Extractives of *Mammea americana* L. Part IV.[1] Identification of New 7,8-Annulated Relatives of the Coumarins Mammea A/AA, A/AB, B/AA, and B/AB, and New Members of the 6-Acyl Family B/AA, B/AB, and B/AC

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Six new coumarins of the 4-n-propyl series and two of the 4-phenyl series have been identified from *Mammea americana* L. Three of the former, mammea B/AA, B/AB, and B/AC, have the 5,7-dihydroxy-4-n-propylcoumarin core carrying an 8-(3-methylbut-2-enyl), grouping, and are differentiated by the 6-acyl substituent, which is 3-methylbutyryl (Ia), 2-methylbutyryl (Ib), or butyryl (Ic). The other three 4-n-propyl compounds have the same core but a 7,8-fused α-(hydroxyisopropyl)dihydrofuran system. The same three acyl variations are present, but at position 6 (VIIa—c). The two 4-phenylcoumarins found have also a 7,8-fused α-(hydroxyisopropyl)dihydrofuran system and possess either a 6-(3-methylbutyryl) or a 6-(2-methylbutyryl) substituent (VIa and b). There is mass spectral evidence of a shorter-chain member.

Structural evidence is based on spectral studies, supported by chemical interconversions involving mammea compounds of known structure.

SEVENTEEN 4-alkyl or 4-aryl coumarins have previously been identified in the seed extract of *Mammea americana* L.[1-8] Three insecticidal members having 4-(1-acetoxypropyl) side-chains are considered in the following paper and, with the eight new compounds reported in the present paper, a total of twenty-eight related coumarins have now been identified in this remarkably rich source

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[1] Part III, L. Crombie, D. E. Games, N. J. Haskins, and G. F. Reed, preceding paper.

[2] L. Crombie, D. E. Games, N. J. Haskins, G. F. Reed, R. A. Finnegan, and K. E. Merkel, *Tetrahedron Letters*, 1970, 3979.

[3] L. Crombie, D. E. Games, and A. McCormick, *Tetrahedron Letters*, 1966, 151; *J. Chem. Soc.* (*C*), 1967, 2545.

[4] L. Crombie, D. E. Games, and A. McCormick, *Tetrahedron Letters*, 1966, 145; *J. Chem. Soc.* (*C*), 1967, 2553.

[5] L. Crombie, D. E. Games, N. J. Haskins, and G. F. Reed, *Tetrahedron Letters*, 1970, 251; *J.C.S. Perkin I*, following paper.

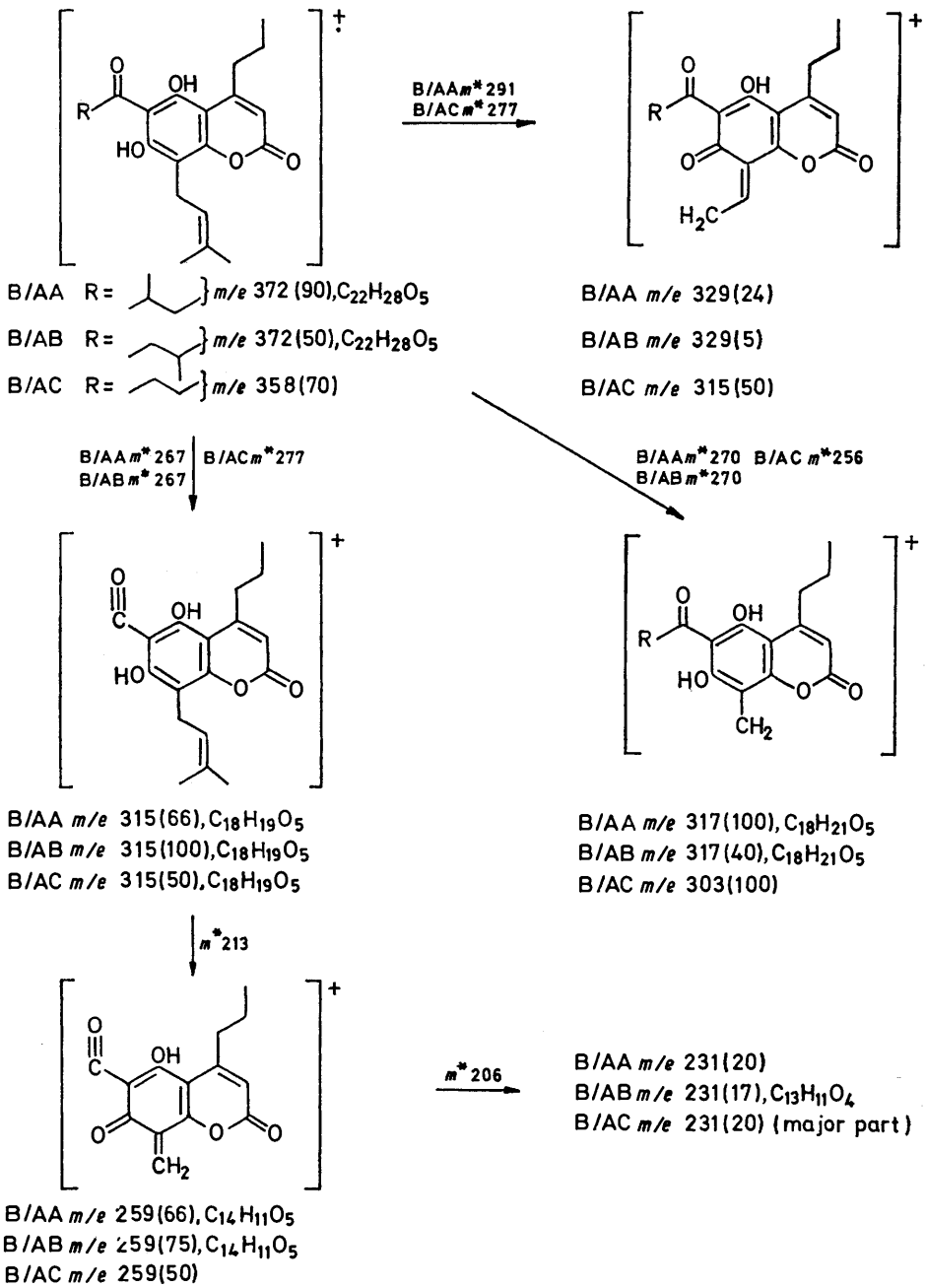
[6] R. A. Finnegan and W. H. Mueller, *Chem. and Ind.*, 1964, 1065; *J. Org. Chem.*, 1965, **30**, 2342.

[7] R. A. Finnegan, M. P. Morris, and C. Djerassi, *J. Org. Chem.*, 1961, **26**, 1180.

[8] C. Djerassi, E. J. Eisenbraun, R. A. Finnegan, and B. Gilbert, *J. Org. Chem.*, 1960, **25**, 2164, 2169.

of biogenetic variants. There is evidence that still others are present. Three of the new coumarins are mammeas B/AA (Ia), B/AB (Ib), and B/AC (Ic). The other five [(VIa and b) and (VIIa—c) are tricyclic, presence of compound (VIc) or (VId) in some samples is mentioned later in connection with the mass spectra.

Because of isolation difficulties, the approach of Part III [1] was followed, with separation into small



SCHEME 1 Mass spectral fragmentations of mammea B/AA, B/AB, and B/AC. Differences in major ion abundances were observed with an MS12 spectrometer (F. Scheinmann, personal communication)

having a five-membered ring attached to the 7- and 8-positions. Mammeigin [6] (A/A cyclo D) [3] and certain other related coumarins [9–11] have six-membered attachments to these positions. Evidence for the groups of congeners. Spectral methods were then employed for structure deduction and the conclusions were checked by synthesis and chemical interrelations.

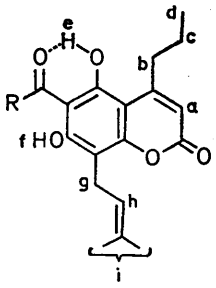
Continued chromatographic investigation of the light

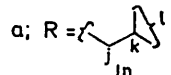
[9] I. Carpenter, E. J. McGarry, and F. Scheinmann, *Tetrahedron Letters*, 1970, 3983; a full account has recently appeared: *J. Chem. Soc.* (*C*), 1971, 3783.

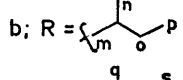
[10] D. E. Games and N. J. Haskins, *Chem. Comm.*, 1971, 1005.

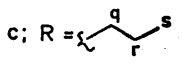
[11] D. P. Chakraborty and B. C. Das, *Tetrahedron Letters*, 1966, 5727.

petroleum extracts of the seeds of *M. americana* gave yellow crystalline material (Q3), m.p. 109°. Mass measurement of the molecular ion agreed with the formula $C_{22}H_{28}O_5$ for the major component. The i.r. spectrum [$\nu_{max.}$ (CCl_4) 3330, 1747, 1627, and 1595 cm^{-1}] was similar to those of other 5,7-dioxygenated coumarins,[1-8] and u.v. data (Table) supported a 6-acylated 4-alkyl-5,7-dihydroxycoumarin type.[3,4] Analysis of the n.m.r. data showed the major component to be (Ia), with some (Ic) present. Proton relationships were confirmed by double-resonance methods. Irradiation at τ 4·82 caused collapse of the doublet at τ 6·49 from the 3-methylbut-2-enyl chain and irradiation at τ 7·8 caused collapse of the doublets at τ 7·00 and 9·02 to singlets, confirming the assignment for the 6-(3-methylbutyryl) substituent. In the case of the 4-substituent, irradiation at τ 8·3 caused collapse of triplets at 8·98 and 7·05 to singlets. The mass spectrum also showed Q3 to be a mixture of (Ia) and (Ic), the former predominant. Fragmentation of the molecular ion, *m/e* 372, by loss of a butenyl radical to give *m/e* 317 and by loss of a butyl radical to give *m/e* 315, followed by loss of butene to give *m/e* 259, is characteristic of 5,7-dihydroxycoumarins possessing 3-methylbut-2-enyl and 2-methylbutyryl or 3-methylbutyryl substituents, and is consistent with structure (Ia) (see Scheme 1). The presence of (Ic) is inferred from ions at *m/e* 358 and 303 (Scheme 1).



(I) a; R = 

b; R = 

c; R = 

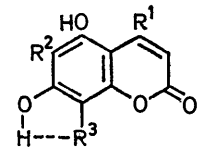
τ Values		
a	4·17 (1H, s)	
b	7·05 (2H, t, *J* 7 Hz)	
c	8·2—8·4 (2H, m)	
d	8·98 (3H, t, *J* 7 Hz)	
f	2·46 (1H, s) *	
g	6·49 (2H, d, *J* 7 Hz)	
h	4·82 (1H, m)	
i	8·15, 8·24 (both 3H, s)	
(Ia)	e	−5·20 (1H, s) *
	j	7·00 (2H, d, *J* 7 Hz)
	k	7·8 (1H, m)
	e	9·02 (6H, d, *J* 7 Hz)
(Ib)	e	−4·70 (1H, s) *
	m	6·2 (1H, m)
	n	8·82 (3H, d, *J* 7 Hz)
	o	8·2—8·4 (2H, m)
	p	9·08 (3H, t, *J* 7 Hz)
(Ic)	e	−5·23 (1H, s) *
	q	6·90 (2H, t, *J* 7 Hz)
	r	8·2—8·4 (2H, m)
	s	8·99 (3H, t, *J* 7 Hz)

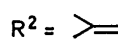
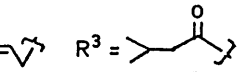
N.m.r. data for partially synthetic specimens.

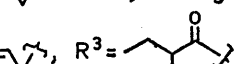
* Exchanged by D_2O.

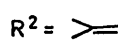
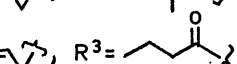
A second yellow fraction (Q4), m.p. 114°, had u.v. and i.r. characteristics similar to Q3. The n.m.r. and mass spectra showed it to be predominantly the 6-(2-methylbutyryl)coumarin (Ib), contaminated with some butyryl (Ic) and 3-methylbutyryl (Ia) compounds. Attention was then turned to the Q5 fraction, yellow, m.p. 81°, which showed similar u.v. and i.r. data to Q3 and Q4. The n.m.r. and mass spectral information showed this to be predominantly the 6-butyrylcoumarin (Ic), containing some 6-(2-methylbutyryl) (Ib) and 6-(3-methylbutyryl) (Ia) relatives.

These spectral deductions were confirmed by isomerising the known [3] mammea B/BA (IIa), B/BB (IIb), and B/BC (IIc) to mammea B/AA (Ia), B/AB (Ib), and B/AC (Ic), respectively, by treatment with methanolic 5% potassium hydroxide, followed by acidification. Mammea B/AA (Ia) and B/AB (Ib) were also prepared

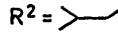


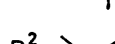
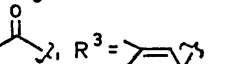
(II) a; R^1 =  , R^2 =  , R^3 = 

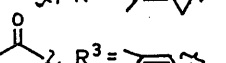
b; R^1 =  , R^2 = , R^3 = 

c; R^1 =  , R^2 =  , R^3 = 

d; R^1 =  , R^2 = , R^3 = H

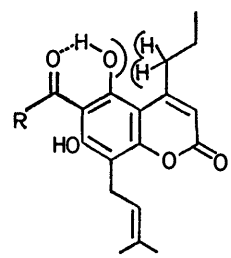
e; R^1 =  , R^2 =  , R^3 = H

f; R^1 = Ph, R^2 =  , R^3 = 

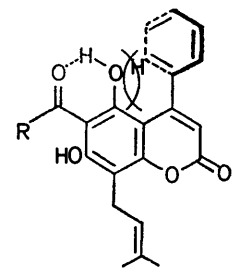
g; R^1 = Ph, R^2 = , R^3 = 

by treating the acylcoumarins (IId and e) with 2-methylbut-3-en-2-ol and boron trifluoride–ether complex.[10] Comparison of spectral and chromatographic data of these pure compounds and their mixtures with the substances isolated confirmed the deductions made.

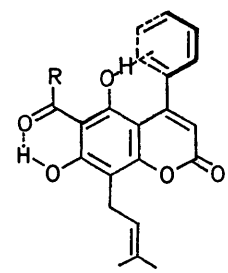
In the n.m.r. spectra of the 6-acylcoumarins (Ia—c) two phenolic hydroxy-groups resonate sharply at



(III)



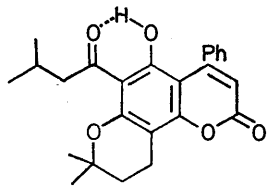
(IVa)



(IVb)

τ *ca.* −5 and *ca.* 2·5, a situation not markedly different from those for the 8-acyl isomers (IIa and b) [τ *ca.*

—4·5 and *ca.* 3, both sharp (Part I, Table 2)]. On the other hand, in the 4-phenyl series the two hydroxy-groups of the 6-acyl series have broadened resonances near τ −1 and 0 and an exchange situation is indicated, with the 8-acyl carbonyl group changing its position between a 5- and a 7-bonding phenolic hydroxy-group on the n.m.r. time-scale. The 4-phenyl-8-acyl series (OH, sharp resonances, τ *ca.* −4·5 and *ca.* 4) resembles in type the 4-alkyl-8-acyl series. Molecular models show that there is a large steric effect from the 4-aryl group, which must be twisted out of plane by the 5-hydroxy-group. This effect is absent in the 4-alkyl series, and the expected 5,6-chelate, which has a favourable bond-fixation arrangement, is formed (III). The



(V)

presence of the out-of-plane 4-aryl group is envisaged as bringing the energies of the two forms (IVa and b) closer together, destabilising (IVa) by steric compression and providing, in the form (IVb), an aryl acceptor seat for the 5-hydroxy-group hydrogen bond. The differences in the hydroxy-resonance patterns for the 6- and 8-acyl compounds of the 4-aryl series is known to be a valuable criterion for orientation purposes.[4,11]

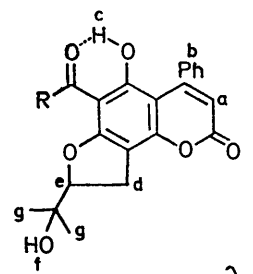
A fourth yellow crystalline material (P), isolated chromatographically from the *M. americana* extract, had m.p. 110—115°; mass measurement of the molecular ion indicated the formula $C_{25}H_{26}O_6$, though combustion analysis results were poor. T.l.c. gave an unresolvable spot but careful column chromatography gave two yellow fractions, P1, m.p. 110—115°, and P2, m.p. 97—105°, which differed in the 1250—1000 cm^{-1} region of the i.r. spectrum. The i.r. spectra of P1 and P2, and their u.v. data (Table), were indicative of a

U.v. data for natural and synthetic coumarins in ethanol

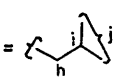
		$\lambda_{max.}$/nm (log ε)									
Mixture Q3	0·01N-HCl			284 (4·38)			329 (3·95)				
	0·01N-KOH	232 (4·34)				300 (4·28)			380 * (4·02)	415 (4·11)	
Mixture Q4	0·01N-HCl			284 (4·42)			328 (3·97)				
	0·01N-KOH	237 (4·19)				298 (4·25)			378 * (3·97)	410 (4·09)	
Mixture Q5	0·01N-HCl			284 (4·36)			329 (3·96)				
	0·01N-KOH	232 (4·34)				300 (4·27)			380 * (4·02)	415 (4·11)	
Coumarin (Ia)	0·01N-HCl			284 (4·43)			329 (4·00)				
	0·01N-KOH	232 (4·25)				305 (4·24)			374 * (4·00)	415 (4·08)	
Coumarin (Ib)	0·01N-HCl			286 (4·35)			325 (3·96)				
	0·01N-KOH	238 (4·25)				307 (4·28)			380 (3·94)	415 (3·96)	
Coumarin (Ic)	0·01N-HCl			285 (4·39)			323 (3·98)				
	0·01N-KOH	239 (4·23)				300 (4·25)			380 * (3·99)	410 (4·08)	
Mixture P	0·01N-HCl	232 (4·11)		282 (4·39)				348 (4·01)			
	0·01N-KOH		249 (4·21)	280 * (4·05)		316 (4·05)					428 (3·95)
Mixture P1	0·01N-HCl	232 (4·10)		283 (4·37)				348 (3·99)			
	0·01N-KOH		249 (4·20)			316 (4·03)					429 (3·99)
Mixture P2	0·01N-HCl	232 (4·12)		283 (4·40)				348 (4·00)			
	0·01N-KOH		249 (4·22)			316 (4·06)					430 (4·00)
Coumarin (V)	0·01N-HCl	227 (4·16)		287 (4·45)				338 (4·05)			
	0·01N-KOH		248 * (4·32)	293 (4·12)		318 (4·16)					420 (3·93)
Coumarin (VIa)	0·01N-HCl	232 (4·10)		282 (4·39)				348 (3·99)			
	0·01N-KOH		249 (4·21)			316 (4·04)					430 (3·98)
Coumarin (VIb)	0·01N-HCl	228 (4·10)		280 (4·38)				347 (3·97)			
	0·01N-KOH		247 (4·20)			312 (4·05)					425 (3·96)

* Inflection.

5,7-dihydroxy-4-phenylcoumarin with a 6-acyl substituent,[4] and the u.v. data were also similar to those of the acid-cyclisation product (V) derived from mammea



(VI) a; R =



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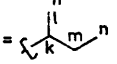

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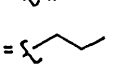

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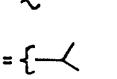


τ Values

a 4·09 (1H, s)
b 2·64 (5H, m)
d 6·69 (2H, d, *J* 9 Hz)
e 5·09 (1H, t, *J* 9 Hz)
f 8·03 (1H, s) *
g 8·57 (3H, s)
8·69 (3H, s)

(VIa) c −4·46 (1H, s) *
h 7·02 (2H, m)
i 7·8 (1H, m)
j 9·04 (6H, d, *J* 7 Hz)

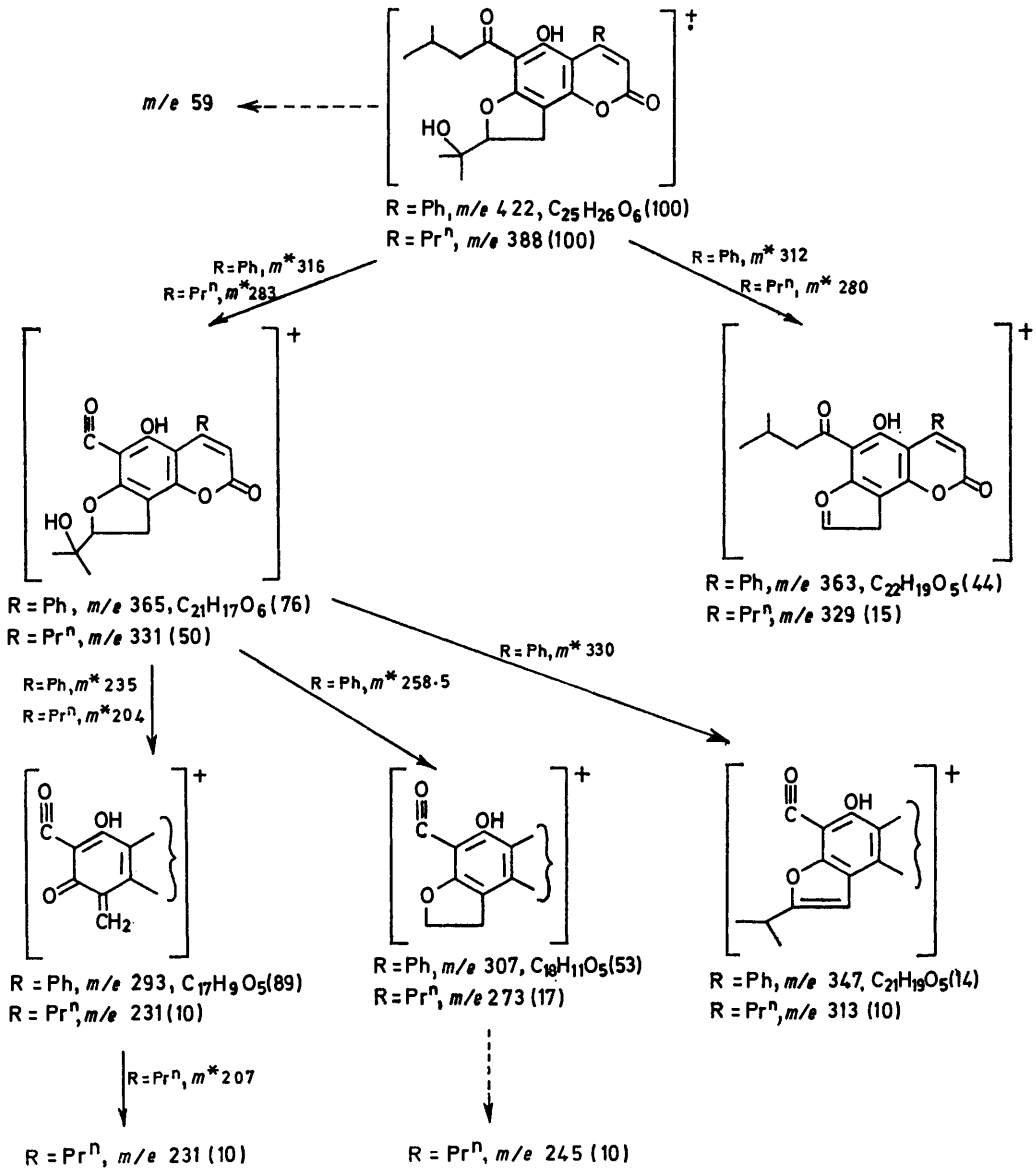
(VIb) c −4·60 (1H, s) *
k 6·35 (1H, m)
e 8·85 (3H, dd, *J* 7 and 2 Hz)
m 8·2—8·4 (2H, m)
n 9·11 (3H, t, *J* 7 Hz)

N.m.r. data for partially synthetic specimens.
* Exchanged by D_2O.

A/AA (Table).[6] The n.m.r. spectrum of P1 indicated it to be predominantly (VIa), together with a little of the isomeric (VIb), and the P2 spectrum showed that, conversely, it was predominantly (VIb) with a little (VIa): proton relationships were confirmed by double-resonance. The mass spectral fragmentations of both P1 and P2 were consistent with the presence

of both a 5-acyl substituent [1,3,4] and a α-(hydroxyisopropyl)dihydrofuran system.[1,12]

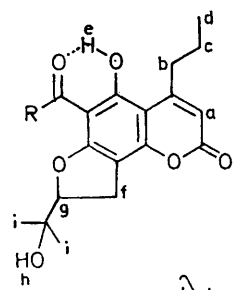
To check these conclusions, coumarins (VIa and b) were prepared by treatment with *m*-chloroperbenzoic acid of mammea A/AA (IIf) and mammea A/AB (IIg), respectively, and compared with the fractions P1 and P2. This revealed that a number of additional ions were present in the spectra of P1 and P2. The presence of these extra ions [*m/e* 388(28), 374(9), 331(10), and 259(6·5)] is consistent with replacement of a 4-phenyl substituent by 4-n-propyl and indicates the presence of structures (VIIa—c) or their 5,6-fused isomers (Scheme 2). There was also present in the mass spectra of P, P1, and P2 an ion at *m/e* 408 of much greater intensity than expected for the isotope peak of *m/e* 407. This ion (M^+, 408), together with ions at *m/e* 393, 375, and 349, would be expected to originate from structures (VIc and d). The alternative 5,6-fused isomers may be discounted, as they would have different t.l.c. behaviour from (VIa and b). Other major ions in the mass spectrum coming from (VIc and d), formed by initial acyl cleavage and subsequent fragmentation, would be the same as those similarly formed from (VIa and b) (Scheme 2) and not be informative.



SCHEME 2 Mass spectral fragmentations of 7,8-fused mammea compounds. The 4-phenylcoumarin possessing a 6-(2-methylbutyryl) side chain (VIa) and the 4-n-propylcoumarins possessing 6-(2-methylbutyryl) (VIIb) and 6-(butyryl) (VIIc) side chains display similar fragmentations

[12] F. M. Abdel-Hay, E. A. Abu-Mustafa, B. A. H. El-Tawil, M. B. E. Fayez, C. S. Barnes, and J. L. Occolowitz, *Indian J. Chem.*, 1967, **5**, 89; M. Shipchandler and T. O. Soine, *J. Pharm. Sci.*, 1968, **57**, 741.

Substance P gave the expected mono-acetate under mild acetylation conditions, and t.l.c. comparisons with the monoacetates of the partially synthetic (V1a and b) (see before) revealed the presence of a further acetate spot due to minor components in P. In view of the mass spectral results, comparison (t.l.c.) was made with the acetates of the already known [1] 5,6-fused 4-n-propyl α-(hydroxyisopropyl)dihydrofuran-fused coumarins. No correspondence was observed. This suggested that structures (VIIa—c) with the 7,8-fusion



(VII) a; R = 

b; R = 

c; R = 

	τ Values
a	4·19 (1H, s)
b	7·05 (2H, t, *J* 7 Hz)
c	8·2—8·4 (2H, m)
d	9·00 (3H, t, *J* 7 Hz)
f	6·75 (2H, d, *J* 9 Hz)
g	5·10 (1H, t, *J* 9 Hz)
h	7·72 (1H, s) *
i	8·69, 8·55 (both 3H, s)
	(VIIa)
e	−5·10 (1H, s) *
j	7·04 (2H, m)
k	7·8 (1H, m)
l	8·96 (6H, d, *J* 7 Hz)
	(VIIb)
e	−5·23 (1H, s) *
m	6·30 (1H, m)
n	8·92 (3H, dd, *J* 2 and 7 Hz)
o	8·2—8·4 (2H, m)
p	9·02 (3H, t, *J* 7 Hz)
	(VIIc)
e	−4·95 (1H, s) *
q	6·88 (2H, t, *J* 7 Hz)
r	8·2—8·4 (2H, m)
s	9·00 (3H, t, *J* 7 Hz)

N.m.r. data for partially synthetic specimens.

* Exchanged by D_2O.

were probably those of the new compounds. These candidates were prepared by treatment of mammea B/AA (Ia), B/AB (Ib), and B/AC (Ic) with *m*-chloroperbenzoic acid. The spectral data were those expected from the information already accumulated and supported the deductions made. Comparisons by t.l.c., of both acetylated and non-acetylated specimens, with the natural materials were also in agreement with their presence in the latter. In a report adjacent to our preliminary communication, an account of the occurrence of (Ib), (VIb), and (VIIb) in *Mammea africana* bark was given by Scheinmann *et al.*[9] These specimens, and specimens of two other new coumarins, are reported by them to show *two* chelated hydroxy-resonances in the n.m.r. We have always found the observation of more than one such resonance to be a reliable criterion of lack of homogenity in the natural products, and this is borne out by the observation of single sharp resonances for all the synthetic samples made in our laboratory. We conclude that these authors were handling mixtures of related compounds which were difficult to separate.

EXPERIMENTAL

For general experimental conditions and the meaning of symbols, see Part I.[3] N.m.r. data were measured at 100 MHz for solutions in deuteriochloroform and i.r. data for solutions in chloroform, unless stated otherwise. Detailed n.m.r. and mass spectral data for compounds marked with an asterisk are deposited with the N.L.L. as Supplementary Publication No. SUP 20427 (13 pp., 1 microfiche).†

Isolation of Mammea B/AA, B/AB, and B/AC.—For extraction of *Mammea americana* seeds see Part I.[3] Chromatography on alumina of the yellow crystal fractions described in Part I yielded yellow crystalline materials which differed in i.r. spectra from mammea A/AB and mammea A/AA; the crystals were eluted from the column before mammea A/AB. Repeated chromatography on alumina (Woelm acid, activity III) gave 5,7-dihydroxy-8-(3-methylbut-2-enyl)-6-(3-methylbutyryl)-4-propylcoumarin (mammea B/AA; isomammein), contaminated with some mammea B/AC, m.p. 109° (Q3) * [Found: *M* (mass spec.), 372·1937 ± 18. Calc. for $C_{22}H_{28}O_5$: *M*, 372·1937], $\nu_{max.}$ (CCl_4) 3330, 1747, 1627, and 1595 cm^{-1}, $\nu_{max.}$ (mull) 3360, 1705, 1620, and 1530 cm^{-1}.

Also isolated was yellow crystalline material, m.p. 114°, (Q4),* shown to be a mixture 5,7-dihydroxy-8-(3-methylbut-2-enyl)-6-(2-methylbutyryl)-4-propylcoumarin (mammea B/AB) with some mammea B/AA [Found: C, 70·7; H, 7·6%; *M* (mass spec.), 372. Calc. for $C_{22}H_{28}O_5$: C, 70·95; H, 7·6%; *M* 372], $\nu_{max.}$ (CCl_4) 1748, 1625, 1590, and 1555 cm^{-1}, $\nu_{max.}$ (mull) 3370, 1715, 1620, and 1590 cm^{-1}.

A further yellow crystalline material (Q5) had m.p. 81° and was a mixture consisting mainly of 6-butyryl-5,7-dihydroxy-8-(3-methylbut-2-enyl)-4-propylcoumarin (mammea B/AC) with some B/AA [Found: *M* (mass spec.), 358·1780 ± 12. Calc. for $C_{21}H_{26}O_5$: *M*, 358·1780], $\nu_{max.}$ 3360, 1705, 1620, and 1580 cm^{-1}.

Isomerisation of Mammea B/BA (Mammein).—Mammea B/BA (500 mg) and methanolic 5% potassium hydroxide (5 ml) were kept at 20° overnight, poured into water (20 ml), and acidified with 2N-hydrochloric acid. Extraction with ether gave a gum which yielded the yellow *mammea B/AA* * (isomammein) (Ia) (400 mg), m.p. 119—121°, closely similar to the natural material (i.r. and t.l.c. comparison). [Found: C, 70·8; H, 7·45%; *M* (mass spec.), 372·1937 ± 18. $C_{22}H_{28}O_5$ requires C, 70·95; H, 7·6%; *M*, 372·1937], $\nu_{max.}$ (CCl_4) 3330, 1747, 1627, and 1595 cm^{-1}.

Isomerisation of Mammea B/BB.—Similar treatment of mammea B/BB gave yellow needles of *mammea B/AB** (Ib), m.p. 98—100° (from chloroform–hexane) [Found: C, 70·85; H, 7·5%; *M* (mass spec.), 372·1937 ± 18. $C_{22}H_{28}O_5$ requires C, 70·95; H, 7·6%; *M*, 372·1937], $\nu_{max.}$ 1750, 1620, 1595, and 1560 cm^{-1}, $\nu_{max.}$ (mull) 3360, 1710, 1695, 1615, and 1590 cm^{-1}. Comparison with natural material involved t.l.c., n.m.r., and i.r. scrutiny.

Isomerisation of Mammea B/BC.—Similar treatment of mammea B/BC gave yellow needles of *mammea B/AC** (Ic), m.p. 127—128·5° (from chloroform–hexane) [Found: C, 70·5; H, 7·4%; *M* (mass spec.), 358·1780 ± 18. $C_{21}H_{26}O_5$ requires C, 70·35; H, 7·3%; *M*, 358·1780], $\nu_{max.}$ (mull) 3390, 1725, 1715, 1620, 1603, and 1585 cm^{-1}, $\nu_{max.}$ (CCl_4) 3350, 1745, 1628, and 1590 cm^{-1}.

Isolation of Crystalline Material P.—Preparative layer chromatography of the insecticidally active fractions (following paper) yielded a green fluorescent band of R_F value intermediate between that of the insecticidal material and the origin. Treatment of the yellow gum obtained with ether–light petroleum (b.p. 60—80°) gave yellow

† Details of Supplementary Publications are given in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (Notice to Authors No. 7).

crystals (P), m.p. 90—110°. Further quantities were obtained by chromatography of the residues of mammea A/AB-containing fractions [silica gel (Woelm Activity III); chloroform as eluant]. Samples of material P obtained from various sources showed closely similar i.r. spectra though slight differences were present in the 1100—1250 cm^{-1} region. Repeated preparative layer and column chromatography effected only partial purification. Two samples, P1 and P2, were eventually obtained, each of which was predominantly one compound. Material P* [Found: *M* (mass spec.), 422·1739 ± 15. Calc. for $C_{25}H_{26}O_6$: *M*, 422·1729] had $\nu_{max.}$ 1725 and 1615 cm^{-1}, $\nu_{max.}$ (mull) 3460, 3420, 3240, 1715, 1610, and 1565infl cm^{-1}. Sample P1*, m.p. 110—115°, had $[\alpha]_D^{24}$ −2·82° (*c* 0·71 in EtOH), with i.r. and u.v. data similar to those of P, except for some slight differences in the 1250—1000 cm^{-1} region [i.r. (mull)]. Treatment of P1 with acetic anhydride–pyridine at room temperature gave a monoacetate, m.p. 100—102°, $\nu_{max.}$ (mull) 3440, 3380, 3250, 1775, 1705, 1685, and 1600 cm^{-1}, $\lambda_{max.}$ 232, 255, 270infl, and 333 nm (log ε 4·30, 4·24, 4·05, and 4·10). T.l.c. [benzene–ethyl acetate (8 : 2)] showed the acetate to be a mixture of at least two compounds which corresponded in R_F values with the acetates of the α-(hydroxyisopropyl)dihydrofurans (VIa and b) and (VIIa and b). Sample P2*, m.p. 97—105°, $[\alpha]_D^{24}$ −6·7° (*c* 0·475 in EtOH), had i.r. and u.v. data similar to those of P and P1 except for slight differences in the 1250—1000 cm^{-1} region [i.r. (mull)]. Other samples showed larger amounts of the 4-n-propyl coumarin.

Epoxidation of Mammea A/AA (Mammeisin) Diacetate.—Mammea A/AA diacetate [4] was treated with *m*-chloroperbenzoic acid as previously described to give the non-crystalline diacetate * [Found: M^+ (mass spec.), 506·1941 ± 25. Calc. for $C_{29}H_{30}O_8$: *M*, 506·19405], $\nu_{max.}$ 1780, 1740, 1615, and 1595 cm^{-1}, $\nu_{max.}$ (film) 1780, 1740, 1720, 1615, and 1595 cm^{-1}, $\lambda_{max.}$ 227infl, 244, 282, and 320infl nm (log ε 4·07, 3·98, 3·84, and 3·59).

Reaction of m-*Chloroperbenzoic Acid with Mammea A/AA (Mammeisin).*—Mammea A/AA was treated with *m*-chloroperbenzoic acid to give 1,2-*dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-4-(3-*methylbutyryl*)-6-*phenylfuro*[2,3-h][1]*benzopyran*-8-*one* * (VIa), yellow crystals, m.p. 115—117° † (from ether–light petroleum) [Found: C, 71·2; H, 6·3; *M* (mass spec.), 422·1729 ± 20. $C_{25}H_{26}O_6$ requires C, 71·05; H, 6·2%; *M*, 422·1729], $\nu_{max.}$ 1720 and 1610 cm^{-1}, $\nu_{max.}$ (CCl_4) 1755 and 1615 cm^{-1}, $\nu_{max.}$ (mull) 3460, 3420, 3240, 1715, and 1610 cm^{-1}. Comparison of this compound with the natural material P1 showed that P1 was contaminated with some of the isomeric compound (V1b). Treatment of (VIa) with pyridine–acetic anhydride at room temperature gave a white crystalline *monoacetate*,* m.p. 105—109° [from ether–light petroleum (b.p. 40—60°)] [Found: C, 69·7; H, 6·25%; *M* (mass spec.), 464·1835 ±23. $C_{27}H_{28}O_7$ requires C, 69·8; H, 6·1%; *M*, 464·1835], $\nu_{max.}$ 1760, 1730, and 1615 cm^{-1}, $\nu_{max.}$ (mull) 3425, 3250, 1775, 1708, 1690, and 1613 cm^{-1}.

If the reaction was worked up immediately, n.m.r. examination of the product indicated that it was mainly the epoxide, which was slowly converted into the α-(hydroxyisopropyl)dihydrofuran. The presence of the epoxide was confirmed by immediate treatment of the mixture with pyridine–acetic anhydride; the diacetate was then isolated, and was identical with the epoxide from mammea A/AA diacetate (i.r., n.m.r., t.l.c.).

Reaction of m-*Chloroperbenzoic Acid with Mammea A/AB.*—Mammea A/AB was treated with *m*-chloroperbenzoic acid to give yellow crystals of 1,2-*dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-4-(2-*methylbutyryl*)-6-*phenylfuro*[2,3-h][1]*benzopyran*-8-*one* * (VIb), m.p. 115—117° [Found: C, 70·5; H, 6·3%; *M* (mass spec.), 422·1729 ± 20. $C_{25}H_{26}O_6$ requires C, 71·05; H, 6·2%; *M*, 422·1729], $\nu_{max.}$ 1725, 1615, and 1520 cm^{-1}, $\nu_{max.}$ (mull) 3400, 1735, 1715, and 1620 cm^{-1}. Comparison of this compound (i.r., n.m.r., t.l.c.) with the natural material P2, showed that P2 was mainly (VIb) contaminated with some of the isomeric compound (VIa).

Treatment of the compound with acetic anhydride–pyridine at room temperature gave a white crystalline *monoacetate*,* m.p. 84—89° (from hexane) [Found: C, 69·5; H, 6·3%; *M* (mass spec), 464·1835 ± 23. $C_{27}H_{28}O_7$ requires C, 69·8; H, 6·1%; *M*, 464·1835], $\nu_{max.}$ 1765, 1690, and 1620 cm^{-1}, $\nu_{max.}$ (mull) 3460, 3400, 3280, 1780, 1710, 1680, and 1615 cm^{-1}, $\lambda_{max.}$ 231, 254, and 330 nm (log ε 4·27, 4·22, and 4·10).

Reaction of m-*Chloroperbenzoic Acid with Mammea B/AA (Isomammein).*—Mammea B/AA was treated with *m*-chloroperbenzoic acid as previously described to give the crystalline 1,2-*dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-4-(3-*methylbutyryl*)-6-*propylfuro*[2,3-h][1]*benzopyran*-8-*one* * (VIIa), m.p. 72—77° (from chloroform–hexane) [Found: C, 67·8; H, 7·1%; *M* (mass spec.), 388·1886 ± 19. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·25%; *M*, 388·1886], $\nu_{max.}$ 1730 and 1625 cm^{-1}, $\nu_{max.}$ (mull) 3440, 3360, 1738, 1708, and 1630 cm^{-1}, $\lambda_{max.}$ 222, 282, and 332 nm (log ε 4·18, 4·49, and 4·07). The compound gave a white crystalline *monoacetate*,* m.p. 132—134° (from chloroform–hexane) [Found: C, 66·55; H, 7·05%; *M* (mass spec.), 430·1991 ±22. $C_{24}H_{30}O_7$ requires C, 66·95; H, 7·0%; *M*, 430·1991], $\nu_{max.}$ 1770, 1730, 1690, and 1620 cm^{-1}, $\nu_{max.}$ (mull) 3470, 1765. 1730, 1705, and 1620 cm^{-1}, $\lambda_{max.}$ 225, 254, and 325 nm (log ε 4·20, 4·22, and 4·07).

Reaction of m-*Chloroperbenzoic Acid with Mammea B/AB.*—Mammea B/AB was treated with *m*-chloroperbenzoic acid to give the crystalline 1,2-*dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-4-(2-*methylbutyryl*)-6-*propylfuro*[2,3-h][1]*benzopyran*-8-*one* * (VIIb), m.p. 92—94° (from ether–hexane) [Found: M^+, 388·1886 ± 19. Calc. for $C_{22}H_{28}O_6$: *M*, 388·1886], $\nu_{max.}$ 1740 and 1620 cm^{-1}, $\nu_{max.}$ (mull) 3400, 1745, 1710, and 1625 cm^{-1}.

Treatment of (VIIb) with pyridine–acetic anhydride at room temperature gave a *monoacetate*,* m.p. 102—105° (from chloroform–hexane) [Found: C, 66·7; H, 6·9%; *M* (mass spec.), 430·1991 ± 22. $C_{24}H_{30}O_7$ requires C, 66·95; H, 7·0%; *M*, 430·1991], $\nu_{max.}$ 1775, 1730, 1690, and 1620 cm^{-1}, $\nu_{max.}$ (mull) 3470, 1765, 1730, 1705, and 1620 cm^{-1}, $\lambda_{max.}$ 225, 255, and 325 nm (log ε 4·09, 4·11, and 4·00).

Reaction of m-*Chloroperbenzoic acid with Mammea B/AC.*—Mammea B/AC was treated with *m*-chloroperbenzoic acid to give yellow crystals of 4-*butyryl*-1,2-*dihydro*-5-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-6-*propylfuro*[2,3-h][1]*benzopyran*-8-*one* * (VIIc), m.p. 75—81° (from chloroform–hexane) [Found: *M* (mass spec.), 374·1729 ± 18. $C_{21}H_{26}O_6$ requires *M*, 374·1729], $\nu_{max.}$ 3420, 1730, and 1615 cm^{-1}, $\nu_{max.}$ (mull) 3400, 1720, and 1620 cm^{-1}.

For acknowledgements, see Part III.[1]

[2/205 *Received*, 1*st February*, 1972]

† Merkel has reported a much higher m.p.[13]

[13] K. E. Merkel, Ph.D. Thesis, University of New York, Buffalo, 1970.