SUMMARY

By the Ritter reaction of p-menthan-8-ol with propio- and benzonitriles the corresponding secondary amides, not previously described have been synthesized. The use in this reaction of α-terpineol and benzonitrile led to the formation of a mixture of N-(p-menth-1-en-8-yl)-benzamide and N,N-(p-menth-1,8-diyl)dibenzamide. A trans-diamide was also obtained in the reaction of P-terpineol with isovaleronitrile. The use of propionitrile as the nucleophile led to the formation from P-terpineol of 2-ethyl-4,4,8-trimethyl-8-propionamido-3-azobicyclo[3.3.1]non-2-ene.

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STRUCTURE OF FERULIDE

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The structure of a new sesquiterpene lactone — ferulide from *Ferula penninervis* Regel et Schmalh — has been established on the basis of its spectral characteristics. This compound has the composition $C_{20}H_{24}O_5$, mp 135-137°C.

On standing, the mother liquor from ferolide — a sesquiterpene lactone isolated previously from the seeds of *Ferula penninervis* Regel et Schmalh [1] — deposited crystals of a new compound with mp 135-137°C, composition $C_{20}H_{24}O_5$ (I).

The IR spectrum of (I) had the absorption bands of the carbonyl of a γ-lactone ring (1790 cm^{-1}), of an α,β-conjugated C=O of an ester group (1720 cm^{-1}), and bands characteristic for a guaiadienone grouping (1690, 1650, and 1620 cm^{-1}). The mass spectrum showed, in addition to the peak of the molecular ion (M^+ 344), the peak of an ion with m/z 244 [M — 100]. The splitting out of an ion with m/z 100 is possible if the ester group in (I) contains a senecionic, angelic, or tiglic acid residue. This and other questions of the structure of the compound under investigation were solved by considering the characteristics of the proton magnetic resonance spectra.

The PMR spectrum of (I) ($CDCl_3$, 0 — TMS, Varian SC-300) had one-proton multiplets at 5.69 and 6.16 ppm with half widths of 4 Hz from two olefinic protons, and the signals of the protons of five methyl groups: 1.54 (s), 1.91 (d, ^4J = 1.2 Hz), 2.15 (d, ^4J = 1.2 Hz), 2.24, and 2.29 ppm (br.s). In the homonuclear double proton-proton resonance spectrum, when the transitions of the nuclei of the olefinic proton with a CS of 5.69 ppm were saturated, the doublets of methyl groups at 1.91 and 2.15 ppm were synchronously converted into singlets. Consequently, the ester group of the compound contains a semecionic acid residue (5.69, 1.91, and 2.15 ppm).

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The value of the chemical shift of the olefinic proton in the spectrum (6.16 ppm) was identical with that of H-3 (under similar conditions of recording the spectra) of leucomisin (6.15 ppm) and of austricin (6.16 ppm), and the 5α-OH of achillin (6.15 ppm) [2] — sesquiterpene lactones ith a guaiadienone structure of the main skeleton. Furthermore, the doublet-resonance spectrum showed the existence of allyl interaction between the olefinic proton at 6.16 ppm and the methyl group at 2.29 ppm with $^4J = 1.3$ Hz. According to the value of the chemical shift, the second broadened singlet at 2.24 ppm undoubtedly belonged to a methyl group located at another double bond for the protons of which no allyl interaction with the olefinic proton at 6.16 ppm was observed.

In the PMR spectrum of (I) there was a doublet of doublets with $^3J = 11.3$ and 8.8 Hz at 4.72 ppm. When the proton (H-6) corresponding to the signal was irradiated with a radiofrequency field the nature of the splitting of two other signals changed: a multiplet at 2.87 ppm (H-7) was converted into a doublet of doublets with $^3J = 12.8$ and 2.9 Hz, and a doublet with broadened lines at 3.70 ppm having $^3J = 11.3$ Hz (H-5) was converted into a broadened singlet. When using the multifrequency resonance procedure it was also found that the broadened lines of the doublet at 3.70 ppm were due to long-range spin—spin coupling of H-5 with the protons of two methyl groups (2.24 and 2.29 ppm) at double bonds, and that H-7 interacted vicinally with two protons (1.82 and 2.08 ppm) of a neighboring methylene group as well.

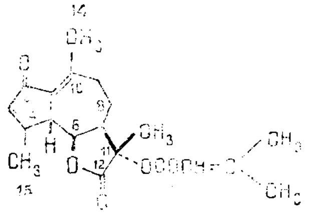
On the basis of the facts given above, it was established that the compound under investigation was a sesquiterpene lactone with a quaiadienone structure of the main skeleton and with attachment of the lactone ring at C-6 and C-7.

The presence in the PMR spectrum of a 3-H singlet at 1.54 ppm and the absence of the signals of an exocyclic methylene group and of a proton at an acyl function showed the mutually geminal positions of the ester group and the third methyl group at C-11 of the lactone ring.

We established that the compound under investigation was a new sesquiterpene lactone of structure (I) and have called it ferulide. On the basis of the results of a detailed analysis of all the characteristics of the PMR signals, we suggest the cis-linkage of the lactone ring and the β- and α-orientations for the methyl and ester groups at C-11, respectively.

The detection of this compound apparently indicates that the presence of a guaiadienone grouping is characteristic for the sesquiterpene lactones produced by the giant fennels of Central Asia [3-5].

Thus, for the new sesquiterpene lactone, ferulide, we propose the structure of 2-oxo-11α-senecionyl-5β,6α,7α(H)-guaia-3,10-dien-6,12-olide (I).



SUMMARY

The structure of a new sesquiterpene lactone — ferulide, from *Ferula penninervis* Regel et Schmalh — has been established on the basis of its spectral characteristics.

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