

## Structure of moreollin, a pigment isolated from *Garcinia morella* Dessler

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**Abstract.** The structure of moreollin (3), isolated from the seed coat of *G. morella*, and its isomerised product, isomoreollin (4) have been established as the ethanol adducts of morellin (1) and isomorellin (2) on the basis of p.m.r., c.m.r., mass spectrometry and confirmed by partial synthesis from morellin (1) and isomorellin (2).

**Keywords.** Structure elucidation; complex xanthone; p.m.r.; c.m.r.; mass spectra.

### 1. Introduction

The extracts of the pericarp of the seeds of *Garcinia morella* Dessler were shown to possess antimicrobial properties (Chopra *et al* 1957). Several crystalline compounds, morellin, neomorellin, dihydroisomorellin, ethoxydihydroisomorellin, morellic acid and isomorellic acid have been isolated and their structures elucidated (Venkataraman 1973). The mother liquors, after the removal of morellin, afforded (Krishna Murthy and Rao 1953) lemon yellow crystalline compound, moreollin (3) (m.p.168°). The structure of moreollin is deduced as the ethanol adduct of morellin (1) from its chemical reactions, spectral data and partial synthesis and is described in this paper. A preliminary report on the structure of moreollin has already been published (Subba Rao *et al* 1973).

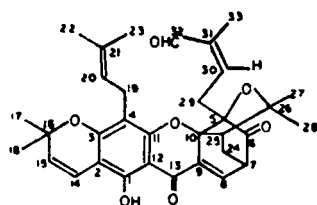
### 2. Results and discussion

Elemental analysis of moreollin (3) indicated a molecular formula of  $C_{35}H_{42}O_8$ . This was confirmed from its high resolution mass analysis ( $M^+$  found 590.2888; calculated mass for the molecular formula 590.2880). The UV spectrum of moreollin showed absorptions at 235, 266, 275, 305, 316 and 365 nm, similar to that observed for morellin (1). The IR spectrum of moreollin indicated the presence of a phenolic hydroxyl ( $3400\text{ cm}^{-1}$ ), a saturated ketone ( $1740\text{ cm}^{-1}$ ), an unsaturated aldehyde group ( $1680\text{ cm}^{-1}$ ) and a chromanone carbonyl group ( $1650\text{ cm}^{-1}$ ) in addition to the aromatic absorptions at 1630, 1610 and  $1595\text{ cm}^{-1}$ . The PMR spectrum of moreollin showed the presence of eight methyl groups, three vinylic hydrogens, an aldehyde proton and a hydrogen bonded phenolic hydroxyl group. This is discussed separately.

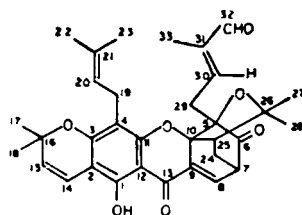
Moreollin afforded an amorphous diacetate  $C_{39}H_{48}O_{19}$ , with acetic anhydride in pyridine but could not be recovered on hydrolysis. Catalytic hydrogenation revealed the presence of three double bonds in moreollin but the products, which could not be separated into pure crystalline compounds, were found to be mixtures of dihydro-, tetrahydro-, and hexahydro derivatives of moreollin from their mass spectral analysis.

On boiling with acetic acid for 30 min, moreollin is isomerised to a crystalline, compound, isomorellin (4)  $C_{35}H_{42}O_8$ , m.p.  $148^\circ$ . The UV and the IR absorption spectra are similar to those of moreollin. However, the PMR spectrum showed differences in the chemical shifts of the vinylic, aldehyde, and the hydroxyl protons.

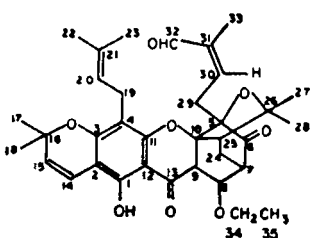
Prolonged treatment of moreollin or isomorellin with pyridine afforded isomorellin (2),  $C_{33}H_{36}O_7$ , identified by comparison with an authentic sample. The structure of isomorellin (2) has been conclusively established by x-ray diffraction data (Kantha *et al* 1963), PMR analysis (Nair and Venkataraman 1964, Philipsborn 1974) and other chemical evidences (Rathnamala 1977). It follows, therefore, that moreollin and isomorellin are derivatives of morellin (1) and appear to differ only in the configuration of the side chain containing the  $\alpha,\beta$ -unsaturated aldehyde group similar to that observed between morellin (1) and isomorellin (2). Further evidence for the structures of moreollin and isomorellin as the ethanol adducts of morellin (1) and isomorellin (2) respectively was obtained from a study of their PMR, CMR, and mass spectral data, and confirmed by partial synthesis.



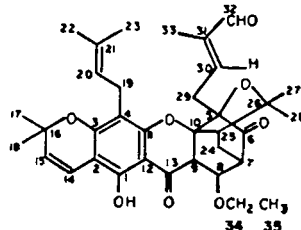
MORELLIN (1)



ISOMORELLIN (2)



MOREOLLIN (3)



ISOMORELLIN (4)

## 2.1. PMR spectra of moreollin (3) and isomorellin (4)

The PMR spectrum of moreollin (3) (figure 1) differs from that of morellin (1) or isomorellin (2) in several respects, the most striking ones being the absence of the vinylic hydrogen at  $C_8$  and the appearance of an extra methyl signal as a triplet at  $\delta$  1.15 ( $J=6\text{Hz}$ ) superimposed on a tertiary methyl signal. The presence of a triplet methyl signal indicates clearly that the new pigment contains an ethyl group. The other six methyl signals appear between  $\delta$  1.35 and 1.8. A set of multiplets between

$\delta$  2.46 to 3.74 account for 11 protons, three more as compared to morellin (1), in the same region. These are due to the protons attached to the  $C_9$  and  $C_{34}$  carbons. A new signal, which appeared at  $\delta$  4.5 (d,  $J=4$  Hz), is due to the tertiary proton at  $C_8$ . The triplet at  $\delta$  5.0 could be ascribed to the vinylic proton of  $C_{20}$ , coupled to methylene protons of  $C_{19}$ . The doublets at  $\delta$  5.5 and 6.6 are due to the vinylic protons in the 2,2-dimethylchromene system. In addition, there are two protons appearing as a pair of superimposed quartets at  $\delta$  3.55 indicating the presence of two nonequivalent  $-O-CH_2-$  protons. The vinylic proton at  $C_{30}$  appears at  $\delta$  6.86 as a triplet ( $J=4$  Hz). The aldehyde proton and the chelated hydroxyl appear at  $\delta$  10.18 and 11.85, respectively. The above PMR data clearly indicate that the new pigment is an ethanol adduct of morellin (1) or isomorellin (2) and is represented either by (3) or (4).

The PMR spectrum of isomoreollin (figure 2) closely resembles that of moreollin and shows differences only in the chemical shifts due to the aldehyde,  $\delta$  9.36 and the

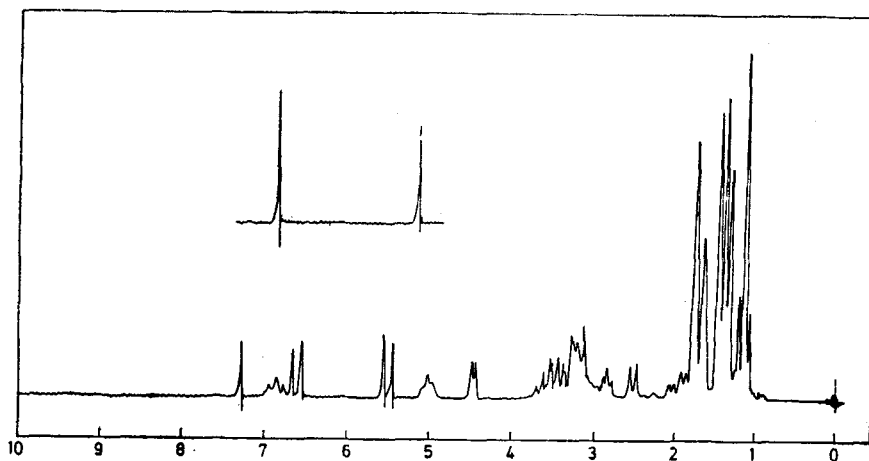


Figure 1. PMR spectrum of moreollin.

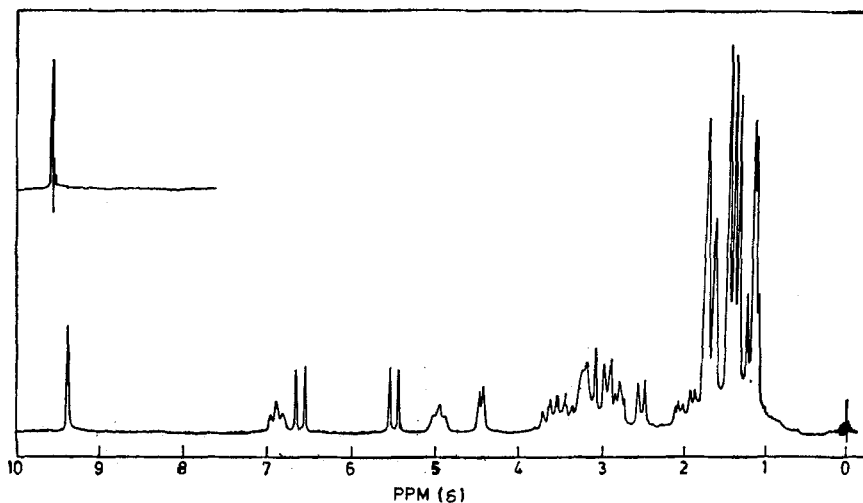


Figure 2. PMR spectrum of isomoreollin.

chelated hydroxyl  $\delta$  11.76 protons. Like moreollin, isomoreollin also has 8 methyl groups. A new three proton resonance appears as a triplet at  $\delta$  1.15 due to the ethyl methyl protons ( $\text{CH}_2\text{CH}_3$ ). The other six methyl signals appear between  $\delta$  1.18 and 1.8. The multiplet in the region  $\delta$  2.46 to 3.74 integrates to 11 protons, similar to that of moreollin. The three new protons are due to those attached to  $\text{C}_9$  and  $\text{C}_{34}$  carbons. The tertiary proton at  $\text{C}_8$  appears as a doublet of doublets at  $\delta$  4.45. The vinylic protons at  $\text{C}_{20}$  and  $\text{C}_{30}$  appear as triplets at  $\delta$  4.95 and 6.9 respectively. The vinylic protons at  $\text{C}_{14}$  and  $\text{C}_{15}$  appear as doublets at  $\delta$  5.15 and 6.6.

The PMR spectra of *cis* and *trans*-2-enals have been well documented (Stevens *et al* 1973). In line with this observation, moreollin contains a *cis*-2 enal moiety as in morellin (1) and is, therefore, the ethanol adduct of morellin as represented in the structure (3). Hence isomoreollin has the structure (4). This is confirmed as follows.

## 2.2. CMR spectra of moreollin (3) and isomoreollin (4)

The proton-noise decoupled CMR spectra of morellin (1), isomorellin (2), moreollin (3) and isomoreollin (4) are illustrated in figure 3 and 6 and the individual assignments are depicted in table 1. Assignments are based on off-resonance decoupling experiments,

Table 1. Carbon (Proton and noise decoupled) chemical shifts.

Carbon number	Morellin	Moreollin	Isomorellin	Isomoreollin
1	157.4	156.7	157.4	156.8
2	103.2	103.3	102.9	103.4
3	161.0	161.1	161.1	161.1
4	107.8	109.2	107.7	109.3
5	83.6	82.1	83.1	82.1
6	202.5	208.3	202.8	208.3
7	46.6	44.2	46.6	44.2
8	135.1	72.6	135.5	72.6
9	133.2	43.8	133.1	43.8
10	90.3	88.5	90.5	88.5
11	156.9	155.8	157.0	155.0
12	100.1	102.0	100.2	102.1
13	178.0	193.7	178.8	193.6
14	115.0	115.4	115.0	115.6
15	126.1	126.6	126.7	126.6
16	78.6	78.6	78.5	78.6
17	27.9	27.4	27.0	27.8
18	28.1	28.3	28.0	28.3
19	21.3	21.6	21.3	21.7
20	121.7	122.7	121.6	122.8
21	131.8	131.5	131.7	131.6
22	285.4	25.4	25.4	25.7
23	17.9	18.1	17.8	18.1
24	24.9	20.1	24.9	20.1
25	48.7	49.1	48.7	49.2
26	83.8	86.2	83.7	86.2
27	29.6	29.8	29.6	29.9
28	28.6	28.6	28.6	28.6
29	26.5	25.7	27.0	27.4
30	139.5	142.9	146.2	149.0
31	137.4	137.2	139.8	140.1
32	189.1	191.4	194.1	195.2
33	16.1	16.5	9.3	8.1
34	—	63.9	—	63.9
35	—	15.2	—	15.2

an analysis of the partially decoupled spectrum, selective decoupling experiments and comparison of the spectra with that of morellin (1) and isomorellin (2). The salient features of the spectra are presented below.

It is clear from the CMR data that the  $C_8$  and  $C_9$  carbons appeared at  $\delta$  135 and 133 in morellin (1) and isomorellin (2) respectively. These two carbons 8 and 9 are shifted to  $\delta$  72.6 and 43.8 respectively in the spectrum of moreollin (3) and isomoreollin (4). Further the spectrum also showed the presence of two additional carbon atoms, 34 and 35, at  $\delta$  63.9 and 15.2 in moreollin and isomoreollin respectively. Furthermore, it was observed that saturation of the 8,9 double bond in morellin (1) and isomorellin (2) results in pronounced change in the chemical shifts of a number of carbon atoms. Thus, both the carbonyl carbons at positions 6 and 13 were shifted downfield by 5.8 and 5.7  $\delta$  respectively, while the carbons at 24 and 7 suffered an up-field shift of 4.8 and 2.4  $\delta$  respectively. The carbon atoms 5 and 10 were shielded whereas the carbons—30, 12, 26 and 4 were deshielded to a considerable extent.

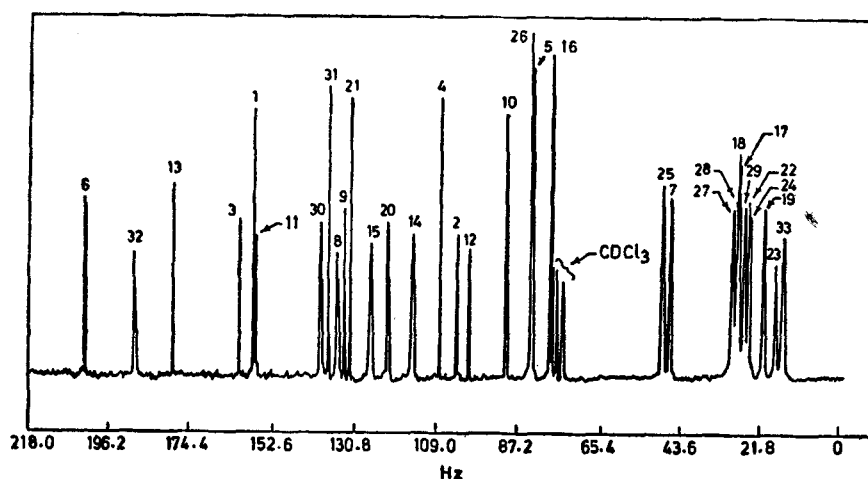


Figure 3. CMR spectrum of moreollin.

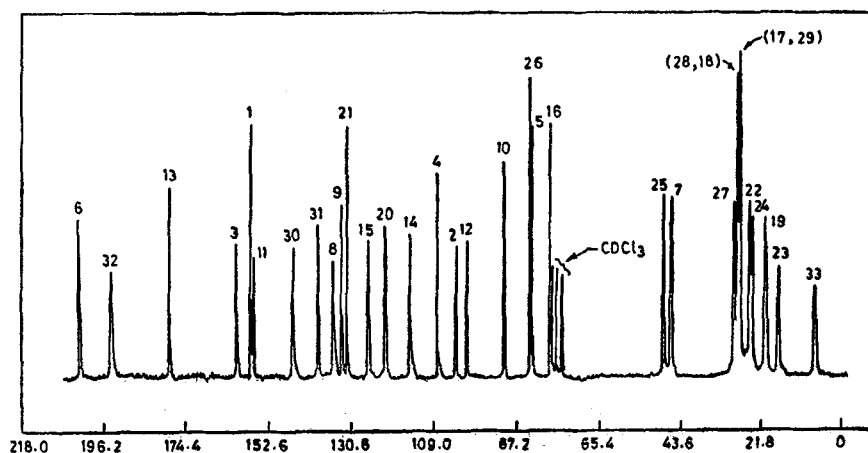


Figure 4. CMR spectrum of isomorellin.

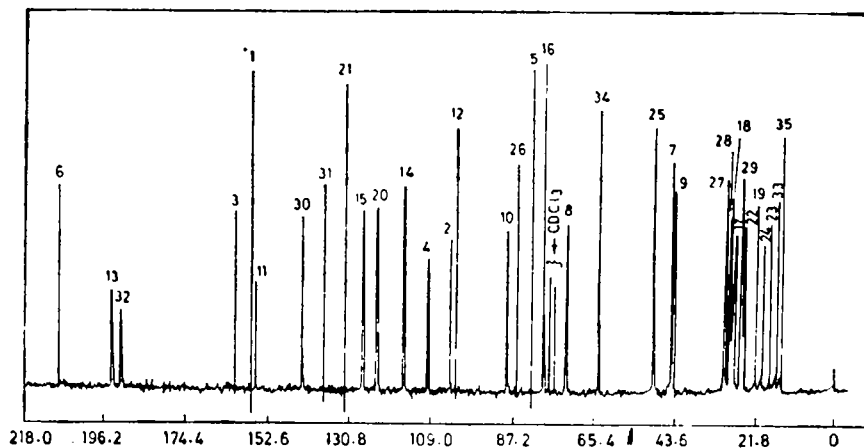


Figure 5. CMR spectrum of moreollin.

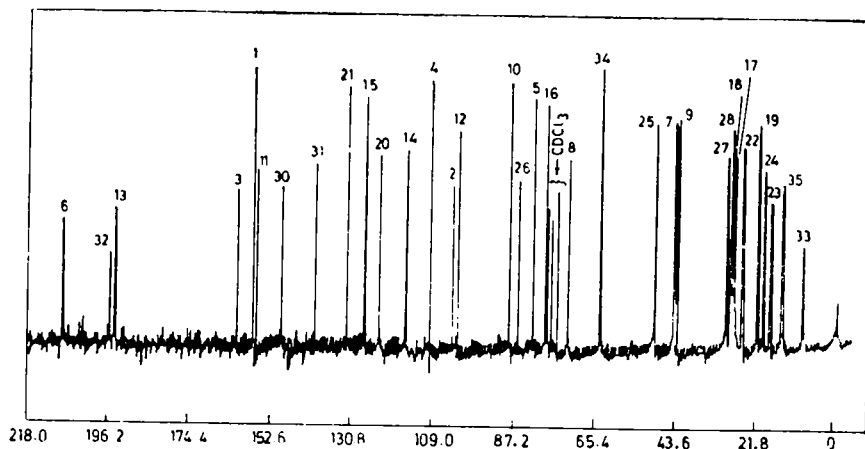


Figure 6. CMR spectrum of isomoreollin.

The  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts and the C, H coupling constants of the aldehyde side chain in morellin (1), isomorellin (2), moreollin (3) and isomoreollin (4) are presented in table 2. The long range coupling constants  $^3J_{\text{C,H}}$  of the aldehyde carbon were obtained from selective decoupling experiments.

It is well known that *cis*-substituents on an olefinic double bond lead to a shielding effect (de Haam and Van de Veen 1973) probably due to the Van der Waals interaction of the hydrogens and subsequent polarization of the C—H bonds. Hence, the lower  $\delta$  value of the aldehyde carbon [ $\delta$  189.1 in morellin (1) and  $\delta$  191.0 in moreollin (3)] is assigned to the *cis*-configuration of CHO and  $\text{CH}_2$  groups (*Z*-isomer) whereas the higher value [ $\delta$  194.1 in isomorellin (2) and  $\delta$  195.2 in isomoreollin (4)] corresponds to the *trans*- (or *E*) isomer. As expected, the reverse phenomenon, i.e., deshielding, was observed for the methyl carbon in morellin (16.0) and moreollin ( $\delta$  16.1) compared to isomorellin ( $\delta$  8.1) and isomoreollin ( $\delta$  9.3). This assignment was fully supported by the magnitude of the vicinal C, H reduced coupling constants of the aldehyde carbon,  $^3J_{\text{C,H trans}}=9.8$  Hz (morellin), 9.9 Hz (moreollin) and  $^3J_{\text{C,H cis}}=$

Table 2.  $^{13}\text{C}$  and  $^1\text{H}$  resonances and coupling constants.

	Morellin (1)	Moreollin (3)	Isomorellin (2)	Isomoreollin (4)
$\delta_{\text{CHO}}$	189.1	191.0	194.1	195.2
$\delta_{\text{CHO}}$	9.55	10.16	9.21	9.44
$\delta_{\text{CH}_3}$	16.0	16.1	8.1	9.3
$\delta_{\text{H}}$	6.02	6.86	6.36	6.90
$^3J_{\text{CHO, H}}^{\text{trans}}$	9.8 Hz (reduced)	9.9 Hz (reduced)		
$^3J_{\text{CHO, H}}^{\text{cis}}$			7.8 Hz (reduced)	8.9 Hz (reduced)
$^3J_{\text{CH}_3, \text{H}}^{\text{trans}}$			6.5 Hz	
$^3J_{\text{CH}_3, \text{H}}^{\text{cis}}$	6.1 Hz (reduced)			

1. Carbon and proton chemical shifts relative to internal TMS=0.

2. The reduced C, H coupling constants originate from double resonance experiments, the true values from single resonance, nondecoupled spectra.

7.8 Hz (isomorellin) and 8.9 Hz (isomoreollin). The corresponding reduced coupling constants of the methyl carbon are only slightly larger for the *trans* interaction (6.5 Hz) than for the *cis* interaction (6.1 Hz).

The vicinal  $^{13}\text{C}$ ,  $^1\text{H}$  coupling constants of several  $\alpha$ ,  $\beta$ -unsaturated aldehydes and acids have been investigated as model compounds (Philipsborn 1974). The data obtained from the model study are in close agreement with that obtained for morellin, isomorellin, moreollin and isomoreollin thus confirming the configuration of the side chain containing the aldehyde group in these compounds.

### 2.3. Mass spectrum of moreollin (3)

The mass spectrum of moreollin (3) is illustrated in figure 7 and the possible fragmentation pattern is presented in the Chart 1. The mass spectrum of isomoreollin (4) and its fragmentation pattern is identical to that of moreollin (3).

The molecular ion (A) which also happens to be the base peak appears at  $m/e$  590. Loss of methyl radical probably from the chromens part of the molecule gives the ion (B) at  $m/e$  575, which then eliminates a molecule of ethanol affording the ion (D), occurring at  $m/e$  529. In an alternative pathway the molecular ion (A) loses a molecule of ethanol and a methyl radical in successive steps to generate the ion (D). The molecular ion (A) undergoes a facile retro Diels-Alder type fragmentation to give the ions E ( $m/e$  304) and F ( $m/e$  286). The ion (C) with  $m/e$  544 is equivalent to the molecular ion of morellin and hence can be expected to undergo further fragmentation characteristic of the morellin molecule. The occurrence of significant peaks at  $m/e$  405(I), 287(J), 331(L) and 215(H) support this.

The facile fragmentation of the elements of ethanol from the molecular ion (A) to give an ion corresponding to the molecular ion of morellin (1) supports the earlier conclusion that moreollin is an ethanol addition product of morellin (1). It is interesting to note that the  $\gamma$ -pyrone ring of morellin (1) does not undergo a direct retro

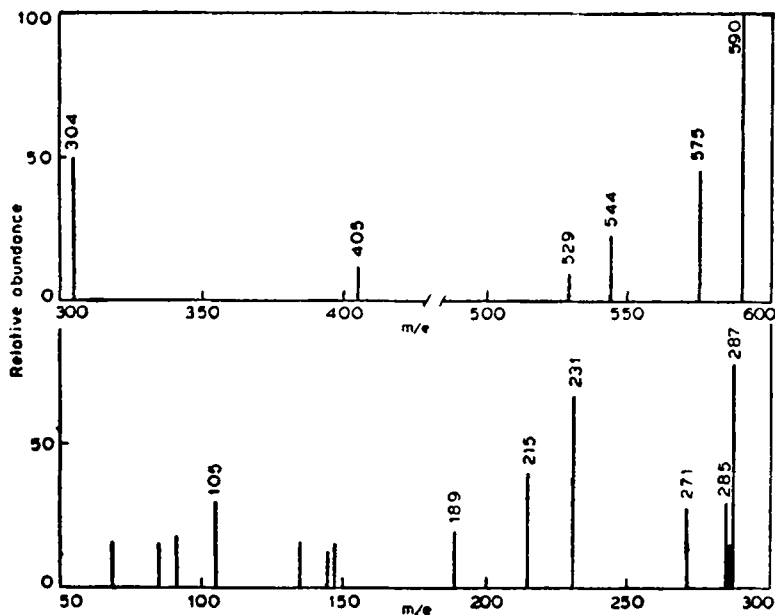
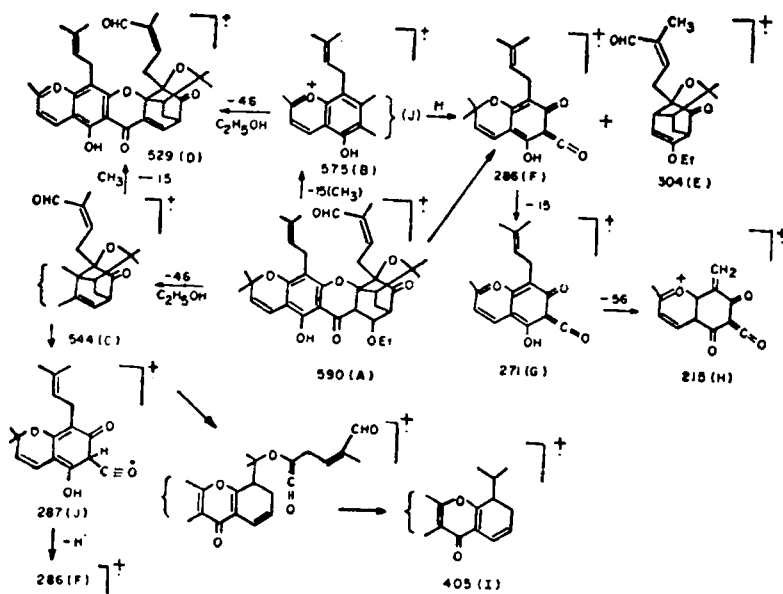


Figure 7. Mass spectrum of moreollin.



Diels-Alder type fragmentation to give an ion at  $m/e$  258, because of the presence of the double bond at the 8 position (Yemul and Rama Rao 1974). But a facile fragmentation of this type occurs in the case of moreollin (3), giving an intense peak at  $m/e$  304 (E) (50%). This shows that the 8-9 double bond present in moreollin (1), is absent in this compound which is in agreement with the proposed structure.



#### 2.4. Partial synthesis of moreollin (3) and isomoreollin (4)

Moreollin (1) was refluxed in ethanol with potassium acetate for 2 hr and the resulting product was chromatographed on neutral alumina. This was subjected to further purification using extensive preparative TLC. A small amount of a yellow crystalline product, m.p. 168° was obtained and this was identified as moreollin (3) by comparison with the authentic sample (mixed melting point and spectral data).

Isomoreollin (4) was similarly prepared from isomorellin (2) and the product was compared with the authentic specimen. A compound, ethoxy dihydroisomorellin has been isolated from the seed coat extracts of *G. morella* (Bhatt *et al* 1964). This compound appears to be identical with isomoreollin (4) although direct comparison of the compounds could not be made possible due to lack of ethoxy dihydroisomorellin.\* The preparation of moreollin (3) and isomoreollin (4) from morellin (1) and isomorellin (2) conclusively establishes the structures and the configuration proposed for them.

### 3. Biogenesis of moreollin

Moreollin (3) appears to be a natural product and not an artefact since it was isolated from the seed coat of *G. morella* even by extraction with light petroleum after the separation of morellin (1). During the extraction process, absolute care was taken to avoid the use of ethanol. Isomoreollin (4) or ethoxydihydroisomorellin, which is an ethanol adduct of isomorellin must be an artefact since isomorellin (2) was completely absent in the extracts of *G. morella* or other *Garcinia* species.

The biogenesis of morellin (1) as suggested, (Quillinan and Scheinmann 1971) involves a Claisen rearrangement of the 5, 6-(1, 1-dimethylallyl) ether obtained from 1, 3, 5, 6-tetrahydroxyxanthone, followed by an intramolecular Diels-Alder reaction on the intermediate dienone resulting in the formation of desoxymorellin. Further transformations leading to morellin (1), morellic acid and dihydromorellin have been postulated (Venkataraman 1973).

Moreollin (3), probably, follows the same biogenetic pathway as morellin (1), except that an additional two carbon unit as ethoxyl group is present at C<sub>8</sub>. The presence of an ethoxyl group is rare among natural products but not unknown (Anjaneyulu *et al* 1975; Shienthong *et al* 1974). The origin of these two carbon units appears to be similar to that postulated for furans (Birch *et al* 1969; Diment *et al* 1969).

### 4. Experimental

#### 4.1. General

Melting points and boiling points reported herein are uncorrected. Infrared absorption spectra were recorded on a Perkin-Elmer model 700, or Perkin-Elmer infracord model 137B. The ultraviolet absorption spectra were recorded on a Unicam model SP 700A recording spectrophotometer in 95% ethanol. The proton magnetic reson-

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We are indebted to Prof. K Venkataraman, NCL, Poona, for this kind information.

ance spectra were recorded in deuteriochloroform solution unless otherwise mentioned, either on a Varian HA-100D or a Varian T-60 spectrometer, using tetramethyl silane as an internal reference and chemical shifts are quoted as  $\delta$  (parts per million) downfield from the reference. The CMR spectra were obtained in 0.57 molar  $\text{CDCl}_3$  solutions on a Varian-XL-15-FT instrument at 25.2 MHz and with the aid of a 620-1-16K computer. The mass spectra were obtained on an Atlas CH-7 or an A.E.I. M.S. 902 instrument.

#### 4.2. Isolation of morellin (1) and moreollin (3) from seed coat extracts of *G. morella*

##### Morellin (1)

Powdered seed coat (500 g from 1.5 kg air dried seeds of Mysore gamboge tree) was defatted with light petroleum ( $4 \times 500$  ml). After removal of the last traces of the solvent by suction, percolation was continued with cold acetone and the acetone extract (2.5 l) concentrated to about 100 ml *in vacuo*. The dark brown residue was stirred with boiling ethanol (800 ml) to form a clear solution which on slow cooling deposited morellin (1) as crystals (*ca.* 81 g). On concentration of the filtrate a further quantity (*ca.* 9.5 g) of morellin (1) crystallised which was removed by filtration. Recrystallisation from ethanol afforded bright orange yellow prismatic needles, m.p. 158.9°.  $[\alpha]_D^{26} -628^\circ$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  236, 289, 365 nm ( $\epsilon$ , 31620, 19050, 15140);  $\nu_{\text{max}}$ : 1740, 1670, 1645, 1630, 1590  $\text{cm}^{-1}$ ;  $\delta$ : 1.33 (s, 3H), 1.5 (s, 3H), 1.53 (s, 6H), 1.70 (s, 1H), 1.75 (s, 3H), 1.80 (s, 3H), 2.3 (d,  $J=4.5$  Hz, 2H), 2.65 (distorted q, 2H), 5.57 (d,  $J=10$  Hz, 1H), 6.02 (t,  $J=8$  Hz, 1H), 6.64 (d,  $J=10$  Hz, 1H), 7.6 (d,  $J=7$  Hz, 1H), 9.55 (s, 1H,  $\text{CHO}$ ), 12.77  $\delta$  (s, 1H, phenolic  $\text{OH}$ ).  $M^+$  (%), 544 (100), 529 (30), 501 (34), 488 (5), 405 (45), 363 (26), 307 (16), 287 (37), 231 (27).

Analysis: Found: C, 70.95; H, 6.51. Calculated for  $\text{C}_{33}\text{H}_{36}\text{O}_7$   
C, 71.11; H, 6.62%

##### Moreollin (3):

(i) The mother liquors in the previous experiment, were kept for 2 to 3 weeks. Moreollin (3) (1.89 g) was deposited as thick lemon yellow prisms. It was recrystallised from acetone-ethanol, had a melting point 168°;  $[\alpha]_D^{26} -21.03^\circ$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  235, 266, 275, 305, 316, 365 nm ( $\epsilon$ , 25120, 39810, 41600, 18200, 13800, 4070),  $\nu_{\text{max}}$  3400, 1740, 1680, 1650, 1630, 1610, 1595  $\text{cm}^{-1}$ ;  $\delta$ : 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  $\text{D}_2\text{O}$ ).

$M^+$  (%), 590 (100), 575 (46), 544 (24), 529 (10), 405 (12), 304 (50), 287 (78), 231 (68), 215 (40), 189 (20), 147 (16), 145 (12), 105 (30), 91 (18), 85 (15), 69 (16). High resolution mass analysis (Found: 590.2888; required mass for  $\text{C}_{33}\text{H}_{42}\text{O}_8$ : 590.2880).

Analysis: Found: C, 70.95; H, 7.01.  $\text{C}_{35}\text{H}_{42}\text{O}_8$  requires  
C, 71.17; H, 7.11%

(ii) The acetone extract, as obtained in the previous experiment, was concentrated

to a small volume (500 ml). It was diluted by adding HCl (150 ml) and kept for 2 to 3 weeks at room temperature. Lemon yellow hexagonal crystals which were deposited were collected by filtration. The above solid was recrystallised from acetone to give moreollin (12) (1.2 g), m.p. 168° identical in all respects (IR, PMR, melting and mixed melting points) with the sample obtained in the previous experiment.

#### 4.3. Conversion of moreollin (3) to isomoreollin (4)

Moreollin (3) (0.1 g) was refluxed in acetic acid (5 ml) for 0.5 hr, diluted with water (2 ml) and recrystallization ethanol yielded isomoreollin (4) as lemon yellow prisms (0.042 g), m.p. 148°,  $[\alpha]_D^{25} -22.03^\circ$ ;  $\lambda_{\max}$  227, 267, 275, 317, 363 nm ( $\epsilon$ , 31620, 33880, 34670, 13800, 2818);  $\nu_{\max}$ , 3350, 1740, 1680, 1650, 1630, 1620, 1590  $\text{cm}^{-1}$ ,  $\delta$ , 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, non-equivalent  $-\text{OCH}_2 \text{CH}_3$ ), 4.45 (dd,  $\text{CHOCH}_2 \text{CH}_3$ ), 4.95 (t,  $J=7$  Hz, 1H), 9.36 (s, 1H,  $=\text{CHO}$ ), 11.76, (s, 1H, phenolic  $\text{OH}$ ).

Analysis: C, 70.81, H, 6.98

$\text{C}_{35}\text{H}_{42}\text{O}_8$  requires, C, 71.17, H, 7.117%.

#### 4.4. Isomorellin (2) from moreollin (3)

Moreollin (0.5 g) was refluxed with pyridine for 1 hr. The solution was poured into ice cold water and was extracted with ether (50 × 3 ml). The combined extract was washed with 5% aqueous hydrochloric acid and subsequently by 5% sodium bicarbonate solution. This was dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was extracted with hexane. Hexane extract was concentrated to dryness and was recrystallized from methanol, m.p. 119-20°. The product was identified by mixed melting point and comparison of spectra of an authentic sample of isomorellin (2).

#### 4.5. Moreollin (3) from morellin (1)

Morellin (1) (5 g) was refluxed with ethanolic potassium acetate (5%, 100 ml, pH, 8.5) for 2 hr. The lemon yellow product obtained after dilution with water (500 ml) was thoroughly washed with water, dried and purified by TLC ( $\text{CHCl}_3$ ). On crystallisation from acetone, moreollin (3) separated as hexagonal lemon yellow crystals, m.p. 166-8° (0.71 g). The identity of this material was established by mixed melting point and by comparison of spectra.

#### 4.6. Diacetyl moreollin

Moreollin (3) (0.2 g) was taken up in acetic anhydride (20 ml) and a drop of pyridine. This was heated on a steam bath for four hours. Acetic anhydride was then removed *in vacuo* and the residue was diluted with water. This was extracted with ether and washed with 10% sodium bicarbonate solution and dried over anhydrous sodium sulfate. Solvent was evaporated to dryness and the solid obtained was crystallised from benzene-hexane (1:1), m.p. 170° (yellow microcrystalline solid)  $\nu_{\max}$  1740, 1680, 1650, 1630, 1620, 1590  $\text{cm}^{-1}$ .

(Found: C, 68.48; H, 7.235,  $C_{39}H_{46}O_{10}$  requires  
C, 69.4; H, 6.82%)

Isomoreollin (4) was acetylated with acetic anhydride in dry pyridine as above and the resulting compound was identical with that obtained from moreollin (3).

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