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ISOLATION AND STRUCTURE OF MAMMEA B/BA, B/BB, B/BC AND C/BB: A GROUP OF 4-n-PROPYL- AND 4-n-AMYL-COUMARIN EXTRACTIVES OF MAMMEA AMERICANA L.

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PREVIOUS investigators[1] have reported the occurrence of a 4-alkylated-coumarin, mammein (I), in the seeds of the insecticide-bearing plant Mammea americana L. (Guttiferae).[2] A combination of column, thick-layer and thin-layer chromatography has now led to the isolation of four 4-alkyl-coumarins from this source and it would appear that mammein of the literature[1] is a mixture of two of these. The compounds are designated mammea B/BA* m.p. 123° (I), mammea B/BB m.p. 117-118° (II), mammea B/BC m.p. 129° (III) and mammea C/BB m.p. 100-101° (IV).

All four are isopentenylated at C_6 but at C_8 isovaleryl, 3'-methylbutyryl (anteiso)† and butyryl** side-chains are represented. Three are representatives of the 4-n-propyl series but the fourth is an n-pentyl compound.

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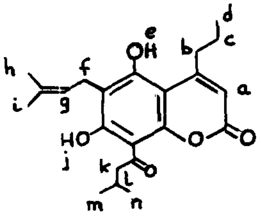
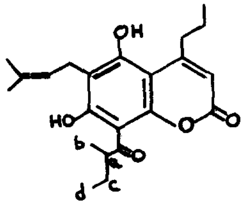
* In order to avoid proliferation of closely related trivial names, and because the extract contains still more close structural relatives, a coding system is used here. The letter to the left of the stroke identifies the 4-substituent of the coumarin, that immediately to the right the orientation of alkenyl and acyl substituents at 6- and 8- (A = 6-acyl, 8-alkenyl and B the reverse), and the second letter to the right of the stroke the nature of the acyl residue. A prefix cyclo is used when heterocyclisation has occurred e.g. (II) of the next communication.



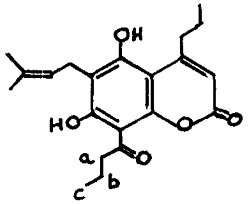
(I) B/BA

a	τ	4.10	(1) s.	
b		7.06	(2) t.	*J* 7 c/s.
c		8.2-8.6	(2) m.	
d		8.96	(3) t.	*J* 7
e		2.78	(1) s.	
f		6.54	(2) d.	*J* 7
g		4.75	(1) m.	
h		8.12	(3) s.	
i		8.19	(3) s.	
j		-4.71	(1) s.	
k		6.88	(2) d.	*J* 7
l		7.8	(1) m.	
m n		8.95	(6) d.	*J* 7



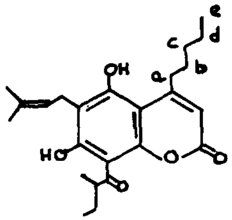
(II) B/BB

a	τ	6.15	(1) m.	
b		8.80	(3) d.	*J* 7 c/s.
c		8.2-8.6	(2) m.	
d		9.0	(3) t.	*J* 7 c/s.



(III) B/BC

a	τ	6.80	(2) t.	*J* 7 c/s.
b		8.2-8.6	(2) m.	
c		8.99	(3) t.	*J* 7



(IV) C/BB

a	τ	7.11	(2) t.	*J* 7 c/s.
b c d		8.2-8.6	(6) m.	
e		9.05	(3) t.	*J* 7

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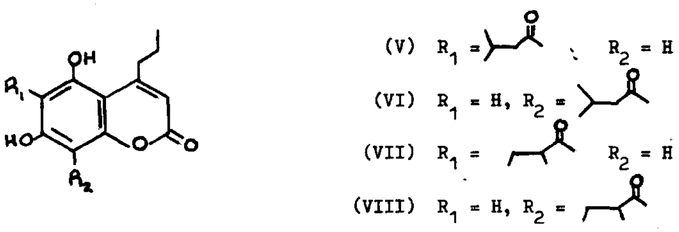
† Residues with such branching occur, for example, in calophyllolide,[3] inophyllolide,[3] and costatolide,[4] compounds also found in the Guttiferae.

** Butyryl residues attached to a phloroglucinol nucleus occur in Aspidium species.[5]



Number of protons in parentheses, s = singlet, d = doublet, t = triplet, m = multiplet. In (II)-(IV) the protons omitted have τ values etc. similar to those in (I) or related structures.

The molecular formulae for mammea B/BB, $C_{22}H_{28}O_5$ and C/BB, $C_{24}H_{32}O_5$ were established by accurate mass-measurements (372.1936 ± 5 p.p.m. and 400.2264 ± 5 p.p.m. respectively) and those for B/BA, $C_{22}H_{28}O_5$, and B/BC $C_{21}H_{26}O_5$ by mass-measurement and analysis. Infrared [all show bands near ν 1720 and 1600 cm^{-1} ($CHCl_3$; coumarin and chelated acetyl)] and ultraviolet data, mass spectral information and N.M.R. results lead to the structures shown with N.M.R. assignments as indicated. The 6-isopentenyl, 8-acyl arrangement is assigned from both ultraviolet data and N.M.R. criteria. Thus 6- and 8-acylated 5,7-dihydroxycoumarins undergo characteristically different base-shifts in the ultraviolet as indicated in the table for the synthetic coumarins (V)-(VIII) which were independently oriented by the Gibbs test under spectrophotometric control.[6,7] Clearly these four mammea compounds belong to the 8-acyl series and in confirmation one hydroxyl in each compound is chelated (τ near -4.7) and one not (τ near 2.8). There is an absence in the natural compounds of the exchange phenomenon described for 6-acyl derivatives in the next communication.

Mammein of the literature[1] has m.p. 128-129.5° but degradation was done on material m.p. 124-128°.[1] Dr. R. A. Finnegan has kindly supplied us with an authentic sample which in our hands has m.p. 126-127°. Mass spectral examination shows it to consist of mammea B/BA and B/BC in the

Ultraviolet Data in Ethanol.[a]

Synthetic coumarin (VII)[b]

N/100 HCl			282 (4.42)	325 (4.07)	
N/100 KOH	237 (4.19)		297 (4.25)	368 (4.11)	400 (4.12)

Synthetic coumarin (VIII)[b]

N/100 HCl	219 (4.42)		290 (4.35)	317 (4.21)	
N/100 KOH	222 (4.21)	254 (3.91)		328 (4.51)	

Mammea B/BA (I)

N/100 HCl	223 (4.57)	252 (4.03)	293 (4.39)	322.5(4.23)	
N/100 KOH	225 (4.50)	253.5 (4.24)		322.5 (4.52)	

Mammea B/BB (II)

N/100 HCl	222 (4.46)		295 (4.37)	320 (4.23)	
N/100 KOH	225 (4.24)	257 (4.05)		333 (4.53)	

Mammea B/BC (III)

N/100 HCl	223 (4.58)	252 (4.03)	293 (4.41)	322 (4.26)	
N/100 KOH	225 (4.53)	253 (4.26)		332 (4.56)	

Mammea C/BB (IV)

N/100 HCl	222 (4.50)		294 (4.40)	322 (4.25)	
N/100 KOH	229 (4.20)	257 (4.14)		333 (4.54)	

[a] $\lambda_{max.}$ (log $\varepsilon_{max.}$) [b] Synthetic coumarins (V) and (VI) have very similar spectra to (VII) and (VIII) respectively.

approximate ratio 2.5 : 1 with traces of three other components (mol. wt. 386, 388 and 400) and this agrees with a thin-layer chromatographic examination Butyric acid was detected in the degradation of mammein[1] and seems more satisfactorily accounted for as arising from the butyryl residue of B/BC than as coming from C_4 and its propyl addendum. Our specimens of B/BA have frequently contained up to 10% B/BC, and *vice versa*, despite careful purification.

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