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CANDICANIN, A NOVEL BICOUMARINYL DERIVATIVE FROM THE ROOTS OF HERACLEUM CANDICANS

M. Bandopadhyay, S.B. Malik and T.R. Seshadri,

Department of Chemistry, University of Delhi, Delhi-7, India.

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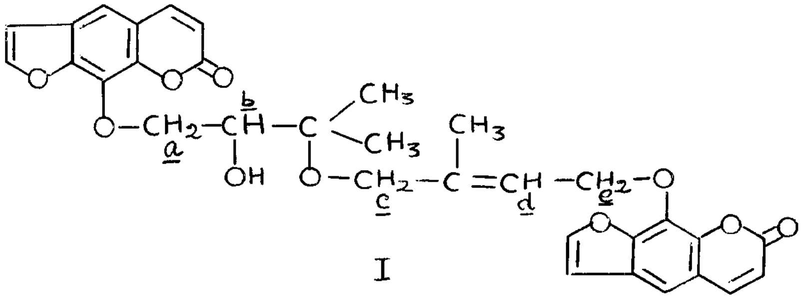
In our earlier communication[1,2] on the chemical components of the roots of H. candicans three new coumarins isoheraclenin, tert-O-methyl herclenol and tert-O-glucosyl heraclenol were reported besides seven other known coumarins. We now describe a novel coumarin derivative obtained from the ether extract of the roots. It had been named candicanin.

Repeated chromatography of the ether extract of the defatted roots on silica gel column gave candicanin as a colourless compound (0.002% yield) by elution with benzene:EtOAc (1:1), m.p. 153°, $C_{32}H_{26}O_{10}$ [redacted] with λ_{max}^{EtOH} and 300 nm (log ϵ 4.64 and 4.36) and $\nu_{max}^{(KBr)}$ 3625 cm^{-1} (-OH), 1725 cm^{-1} (lactone C=O), 1100 cm^{-1} (aliphatic ether) and 1030 cm^{-1} (benzofuran). It gave marked bluish green fluorescence on T.L.C. plate in UV light. Candicanin was hydrolysed with $HOAc/H_2SO_4$ on a steam bath for 3 hrs. The product gave three spots on T.L.C. Two of them were identified as belonging to heraclenol and xanthothoxol. Candicanin gave an acetate by treatment with cold Ac_2O/pyridine. The NMR spectra of the compound and of its acetate and the mass spectrum of the acetate finally established the structure as tert-O-imperatorinyl heraclenol (I).



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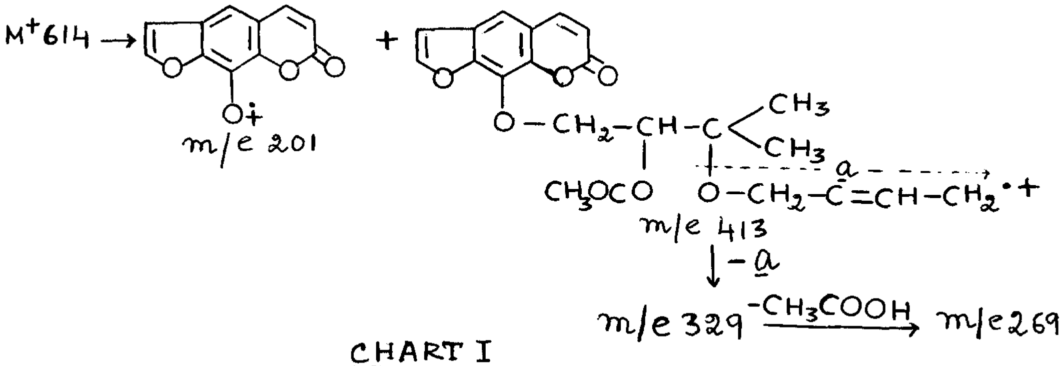

CHART I

The NMR spectrum[3], ($CDCl_3$)(δ): 1.30 and 1.35(3H,s) $C<^{CH_3}_{CH_3}$, 1.8(3H,s, $=C-CH_3$), 2.90(1H,s,$-O\underline{H}$), 4.00(2H,dd,J=4 c/s,CH_2-$\underline{a}$), 4.30 and 4.40(2H,d, J=2.5 c/s, CH_2-$\underline{c}$), 4.60(1H,m,-CH-$\underline{b}$), 5.0(2H,m,CH_2-$\underline{e}$), 5.2(1H,t,-CH-$\underline{d}$) and characteristic peaks for the furanocoumarin skeleton; integration of the spectrum showed there were two furanocoumarin skeletons. In the spectrum of the acetate the signal for -OH was absent and one $-OCOCH_3$ came as singlet at 2.15δ; the proton (b) at 4.60δ was shifted to 5.30δ and also $-CH_2$-$\underline{a}$ suffered 0.2 downfield shift; these features were earlier noticed in the case of acetate of tert-O-methyl heraclenol. The mass spectrum of the acetate had significant peaks at m/e 614, 413, 329, 269, 202 and 201 and can be reationalised as described in Chart I.

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