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THE NEOFLAVONOIDS AND 4-ALKYLCOUMARINS FROM MAMMEA AFRICANA G. DON

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A previous communication[1] on the extractives from the heartwood of M. africana G. Don (Guttiferae) reported the structures of seven xanthones from a chloroform extract which also contained a complex mixture of coumarins. The bark of this tree proved to be a richer source of the coumarins which were obtained, devoid of the xanthones, by extraction with benzene. By a combination of column and repetitive preparative TLC on silica gel G (Merck) we have isolated mammea B/BB and mammea A/AA (mammeisin), previously isolated from the seeds of M. americana L.[2] together with three pairs of closely related coumarins. These compounds are designated MAB 1 (which is identical to the known mammea A/AB[2]), $C_{25}H_{26}O_5$, m.p. 75°, MAB 2, $C_{22}H_{28}O_5$, m.p. 115-116°, MAB 3, $C_{25}H_{26}O_6$, m.p. 134° (dec.), MAB 4, $C_{22}H_{28}O_6$, m.p. 83-84°, MAB 5, $C_{25}H_{24}O_5$, m.p. 78-80°, and MAB 6, $C_{22}H_{26}O_5$, all of which appear to be optically inactive by c.d. measurements. The spectral data show that the coumarins MAB 1-6 are all derived from 5,7-dihydroxycoumarin having a 2-methylbutanoyl substituent at C-6, with either a phenyl or propyl group at C-4 and a dimethylallyl group (or cyclised derivative) at C-8. Thus in the infrared spectrum of each compound there are peaks at 3400 cm^{-1} (νOH), 1720 (νC = O, lactone) and 1615 cm^{-1} (νC = O, hydrogen bonded acyl ketone). The u.v. spectra (Table 1) show the coumarin chromophore and are particularly useful in locating the acyl group at C-6 by the characteristic bathochromic shifts of the long wavelength bands to above 400 nm in alkaline media.[2] In accordance with this orientation the 6-acylcoumarins are all yellow and give a green colour with ethanolic ferric chloride.[2] The n.m.r. spectrum (Table 2) of each compound is consistent with a 2-methylbutanoyl side chain at C-6,[2] a vinyl proton at C-3 and either a C-4 propyl (for MAB 2, MAB 4, and MAB 6) or a C-4 phenyl (for MAB 1, MAB 3 and MAB 5) substituent. The nature of the C-8 substituent varies from a 3,3-dimethylallyl side chain, for MAB 1 and MAB 2, to a hydroxyisopropyldihydrofuran, for MAB 3 and MAB 4, to a 2,2-dimethylpyran ring for MAB 5 and MAB 6. The mass spectra of all these compounds exhibit peaks at M-57 due to the elimination of a butyl radical from the acyl side chain at C-6. In

TABLE 1

Ultraviolet data for Mammea africana G. Don coumarins

λ_{max}^{MeOH} (nm) (logε)

MAB 1	0.1N HCl	232 (4.24)	282 (4.47)	336 (4.01)		
	0.1N KOH	237 (4.35)	300 (4.27)		390 (3.97)	422 (4.03)
MAB 2	0.1N HCl	220 (4.21)	284 (4.44)	326 (3.97)		
	0.1N KOH	236 (4.24)	300 (4.26)		381 (3.96)	408 (4.02)
MAB 3	0.1N HCl	229 (4.25)	281 (4.48)	345 (4.03)		
	0.1N KOH	240 (4.28)	282 (4.14)	320 (4.33)		424 (3.92)
MAB 4	0.1N HCl	222 (4.17)	282 (4.45)	335 (4.01)		
	0.1N KOH	240 (4.18)	285 (4.10)			406 (4.01)
MAB 5	0.1N HCl	233 (4.36)	286 (4.46)	335 (3.76)		
	0.1N KOH	250 (4.30)	310 (4.31)			430 (3.69)
MAB 6	0.1N HCl	227 (4.25)	285 (4.20)	330 (3.72)		
	0.1N KOH	246 (4.16)	307 (4.25)			410 (3.74)

TABLE 2

The n.m.r. spectra of the coumarins from Mammea africana G. Don

τ values (no. of H, J in Hz)

MAB	C-3 H	C-4 substituent[e] 1'H	2'H	3'H	C-5 OH	C-6 substituent[e] 2'H	2'CH_3	3'H	3'CH_3	C-8 substituent[e] 1'H	2'H	3'CH_3
1[a,c]	4.08s (1H)	2.53 (5H)			0.67b	6.24m (1H)	8.93d (3H,7)	~8.40m (2H)	9.06t (3H,7)	6.52d (2H,7)	4.71t (1H,7)	8.11s(3H) 8.27s(3H)
2[b,c]	4.29s (1H)	7.13t (2H,6.5)	8.50m (2H)	9.02t (3H,7)	-4.5s -4.58s (1H)	6.34m (1H)	8.87d (3H,7)	~8.50m (2H)	9.13t (3H,7)	6.58d (2H,7)	4.94t (1H,7)	8.22s(3H) 8.32s(3H)
3[b,d]	4.33s (1H)	2.84 (5H)			-4.55s -4.42s (1H)	6.46m (1H)	8.90d[f] (3H,7)	~8.50m (2H)	9.14t (3H,7)	6.70d (2H,10)	5.20t (1H,10)	8.62s(3H) 8.74s(3H)
4[b,d]	4.34s (1H)	7.18t (2H,7)	8.50m (2H)	9.00t (3H,7)	-5.07s -4.91s (1H)	6.44m (1H)	8.87d (3H,7)	~8.50m (2H)	9.05t (3H,7)	6.85d (2H,9)	5.24t (1H,9)	8.63s(3H) 8.76s(3H)
5[a,d]	4.00s (1H)	2.60 (5H)			-4.72 s -4.83 s (1H)	6.31m (1H)	8.82d (3H,7)	~8.40m (2H)	9.09t (3H,7)	3.08d (1H,10)	4.36d (1H,10)	8.42s (6H)
6[a,d]	4.02s (1H)	7.03t (2H,6)	8.40m (2H)	8.92t (3H,7)	-5.40 s -5.52 s (1H)	6.23m (1H)	8.78d (3H,7)	~8.40m (2H)	9.03t (3H,7)	3.10d (1H,10)	4.38d (1H,10)	8.43s (6H)

[a] at 60 MHz

[b] at 100 MHz

[c] in CCl_4

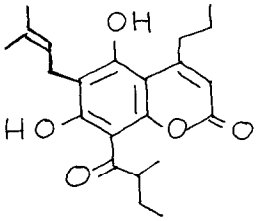
[d] in $CDCl_3$

[e] side chains & rings numbered starting with the benzylic position as 1'

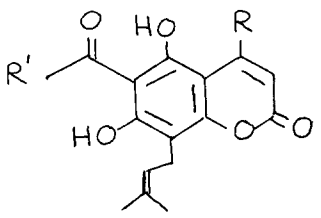
[f] some further splitting of doublet occurred to the extent of 2.5 Hz

MAB 1 has C-7 OH at 0.67 τ
MAB 2 has C-7 OH at 2.50 τ
MAB 3 has t-OH at 7.59 τ
MAB 4 has t-OH at 7.84 τ

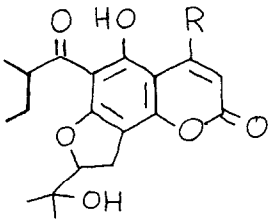
addition, the spectra of MAB 1, MAB 2 and mammea B/BB show the further loss of 56 m.u. from the M-57 ion and 55 m.u. from the molecular ion due to the respective loss of a butene molecule or a butenyl radical by the fragmentation of the 3,3-dimethylallyl side chain.



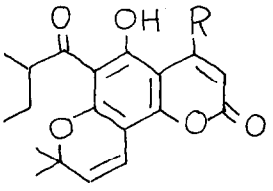
Mammea B/BB



Mammea A/AA; R = Ph, R' = CH_2CHMe_2
MAB 1;. R = Ph, R' = $CHMeCH_2Me$
MAB 2; R = $(CH_2)_2CH_3$, R' = $CHMeCH_2Me$

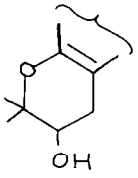


MAB 3; R = Ph
MAB 4; R = $(CH_2)_2CH_3$



MAB 5; R = Ph
MAB 6; R = $(CH_2)_2CH_3$

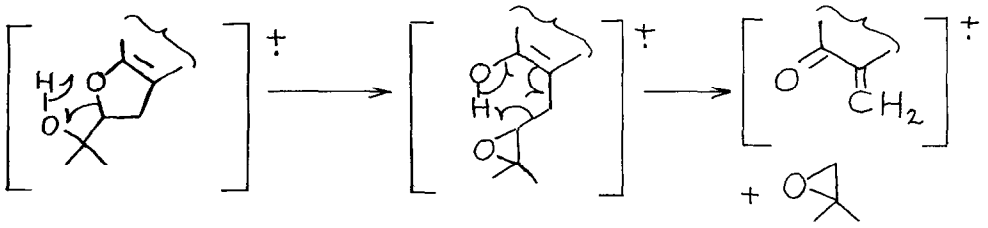
The absence of the M-57-56 and M-55 fragments from the spectra of MAB 3 and MAB 4, MAB 5 and MAB 6 together with the changes in the n.m.r. spectra (Table 2) suggested that the dimethylallyl substituent had been incorporated into a ring system. In the case of MAB 3 and MAB 4 the protons at C-2' and C-3' on the dihydrofuran ring constitute an A_2X system giving rise to the doublet 6.70τ and the triplet at 5.20τ (Table 2). The alternative dihydro pyranol structure (I) for these compounds may be excluded on the grounds that the corresponding protons would constitute an ABX system and would give rise to multiplets around 6.3τ and 7.2τ.[4]



(I)

Although water was not readily lost from the molecular ions of MAB 3 and MAB 4 in the mass spectra, the M-57 fragments underwent the loss of the elements of water to give the ions at M-75 (35%). A metastable ion at m/e 235 in the spectrum of MAB 3 shows that the M-129

fragment arises directly from the M-57 ion. These M-129 ions from both MAB 3 and MAB 4 may result from rearrangements leading to the elimination of isobutene oxide from the M-57 fragments as outlined below.



The occurrence of signals due to two neighbouring vinyl protons and two equivalent methyl groups in the n.m.r. spectra of MAB 5 and MAB 6 show the presence of a 2,2-dimethylpyran ring.[5] This was supported by the mass spectra where the 2,2-dimethylpyran rings underwent the characteristic loss of a methyl group to form the extremely stable benzopyrylium ions which are responsible for the base peaks at M-15 in these spectra.

The evidence is thus in excellent agreement with the structures we propose although the presence of two hydrogen bonded hydroxyl signals in the n.m.r. spectra of MAB 2-6 may suggest isomeric impurities. However, such impurities could not be detected by TLC.

Six of the coumarins, mammea B/BB, A/AA and MAB 1-4, have also been isolated independently by Professor Crombie and Dr. Games and we thank them for an exchange of information and manuscripts prior to publication. We thank S.R.C. for grants to I.C. and E.J.M. and for equipment.

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2. L. Crombie, D.E. Games and A. McCormick, J. Chem. Soc., (C) 2545 and 2553 (1967).
3. Similar data have been obtained by I.O. Sutherland, unpublished work, for a synthetic 2-hydroxyisopropylcoumaran. We are indebted to Dr. Sutherland for this information.
4. B.F. Burrows, N. Finch, W.D. Ollis and I.O. Sutherland, Proc. Chem. Soc., 150 (1959) and unpublished work; T.R. Seshadri, M.S Sood, K.L. Handa and Vishwapaul, Tetrahedron, 23, 1883 (1967).
5. e.g. B. Jackson, H.D. Locksley and F. Scheinmann, J Chem. Soc., (C), 2500 (1967).