STRUCTURE AND CONFIGURATION OF JURMOLIDE

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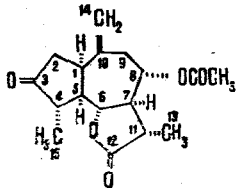
Continuing a study of the lactones of the epigeal part of Jurinea maxima [1], the benzene fractions after the isolation of salonitenolide and salonitolide were combined and rechromatographed on a column of alumina. The column was washed with mixtures of petroleum ether and benzene in ratios of (8:2, 7:3, and 1:1). From the fractions eluted by petroleum ether–benzene (1:1) we isolated a substance with the composition $C_{17}H_{22}O_5$, mp 136–137°C (ethanol), $[\alpha]_D^{18}$ + 102.7° (c 0.74; chloroform), which proved to be a new sesquiterpene lactone and has been called jurmolide. Jurmolide is readily soluble in acetone and chloroform and is insoluble in petroleum ether and water. On TLC (alumina; ethyl acetate system), it has R_f 0.82. Its IR spectrum shows the absorption bands of a γ-lactone carbonyl (1781 cm^{-1}), an ester group (1740 and 1240 cm^{-1}), and a double bond (1645 cm^{-1}). A maximum in the UV spectrum at 280 nm (log ε 2.1) shows the presence of a carbonyl group in a five-membered ring, and in the IR spectrum the band of this group fuses with the absorption band of the ester group. In the NMR spectra of jurmolide (taken on a JNM-4H-100/100-MHz instrument in $CDCl_3$, the chemical shifts are given in the δ scale from the signal of MHDS taken as 0), at 4.74 and 5.08 ppm there are one-proton signals due to the protons of a exomethylene group. Doublets at 1.16 ppm (J = 8 Hz), and 1.27 ppm (J = 6 Hz) correspond to the protons of two secondary methyl groups. A three-proton singlet at 2.05 ppm relates to the protons of the methyl of an acetyl gruup. The geminal proton at 4.89 ppm is represented in the form of a multiplet. A triplet at 3.99 ppm ($J_1 = J_2 = 9$ Hz) corresponds to the lactone proton. The composition, spectral characteristics, and reduction of azulene on dehydration over selenium show that jurmolide is a guaianolide. On heating, jurmolide dissolved in a 5% aqueous solution of KOH. The solution was acidified with 10% H_2SO_4 to pH 1 and extracted with chloroform. The extract was washed with 3% sodium bicarbonate solution and with water. After the elimination of the solvent, crystals were obtained of a hydroxy lactone with mp 178–179°C which, by comparison of IR spectra and a mixed melting point, were identified as isoamberboin [2].

Consequently, jurmolide has the structure of 8α-acetoxy-3-oxo-1:5:7α(H),4:6:11β(H)-guai-10(14)-en-6, 12-olide:



LITERATURE CITED

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2. A. Corbella et al., Chem. Commun., 7, 386 (1972).

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