MICROLOBIDENE — A TERPENOID COUMARIN FROM *Ferula microloba* WITH A NEW TYPE OF TERPENOID SKELETON

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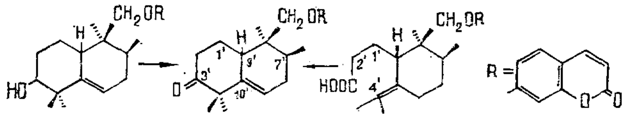
Continuing the separation of the coumarins of *Ferula microloba* Boiss. [1], we have isolated a coumarin which we have called microlobidene.

Microlobidene (I) is an optically active compound with $[\alpha]_D^{20}$ +56° (c 0.5 $CHCl_3$), composition $C_{24}H_{30}O_4$, M^+ 382, mp 142-143°C and, according to its UV spectrum, belongs to the 7-hydroxycoumarin derivatives. In the IR spectrum there are absorption bands of a hydroxy group (3575 cm^{-1}), the carbonyl of an α-pyrone (1730 cm^{-1}), and an aromatic nucleus (1620, 1560, 1520 cm^{-1}).

In the PMR spectrum of (I) (100 MHz, HMDS, $CDCl_3$, δ, ppm) in addition to the signals of a 7-substituted coumarin nucleus there are signals from an olefinic proton (5.37; m, 1 H, $W_{1/2}$ = 7.5 Hz), and of the hemihydroxylic proton (3.38; m, 1 H, $W_{1/2}$ = 7 Hz), and the appearance of a signal from an aryloxymethylene group in the form of a singlet (3.75; s, 2 H) shows that it is attached to a quaternary carbon atom, as in kamolol and kamolone [2]. Then in the strong-field region signals are observed from a secondary methyl group (0.90; d, 3 H, J = 7 Hz) and from three tertiary methyl groups (1.03; s, 6 H; 0.99; s, 3 H), while when the PMR spectrum was taken in pyridine the last signals resonated in the region of 1.01 ppm (s, 6 H), and 1.23 ppm (s, 3 H).

On the basis of the spectra and in view of the composition $C_{24}H_{30}O_4$, it can be stated that the terpenoid moiety of microlobidene is bicyclic. The presence of an olefinic proton and the absence of a vinyl methyl group indicates that the double bond is tetrasubstituted and is present either at $\Delta^{4'(10)}$, $\Delta^{10'(5')}$, $\Delta^{8(9')}$, or $\Delta^{9'(1')}$.

Taking into account the fact that, on the one hand, the PMR spectra of microlobidene and of kamolone are somewhat similar (the spectrum of (I) also has the signal from a secondary methyl group and the signal from the $-CH_2OR$ group appears in the form of a singlet), and, on the other hand, the spectrum of microlobidene is close to those of compounds of the iresane series (the presence of signals from three tertiary methyl groups [3]), it was assumed that microlobidene has the structure (I). This hypothesis is confirmed by the fact that galbanic acid (II) has the 3',4'-seco structure [4]. The closure of the ring at these carbon atoms should lead to the skeleton of (I).



I III II

Galbanic acid (II) was subjected to dehydration with the aid of phosphorus pentoxide (P_2O_5), and an amorphous product was obtained — a bicyclic sesquiterpenoid 7-O-coumarin (III) with the composition $C_{24}H_{28}O_4$, M^+ 380, R_f 0.6 (chloroform—ethyl acetate (2:1)), the IR spectrum of which contained absorption bands of a carbonyl group in a six-membered ring and of an α-pyrone (1720, 1730 cm^{-1}) and also the absorption bands of an aromatic nucleus (1620, 1570, 1520 cm^{-1}). The PMR spectrum of (III) has signals with (ppm): 0.94, d, 3 H, J = 7 Hz ($C\underline{H}_3-CH-$); 1.09, s, 6 H; 1.14, s, 3 H (CH_3-C-); 3.82, s, 2 H ($-CH_2OR$); 5.44, m, 1 H, $W_{1/2}$ = 7.5 Hz ($HC=C-$); 7.12, d, 1 H, $J_{3,4}$ = 10 Hz (H_3); 7.51, d, 1 H, $J_{4,3}$ = 10 Hz (H_4); 6.70, m, 2 H (H_6 and H_8); and 7.26, d, 1 H, $J_{5,6}$ = 10 Hz (H_5). The PMR spectrum of (III) is similar to to that of microlobidene, with a difference in the absence of the signal from a gem-hydroxylic proton in the spectrum of the product of the dehydration of (II). Their mass spectra differ by two mass units. It was assumed that (III) was the ketone of (I). In actual fact, when

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microlobidene was oxidized with chromium trioxide in acetone, a ketone was obtained which proved to be identical with the dehydration product (III) of galbanic acid.

Thus, it has been established that microlobidene has the structure (I) with a new type of terpenoid skeleton [7-(3'-hydroxy-4',4',7',8'-tetramethyl-$\Delta^{10'(5')}$-decalin-8'-ylmethylenoxy]coumarin.

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COUMARINS OF *Seseli peucedanoides*

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Two substances have been obtained by column chromatography on alumina (Al_2O_3, activity grade IV, 80 × 4 cm) of 3 g of an extract obtained by three steepings with acetone at room temperature of 400 g of the roots of *Seseli peucedanoides* (Bieb.) K.-Pol., collected in the Nakhichevan ASSR. Fractions 155-159, eluted with petroleum ether—chloroform (5:1) yielded substance (I) with the composition $C_{19}H_{20}O_5$, mp 137-139°C (from petroleum ether—chloroform).

In the region of characteristic frequencies, the IR spectrum of substance (I) contains absorption bands of the carbonyl groups of a δ-lactone and of an α,β-unsaturated ester (1718 cm^{-1}), of an aliphatic double bond (1657 cm^{-1}), of a benzene ring (1630, 1675 cm^{-1}), and of a gem-dimethyl grouping (1390, 1370, cm^{-1}). The presence and nature of an ester group were elucidated by the saponification of substance (I). This gave a hydroxydihydrofurocoumarin with the composition $C_{14}H_{14}O_4$, mp 189-191.5°C, and an acid with composition $C_5H_8O_2$, mp 68°C, which was identified by a comparison of IR spectra [1] as senecioic. The IR spectrum of the saponified product had the bands characteristic for oxydihydrofurocoumarins (3470, 1710, 1630, 1575 cm^{-1}). The results of a comparison of the IR spectra of substance (I) and its saponified product with the spectra of pranchimgin [1] and of marmesin, respectively, showed their identity.

Fractions 169-179, eluted with the same mixture of petroleum ether and chloroform (5:1) yielded substance (II) with the composition $C_{19}H_{30}O_5$, mp 104-105°C (petroleum ether—chloroform). The IR spectrum of (II) showed absorption bands at (cm^{-1}) 1730 (CO of a δ-lactone ring), 1718 (CO of an α,β-unsaturated ester), 1630, 1572 (dihydrofurocoumarin system), 1387, 1370 (gem-dimethyl grouping). Saponification of the substance by the usual method [2] led to an oxydihydrofurocoumarin with the composition $C_{14}H_{14}O_4$, mp 189-191.5°C (ν_{max} 3470, 1710, 1630, 1575 cm^{-1}) and an acid with the composition $C_5H_6O_2$, mp 44-45°C, which were identified by a comparison of IR spectra as marmesin and angelic acid [1]. Consequently, substance (II) was deltoin. The IR spectra of the compounds compared coincided completely.

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