Tetrahedron Letters No.2, pp. 145-149, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ISOLATION AND STRUCTURE OF MAMMEA A/BA, A/AB AND A/BB: A GROUP OF 4-ARYL-COUMARIN EXTRACTIVES OF MAMMEA AMERICANA L.

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(Received 19 November 1965)

THE 4-phenyl coumarins mammeisin (I)[1] and mammeigin (II)[2] have been reported in the rind and seed-oil respectively of Mammea americana L. Continuing our investigation of the fresh seeds we have isolated three new 4-phenyl coumarins, mammea A/BA, colourless needles m.p. 125-126° (III), mammea A/AB, yellow needles m.p. 107-108° (IV), mammea A/BB, colourless needles m.p. 124-125° (V), together with mammeisin (A/AA), yellow needles, and mammeigin (A/A cyclo D), yellow needles.* The three new coumarins are isomeric with mammea A/AA, $C_{25}H_{26}O_5$ (accurate mass measurement and analysis). Two unrelated natural products, 2-methoxy-xanthone† (m.p. and mixed with a synthetic specimen 131°), and the triterpene friedelin were also isolated during the chromatographic separation.

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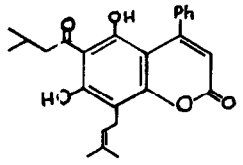
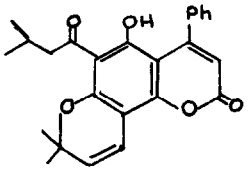
* The yellow 6-acyl compounds give an olive-green ferric chloride colour; the colourless 8-acyl a brown purple.

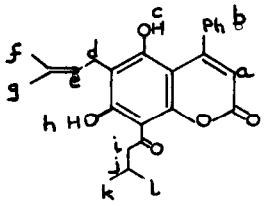
† This has lately been found in Kielmeyra coriacea Mart., another member of the Guttiferae.[3] Both xanthones and coumarins are known to occur in this family but the two have not previously been found together.[4] Very recently 2-hydroxyxanthone has been reported in M. americana.



(I) (A/AA)

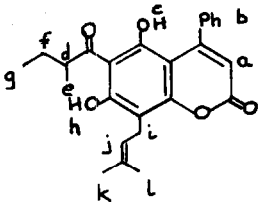


(II) (A/A cyclo D)



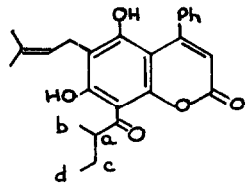
(III) (A/BA)

a	τ	4.21	(1) s.
b		2.57	(5) s.
c		4.10	(1) s.
d		6.81	(2) d. J 7 c/s.
e		4.97	(1) m.
f		8.32	(3) s.
g		8.37	(3) s.
h		-4.53	(1) s.
i		6.92	(2) d. J 7
j		7.8	(1) m.
k		8.96	(6) d. J 7
l			



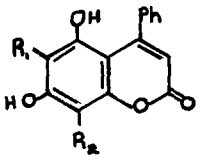
(IV) (A/AB)

a	τ	4.18	(1) s.
b		2.55	(5) s.
c		-0.93	(1) broad
h		0.10	(1) " "
d		6.35	(1) m.
e		8.93	(3) d. J 7 c/s.
f		8.2-8.6	(2) m.
g		9.18	(3) t. J 7
i		6.51	(2) d. J 7
j		4.78	(1) m.
k		8.12	(3) s.
l		8.28	(3) s.

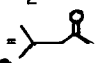


(V) (A/BB)

a	τ	6.13	(1) m.
b		8.74	(3) d. J 7 c/s.
c		8.2-8.6	(2) m.
d		8.98	(3) t. J 7



(VI) R_1 =  R_2 = H

(VII) R_1 = H, R_2 = 

(VIII) R_1 =  R_2 = H

(IX) R_1 = H, R_2 = 

The structures of the three new 4-phenyl-coumarins rest on a combination of spectroscopic data. Classification as acylated and alkylated 4-phenyl 5,7-dihydroxycoumarins follows from the ultraviolet data in neutral and acid medium which also allows mammea A/AB to be placed in the 6-acyl class like A/AA whilst A/BA and A/BB are 8-acyl compounds. Mass spectral data also support the structures (III)-(V). N.M.R. assignments for the protons are as shown by the formulae and it is noteworthy that 8-acyl compounds show one hydroxyl resonance due to the 7-chelated hydroxyl near τ -4.5 and one due to the unchelated 5-hydroxyl near 4.1. On the other hand, 6-acyl compounds show two hydroxyls (deuteration) as broad bands near τ -1.0 and 0.1. This is ascribed to a chelation exchange phenomenon involving the 5- and 7-hydroxyls and is being investigated further: it provides a useful orientation criterion in this type of system.*

In agreement with the structures proposed, mammea A/BA (III) can be isomerised by 5% methanolic potassium hydroxide to give A/AA (I) whilst with the same reagent mammea A/BB gives A/AB.

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* What appears to be a related phenomenon in phloroacetophenones has been reported[5] but not ascribed to exchange.

Ultraviolet Data in Ethanol [a]

Synthetic coumarin (VIII)[b]					
N/100 HCl	237 (4.09)		283 (4.31)	335 (4.01)	
N/100 KOH	239 (4.23)		287 (4.21)	376 (4.03)	404 (4.12)
Mammea A/AB (IV)[c]					
N/100 HCl	233 (4.14)		283 (4.47)	333 (4.01)	
N/100 KOH	238 (4.35)		293 (4.31)	394 (3.96)	428 (4.11)
Synthetic coumarin (IX)[b]					
N/100 HCl	223 (4.41)		289 (4.37)	327 (4.19)	
N/100 KOH	227 (4.35)	257 (4.15)		333 (4.56)	
Mammea A/BA (III)					
N/100 HCl	225 (4.46)		294 (4.36)	332 (4.25)	
N/100 KOH	233 (4.40)	261 (4.19)		337 (4.60)	
Mammea A/BB (V)					
N/100 HCl	227 (4.45)		294 (4.38)	333 (4.24)	
N/100 KOH	234 (4.39)	263 (4.19)		337 (4.58)	

[a] $\lambda_{max.}$ (log $\varepsilon_{max.}$), [b] Synthetic coumarins (VI) and (VII) have similar spectra to (VIII) and (IX) respectively. [c] The spectra of mammea A/AA (I) and A/A cyclo D (II) are similar.

We thank Dr. R. A. Finnegan (University of New York, Buffalo) for samples of mammeisin and mammeigin, Dr. R. Stevenson (Brandeis University, Waltham, Mass.) for a specimen of friedelin, and Dr. H. Suschitzky (Royal College of Advanced Technology, Salford) for a specimen of synthetic 2-methoxyxanthone.

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