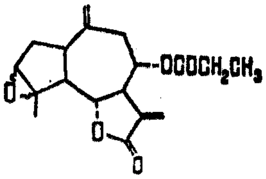
en-membered ring. In the weak fields there are doublets of one proton each at 5.49 and 6.07 ppm with $^4J = 3$ Hz each, the protons of an exomethylene group at a lactone ring. A multiplet signal (5.07 ppm, $\Sigma J = 24$ Hz) of a hemiacyl proton presupposes interaction with several vicinal protons, which permits the C-8 position to be assigned to the proprionic acid residue.

It follows from the facts given that pyrethrin is a guaianolide and has the following structure:



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FEROLIDE — A NEW LACTONE FROM *Ferula penninervis*

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UDC 547.314

On separating a chloroformic extract of *Ferula penninervis* Rgl. et Schmalh., together with the grilactone and the coumarin aurapten isolated previously [1], by chromatography on silica gel [hexane—ethyl acetate (3:1)] we isolated a new lactone, which we have called ferolide (I).

Ferolide has the composition $C_{22}H_{26}O_7$, M^+ 402; mp 178-179°C (decomp), $[\alpha]_D^{20}$ −10.3° (c 0.55; chloroform). UV spectrum: λ_{max} 255 nm (log ε 4.33). IR spectrum, ν_{max}^{KBr} cm^{-1}: 1800 (C=O of a γ-lactone with an ester grouping in the α position to the lactone carbonyl); 1745 ($OCOCH_3$); 1710 (OCO—HC=C), 1690 (—C=C—CO—C=C—) 1640 and 1620 (C=C).

The following resonance signals have been observed in the PMR spectrum of ferolide ($CDCl_3$): H-3 (br.s, 6.05 ppm); H-6 (q, 4.55 ppm, $J_{6,7} = 10$ Hz, $J_{6,5} = 11.0$ Hz); and H-8 (sx, 5.52 ppm $J_{8,9} = 2.0$ Hz, $J_{8,9'} = J_{8,7} = 11$ Hz).

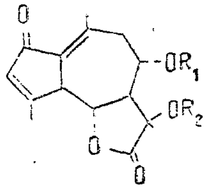
A broadened singlet (6 H) at 2.16 ppm and a singlet (1 H) at 6.05 ppm in association with the results of UV and IR spectroscopy show the presence of a guaiadiene grouping in the molecule.

The fact that ferolide is a guaianolide was confirmed by the production of chamazulene on dehydrogenation with selenium. On the sextet at 5.52 ppm is superposed the singlet of a H-17 olefinic proton. The singlet nature of the olefinic proton together with the singlets of vinylmethyl groups at 2.16 ppm (3 H) and 2.04 ppm (3 H) indicates that one of the acid residues in the ferolide molecule is that of senecioic acid, as was shown by the saponification of ferolide at room temperature with 5% ethanolic caustic soda and the isolation of the acid.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 533, July-August, 1983. Original article submitted February 25, 1983.

0009-3130/83/1904-0506$07.50

The value of the H-8 chemical shift (5.52 ppm) shows that an unsaturated aliphatic acid, in this case senecioic acid, is present at C-8 [2]. In the 2.04 ppm region there is the superposition of the signals of a vinylmethyl group at C-19 and of the methyl group of an acetic acid residue. On the basis of the facts given above, the structure of 11-acetoxy-2-oxo-8-senecioyloxy-guaia-3,10-dien-6,12-olide is justified for ferolide.



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TRANSFORMATIONS OF 4-HYDROXYMETHYL-2-CARENE UNDER THE CONDITIONS OF HETEROGENEOUS HYDROGENATION

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UDC 547.597.1:66.092.17

The main product of the hydrogenation of 2- and 3-carenes (I and II) in the liquid phase over Pt is carane [1]. The hydrogenation of the same terpenes over Pd leads to the formation of 1,1,4-trimethylcycloheptane [1]. It was assumed that the formation of compounds with a cycloheptane skeleton was connected with the occurrence of a reaction in which (I) was dehydrogenated to cara-2,4-diene with its subsequent tautomeric transformation into 3,7,7-trimethylcyclohepta-1,3,5-triene [2]. It is known that the liquid-phase hydrogenation over Pt of 4-hydroxymethyl-2-carene (III) – an oxygen-containing terpenoid with a bicyclic structure similar to that of (I) – gives 4-hydroxymethylcarane [3].

We now give the results of a study of the liquid-phase and gas-phase hydrogenation of (III) over palladized carbon (2% of Pd).

Liquid-phase hydrogenation was carried out at 20–80°C and atmospheric pressure in octane and glacial acetic acid for 24 h at a substrate:catalyst ratio of 10:1, and vapor-phase hydrogenation at 200-250°C in a catalytic apparatus in a current of H_2 with a time of contact of (III) and catalyst of 0.91-0.98 sec.

The composition of the hydrogenate was monitored by GLC.

When (III) was hydrogenated at 20°C no transformations whatever were observed. When the temperature was raised to 80°C in octane, a mixture of hydrocarbons (4%) consisting of 1,1,4,5-tetramethylcycloheptane (IV) (80%), 4-methylcarane (V) (15%), and 4-isopropyl-1,2-dimethylbenzene (VI) (5%) was formed. The hydrogenation of (III) in glacial acetic acid at 80°C led to the production of these hydrocarbons (7%) and the acetate of 4-hydroxymethyl-2-carene (VII) (36%). The properties of the (VII) isolated corresponded to those given in the literature [3].

In the vapor-phase hydrogenation of the (III) with its complete conversion, the hydrogenate contained (IV) (65-45%), (V) (14-9%), (VI) (18-30%), and an unidentified substance (3-16%) which could not be isolated because of its ready isomerization and which is presumed to be 4-isopropenyl-1,2-dimethylbenzene. The components of the hydrogenate were isolated by the PGLC method and were identified from their physicochemical properties and spectral characteristics.

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 534, July-August, 1983. Original article submitted February 21, 1983.

0009-3130/83/1904-0507$07.50