflections. The data from the x-ray experiment were deposited in the Cambridge Crystallographic Data Centre (CCDC 814980).

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