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TRITERPENOIDS FROM MANGIFERA INDICA : I.
THE STRUCTURE OF MANGIFEROLIC ACID.

S.Corsano and E.Mincione
Istituto di Chimica Organica dell'Università, Roma

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In the course of an investigation on the constituents of the resin from Mangifera Indica, we have obtained by extraction with sodium carbonate an acidic fraction, which was chromatographated over silica gel to give several components. We report in this communication the elucidation of the structure of the major component, which we have named "mangiferolic" acid (I), first example of triterpenic acid containing a cyclopropane ring.

Mangiferolic acid (I) $C_{30}H_{48}O_3$ (+) m.p. 181-183°, $[\alpha]_D$ + 49°, revealed its nature as an $\alpha\beta$-unsaturated acid by its ultraviolet absorption (λ_{max} 217 mμ, ε = 11.300) and by its infrared spectrum: ν_{max} (KBr) 1695 cm^{-1} ($\alpha\beta$-unsaturated acid), 1650 cm^{-1} (conjugated double bond). The presence of an hydroxyl group has been revealed by the infrared spectrum of the methyl ester (II) $C_{31}H_{50}O_3$ m.p. 94-96°, $[\alpha]_D$ + 51°, which showed ν_{max} (CS_2) 3570 cm^{-1} (OH), 1715 cm^{-1} ($\alpha\beta$-unsaturated ester), 1650 cm^{-1} (conjugated double bond). The NMR spectrum of the methyl ester

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(+) Satisfactory analyses have been obtained for all compounds reported. Melting points were determined on a Kofler block and have not been corrected. Specific rotations were determined in chloroform solution at room temperature. NMR spectra were carried out on a Varian A 60 spectrometer. Chemical shifts are quoted in δ values downfield from tetramethylsilane as internal standard.

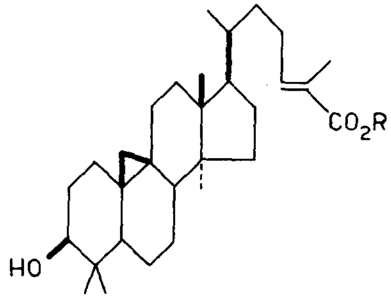
(II) (in CCl_4) showed a pair of doublets centered at δ 0.37 and δ 0,58 (2H) (J = 4 c/s) indicative of two non-equivalent hydrogen atoms on a cyclopropane ring [1]; a peak at δ 1.8 (3H) indicative of a vinylic methyl; a quartet centered at δ 3.18 (1H) attributable to a proton α to an hydroxyl group; a triplet centered at δ 6.63 (1H) assignable to an olefinic proton shifted to low field by the close proximity of the ester group.

The conjugated double bond of mangiferolic acid was readily hydrogenated on palladised charcoal, yielding a dihydro-acid (III) $C_{30}H_{50}O_3$ m.p. 178-180°, 215-220°, $[\alpha]_D$ + 40°, which showed no selective absorption between 220 and 300 mμ ; therefore mangiferolic acid has only one double bond.

These results suggested a close relationship between mangiferolic acid and cycloartenol (IV). Moreover the unusually large shift to low field observed for the vinylic methyl peak suggested that this methyl and the carboxyl group are attached to the same unsaturated carbon atom at position 25 [2].

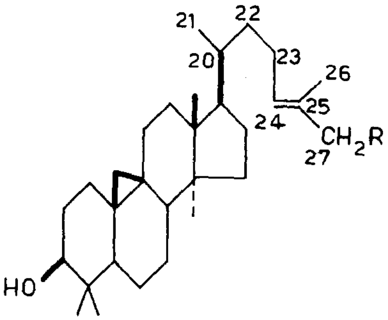
This assumption has been confirmed by reduction of mangiferolic acid with $AlLiH_4$ to a diol (V) $C_{30}H_{50}O_2$ m.p. 153-155°, $[\alpha]_D$ + 49°, which in its NMR spectrum showed the vinylic methyl peak shifted to higher field at δ 1.64.

It was possible to correlate this diol (V) with a known derivative of cycloartenol (IV) as follows. Catalytic hydrogenation of (V) with palladised charcoal gave two products: a small amount of a dihydro-diol (VI) $C_{30}H_{52}O_2$ m.p. 149-152°, $[\alpha]_D$ + 42° and, as principal product, a saturated alcohol by hydrogenolysis of the primary alcohol group and reduction of the double bond. This saturated alcohol $C_{30}H_{52}O$ m.p. 108-110°, $[\alpha]_D$ + 48° was identical in all respect with a known sample of



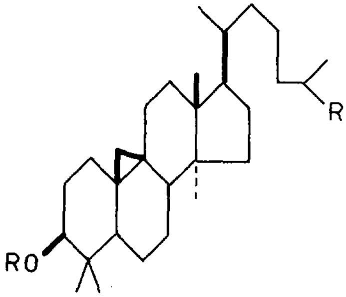
I : R = H

II : R = CH_3



IV : R = H

V : R = OH

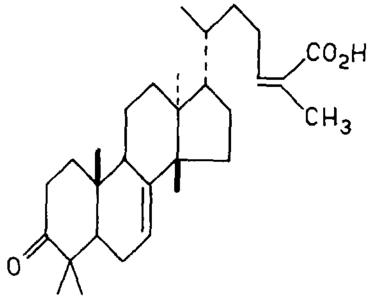


III : R = H ; R' = COOH

VI : R = H ; R' = CH_2OH

VII : R = H ; R' = CH_3

VIII : R = $OCOCH_3$; R' = CH_3

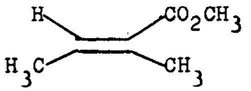


XI

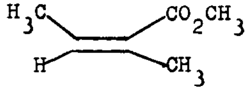
of cycloartanol (VII) (mixed melting point, $[\alpha]_D$, NMR and IR spectra). Moreover acetilation gave a compound $C_{32}H_{54}O_2$ m.p. 131-132°, $[\alpha]_D$ + 57°, which showed identical properties with a sample of cycloartanyl acetate (VIII) (mixed melting point, $[\alpha]_D$, IR spectra).

Mangiferolic acid must therefore be considered as 3β -hydroxy cycloart-24-en-26(or 27)-oic-acid.

The stereochemistry of the terminal conjugated double bond has been established on the basis of NMR data reported for a number of cis-trans pairs of $\alpha\beta$-unsaturated esters 3). Since it is well known that β -olefinic proton cis to the carbomethoxy group is, without exception, significantly more deshielded than the trans, the trans structure (I) can be assigned to mangiferolic acid by a comparison between δ values of the β -olefinic protons of methyl mangiferolate, methyl tiglate (IX) and methyl angelate (X) (table I)



IX



X

TABLE I(+)

Methyl ester	β H	Δ (a)
Me.tiglate	6.73	0.75
Me angelate	5.98	
Me.mangiferolate	6.63	0.72
Me.masticadienonate	5.91	

(+) Measurements in CCl_4 solution
(a) $\Delta = \delta$ cis - δ trans

The NMR spectrum of methyl masticadienonate shows the β-olefinic proton of the terminal conjugated ethylenic linkage considerably more shielded than that of methyl mangiferolate, and the difference in their chemical shifts is nearly the same as that between methyl tiglate and methyl angelate (table I). We propose therefore modifying the configuration of masticadienonic acid from the trans form, suggested by D.H.R. Barton and E. Seoane 4) to the cis form (XI).

An investigation on the other acidic components is at present in progress in this Institute.

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