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A REVISED STRUCTURE FOR HERMONIONIC ACID

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Abstract: Hermonionic acid and its decarboxylated product have been isolated from Garcinia quaesita. ^{13}C NMR spectral and chemical evidence indicate that hermonionic acid is 2-O-[2-(3-methylbut-2-enyl)-3-methoxy-4-hydroxy-5-(3,7-dimethylocta-2,6-dienyl]-4-methoxy-5-(3-methylbut-2-enyl -6-hydroxybenzoic acid. The previously assigned dienone structure for this acid is incorrect.

The bark hot light petroleum extractives of Garcinia quaesita Kosterm. on combined column and preparative thin layer chromatographic separations gave an acid (1) which was identical (Co-TLC, IR, ^1H NMR, MS) with hermonionic acid[1] previously obtained from Garcinia hermonii Kosterm. The decarboxylated hermonionic acid (2) was also isolated as a minor product. Their molecular formulae were shown by high resolution mass spectrometry to be $C_{35}H_{46}O_7$ and $C_{34}H_{46}O_5$ respectively. The acid on heating at 180°C gave a decarboxylated product which was identical with the minor natural product (2). Both 1 and 2 had signals for seven allylic methyl groups (δ_H 1.59-1.75 singlet), four olefinic protons (δ_H 4.90-5.30, multiplet) and six benzylic protons (δ_H 3.25, triplet) in their ^1H NMR spectra. The presence of two isoprenyl and one geranyl groups directly attached to the aromatic ring(s) can be discerned from the above. The acid (1) had two chemically different methoxy groups (δ_H 3.70 and 3.80) whilst in 2 the two methoxy groups were chemically similar (δ_H 3.70). The acid (1) contained only two aromatic protons both of which appeared as singlets (δ_H 5.66 and 6.50). Whereas 2 had three aromatic protons, one of which appeared as a singlet (δ_H 6.4) and the other two as a meta- coupled pair (δ_H 5.87 and 6.03, J=2Hz). 1 had a chelated OH signal (δ_H 12.4) which was absent in 2 and it answered the Gibbs test. Both 1 and 2 gave diacetate (Ac_2O-pyridine) confirming that they are dihydroxy derivatives possessing the same skeleton.

Treatment of the acid (1), with p-toluenesulphonic acid yielded a decarboxylated cyclised product (3) in which one isoprenyl group and one geranyl group cyclised with an ortho- hydroxy group in each case. As in 2 the two methoxy groups in 3 were chemically similar (δ_H 3.70). Dimethyl octahydrohermonionic acid when treated with acetyl chloride/conc. H_2SO_4 gave a xanthone, $C_{32}H_{56}O_6$(M^+ 596). Its ^1H NMR, MS data and comparison of its UV, data with those for tetraoxygenated xanthones showed the xanthone to be 1,3,6,7-tetramethoxy-2,5-di-(3-methylbutyl)-8-(3,7-dimethyloctyl)-xanthen-9-one (4). From the above data two possible structures (1 and 5) for hermonionic acid can be written at this stage. The presence of the intense fragment ion pair at m/z 235 and 327 (Scheme 1) and the absence of the pair at m/z 259 and 303 strongly favours the structure 1 for hermonionic acid.

Hermonionic acid was first isolated[1] from Garcinia hermonii and was assigned the structure 6. Though its ^1H NMR spectrum had a 6H single triplet at δ_H 3.25, four of these protons were erroneously considered to be due to the allylic protons of the two isoprenyl chains of the cyclohexadienone ring of 6. These type of protons are known[2,3] to resonate at δ_H 2.3-2.7. Besides, the ^{13}C NMR spectrum of hermonionic acid showed no signals in the range 45-90 ppm. A singlet around δ_C 57 for the saturated tertiary aliphatic carbon should be present in the spectrum of hermonionic acid if it had structure 6.

The δ_C assignments for hermonionic acid are given in Fig. 1 and the mass spectral fragmentations are shown in Scheme 1.

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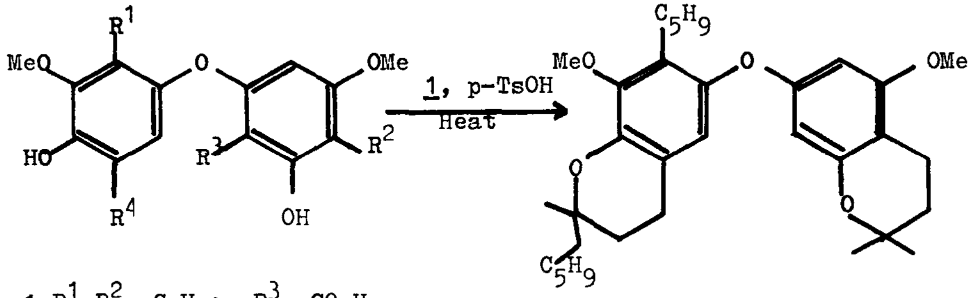
see the ^{13}C NMR spectral data of zeylaxanthonone[4] and colupulone.[5]



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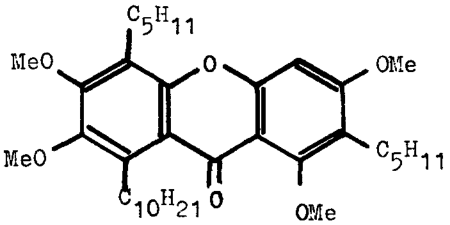
1 $R^1 = R^2 = C_5H_9$; $R^3 = CO_2H$

$R^4 = C_{10}H_{17}$

2 $R^1 = R^2 = C_5H_9$; $R^3 = H$; $R^4 = C_{10}H_{17}$

5 $R^1 = R^4 = C_5H_9$; $R^3 = CO_2H$; $R^2 = C_{10}H_{17}$

$\underline{1} \xrightarrow[\text{c) } CH_3COCl/H_2SO_4]{\text{a) } H_2/Pt_2O \quad \text{b) } Me_2SO_4}$



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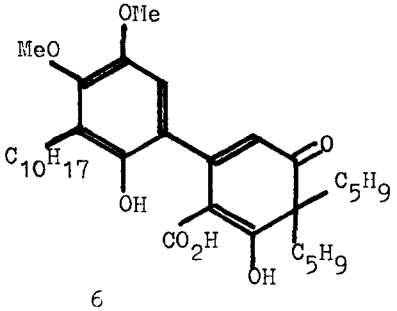

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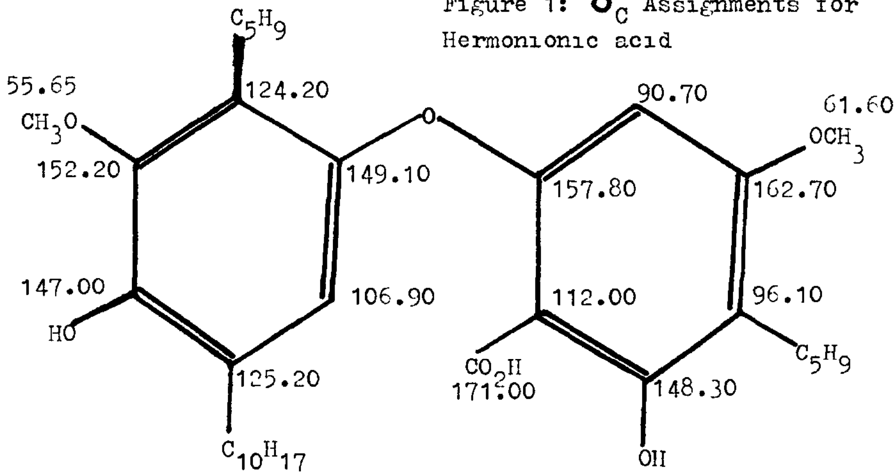
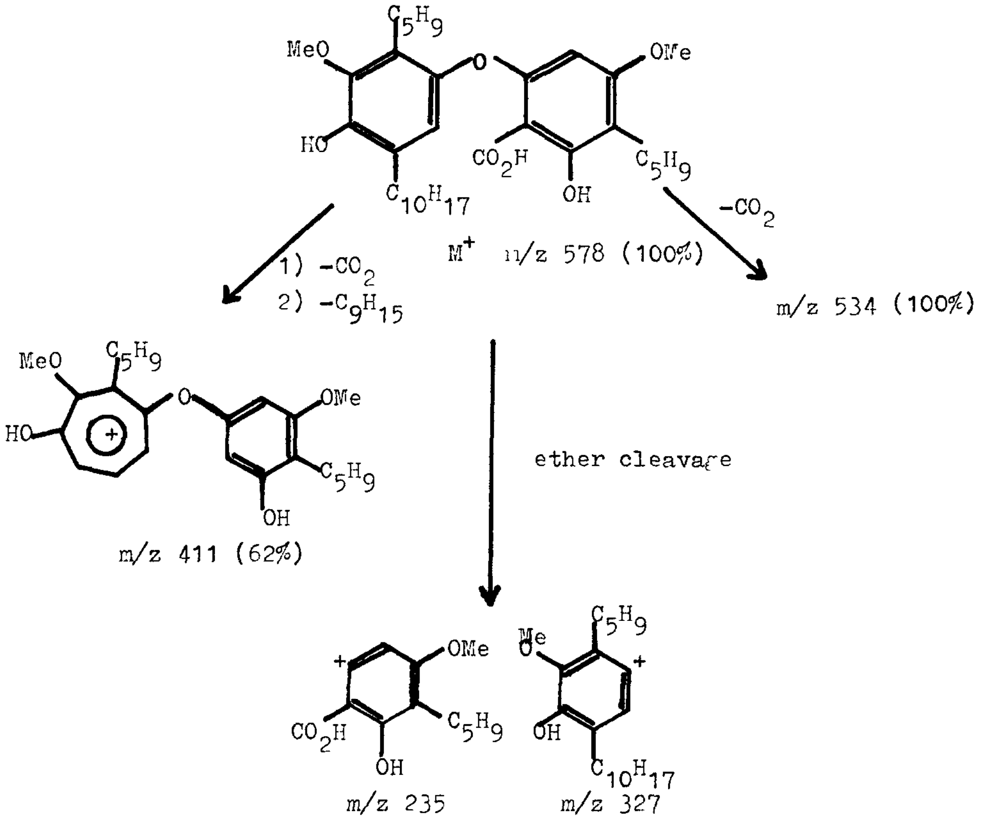


Figure 1: δ_C Assignments for Hermonionic acid



SCHEME 1: Mass Fragmentations of Hermonionic acid

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