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# THE STRUCTURE OF MOREOLLIN

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Moreollin, m.p. 168°; $[\alpha]_D^{26°}$ -21.03; $\lambda_{max}^{EtOH}$ 235, 266, 275, 305, 316, 365 nm ($\epsilon$ 25120, 39810, 41690, 18200, 13800, 4070); $\nu_{max}^{nujol}$ 3400, 1740, 1680, 1650, 1630, 1610, 1595 cm$^{-1}$; $\delta_{CDCl_3}$ 1.15 (*t*, 3H), 1.18 (*s*, 3H), 1.35 (*s*, 3H), 1.4 (*s*, 3H), 1.5 (*s*, 3H), 1.7 (*bs*, 3H), 1.8 (*bs*, 6H), 3.55 (2H), 4.5 (*d*, J = 4 Hz, 1H), 5.0 (*t*, 1H), 5.5 (*d*, J = 10 Hz, 1H), 6.6 (*d*, J = 10 Hz, 1H), 6.9 (*t*, J = 7 Hz, 1H); 10.18 (*s*, 1H), 11.85 (*s*, 1H phenolic OH exchanged with $D_2O$), was isolated as a minor constituent along with morellin (*1*) from the neutral fraction of the seed coat of *Garcinia morella*[1]. High resolution mass analysis of moreollin indicated the molecular formula as $C_{35}H_{42}O_8$ (Found: 590.2888; Calculated mass for the formula 590.2880). Moreollin, on boiling with acetic acid, isomerised to isomoreollin, m.p.148°, $[\alpha]_D^{26°}$ -22.03; $\lambda_{max}$ 227, 267, 275, 317, 363 nm ($\epsilon$ 31620, 33880, 34670, 13800, 2818); $\nu_{max}$ 3350, 1740, 1680, 1650, 1630, 1620, 1590; $\delta_{CDCl_3}$ 1.15 (*t*, 3H), 1.15 (*s*, 3H), 1.35 (*s*, 3H), 1.4 (s, 3H), 1.5 (*s*, 3H), 1.7 (*bs*, 3H), 1.8 (*bs*, 6H), 3.55 (*m*, nonequivalent $-OC\underline{H}_2CH_3$), 4.45 (*dd*, $C{<}^{OCH_2CH_3}_{\underline{H}}$), 4.95 (*t*, J = 7 Hz, 1H), 5.5 (*d*, J = 10 Hz, 1H),

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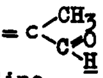
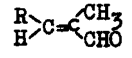
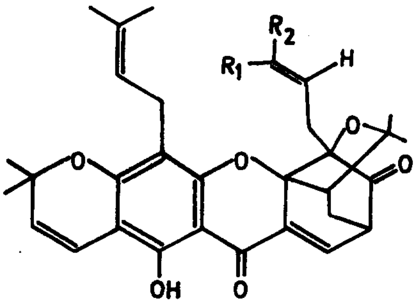
6.6 (d, J = 10 Hz, 1H), 6.9 (t, J = 7 Hz, 1H), 9.36 (s, 1H  $=C(CH_3)-C(=O)\underline{H}$ ), 11.76 (s, 1H, phenolic O<u>H</u>). Prolonged treatment with pyridine moreollin gave isomorellin (<u>2</u>) whose structure was deduced from x-ray diffraction data[2], p.m.r. spectral analysis[3] and other chemical evidence[4]. Unlike morellin, moreollin and isomoreollin did not show any antimicrobial activity. Moreollin and isomoreollin resembled dihydroisomorellin[5] in its spectral properties indicating the absence of $\Delta^{8(9)}$ double bond in conjugation with the chromanone carbonyl group.

The p.m.r. spectrum of moreollin is different from that of morellin or isomorellin and shows eight methyl resonances - one additional methyl group appeared as a triplet at $\delta$,1.15 (J = 6 Hz) superimposed on a tertiary methyl signal. The vinylic proton of the bicyclooctene system of morellin or isomorellin is absent in moreollin and isomoreollin and a new proton appears as a doublet of doublets at $\delta$,4.5 (J = 4 Hz, 1 Hz). In addition there are two protons appearing as a pair of quartets superimposed at $\delta$,3.55 indicating the presence of two nonequivalent $-OC\underline{H}_2-$ protons. The aldehyde proton and the chelate hydroxyl appear at $\delta$,10.18 and 11.85 respectively. These results suggest that the new pigment is an ethanol adduct of morellin (<u>1</u>) or isomorellin (<u>2</u>) and is represented by (<u>3</u>) or (<u>4</u>). This is confirmed from the mass spectrum of moreollin which contains a major fragment, M/e 544 corresponding to the loss of ethanol.

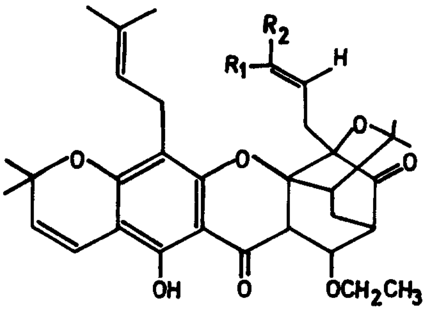
The p.m.r. spectrum of isomoreollin closely resembles that of moreollin and shows differences in the chemical shifts due to the aldehyde $\delta$, 9.36 and the chelated hydroxyl $\delta$, 11.76 protons. The p.m.r. spectra of <u>cis</u> and <u>trans</u>-2-enals of the type  $R(H)C=C(CH_3)CHO$ have been well characterised[6,7]. It is shown that the aldehyde proton appears at $\delta$,10.00 in <u>cis</u>-2-enals while the corresponding <u>trans</u> compounds show resonances due to the aldehyde proton at $\delta$,9.3. In line with this observation, moreollin contains the cis-2-enal moiety as in morellin (1) and is, therefore, the ethanol adduct of morellin as represented in (3). This is confirmed by a partial synthesis of moreollin (3) from morellin (1) using ethanolic potassium acetate. Isomoreollin has the structure (4). These observations will be further substantiated from their $^{13}C$ NMR spectral analysis which is now in progress.

Ethoxydihydroisomorellin (4) has been isolated[5] from the pericap of the seeds of Garcinia morella. Isomoreollin appears to be identical with this compound from the published data, although a direct comparison of the samples could not be made due to lack of material.



(1), $R_1$ = CHO ; $R_2$ = Me

(2), $R_1$ = Me ; $R_2$ = CHO



(3), $R_1$ = CHO ; $R_2$ = Me

(4), $R_1$ = Me ; $R_2$ = CHO

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## References

1. D.V.Krishna Murthy and P.L. Narasimha Rao, J.Sci.Ind.Res., **12B**, 565 (1953).
2. G.Kartha, G.N.Ramachandran, H.B.Bhat, P.M.Nair, V.K.V.Raghavan and K.Venkataraman, Tet.Lett., 459 (1963).

3. P.M.Nair and K.Venkataraman, Ind.J.Chem., **2**, 402 (1964).

4. Morellin and isomorellin differ in the configuration of the side chain containing the aldehyde group. We have stereoselectively decarbonylated morellin and isomorellin using Wilkinson's catalyst and the resulting olefins have been shown to possess the 'E' and 'Z' configuration respectively. The structures were further confirmed by an independent study of the $^{13}$C NMR on morellin and isomorellin (G.S.R.Subba Rao, S.Ratna Mala, V.Surendranath, W.V.Philipsborn and U.Vogelli - to be published).

5. H.B.Bhat, P.M.Nair, and K.Venkataraman, Ind.J.Chem., **2**, 405 (1964).

6. D.J.Faulkner, Synthesis, **4**, 177 (1971).

7. K.L.Stevens, L.Jurd and G.Manners, Tet.Lett., **31**, 2955 (1973).