

# A NEW COUMARIN FROM THE ROOTS OF *Ferula pseudooreoselinum*

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UDC 547.314

From the neutral part of the resin of the roots of *Ferula pseudooreoselinum* (Rgl. et Schmalh) K. Pol., by chromatography on neutral  $\text{Al}_2\text{O}_3$  (activity grade II) and elution with chloroform we have isolated a new coumarin,  $\text{C}_{29}\text{H}_{38}\text{O}_6$ , mol. wt. 482 (mass spectrometry), mp 176–178°C (from aqueous ethanol),  $[\alpha]_D^{20} - 26^\circ$  (c 2; ethanol),  $R_f$  0.16; UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}}$  325, 252, 218 nm (log  $\epsilon$  4.11, 3.23, 4.18). IR spectrum,  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$ : 3600, 3500, 3060, 1740 (lactone C=O), 1712 (ester C=O), 1618, 1513, 1240 (v.s, ester C–O) (Fig 1a). NMR spectrum,  $\delta^{\text{CDCl}_3}$ , ppm: 7.63 and 6.23 (doublets, 1H,  $J=9$  Hz) – H-4 and H-3; 7.33 (doublet, 1H,  $J=7$  Hz) – H-5; 6.87 (singlet, 1H) – H-8; 6.82 (quartet, 1H,  $J_1=7$  Hz,  $J_2=2$  Hz) – H-6; 6.02 (octet, 1H,  $J_1=7.5$  Hz,  $J_2=1.5$  Hz) – olefinic proton in an angeloyl residue; 4.60 (multiplet, 1H) –  $\text{C}_3\text{--H}$ ; 4.41 and 4.13 (two quartets, each 1H,  $J_1=11$  Hz,  $J_2=4$  Hz;  $J_1=11$  Hz,  $J_2=6$  Hz) –  $\text{O--CH}_2\text{--C}_9$ ; 1.85–2.06 – two  $\text{CH}_2$  groups in an angeloyl residue; 1.23 (singlet, 3H) –  $\text{C}_8\text{--CH}_3$ ; 0.99 (singlet, 3H) –  $\text{C}_4\text{--CH}_3$ ; 0.92 (singlet, 6H) –  $\text{C}_4\text{--CH}_3$  and  $\text{C}_{10}\text{--CH}_3$  (Fig. 2).

The spectral information permitted the assumption that the coumarin under investigation was an ester of an ether of umbelliferone and a sesquiterpene compound.

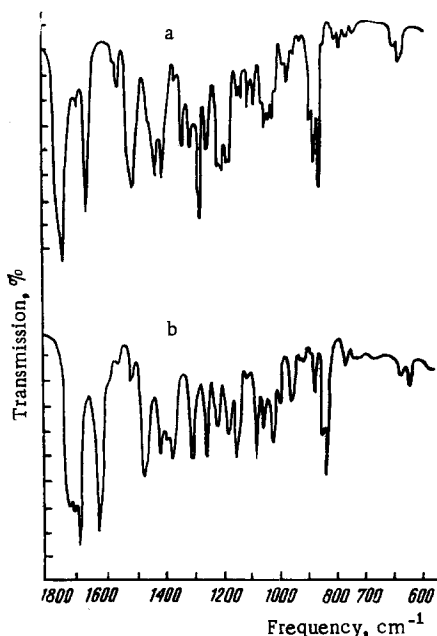


Fig. 1. IR spectra of isosamarandin acetate (a) and of isosamarandin (b) (paraffin oil, UR-10).

When the coumarin was dehydrogenated by being heated with selenium (0.2:0.2) in the usual way [1] at 250–300°C for 1 h, 1,2,5,6-tetramethylnaphthalene with mp 112–113°C (from ethanol) was formed. This shows that the sesquiterpene part of the coumarin has the carbon skeleton characteristic of farnesiferol [2].

Saponification of the coumarin for 10 h gave tiglic acid with mp 56–57°C (from aqueous ethanol), and a substance,  $\text{C}_{24}\text{H}_{32}\text{O}_5$ , mp 215°C,  $[\alpha]_D^{20} + 28^\circ$  (c 0.5 ethanol). On the basis of the spectral and chemical characteristics of the initial coumarin and the saponified product, it was assumed that the latter may be isosamarandin – the isomer of samarcandin at the  $\text{C}_3$  secondary OH bond; i.e., in the saponified coumarin the OH group must be equatorial. To confirm this, samarcandin [1, 3] was converted into samarcandone, which, on reduction with  $\text{NaBH}_4$ , formed isosamarandin with mp 215°C, giving no depression of the melting point with the presumed isosamarandin (Fig. 1b) from the natural coumarin.

Thus, the coumarin investigated is an ester of tiglic acid and isosamarandin. However, it is more likely that in the natural coumarin the ester group is of the angelic acid type. This conclusion is based on the observation in the NMR spectrum of the coumarin under consideration of a signal with  $\delta$  6.02 ppm (octet, 1H,  $J_1=7$  Hz,  $J_2=2$  Hz) which is characteristic for the olefinic proton in an angeloyl residue [4].

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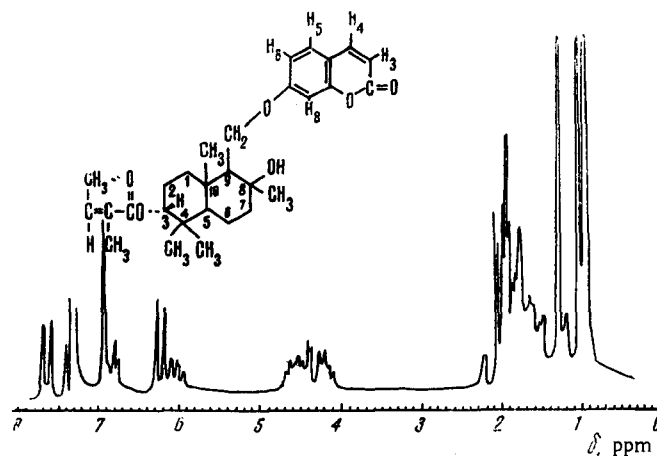


Fig. 2. NMR spectrum of isosamarcandin angelate (CDCl<sub>3</sub>, Varian HA-100).

The ester group is located at the secondary OH group in the C<sub>3</sub> position. Thus, the signal in the NMR spectrum with  $\delta$  4.60 ppm (multiplet, 1H) corresponding to the proton in the ester group is shifted upfield and appears in the saponified coumarin at  $\delta$  3.16 ppm.

On the basis of what has been said, it may be considered that the coumarin isolated from Ferula pseudooreoselinum is an ester of angelic acid and isosamarcandin at the C<sub>3</sub> secondary OH group.

#### LITERATURE CITED

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