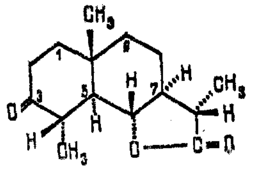
The catalytic hydrogenation of α-santonin in the presence of 10% Pd/C gave γ-tetrahydrosantonin, which was isomerized by $HClO_4$ into α-tetrahydrosantonin [1, 2], identical in its physicochemical constants, spectral characteristics, and according to a mixed melting point, with artepaulin. Consequently, artepaulin has the structure and configuration of 3-oxo-5,7α(H),4,6,11β(H)-eudesman-6,12-olide (I).



I

The ^{13}C NMR spectrum (Bruker WP-80, 20.1 MHz, $CDCl_3$, 0 — TMS) of artepaulin obtained under the conditions of complete and partial decoupling (off-resonance) from protons confirmed the structure (I) proposed for it.

When the column was eluted with ether, a crystalline substance (II), $C_{15}H_{18}O_3$, mp 169-171°C (ethanol), M^+ 246, was isolated. (II) was identified by IR, NMR, and mass spectroscopy and a mixed melting point as α-santonin [3, 4].

Trials in the All-Union Scientific-Research Institute of Chemical Plant Protecting Agents showed that α-santonin inhibits the development of late blight of tomato.

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BIOMIMETIC SYNTHESIS OF β-DUVA-3,8,13-TRIENE-1,5-DIOL BY THE PHOTOSENSITIZED OXIDATION OF ISOCEMBROL

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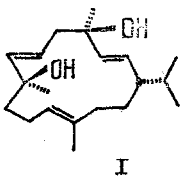
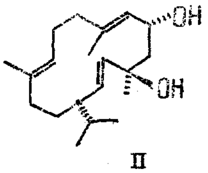
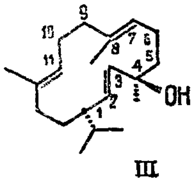
β-Duva-3,8,13-triene-1,5-diol (1S,4R,8S-cembra-2E,6E,11E-triene-4,8-diol) (I) was isolated by Rowland [1] from the leaves of the tobacco plant *Nicotiana tabacum* L. The stereochemistry of this compound was determined by Enzell [2] and as the last stage of its biosynthesis the allylic isomerization of another cembrane derivative present in tobacco leaves, the diol (II), was suggested [2].



I



II



III

We have established that the diol (I) can be obtained by photooxidation from a simpler precursor also present in tobacco leaves — isocembrol (III) [3].

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The reaction, the reduction of the intermediate hydroperoxides, and the separation of the products were performed under conditions analogous to those described for the photooxidation of cembrene [4]. The yield of diol (I) amounted to 17.5% on the isocembrol that had reacted and was of the order of 26% of the total amount of diols formed. The compound isolated had mp 150-152°C (from acetonitrile), $[\alpha]_D^{29}$ + 40.8° (c 6.93; chloroform). According to the literature [1]; mp 150-152°C, $[\alpha]_D^{25}$ + 40°. The PMR and IR spectra corresponded to those given by Rowland and Roberts [1].

In the reaction under investigation, the products of oxidation at the C_{11} bond of isocembrol were also obtained, and these will be described in a separate communication. The formation of the diol (I) (more accurately, the corresponding hydroperoxide) is a stereospecific process. The C_8 epimer of the diol (I) is produced in very small amounts, if at all, and we have not yet succeeded in detecting it.

The photooxidation of isocembrol is a model of the biosynthesis of the diol (I). Terpenoid hydroperoxides as products of the photooxidation of the corresponding olefins have been detected in recent years [5] in the green parts of plants. This indicates an appreciable contribution of photooxidation to the processes involved in the secondary metabolism of unsaturated terpenoids, which include cembrane derivatives.

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