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PABULENOL, A BIOLOGICAL TRANSFORMATION PRODUCT OF OXYPEUCEDANIN

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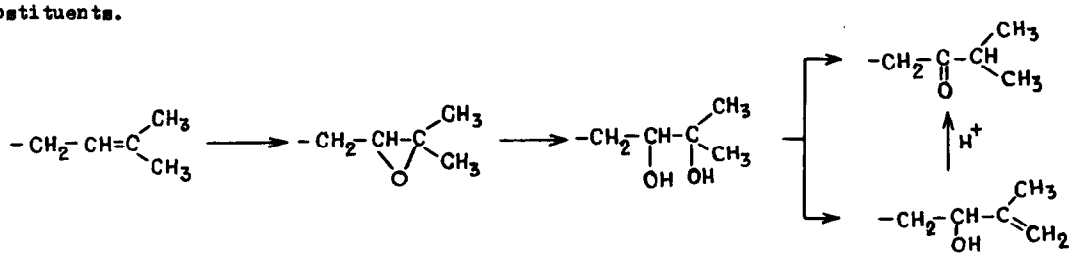
The simultaneous occurrence of the furocoumarins, isoimperatorin (I), oxypeucedanin (II), oxypeucedanin hydrate (III), isooxypeucedanin (IV)[1-2] and pabulenol (V) in Prangos pabularia Lindl. (Umbelliferae) provides circumstantial evidence in support of the following sequence of cellular reactions as visualised by Hendrickson and Richards[3] in their biogenetic codification of isoprenoid substituents.



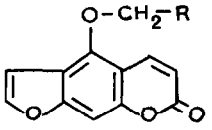
Of these pabulenol (V), $C_{16}H_{14}O_5$ (M^+286.0852), m.p. 134-35°, $[\alpha]_D^{25}$ -3.8° (EtOH), is a new coumarin isolated in 0.005% yield from the root portion of P. pabularia. The present communication deals with the structure elucidation of this compound. Its UV spectrum in the region 225-340 nm $[\lambda_{max}^{EtOH}$ 249.5, 267 and 308 nm (log ε : 4.17, 4.12 and 4.02 respectively)] is typical of a linear furocoumarin bearing similarity with bergapten[4,5] while the IR spectrum revealed a hydroxyl group (2.86μ), a lactone carbonyl (5.85μ), a benzofuran (9.3μ), an aromatic ether (9.05 and 8.24μ) and a terminal methylene (11.2μ). The 100 MHz NMR spectrum (d_6-DMSO) showed the coumarin doublets at δ 6.25 and 8.25 (J=10 Hz), the α-furan proton at δ 7.95 [1H(d), J=2 Hz] while the β-furan merged with the single aromatic proton resulting in a finely split two proton signal at δ 7.24 (J=1 Hz). The three proton multiplet ca δ 4.35 has been assigned to the two methylene and the adjacent methine protons ($OC\underline{H}_2$-$C\underline{H}$-O-) and the signal at δ 5.36 [1H (d), J=4 Hz] disappearing in D_2O, to the hydroxyl proton. A three proton singlet at δ 1.71 has been attributed to the vinyl methyl and the signals [1H (s) each] at δ 5.06 and 4.86 to $=C\underline{H}_2$.

The presence of the hydroxyl group as -CHOH was corroborated from the formation of pabulenol acetate (VI), $C_{18}H_{16}O_6$ (M^+328), m.p. 119.5°, and from the study of its NMR spectrum.

The signal at δ 2.12 [3H (s)] was assigned to the acetoxy function. The carbinol methine proton now appeared downfield at δ 5.65 [1H (t), J = 5 Hz] while the β-furan proton resonated as a doublet at δ 6.96 (J = 3 Hz). The latter was further split by long range coupling with the aromatic proton at δ 7.18 (J = 1 Hz), a characteristic feature of bergaptol derivatives[6]. This demanded the formulation of the side chain in pabulenol acetate as depicted in (VI).

Acid hydrolysis (10% H_2SO_4) of pabulenol afforded isooxypeucedanin (IV) and oxypeucedanin hydrate (III), thereby confirming the presence of an allylic hydroxyl group and a terminal methylene function. Isooxypeucedanin (IV) was obtained from (II) in better yield (60%) by acid catalysed rearrangement with BF_3, compared to the older method using mineral acids[1,7-8] (6%).

All the above data can best be reconciled in structure (V) for pabulenol.



I , R = $-CH=C(CH_3)(CH_3)$ II , R = $-CH-C(CH_3)(CH_3)$ (epoxide) III , R = $-CH(OH)-C(OH)(CH_3)(CH_3)$

IV, R = $-C(=O)-CH(CH_3)(CH_3)$ V , R = $-CH(OH)-C(=CH_2)(CH_3)$ VI , R = $-CH(OAc)-C(=CH_2)(CH_3)$

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