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A NEW GUAIANOLIDE – OPOFERZIN FROM THE ROOTS OF Ferula oopoda

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A new guaianolide with the composition $C_{20}H_{22}O_5$, mp 150-152°C, has been isolated from the resin of the roots of Ferula oopoda, (Boiss. et Buhse) Boiss. It has been established that it corresponds to the structure of 11α-angeloyloxy-2-oxo-5βH, 6αH-guaia-1(10), 3,7- trien-6,12-olide.

Six natural and four artefactual sesquiterpene lactones isolated from the resin of the roots of Ferula oopoda (Boiss. et Buhse) Boiss. have been reported previously [1, 2]. In the present paper we give the results of an investigation of the structure of a new guainolide from this plant material which has the composition $C_{20}H_{22}O_5$, mp. 150-152°C, and has been called opoferzin.

The IR spectrum of opoferzin has absorption of a γ-lactone ring (1770 cm^{-1}), of an α,β-saturated group (700 cm^{-1}), of a conjugated ketone group in a five membered ring (1660 cm^{-1}), and of double bonds in conjugation (1660, 1630 cm^{-1}).

The presence and nature of the ester group was found both by saponification and from the NMR spectrum. On saponification, a distillable acid with mp. 44-45°C was obtained which was identified from its IR spectrum as angelic acid. The NMR spectrum of opoferzin had signals at (ppm) 1.90 (d, J = 7 Hz, $Ch_3{-}CH{=}$, each component being also split into a doublet with J = 1.4 Hz), 2.03 (d, J = 1.4 Hz, $CH_3{-}C{=}$), and 6.14 (m, $-CH{=}$), which are characteristic for an angelic acid residue.

The three-proton singlet at 2.33 and 2.43 ppm and a one-proton singlet at 6.23 ppm in the spectrum indicated the presence in the opoferzin molecule of the cyclopentadiene structural fragment that is characteristic for the sesquiterpene lactams badkhyzin [1], talassins A and B [3], diversolide [4], olgin, and olgoferin [5].

Thus, of the three methyl groups of the guaiane hydrocarbon skeleton two are vinyl methyls (at C_4 and C_{10}). The third methyl group (at C_{11}) appeared in the NMR spectrum in the form of doublet at 1.80 ppm (J = 1.4 Hz). The nature of the splitting and the value of the chemical shift of the latter indicated the methyl of a gem-ester group [3, 5].

As the PMR spectrum showed, the opoferzin molecule contains four double bonds. One of them is tetrasubstituted and two are trisubstituted, these being located at $C_1{-}C_{10}$, $C_3{-}C_4$, and $C_{17}{-}C_{18}$, respectively. The fourth double bond, also trisubstituted, is located at $C_7{-}C_8$. This was shown by the one-proton signals of an olefinic proton at 6.08 ppm (d, J = 6 Hz) and of the protons of a vicinal CH_2 group (q, 2.82 ppm, J = 6, J = 14.6 Hz; and d, 2.65 ppm, J = 14.57 Hz), which are characteristic for an ABX system.

The lactone proton appeared in the spectrum in the form of a quartet at 4.56 ppm (J = 10.5; J = 1.4 Hz). As can be seen from the spin-spin coupling constants, the last-mentioned proton interacts with one vicinal proton (H-5), the signal of which is represented in the spectrum by a doublet at 3.13 ppm (J = 10.5 Hz). These facts showed the presence of a ring at $C_6{-}C_7$.

The configurations of the C_5 and C_6 asymmetric centers followed from the spin-spin coupling constants of H-5 (10.5 Hz), and also from the results of an x-ray study of sesqui-

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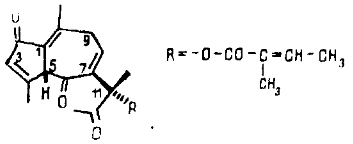
terpene lactones isolated from representatives of the family Apiaceae (Umbelliferae), particularly from the tribes Laserpitieae and Peucedaneae, which indicates that they belong to the new stereostructural type of slovanolide (1S,5R,6R,7S-guaian-6,12-olide) [6].



$$R = -O-CO-\underset{\displaystyle CH_3}{C}=CH-CH_3$$

The stereoposition of the ester group was determined from the following facts. All sesquiterpene lactones of representatives of the family Apiaceae acylated at C_{11}, regardless of their hydrocarbon skeleton, are characterized by the α-orientation of the ester group. This biogenetic feature apparently exists in opoferzin, as well. Consequently, opoferzin has the structure of 11α-angeloyloxy-2-oxo-5βH,6αH-guaia-1(10),3,7 trien-6,12-olide (I).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer in paraffin oil and NMR spectra on a Bruker WP 20°SY spectrometer in $CDCl_3$ solution, TMS – 0.

Isolation of Opoferzin. The resin (10 g) from the roots of Ferula oopoda, obtained by a known method [7], was chromatographed on a column (3.5 × 100 cm) of silica gel L (40/100 μm). Elution was performed with the sequence of solvents decribed in [8]. The fractions eluted by chloroform and preceding the fractions containing badkhyzin yielded opoferzin with the composition $C_{20}H_{22}O_5$, mp. 150-152°C (from ethanol).

Saponification of Opoferzin. The substance (0.1 g) was saponified with 10 ml of a 5% aqueous solution of caustic potash. The reaction mixture was worked up by a known method [7]. A distillable acid with mp. 44-45°C was obtained.

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