Synthesis of the *Mammea* Coumarins. Part 1. The Coumarins of the Mammea A, B, and C Series

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The naturally-occurring *Mammea* coumarins of the 4-phenyl-(mammea A), 4-propyl-(mammea B), and 4-pentyl-(mammea C) series have been prepared by Pechmann condensation of an acylphloroglucinol (3-methylbutyryl-, 2-methylbutyryl-, butyryl-, or 2-methylpropionyl-) with the appropriate β-ketoester to give a mixture of 6- and 8-acyl-5,7-dihydroxycoumarins that could be separated. *C*-Alkylation with 3-methylbut-2-enyl bromide, or 3,7-dimethylocta-2,6-dienyl chloride, in aqueous potassium hydroxide completed the synthesis of the *Mammea* coumarins having unmodified prenyl or geranyl substituents; oxidative modification of the prenyl group led to the mammea cyclo E and cyclo F coumarins. Some mammea cyclo D (chromeno) coumarins were synthesized by reaction of acylcoumarins with 1,1-dimethoxy-3-methylbutan-3-ol.

The insecticidal properties of various parts of the evergreen 'mamey' tree *Mammea americana* L. (Guttiferae), indigenous to the West Indies and Central America, have been documented for a number of years;[1] indeed, preparations from different parts of the tree are used to combat pests and parasites in areas where the tree is native.[1b,f] Investigation has shown that the seeds of the 'mamey apple,' the fruit of *M. americana*, are the most effective source of insecticidal activity, and that this activity appears in the light petroleum extract of the seeds.[1b,c,e] Extensive column and preparative layer chromatography of this extract led to the isolation of over twenty 4-alkyl or 4-aryl-5,7-dioxygenated coumarins.[2] Further examples have been identified by gas chromatography–mass spectrometry (g.c.–m.s.).[3] Some further coumarins of the same type have been isolated, or identified by g.c.–m.s., from other members of the Guttiferae such as *M. africana*,[2a,b,3,4], the Indian trees *M. longifolia*[5] and *Mesua ferrea*,[6] and *Mesua thwaitesii* from Ceylon[7], swelling the group of so-called *Mammea* coumarins to nearly fifty. They can be structurally sub-divided into a 4-phenyl series, designated † mammeas A, a 4-propyl group (mammeas B), and the less common 4-pentyl (mammea C) or 4-(1-methylpropyl) (mammea D) derivatives. The major insecticidal components of *Mammea americana* form another series with a 4-(1-acetoxypropyl) substituent (mammeas E). Within each group, as well as a 5,7-dioxygenation pattern the aromatic ring carries an acyl group, which may be 3- or 2-methylbutyryl, butyryl, or less commonly 2-methylpropionyl, at either the 6- or 8-position. The remaining position (8- or 6-) in the simple derivatives is generally substituted with a 3-methylbut-2-enyl (prenyl) group, but in two cases (surangins A and B)[5] a 3,7-dimethylocta-2,6-dienyl (geranyl) substituent is found. The naturally-occurring coumarins of the mammea A series with an unmodified prenyl substituent thus comprise compounds (**1a**—**g**),[2b,f,4,6a,7] shown with their letter coding designation.

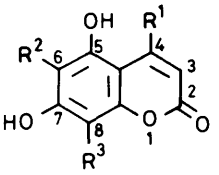
Likewise, the naturally-occurring simple members of the mammea B series are (**1h**—**j**),[2d,4] (**1l**—**n**),[2a,4] either (**1k**) or (**1o**),[3] and (**1p**),[5] whilst (**1q,r**)[2a,4] and (**1t**)[6b] represent the simple natural products of the C and D series, respectively; finally the mammea E series consists of coumarins (**1u,v**),[2e] (**1w**) or (**1x**),[2e] and (**1y**).[5] A 3,4-dihydro derivative of the non-alkylated 4-pentylcoumarin (**1q**) has also been reported from *M. africana*,[8] and a 4-phenyldihydrocoumarin has been isolated from the fern *Pityrogramma calomelanos*.[9]

In some further natural products the prenyl residue has been modified by oxidative cyclisation involving an *ortho* hydroxy group to produce 2,2-dimethylchromene (cyclo D), 3-hydroxy-2,2-dimethyldihydropyran (cyclo E), and 2-(1-hydroxy-1-methylethyl)dihydrofuran (cyclo F) derivatives. Those that have been identified are (**2a**—**i**)[2b,g,3,4,6c] and (**3a**)[10] in the cyclo D series, (**4a**—**c**)[2c,i] in the cyclo E series, with (**5a**—**g**)[2d,4] and (**6a**—**c**)[2c,h,i] in the cyclo F series; two peroxides and a hydroperoxide derivative in the B/cyclo F series have also been isolated.[2c,i] Whether some of these oxidised derivatives are metabolic products or artefacts of the isolation procedure remains uncertain.

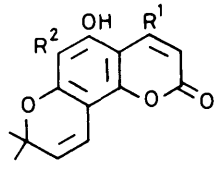
The coumarins A/AA, A/AB, A/BA, A/BB, B/BA, B/BB, B/BC, C/BB, and A/AA cyclo D were found to be uncouplers of oxidative phosphorylation at below 0.5 μg ml^{-1}, and other members of the class not tested probably possess this property.[2e] Mammeas E/BA, E/BB, and E/BC (or E/BD) are also uncouplers, and in addition account for the insecticidal properties of *Mammea americana* extracts; the mammea E coumarin surangin B (**1y**) from *M. longifolia* also displays insecticidal activity.[2e] Surangin A (**1p**) and B, along with mesuol (mammea A/AD), have been reported to have antibacterial properties,[5] and a number of *Mammea* coumarins inhibit the growth of Sarcoma 180 tumour cells.[2h]

This mix of biological activities, and the isolation of some of the *Mammea* coumarins as mixtures of isomers or closely related congeners, has led us to embark on a programme of total synthesis so that the pure compounds may be tested more thoroughly. We report here our efforts in the mammea A, B, and C series, encompassing both the unmodified prenyl (or geranyl) compounds and the cyclo derivatives. Subsequent papers deal

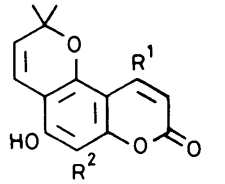
† In this and the following papers we use the letter coding system for these coumarins, introduced earlier (L. Crombie, D. E. Games, and A. McCormick, *Tetrahedron Lett.*, 1966, 151) to avoid the proliferation of very similar trivial names, and extended here. The name mammea is followed by a letter designating the 4-substituent (A = phenyl, B = propyl, C = pentyl, D = 1-methylpropyl, and E = 1-acetoxypropyl) and a stroke separates this from a second letter designating whether a 6- or 8-acyl group is present (A = 6-acyl, B = 8-acyl); a third letter designates the type of acyl substituent (A = 3-methylbutyryl, B = 2-methylbutyryl, C = butyryl, and D = 2-methylpropionyl). Where the prenyl substituent has been modified by cyclisation, the third letter is followed by the prefix cyclo and a fourth letter indicating the type of heterocyclisation [cyclo D = 2,2-dimethylchromene, cyclo E = 3-hydroxy-2,2-dimethyldihydropyran, and cyclo F = 2-(1-hydroxy-1-methylethyl)dihydrofuran].



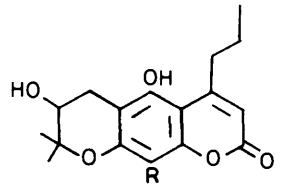
(1) A/AA **a**; R^1 = Ph, R^2 = $COCH_2CHMe_2$, R^3 = $CH_2CH{=}CMe_2$
A/AB **b**; R^1 = Ph, R^2 = $COCHMeCH_2Me$, R^3 = $CH_2CH{=}CMe_2$
A/AC **c**; R^1 = Ph, R^2 = $COCH_2CH_2Me$, R^3 = $CH_2CH{=}CMe_2$
A/AD **d**; R^1 = Ph, R^2 = $COCHMe_2$, R^3 = $CH_2CH{=}CMe_2$
A/BA **e**; R^1 = Ph, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCH_2CHMe_2$
A/BB **f**; R^1 = Ph, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMeCH_2Me$
A/BD **g**; R^1 = Ph, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMe_2$
B/AA **h**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CHMe_2$, R^3 = $CH_2CH{=}CMe_2$
B/AB **i**; R^1 = CH_2CH_2Me, R^2 = $COCHMeCH_2Me$, R^3 = $CH_2CH{=}CMe_2$
B/AC **j**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CH_2Me$, R^3 = $CH_2CH{=}CMe_2$
B/AD **k**; R^1 = CH_2CH_2Me, R^2 = $COCHMe_2$, R^3 = $CH_2CH{=}CMe_2$
B/BA **l**; R^1 = CH_2CH_2Me, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCH_2CHMe_2$
B/BB **m**; R^1 = CH_2CH_2Me, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMeCH_2Me$
B/BC **n**; R^1 = CH_2CH_2Me, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCH_2CH_2Me$
B/BD **o**; R^1 = CH_2CH_2Me, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMe_2$
Surangin A **p**; R^1 = CH_2CH_2Me, R^2 = $(CH_2CH{=}CMeCH_2)_2H$, R^3 = $COCHMeCH_2Me$
q; R^1 = $(CH_2)_4Me$, R^2 = H, R^3 = $COCHMeCH_2Me$
C/BB **r**; R^1 = $(CH_2)_4Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMeCH_2Me$
C/AB **s**; R^1 = $(CH_2)_4Me$, R^2 = $COCHMeCH_2Me$, R^3 = $CH_2CH{=}CMe_2$
D/BB **t**; R^1 = $CHMeCH_2Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMeCH_2Me$
E/BA **u**; R^1 = $CHOAcCH_2Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCH_2CHMe_2$
E/BB **v**; R^1 = $CHOAcCH_2Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMeCH_2Me$
E/BC **w**; R^1 = $CHOAcCH_2Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCH_2CH_2Me$
E/BD **x**; R^1 = $CHOAcCH_2Me$, R^2 = $CH_2CH{=}CMe_2$, R^3 = $COCHMe_2$
Surangin B **y**; R^1 = $CHOAcCH_2Me$, R^2 = $(CH_2CH{=}CMeCH_2)_2H$, R^3 = $COCHMeCH_2Me$



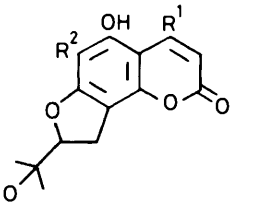
(2) A/AA cyclo D **a**; R^1 = Ph, R^2 = $COCH_2CHMe_2$
A/AB cyclo D **b**; R^1 = Ph, R^2 = $COCHMeCH_2Me$
A/AD cyclo D **c**; R^1 = Ph, R^2 = $COCHMe_2$
B/AA cyclo D **d**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CHMe_2$
B/AB cyclo D **e**; R^1 = CH_2CH_2Me, R^2 = $COCHMeCH_2Me$
B/AC cyclo D **f**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CH_2Me$
B/AD cyclo D **g**; R^1 = CH_2CH_2Me, R^2 = $COCHMe_2$
C/AA cyclo D **h**; R^1 = $(CH_2)_4Me$, R^2 = $COCH_2CHMe_2$
C/AB cyclo D **i**; R^1 = $(CH_2)_4Me$, R^2 = $COCHMeCH_2Me$



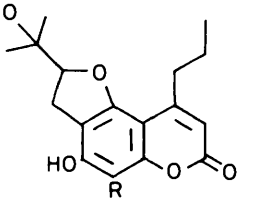
(3) A/BB cyclo D **a**; R^1 = Ph, R^2 = $COCHMeCH_2Me$
B/BB cyclo D **b**; R^1 = CH_2CH_2Me, R^2 = $COCHMeCH_2Me$
C/BB cyclo D **c**; R^1 = $(CH_2)_4Me$, R^2 = $COCHMeCH_2Me$



(4) B/BA cyclo E **a**; R = $COCH_2CHMe_2$
B/BB cyclo E **b**; R = $COCHMeCH_2Me$
B/BC cyclo E **c**; R = $COCH_2CH_2Me$



(5) A/AA cyclo F **a**; R^1 = Ph, R^2 = $COCH_2CHMe_2$
A/AB cyclo F **b**; R^1 = Ph, R^2 = $COCHMeCH_2Me$
A/AC cyclo F **c**; R^1 = Ph, R^2 = $COCH_2CH_2Me$
A/AD cyclo F **d**; R^1 = Ph, R^2 = $COCHMe_2$
B/AA cyclo F **e**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CHMe_2$
B/AB cyclo F **f**; R^1 = CH_2CH_2Me, R^2 = $COCHMeCH_2Me$
B/AC cyclo F **g**; R^1 = CH_2CH_2Me, R^2 = $COCH_2CH_2Me$



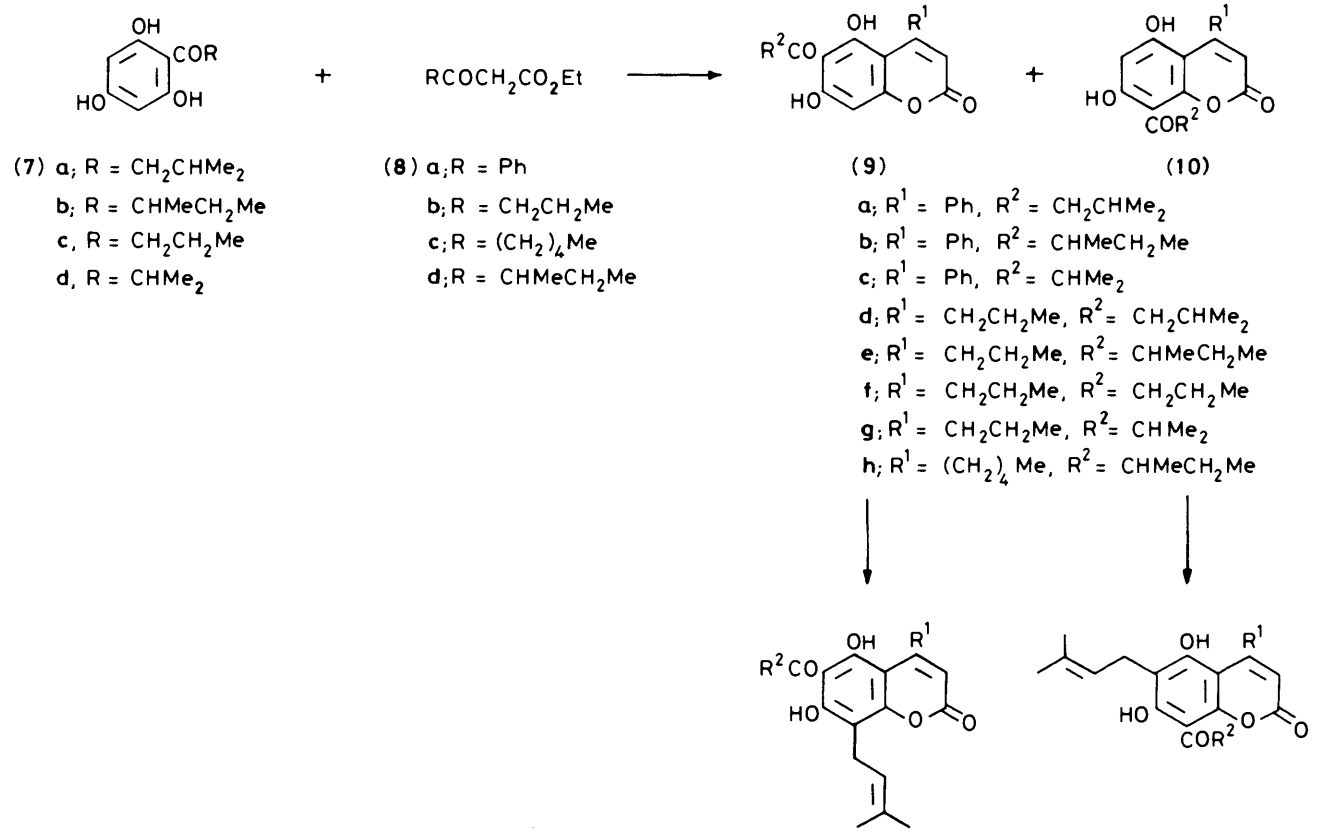
(6) B/BA cyclo F **a**; R = $COCH_2CHMe_2$
B/BB cyclo F **b**; R = $COCHMeCH_2Me$
B/BC cyclo F **c**; R = $COCH_2CH_2Me$

with studies leading to synthesis of mammea D/BB (ferruol A) and the insecticidal mammea E series.*

Results and Discussion

Our approach, outlined in the Scheme, was based on the Pechmann condensation[11] of an acylphloroglucinol (**7**), prepared from phloroglucinol, with an appropriate β-keto ester (**8**) to give a mixture of 6- and 8-acylcoumarins (**9**) and (**10**), respectively, that could be separated and independently *C*-alkylated to insert a prenyl (or geranyl) residue which could subsequently be oxidatively modified if required. This short

* Where side chain chiral centres exist these are in the (±)-form in the synthetic materials, unless stated otherwise, in this and the following papers.



Scheme

route would access both the 6- and 8-acyl series of natural products. Previous synthetic work in our laboratories had laid the foundation for this approach by showing that both 6- and 8-acyl coumarins could be isolated from this type of Pechmann condensation,[2a,b] although the published yields of this reaction, and of the Friedel-Crafts acylation of phloroglucinol, were less than satisfactory. Introduction of the prenyl group into an acylphloroglucinol prior to coumarin formation was discounted based on an earlier report that Pechmann condensation with an alkylated acylphloroglucinol was very inefficient.[12]

A study of the Friedel-Crafts reaction between phloroglucinol and the acid chlorides of 3- and 2-methylbutyric, butyric, and 2-methylpropionic acids in carbon disulphide–nitrobenzene mixtures at reflux in the presence of aluminium trichloride showed that superior yields and cleaner products (free of unchanged phloroglucinol) could be obtained when the molar ratio of aluminium chloride to phloroglucinol was raised to 4:1; reaction time and the grade of aluminium trichloride used were also important (see the Experimental section). Under optimum conditions the acylphloroglucinols (**7a**—**d**) were obtained in up to 80% yields.

The β-keto esters needed for preparation of *Mammea* coumarins of the A, B, and C series are ethyl benzoylacetate (**8a**), ethyl 3-oxohexanoate (**8b**), and ethyl 3-oxo-octanoate (**8c**), respectively. They could be prepared easily by reaction of the appropriate methyl ketone with diethyl carbonate in the presence of sodium hydride (ethyl benzoylacetate is also available commercially). Ethyl 4-methyl-3-oxohexanoate (**8d**) was also obtained by this method, from 3-methylpentan-2-one, as it was hoped that Pechmann condensations with this β-keto ester would lead to the mammea D coumarins.

The Pechmann condensation requires an acidic condensing agent, with sulphuric acid and phosphorus pentaoxide being probably the most commonly used.[11] For the desired condensations of the acylphloroglucinols (**7**) with β-keto esters (**8**) the choice of condensing agent is limited by the labile nature of the acyl group; *Mammea* coumarins have been deacylated by use of 70—75% sulphuric acid, or trifluoroacetic acid.[2c,e,13] Based on earlier studies, [2a,b] it was decided that a mixture of glacial acetic acid containing 5% v/v sulphuric acid would be suitable, and indeed reaction in this medium of the acylphloroglucinols (**7a**—**d**) with ethyl 3-oxohexanoate (**8b**), and of (2-methylbutyryl)phloroglucinol (**7b**) with ethyl 3-oxo-octanoate (**8c**), afforded mixtures of the respective 6- and 8-acyl coumarin isomers (**9d**—**h**) and (**10d**—**h**) in combined yields of 63—70%. The ratio of 6-acyl to 8-acyl isomers was generally *ca.* 3:2. The reaction of (**7b**) with ethyl 4-methyl-3-oxohexanoate (**8d**) failed to produce any coumarin material, so that the mammea D series was not accessible by this route (see following papers). Condensations between the acyl phloroglucinols (**7a,b,d**) and ethyl benzoylacetate (**8a**) proceeded well on a 5 mmol scale in the acetic–sulphuric acid medium, but when scaled up to 20 mmol or more failed to produce much coumarin material; instead substantial amounts of acetophenone were isolated, presumably formed by a competitive retro-Claisen cleavage of the β-keto ester. To combat this, the β-keto ester was added to the reaction mixture in portions over 20 days to afford modest yields (28—36%) of the 4-phenylcoumarin 6- and 8-acyl isomer mixtures (**9a**—**c**) and (**10a**—**c**). Attempts to employ other condensing agents for the Pechmann condensation in order to obtain the 4-(1-methylpropyl)coumarins, or to improve the yields of the 4-phenyl series, were not successful. For example, merely increasing the concentration of sulphuric acid in acetic acid to 10% v/v caused deacylation in a reaction of

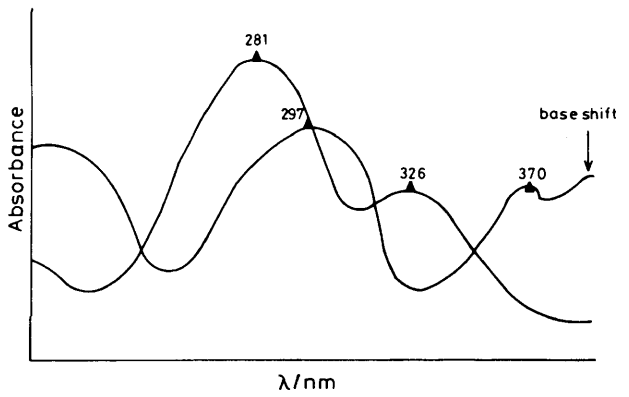


Figure 1. Typical u.v. spectrum of a 6-acyl-5,7-dihydroxycoumarin in ethanol.

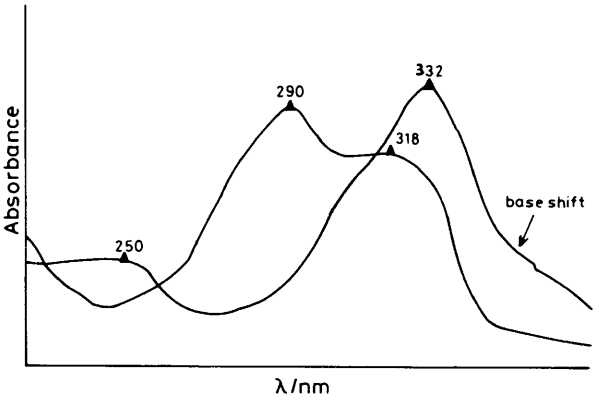


Figure 2. Typical u.v. spectrum of an 8-acyl-5,7-dihydroxycoumarin in ethanol.

(3-methylbutyryl)phloroglucinol (**7a**) with ethyl benzoylacetate (**8a**), to give only 5,7-dihydroxy-4-phenylcoumarin.

The most effective method of separating the 6- and 8-acyl coumarin mixtures for the 4-propyl and 4-pentyl series proved to be fractional crystallisation from chloroform–methanol and up to 75% of each mixture could be separated into the individual isomers in this way. Initial attempts had involved alumina column chromatography, as reported earlier from these laboratories,[2a] but with no improvement on those partial separations. Fractional crystallisation failed in the cases of the 4-phenylcoumarin mixtures, but complete separation could be achieved by column chromatography on silica gel, a technique that had given no separation with 4-propyl- or 4-pentyl-coumarin isomer mixtures. Interestingly, when separating mixtures by crystallisation the first isomer to crystallise is the 6-acylcoumarin if the acyl group is 3-methylbutyryl or butyryl, but is the 8-acyl isomer if the acyl group is 2-methylpropionyl or 2-methylbutyryl.

The orientation of the acyl group in these coumarins was based on ultraviolet absorption data, including the Gibbs test under spectrophotometric control.[14] The 6-acyl isomers all show a characteristic $\lambda_{max.}$ at 614 nm in the Gibbs test, whereas the 8-acyl isomers give no absorption in this region. The u.v. spectra of all the synthetic 6-acylcoumarins are consistent, irrespective of acyl group and C-4 substitution, and in good agreement with earlier published data;[2a,b] the same applies to the synthetic 8-acylcoumarins. Typical spectra in ethanol, and with base-shift, for a 6-acyl and an 8-acyl isomer are shown in Figures 1 and 2, respectively. The base-shifts are characteristically different, and in addition we have found that the presence of a $\lambda_{max.}$ at 281 ± 1 nm in the 6-acyl isomers, and of a $\lambda_{max.}$ at 290 ± 1 nm in the 8-acyl isomers, is a most useful aid to rapid differentiation of isomers without resort to base-shift or Gibbs test. The n.m.r. data have proved to be of limited assistance in distinguishing 6- and 8-acylcoumarin isomers in these series, as the spectra are of very similar appearance. Low solubility necessitated observing the spectra in solvents in which the hydroxy-proton resonances are not always apparent, preventing the use of these signals for orientation purposes, in contrast to the situation in some of the natural *Mammea* coumarins. The assignments to 6- or 8-acyl series based on u.v. data have subsequently been confirmed unequivocally by an *X*-ray crystal structure determination (see the following papers).

We thus had to hand pure samples of the acylcoumarins (**9a**—**h**) and (**10a**—**h**) and the 4-pentylcoumarin (**10h**) had properties in agreement with those reported for the natural material (**1q**) isolated from *M. africana*. The remaining step to complete synthesis of the *Mammea* coumarins with an unmodified prenyl group was thus a *C*-alkylation to insert the C_5 residue. After a number of other methods had been investigated (see below), it was found that alkylation with 3-methylbut-2-enyl bromide (prenyl bromide) in 10% aqueous potassium hydroxide at 0 °C, with 1.5 h as optimum reaction time, worked sufficiently well to be adopted. An increase in the strength of the potassium hydroxide solution, or of reaction time, led to an increase in polyprenylated products, and higher temperatures were avoided initially because of the reported tendency of *Mammea* coumarins to isomerise (from the 8-acyl to 6-acyl series, or *vice versa*) in basic media,[2b,d,e,6a,13] and to deacylate in hot aqueous potassium hydroxide.[13]

Using our method the coumarins with a simple prenyl group in the 4-phenyl, 4-propyl, and 4-pentyl series were prepared without isomerisation in yields, on a once-through basis, of 20—35%. About 35% of starting acylcoumarin could be recovered, so that the *C*-prenylation yields based on converted starting material were 30—45%; no *O*-alkylation was observed. Thus mammea A/AA (**1a**), A/AB (**1b**), and A/AD (**1d**) were prepared from the 6-acylcoumarins (**9a**—**c**), respectively, whilst mammea A/BA (**1e**), A/BB (**1f**), and A/BD (**1g**) were prepared from the 8-acylcoumarins (**10 a**—**c**), respectively. In the 4-propyl series, mammea B/AA (**1h**), B/AB (**1i**), B/AC (**1j**), and B/AD (**1k**) were prepared from (**9d**—**g**), respectively, and prenylation of (**10d**—**g**) led to mammea B/BA (**1l**), B/BB (**1m**), B/BC (**1n**), and B/BD (**1o**), respectively. Lastly, in the 4-pentyl group, mammea C/BB (**1r**) and C/AB (**1s**) were prepared from the acylcoumarins (**9h**) and (**10h**), respectively. The physical and spectral data of these synthetic materials agree in almost all cases with those reported for the naturally-occurring coumarins. The exceptions were synthetic mammea A/AD (**1d**) and A/BB (**1f**), which had lower melting points than those recorded for the natural materials, but no combustion analysis was reported for the former,[6a] and the figures published for the latter were not totally satisfactory.[2b] As all other data for the synthetic materials are in agreement with those of the natural, and satisfactory combustion analyses were obtained, there seems to be no doubt that they have the same structures. Mammea A/BD (**1g**) and C/AB (**1s**) have not yet been isolated as natural products, although they may be present in the extracts; mammea A/BD (isomesuol) has, however, been isolated from base-catalysed isomerisation of mammea A/AD (mesuol; **1d**).[6a] Another reason for preparing (**1g**) and (**1s**) is that the orientation of the acyl groups in the products of *C*-prenylation cannot now be based on a Gibbs test, but instead is based on the analogous base-shift behaviour of the prenylated and non-prenylated coumarins in the u.v. spectrum. To have both the 6-acyl and the corresponding 8-acyl isomer strengthened our conclusions. Typical u.v. spectra are shown in Figures 3 and 4 (*cf.* Figures 1 and 2). ^{1}H N.m.r. spectra of 6-acyl-8-prenylcoumarins were generally very similar to the 8-acyl-6-

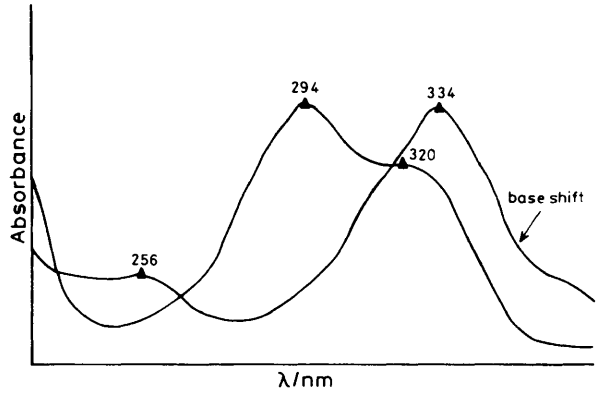


Figure 3. Typical u.v. spectrum of a 6-acyl-5,7-dihydroxy-8-prenylcoumarin in ethanol.

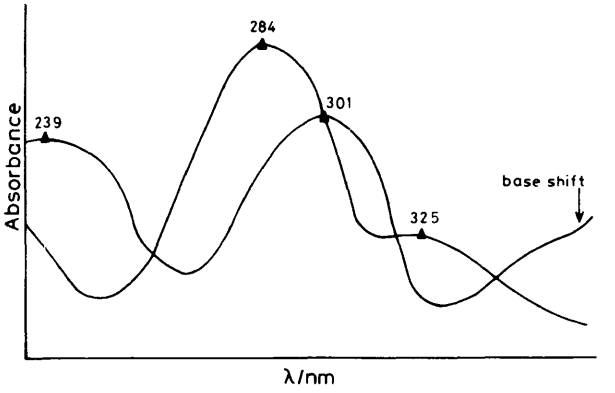
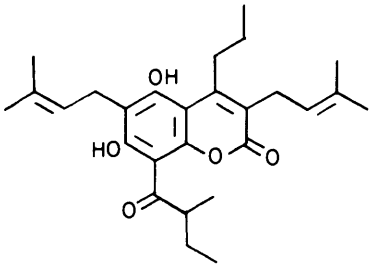


Figure 4. Typical u.v. spectrum of an 8-acyl-5,7-dihydroxy-6-prenylcoumarin in ethanol.

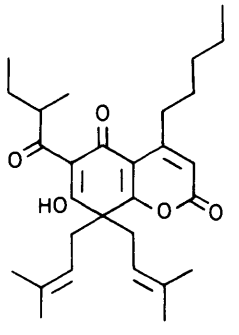
prenyl compounds in the 4-propyl and 4-pentyl series; two hydroxy group resonances were observed, at *ca.* δ 14.7 and 7.0, showing their chelated (to the 5-OH in 6-acylcoumarins, and to the 7-OH in the 8-acyl isomers) and unchelated nature, respectively. In the 4-phenyl (mammea A) series a similar pattern is observed for the 8-acyl-6-prenylcoumarins, but the 6-acyl-8-prenyl compounds show two chelated hydroxy groups at *ca.* δ 9.8 and 11.2, indicating a slow exchange situation on the n.m.r. time scale. Presumably the out-of-plane 4-phenyl group destabilises the expected 5,6-chelate by steric compression and stabilises the 6,7-chelate by providing an acceptor site for a hydrogen-bond involving the 5-hydroxy group, thus bringing the two forms closer in energy.[2d]

Alkylation of the acylcoumarins sometimes produced some polyprenylated material, and in two cases this was examined to determine the nature of such products. From alkylation of the 8-acylcoumarin (**10e**), the 3,6-bisprenylcoumarin (**11**) was isolated in 1% yield along with mammea B/BB (**1m**). The ^{1}H n.m.r. spectrum of (**11**) showed signals for a second prenyl group in a slightly different environment to that at C-6, and the absence of the signal attributable to 3-H in mammea B/BB. Alkylation of the 6-acylcoumarin (**9h**) afforded, in addition to mammea C/AB (**1s**), a further bisprenylated product in 6% yield. The ^{1}H n.m.r. spectrum indicated two *C*-prenyl groups in identical environments and a singlet at δ 6.05 that can be assigned to 3-H. The observation of only one hydroxy group resonance at δ 18.5, *i.e.* unusually strongly chelated, is consistent with disruption of the aromatic ring to give the 8,8-dialkylated product (**12**) or its 5-hydroxy-7-keto tautomer. Both 3,6- and 8,8-bisprenylation have been observed in other alkylation studies with 4-propyl-5,7-dihydroxycoumarin.[15]

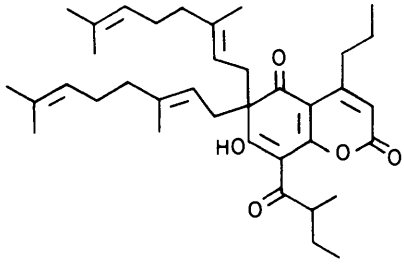
The *C*-alkylation observed in our experiments, in contrast to the *O*-alkylation observed in acetone solvent with potassium carbonate as base (see later), is presumed to arise because



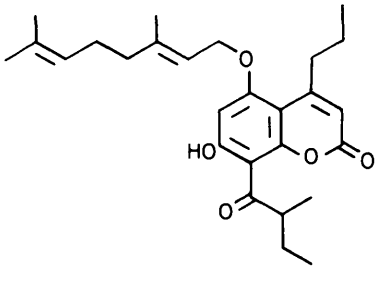
(11)



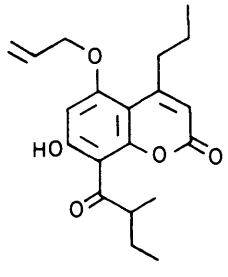
(12)



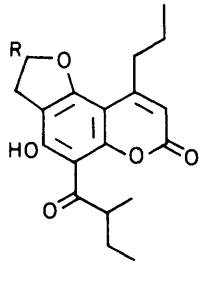
(13)



(14)



(15)



(16) a; R = Me
b; R = OH

hydrogen-bonding of the phenolic oxygen atom in the aqueous reaction mixture creates a solvation shell that disfavours *O*-alkylation. This view is supported by the finding that 2,2,2-trifluoroethanol, a solvent with high hydrogen-bonding capability, can be used to replace water in these alkylations. The preformed dipotassium salt of (**9f**), for example, was treated with prenyl bromide in 2,2,2-trifluoroethanol at 0 °C to afford mammea B/AC (**1j**) in 20% yield. ^{1}H N.m.r. spectra of the crude products, however, showed evidence of some *O*-alkylation so that water was the preferred solvent.

Attempts to prepare the geranyl coumarin surangin A (**1p**) by *C*-alkylation with geranyl bromide or chloride of either the 8-acylcoumarin (**10e**) in 10% aqueous potassium hydroxide at 0 °C, or of the dipotassium salt of (**10e**) in 2,2,2-trifluoroethanol at 0 °C, gave only starting material. The coumarin (**10e**) was eventually alkylated using geranyl chloride and just two equivalents of 10% aqueous potassium hydroxide, in an effort to minimise coumarin isomerisation, but at 40—45 °C for 24 h. Column chromatography of the crude products on silica gel led to the isolation of the 6,6-bisgeranylated pyrone (**13**) in 5% yield, followed by a 1 : 1 mixture of surangin A (**1p**) and its 5-*O*-geranyl isomer (**14**) in 14% yield; this mixture was separated by reverse-phase h.p.l.c. The synthetic surangin A had spectral properties identical to those reported for the natural material,[5] and was identical (t.l.c., m.p., and mixed m.p.) to a sample of the natural material kindly provided by Dr. T. Govindachari. Increased reaction temperature led to a reduced yield of surangin A and an increase in polyalkylation, whereas replacement of the water by 2,2,2-trifluoroethanol at 45 °C resulted in partial isomerisation of the 8-acylcoumarins such that the 6-acyl isomer (**9e**) of the starting material was isolated along with a complex mixture of alkylation products.

Among other methods explored for prenylation of the acylcoumarins, the use of 3-hydroxy-3-methylbut-1-ene with boron trifluoride has been reported to produce mammea B/AA (**1h**) and B/AB (**1i**) in yields of only 2% from the coumarins (**9d,e**), respectively,[15] but in our hands these reactions could not be repeated, and this procedure was not investigated further. Attempts at direct *C*-alkylation with prenyl halides using silver oxide in dioxane,[16] metallic sodium in benzene or ether,[17] potassium and anhydrous zinc chloride in xylene,[18] or potassium methoxide in methanol,[19] all gave no useful alkylation. In an attempt to utilise a three-step *C*-prenylation sequence reported by Murray *et al.*,[20] the *O*-alkylation of the 8-acylcoumarin (**10e**) with 3-chloro-3-methylbut-1-yne and potassium carbonate was undertaken first in acetone solvent, leading only to recovery of starting material, and then in methyl ethyl ketone, affording recovered starting material and a low yield (6%) of the chromeno coumarin mammea B/BB cyclo D (**3b**) (see later). This latter product presumably arises by a thermal cyclisation of the desired 1,1-dimethylpropargyl ether (which would have been reduced to the 1,1-dimethylallyl ether by semi-hydrogenation before thermal Claisen rearrangement to give overall *C*-prenylation). Attempted ring opening of the chromene ring to a prenyl group in compound (**3b**) and in mammea B/AB cyclo D (**2e**) and C/BB cyclo D (**3c**) (see below) by various methods was unsuccessful. In another approach the 8-acyl-4-propylcoumarin (**10e**) was selectively *O*-allylated with allyl bromide–potassium carbonate in acetone to afford (**15**). It was intended that this material would be converted into a 6-allyl coumarin by Claisen rearrangement, followed by oxidative cleavage to an aldehyde that would allow chain extension to a prenyl or a geranyl group. In the event, thermolysis of (**15**) in *N,N*-dimethylaniline led only to the dihydrofurocoumarin (**16a**); this approach was then abandoned although the required aldehyde was eventually prepared, as the hemiacetal (**16b**), by osmium tetraoxide–sodium periodate treatment of mammea B/BB (**1m**).

All the natural *Mammea* coumarins of the A,B and C series having an unmodified prenyl (or geranyl) group had now been prepared, with the exception of mammea A/AC (**1c**), identified by g.c.–m.s. of *Mesua thwaitesii* extracts,[7] so that our attention next turned to the cyclo D, E, and F coumarins.

The Cyclo D Coumarins.—A number of the chromeno coumarins in this series had been prepared prior to our work by treatment of the appropriate acylcoumarin with the acetal 1,1-dimethoxy-3-methylbutan-3-ol in pyridine[21] to produce the mammea cyclo D coumarins (**2a**—**g**).[15] Our efforts in this group were thus limited to preparation, by the same method, of mammea C/AB cyclo D (**2i**), which had been identified by g.c.–m.s. of *Mammea americana* extracts[3] but not yet synthesized, of mammea B/AB cyclo D (**2e**) (already synthesized by Games and Haskins[15]) and the non-naturally occurring B/BB cyclo D (**3b**) and C/BB cyclo D (**3c**) for use in our prenylation studies (see above), and lastly of mammea A/BB cyclo D (**3a**; ponnalide), a coumarin isolated from unripe seeds of *Calophyllum inophyllum*.[22] We have not yet extended our studies to include mammea C/AA cyclo D (**2h**), which had also been identified by g.c.–m.s. of *Mammea americana* extracts,[3] and is thus the only remaining target among the naturally-occurring cyclo D coumarins of the mammea A,B, or C classes.

The Cyclo E and F Coumarins.—In the mammea cyclo E and cyclo F coumarins the prenyl substituent has been oxidatively modified and cyclised by involvement of an adjacent hydroxy group to a 3-hydroxy-2,2-dimethyldihydropyran or a 2-(1-hydroxy-1-methylethyl)dihydrofuran moiety, respectively. They had not, prior to our work, been prepared in a pure state from non-natural precursors; some members of the series had been prepared from natural prenylated materials,[2c,d] but as these were often contaminated with other closely related members of the series, the cyclo coumarins were also obtained impure. The availability from our synthesis of the pure prenylated coumarins prompted a reinvestigation of the oxidative cyclisation.

Mammea B/BA, B/BB, and B/BC (**1l**—**n**) respectively were treated separately with one equivalent of *m*-chloroperbenzoic acid in chloroform containing a trace of toluene-*p*-sulphonic acid; after column chromatography mammea B/BA cyclo E, B/BB cyclo E, and B/BC cyclo E (**4a**—**c**) respectively were each obtained pure in *ca.* 50% yield. This reaction is presumed to involve epoxidation of the prenyl group double bond followed by acid-catalysed ring opening at the tertiary centre with intramolecular capture of the carbonium ion by an adjacent hydroxy group to produce the hydroxydihydropyran ring. The absence from the ^{1}H n.m.r. spectra of (**4a**—**c**) of any low-field signal typical of a chelated hydroxy group confirmed that the new ring is linearly fused at C-(6)–C-(7) of the coumarin nucleus.

Individual treatment of the eight coumarins mammea A/AA, A/AB, B/AA, B/AB, B/AC, B/BA, B/BB, and B/BC (**1a,b,h**—**j**, **l**—**n**) respectively, with *m*-chloroperbenzoic acid in dichloromethane gave, after chromatography, the corresponding pure mammea cyclo F coumarins (**5a,b,e**—**g**) and (**6a**—**c**) respectively in yields of 49—72%. Presumably here, the peracid again forms an epoxide at the prenyl group double bond, but in the absence of added sulphonic acid the epoxide undergoes nucleophilic attack by an adjacent hydroxy group at the less hindered centre to produce the 2-(1-hydroxy-1-methylethyl)dihydrofuran ring. ^{1}H N.m.r. signals at *ca.* δ 14.0 in the spectra of the cyclo F coumarins indicated the presence of a chelated hydroxy group, confirming that the new ring is angularly fused, across C(7)–C(8) for the 6-acyl isomers (**5**) and C(5)–C(6) for the 8-acyl isomers (**6**).

The physical and spectral properties of the synthetic cyclo E and cyclo F coumarins supported the assigned structures and were in agreement with those reported for the naturally-

occurring materials where available. Our experiments therefore provide pure samples of all the clearly identified mammea cyclo E and cyclo F coumarins; as yet we have not prepared mammea A/AC cyclo F and A/AD cyclo F (**5c,d**) respectively, which have been tentatively identified in *M. americana* by mass spectral fragmentation patterns[2d] (mammea A/AD cyclo F has also been identified by g.c.–m.s. of extracts of *Mesua thwaitesii*[7]), nor any mammea C/cyclo F coumarins, although a member of this series with undefined substitution has been reported in *Mammea americana*.[10]

With the few exceptions stated above, and the cyclo F peroxide derivatives,[2c,i] all of the reported naturally-occurring coumarins of the mammea A, B, and C series have now been prepared, including those that have been isolated and those that have been identified by g.c.–m.s. of plant extracts. Attention was then transferred to the limited mammea D series, and especially to the insecticidal mammea E [4-(1-acetoxypropyl)]coumarins and surangin B. Our results in this area are presented in the following papers.[2,3]

Experimental

Unless otherwise stated, the following generalisations apply. Organic solutions were dried over anhydrous $MgSO_4$. Analytical t.l.c. was performed on 20 × 5 cm^2 glass plates coated with silica gel G at a thickness of 0.3 mm, and preparative t.l.c. on 20 × 20 cm^2 plates coated with silica gel HF_{254} at a thickness of 0.8 mm. Separations by column chromatography were carried out on dry columns of Woelm TSC silica, activity III/30 mm, and by high pressure liquid chromatography (h.p.l.c.) using Waters Associates Prep. L. C. System 500 with a Waters Prep. PAK-500 C_{18} column (reverse-phase). All melting points are uncorrected. I.r. spectra were recorded on Perkin-Elmer 710B or Unicam SP 200 spectrometers, and u.v. spectra on a Unicam SP 800 spectrometer in ethanolic solution; base shifts were measured in ethanolic potassium hydroxide solution. Gibbs tests were carried out under spectroscopic control as follows: A weighed sample (3 mg) in pyridine (1 ml) was treated with *N*, 2,6-trichloro-*p*-benzoquinone monoimine in pyridine (6 ml; 0.2% w/v, freshly prepared). The solution was made up to 25 ml with 2% aqueous sodium borate and after 20 min the absorption spectrum was recorded at 600—750 nm against a blank containing buffered reagent only. ^1H N.m.r. spectra were measured on a Jeol JNM-MH-100 spectrometer, operating at 99.8 MHz, with tetramethylsilane as the internal reference; where stated, spectra measured at 250 MHz were recorded on a Bruker WM250 instrument. Hydroxy proton resonances were identified by D_2O exchange. Mass spectra were recorded on AEI MS902 or VG 7070F spectrometers.

Preparation of Acylphloroglucinols.—Aluminium trichloride (0.41 mol; Fluka A. G. puriss, white granules) was added to a stirred suspension of anhydrous phloroglucinol (0.1 mol) in carbon disulphide (60 ml). Nitrobenzene (45 ml) was then added over 30 min forming a homogeneous solution with evolution of hydrogen chloride. The solution was heated under reflux for 30 min, the acyl chloride (0.1 mol) in nitrobenzene (5 ml) was then added over 30 min, and the solution was heated under reflux for a further 30 min before being allowed to cool with stirring. The mixture was poured onto ice–water (400 ml) and hydrochloric acid (3M; 100 ml) was added. The organic solvents were removed by steam distillation, the hot solution remaining was filtered, and the oily residues were extracted several times with boiling water. The combined aqueous solutions when cooled gave the acylphloroglucinol either as an oil which was extracted into ether, to leave a gum after evaporation, or as fine crystals which were collected by filtration. (The use of other grades of aluminium trichloride, of lower ratios of aluminium trichloride to phloroglucinol, or of longer reaction times, led to inferior yields of less pure product). Using this method the following acyl phloroglucinols were prepared.

(3-*Methylbutyryl*)*phloroglucinol* (**7a**): prepared from 3-methylbutyryl chloride as yellow crystals, (80%), m.p. 144—145 °C (lit.,[2a] 145 °C), $\nu_{max.}$(KBr) 3 300, 1 600, and 1 530 cm^{-1}; δ [$(CD_3)_2SO$] 0.94 (6 H, d, *J* 7 Hz, Me_2CH), 1.9—2.2 (1 H, m, Me_2CH), 2.9 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 5.85 (2 H, s, ArH), 10.4 (1 H, br, OH), and 12.4 (2 H, br, chelated OH).

(2-*Methylbutyryl*)*phloroglucinol* (**7b**): prepared from 2-methylbutyryl chloride as an orange-yellow gum[2a] (80%), $\nu_{max.}$($CHCl_3$) 3 550, 3 200, 3 050, 1 600, and 1 530 cm^{-1}; δ [$(CD_3)_2SO$] 0.86 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.1 (3 H, d, *J* 7 Hz, $MeCH$), 1.2—1.8 (2 H, m, *J* 7 Hz, $MeCH_2CH$), 3.75 (1 H, m, CH_2CHCO), 5.80 (2 H, s, ArH), 10.06 (1 H, br, OH), and 12.05 (2 H, br, chelated OH).

Butyrylphloroglucinol (**7c**): prepared from butyryl chloride as orange-yellow crystals (70%), m.p. 175—176 °C (lit.,[24] 179—180 °C), $\nu_{max.}$(Nujol) 3 300, 1 640, and 1 610 cm^{-1}; δ[$(CD_3)_2SO$] 0.9 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.3—1.8 (2 H, m, $MeCH_2CH_2$), 2.94 (2 H, t, *J* 7 Hz, CH_2CH_2CO), and 5.80 (2 H, s, ArH); the hydroxy protons were not discernible.

(2-*Methylpropionyl*)*phloroglucinol* (**7d**): prepared from 2-methylpropionyl chloride as pale yellow crystals (76%), m.p. 197 °C (lit.,[25] 177—178 °C), $\nu_{max.}$(KBr) 3 300, 1 630, and 1 580 cm^{-1}; δ[$(CD_3)_2SO$] 1.1 (6 H, d, *J* 7 Hz, Me_2CH), 3.90 (1 H, m, Me_2CH), 5.70 (2 H, s, ArH), 10.0 (1 H, br, OH), and 11.9 (2 H, br, chelated OH).

Preparation of β-*Keto Esters.*[26]—Sodium hydride (0.86 mol; 50% dispersion in oil) was washed with ether and the ether decanted off. Dry ether (200 ml) and diethyl carbonate (0.82 mol) were added and the stirred mixture was heated to reflux under nitrogen whilst the methyl ketone (0.41 mol) was added over a period of 5 h. Further portions of dry ether were added when the mixture thickened. The cooled mixture was poured into ice–water (600 ml) containing glacial acetic acid (100 ml), the organic layer separated, and the aqueous layer further extracted with ether. The ether extracts were combined and evaporated, and the residue was distilled to yield the β-keto ester. (All the β-keto esters showed spectroscopic indications of both keto and enol forms). By this method the following β-keto esters were prepared:

Ethyl Benzoylacetate (**8a**): prepared from acetophenone (81%), b.p. 104—108 °C at 0.5 mmHg (lit.,[27] 101—106 °C at 1 mmHg), $\nu_{max.}$(film) 2 950, 1 730, and 1 680 cm^{-1}; δ ($CDCl_3$) 1.26 (3 H, t, *J* 7 Hz, $MeCH_2$), 4.00 (2 H, s, $COCH_2CO$), 4.30 (2 H, q, *J* 7 Hz, $MeCH_2O$), and 7.4—8.1 (5 H, m, ArH).

Ethyl 3-*Oxohexanoate* (**8b**): prepared from pentan-2-one (66%), b.p. 94—98 °C at 15 mmHg (lit.,[26] 93—96 °C at 14 mmHg), $\nu_{max.}$(film) 2 950, 1 740, and 1 710 cm^{-1}; δ(CCl_4) 0.96 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.30 (3 H, t, *J* 7 Hz, $MeCH_2O$), 1.4—1.9 (2 H, m, $MeCH_2CH_2$), 2.55 (2 H, t, *J* 7 Hz, $MeCH_2CO$), 3.4 (2 H, s, $COCH_2CO$), and 4.25 (2 H, q, *J* 7 Hz, $MeCH_2O$).

Ethyl 3-*Oxo-octanoate* (**8c**): prepared from heptan-2-one (54%), b.p. 80—82 °C and 0.5 mmHg (lit.,[26] 85—90 °C at 3 mmHg), $\nu_{max.}$(film) 2 950, 1 730, and 1 710 cm^{-1}; δ($CDCl_3$) 0.90 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.28 (4 H, m, $MeCH_2CH_2CH_2$), 1.28 (3 H, t, *J* 7 Hz, $MeCH_2O$), 1.6 (2 H, m, $CH_2CH_2CH_2CO$), 2.54 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 3.44 (2 H, s, $COCH_2CO$), and 4.20 (2 H, q, *J* 7 Hz, $MeCH_2O$).

Ethyl 4-*Methyl*-3-*oxohexanoate* (**8d**): prepared from 3-methylpentan-2-one, (59%), b.p. 104—108 °C at 22 mmHg (lit.,[28] 96—100 °C at 14 mmHg), $\nu_{max.}$(film) 2 950, 1 740, and 1 710 cm^{-1}; δ($CDCl_3$) 0.90 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.10 (3 H, d, *J* 7 Hz, $MeCH$), 1.24 (3 H, t, *J* 7 Hz, $MeCH_2O$), 1.3—1.8 (2 H, m, $MeCH_2CH$), 2.3—2.7 (1 H, m, CH_2CHCO), 3.44 (2 H, s, $COCH_2CO$), and 4.15 (2 H, q, *J* 7 Hz, $MeCH_2O$).

Preparation of 6- *and* 8-*Acyl*-4-*alkyl*-5,7-*dihydroxycoumarins*.—The acylphloroglucinol (1 mol equiv.) was dissolved in the minimum of cold glacial acetic acid and concentrated sulphuric acid was added dropwise with stirring to produce a 5% v/v sulphuric acid in glacial acetic acid mixture. The β-keto ester (1 mol equiv.) was added and the mixture left to stand at room temperature. Any crystals formed were collected by filtration after 2 and 5 days, washed with cold glacial acetic acid and then water, and dried. After 10 days the reaction mixture was poured into ice–water and the resulting precipitate collected and dried. Separation of the isomers was effected by fractional crystallisation from chloroform–methanol. The following coumarins were prepared by this method:

5,7-*Dihydroxy*-6- *and* 8-(3-*methylbutyryl*)-4-*propylcoumarins* (**9d**) and (**10d**). These were prepared as a mixture (18.6 g, 70%) from (3-methylbutyryl)phloroglucinol (18.6 g, 88 mmol) and ethyl 3-oxohexanoate (14 g, 88 mmol). Crystallisation afforded 5,7-dihydroxy-6-(3-methylbutyryl)-4-propylcoumarin (**9d**) as yellow needles, m.p. 228—229 °C (lit.,[12] 228—229 °C), $\nu_{max.}$(Nujol) 3 200, 2 950, 1 690, and 1 610 cm^{-1}; $\lambda_{max.}$ 234infl., 282, and 326 (in base 237, 297, 370, and 403) nm; δ[$(CD_3)_2SO$] 1.0 (9 H, m, Me_2CH and $MeCH_2$), 1.4—1.8 (2 H, m, $MeCH_2$), 2.22 (1 H, m, $CHCH_2CO$), 2.9 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 3.02 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 5.98 (1 H, s, $CH_2C{=}CHCO$), and 6.36 (1 H, s, ArH); the hydroxy protons were not discernible. 5,7-Dihydroxy-8-(3-methylbutyryl)-4-propylcoumarin (**10d**) was obtained as white needles, m.p. 230—232 °C (lit.,[2a] 219 °C), $\nu_{max.}$(Nujol) 2 950, 1 690, 1 630, and 1 600 cm^{-1}; $\lambda_{max.}$ 291 and 318 (in base 250 and 332) nm; δ[$(CD_3)_2SO$] 1.0 (9 H, m, Me_2CH and $MeCH_2$), 1.4—1.8 (2 H, m, $MeCH_2$), 2.2 (1 H, m, $CHCH_2CO$), 2.96 (4 H, m, $CHCH_2CO$ and $CH_2{=}CHCO$), 6.08 (1 H, s, $CH_2C{=}CHCO$), and 6.42 (1 H, s, ArH); the hydroxy protons were not discernible.

5,7-*Dihydroxy*-6- *and* 8-(2-*methybutyryl*)-4-*propylcoumarins* (**9e** and **10e**). These were prepared as a mixture (6.7 g, 69%) from (2-methylbutyryl)phloroglucinol (7.05 g, 34 mmol) and ethyl 3-oxohexanoate (5.3 g, 34 mmol). Crystallisation afforded 5,7-dihydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) as white needles, m.p. 248—250 °C (lit.,[2a] 235—236 °C), $\nu_{max.}$(Nujol) 3 200, 2 950, 1 680, 1 630, and 1 600 cm^{-1}; $\lambda_{max.}$ 290 and 317 (in base 253 and 328) nm; δ[$(CD_3)_2SO$] 0.92 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.0 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.16 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—1.9 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.94 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 3.3 (1 H, m, *J* 7 Hz, CH_2CHCO), 6.04 (1 H, s, $CH_2C{=}CHCO$), 6.48 (1 H, s, ArH), 11.2 (1 H, br, OH), and 11.6 (1 H, s, OH). 5,7-Dihydroxy-6-(2-methylbutyryl)-4-propylcoumarin (**9e**) was obtained as yellow needles, m.p. 209—211 °C (lit.,[2a] 207—208 °C), $\nu_{max.}$(Nujol) 3 300, 2 950, 1 700, 1 640, and 1 620 cm^{-1}; $\lambda_{max.}$ 233infl., 282, and 325 (in base 233, 297, 268, and 397) nm; δ[$(CD_3)_2SO$] 0.92 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.0 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.18 (3 H, d, *J* 7 Hz, *Me*CH), 1.3—1.9 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.92 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 3.9 (1 H, m, CH_2CHCO), 6.0 (1 H, s, $CH_2C{=}CHCO$), and 6.44 (1 H, s, ArH), hydroxy-protons not discernible.

6- *and* 8-*Butyryl*-5,7-*dihydroxy*-4-*propylcoumarins* (**9f**) and (**10f**). These were prepared as a mixture (9.8 g, 63%) from butyrylphloroglucinol (10.6 g, 54 mmol) and ethyl 3-oxohexanoate (8.54 g, 54 mmol). Crystallisation afforded 6-butyryl-5,7-dihydroxy-4-propylcoumarin (**9f**) as yellow needles, m.p. 217—218 °C (lit.,[10] 218—218.5 °C), $\nu_{max.}$(Nujol) 3 300, 2 950, 1 700, 1 640, and 1 620 cm^{-1}; $\lambda_{max.}$ 236infl., 280, and 324 (in base 236, 294, 366, and 398) nm; δ[$(CD_3)_2SO$] 0.94 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.4—1.8 (4 H, m, 2 × $CH_3CH_2CH_2$), 2.76 (2 H, t, $CH_2C{=}CHCO$), 3.0 (2 H, m, CH_2CH_2CO), 5.7 (1 H, s, $CH_2C{=}CHCO$), and 6.08 (1 H, s, ArH); the hydroxy protons were not discernible. 8-Butyryl-5,7-dihydroxy-4-propylcoumarin (**10f**) was obtained as white needles, m.p. 236—238 °C (lit.,[10] 236—238 °C), $\nu_{max.}$(Nujol) 3 300, 2 950, 1 700, 1 640, and 1 610 cm^{-1}; $\lambda_{max.}$ 289 and 317 (in base 252 and 329) nm; δ[$(CD_3)_2SO$] 0.92 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.4—1.8 (4 H, m, 2 × $MeCH_2CH_2$), 2.74 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 2.88 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 6.72 (1 H, s, $CH_2C{=}CHCO$), and 6.06 (1 H, s, ArH); the hydroxy protons were not discernible.

5,7-*Dihydroxy*-6- *and* 8-(2-*methylpropionyl*)-4-*propylcoumarins* (**9g**) and (**10g**). These were prepared as a mixture (15.4 g, 69%) from (2-methylpropionyl)phloroglucinol (15 g, 76 mmol) and ethyl 3-oxohexanoate (12.1 g, 76 mmol). Crystallisation afforded 5,7-dihydroxy-8-(2-methylpropionyl)-4-propylcoumarin (**10g**) as white needles, m.p. 272—273 °C (lit.,[10] 273—274 °C), $\nu_{max.}$(Nujol) 3 200, 2 950, 1 685, 1 645, and 1 600 cm^{-1}; $\lambda_{max.}$ 290 and 316 (in base 253 and 329) nm; δ(C_5D_5N) 0.96 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.28 (6 H, d, *J* 7 Hz, Me_2CH), 1.5—1.8 (2 H, m, *J* 7 Hz, Me CH_2CH_2), 2.96 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 3.92 (1 H, m, Me_2CHCO), 5.96 (1 H, s, $CH_2C{=}CHCO$), and 6.36 (1 H, s, ArH); the hydroxy protons were not discernible. 5,7-Dihydroxy-6-(2-methylpropionyl)-4-propylcoumarin (**9g**) was obtained as yellow needles, m.p. 226—229 °C (lit.,[10] 235—237 °C), $\nu_{max.}$(Nujol) 3 290, 2 950, 1 705, and 1 625 cm^{-1}; $\lambda_{max.}$ 234infl., 281, and 325 (in base 236, 296, 366, and 400) nm; δ(C_5D_5N) 0.9 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.24 (6 H, d, *J* 7 Hz, Me_2CH), 1.3—1.7 (2 H, m, *J* 7 Hz, $MeCH_2CH_2$), 2.84 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 4.16 (1 H, m, *J* 7 Hz, Me_2CHCO), 5.88 (1 H, s, $CH_2C{=}CHCO$), 6.24 (1 H, s, ArH), and 13.5 (2 H, br s, 2 × OH).

5,7-*Dihydroxy*-6- *and* 8-(2-*methylbutyryl*)-4-*pentylcoumarins* (**9h**) and (**10h**). These were prepared as a mixture (22.5 g, 70%) from (2-methylbutyryl)phloroglucinol (15 g, 71 mmol) and ethyl 3-oxo-octanoate (13.2 g, 71 mmol). Crystallisation afforded 5,7-*dihydroxy*-8-(2-*methylbutyryl*)-4-*pentylcoumarin* (**10h**) as white needles, m.p. 218 °C [lit.,[4] 218—220 °C for coumarin (**1q**)], $\nu_{max.}$(Nujol) 3 200, 2 950, 1 680, and 1 630 cm^{-1}; $\lambda_{max.}$ 291 and 317 (in base 250 and 331) nm; δ[$(CD_3)_2SO$] 1.0 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.20 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—1.9 (8 H, m, $MeCH_2CH_2CH_2$ and $MeCH_2CH$), 3.0 (2 H, t, $CH_2C{=}CHCO$), 3.3 (1 H, m, CH_2CHCO), 6.04 (1 H, s, $CH_2C{=}CHCO$), and 6.46 (1 H, s, ArH); the hydroxy protons were not discernible. 5,7-*Dihydroxy*-6-(2-*methylbutyryl*)-4-*pentylcoumarin* (**9h**) was obtained as yellow needles, m.p. 196—197 °C (Found: C, 68.55; H, 7.55%; M^+, 332.1641. $C_{19}H_{24}O_5$ requires C, 68.65; H, 7.28%; *M*, 332.1624); $\nu_{max.}$(Nujol) 2 950, 1 700, and 1 610 cm^{-1}; $\lambda_{max.}$ 235infl., 282, and 325 (in base 235, 297, 370, and 404) nm; δ[$(CD_3)_2SO$] 0.95 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.10 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—1.9 (8 H, m, $MeCH_2CH_2CH_2$ and $MeCH_2CH$), 2.95 (2 H, t, $CH_2C{=}CHCO$), 3.82 (1 H, m, *J* 7 Hz, CH_2CHCO), 5.90 (1 H, s, $CH_2C{=}CHCO$), and 6.32 (1 H, s, ArH); the hydroxy protons not discernible; *m/z* 332 (M^+) and 275 (100%).

Preparation of 6- *and* 8-*Acyl*-5,7-*dihydroxy*-4-*phenylcoumarins*.—These coumarins were prepared using the method detailed above for 4-alkyl coumarins, with the following modification. It was found best to add the β-keto ester in three equal portions over 20 days. Separation of the isomers was achieved by column chromatography on silica gel, eluting with chloroform. Using this method the following coumarins were prepared:

5,7-*Dihydroxy*-6- *and* 8-(3-*methylbutyryl*)-4-*phenylcoumarins* (**9a**) and (**10a**). These were prepared as a mixture (3.6 g, 36%) from (3-methylbutyryl)phloroglucinol (6.1 g, 29 mmol) and ethyl benzoylacetate (5.6 g, 29 mmol). Chromatography afforded 5,7-dihydroxy-8-(3-methylbutyryl)-4-phenylcoumarin (**10a**) as white crystals, m.p. 200—202 °C from chloroform–light petroleum (b.p. 60—80 °C) (lit.,[2b] 196—197 °C) (Found: M^+, 338.1141. Calc. for $C_{20}H_{18}O_5$: *M*, 338.1154); $\nu_{max.}$(KBr) 3 250, 1 690, and 1 600 cm^{-1}; $\lambda_{max.}$ 290 and 326 (in base 251, 334,

and 389) nm; δ($CDCl_3$–CD_3OD) 1.04 (6 H, d, *J* 7 Hz, Me_2CH), 2.28 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 3.14 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 5.94 (1 H, s, PhC=C*H*CO), 6.12 (1 H, s, ArH), and 7.3 (5 H, m, ArH); the hydroxy protons were not discernible; and 5,7-dihydroxy-6-(3-methylbutyryl)-4-phenylcoumarin (**9a**) as yellow needles, m.p. 257—258 °C from chloroform–methanol (lit.,[2b] 244—245 °C) (Found: M^+, 338.1171. Calc. for $C_{20}H_{18}O_5$: *M*, 338.1154); $\nu_{max.}$(KBr) 3 100, 1 680, and 1 610 cm^{-1}; $\lambda_{max.}$ 280 and 333 (in base 290 and 412) nm; δ[$(CD_3)_2SO$] 0.96 (6 H, d, *J* 7 Hz, Me_2CH), 2.2 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 3.04 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 6.02 (1 H, s, PhC=C*H*CO), 6.58 (1 H, s, ArH), and 7.62 (5 H, m, ArH); the hydroxy protons were not discernible.

5,7-*Dihydroxy*-6- *and* 8-(2-*methylbutyryl*)-4-*phenylcoumarins* (**9b**) and (**10b**). These were prepared as a mixture (3.8 g, 35%) from (2-methylbutyryl)phloroglucinol (6.8 g, 32 mmol), and ethyl benzoylacetate (6.21 g, 32 mmol). Chromatography afforded 5,7-dihydroxy-8-(2-methylbutyryl)-4-phenylcoumarin (**10b**) as white plates, m.p. 222—224 °C from chloroform–light petroleum (b.p. 60—80 °C) (lit.,[2b] 210—211 °C) (Found: M^+, 338.1147. Calc. for $C_{20}H_{18}O_5$ *M*, 338.1154); $\nu_{max.}$(KBr) 3 250, 1 680, and 1 620 cm^{-1}; $\lambda_{max.}$ 290 and 328 (in base 252, 333, and 385) nm; δ[$(CD_3)_2SO$] 0.94 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.14 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.0 (2 H, m, $MeCH_2CH$), 3.25 (1 H, m, CH_2CHCO), 5.96 (1 H, s, PhC=C*H*CO), 6.36 (1 H, s, ArH), 7.5 (5 H, m, ArH), and 13.9 (2 H, br s, 2 × OH); and 5,7-dihydroxy-6-(2-methylbutyryl)-4-phenylcoumarin (**9b**) as yellow needles, m.p. 207—209 °C from chloroform–light petroleum (b.p. 60—80 °C) (lit.,[2b] 201—202 °C) (Found: M^+, 338.1141. Calc. for $C_{20}H_{18}O_5$ *M*, 338.1154), $\nu_{max.}$(KBr) 3 050, 1 690, and 1 600 cm^{-1}; $\lambda_{max.}$ 281 and 333 (in base 294 and 412) nm; δ[$(CD_3)_2SO$] 0.85 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.08 (3 H, d, *J* 7 Hz, MeCH), 1.2—1.9 (2 H, m, $MeCH_2CH$), 3.84 (1 H, m, CH_2CHCO), 5.94 (1 H, s, PhC=C*H*CO), 6.5 (1 H, s, ArH), and 7.5 (5 H, m, ArH); the hydroxy protons were not discernible.

5,7-*Dihydroxy*-6- *and* 8-(2-*methylpropionyl*)-4-*phenylcoumarin* (**9c**) and (**10c**). These were prepared as a mixture (2.75 g, 28%) from (2-methylpropionyl)phloroglucinol (3 g, 15.3 mmol) and ethyl benzoylacetate (2.94 g, 15.3 mmol). Chromatography afforded 5,7-dihydroxy-8-(2-methylpropionyl)-4-phenylcoumarin (**10c**) as white needles, m.p. 258—260 °C from chloroform–methanol (lit.,[10] 258—260 °C), $\nu_{max.}$(Nujol) 3 260, 1 690, and 1 630 cm^{-1}; $\lambda_{max.}$ 290 and 328 (in base 253, 333, and 386) nm; δ(C_5D_5N) 1.3 (6 H, d, *J* 7 Hz, Me_2CH), 3.96 (1 H, m, *J* 7 Hz, Me_2CHCO), 5.98 (1 H, s, PhC=C*H*CO), 6.30 (1 H, s, ArH), 7.15—7.4 (5 H, m, ArH), and 13.2 (2 H, br s, 2 × OH); and 5,7-dihydroxy-6-(2-methylpropionyl)-4-phenylcoumarin (**9c**) as yellow needles, m.p. 258—259 °C from chloroform–methanol (lit.,[10] 257—260 °C), $\nu_{max.}$(Nujol) 2 900 and 1 690 cm^{-1}; $\lambda_{max.}$ 282 and 328 (in base 298 and 408) nm; δ(C_5D_5N) 1.20 (6 H, d, *J* 7 Hz, Me_2CH), 4.10 (1 H, m, *J* 7 Hz, Me_2CHCO), 5.86 (1 H, s, PhC=C*H*CO), 6.28 (1 H, s, ArH), 7.22 (5 H, m, ArH), and 13.4 (2 H, br s, 2 × OH).

C-*Prenylation of* 6- *and* 8-*Acyl*-4-*aryl*- *or alkyl*-5,7-*dihydroxycoumarins*.—To the acylcoumarin (1 mol equiv.) in 10% aqueous potassium hydroxide (5 ml) stirred at 0 °C under an atmosphere of nitrogen was added dropwise 3-methylbut-2-enyl bromide (1 mol equiv.) over 1.5 h. After this time the solution was poured into dilute hydrochloric acid and the mixture extracted with ether. The ether extracts were combined, dried, and evaporated and the residue was chromatographed on a silica gel column eluting with chloroform to give initially some gum followed by the *C*-alkylated coumarin. Further elution with chloroform–methanol (20:1 v/v) gave some unchanged coumarin starting material. By this method the following coumarins were prepared:

Mammea A/AA (**1a**). This was prepared from 5,7-dihydroxy-6-(3-methylbutyryl)-4-phenylcoumarin (**9a**) (1 g, 2.96 mmol) as yellow needles (240 mg; 20%), m.p. 98—102 °C from hexane (lit.,[2b] 98—109 °C,[2f] 83—84 °C) (Found: M^+, 406.1176. Calc. for $C_{25}H_{26}O_5$: *M*, 406.1780); $\nu_{max.}$($CHCl_3$) 3 450, 2 950, 1 720, and 1 620 cm^{-1}; $\lambda_{max.}$ 283 and 337 (in base 299 and 392infl.) nm; δ($CDCl_3$) 0.9 (6 H, d, *J* 7 Hz, Me_2CH), 1.74 and 1.88 (6 H, 2 × s, Me_2C=CH), 2.16 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 2.84 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 3.52 (2 H, d, *J* 7 Hz, $ArCH_2CH$), 5.2 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH_2), 5.88 (1 H, s, PhC=C*H*CO), 7.3—7.6 (5 H, m, ArH), 9.8 and 11.2 (each 1 H, s, OH); *m*/*z* 406 (M^+, 85%), 363 (10), 351 (100), 349 (19), and 293 (50).

Mammea A/AB (**1b**). This was prepared from 5,7-dihydroxy-6-(2-methylbutyryl)-4-phenylcoumarin (**9b**) (1 g, 2.96 mmol) as yellow needles (248 mg, 21%), m.p. 109—110 °C from hexane (lit.,[2b] 107—108 °C) (Found: M^+, 406.1776. Calc. for $C_{25}H_{26}O_5$: *M*, 406.1780); $\nu_{max.}$($CHCl_3$) 3 500, 2 950, 1 730, and 1 630 cm^{-1}; $\lambda_{max.}$ 283 and 331 (in base 299 and 392infl.) nm; δ($CDCl_3$) 0.88 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.12 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—1.8 (2 H, m, $MeCH_2CH$), 1.80 and 1.94 (6 H, 2 × s, Me_2C=CH), 3.52—3.84 (3 H, m, $ArCH_2CH$ and CH_2CHCO), 5.4 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH_2), 6.08 (1 H, s, PhC=C*H*CO), 7.44—7.8 (5 H, m, ArH), and 10.1 and 11.2 (each 1 H, s, OH); *m*/*z* 406 (M^+, 52%), 351 (29), 349 (100), and 294 (28).

Mammea A/AD (**1d**). This was prepared from 5,7-dihydroxy-6-(2-methylpropionyl)-4-phenylcoumarin (**9c**) (1 g, 3.1 mmol) as bright yellow needles (240 mg, 20%), m.p. 146—148 °C from hexane (lit.,[6a] 154 °C) (Found: C, 73.25; H, 6.35%; M^+, 392.1614. Calc. for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16%; *M*, 392.1623), $\nu_{max.}$($CHCl_3$) 3 450, 1 730, and 1 630 cm^{-1}; $\lambda_{max.}$ 284 and 338 (in base 299 and 392infl.) nm; δ($CDCl_3$) 1.10 (6 H, d, *J* 7 Hz, Me_2CH), 1.74 and 1.88 (6 H, 2 × s, Me_2C=CH), 3.54 (2 H, d, *J* 7 Hz, $ArCH_2CH$), 3.72 (1 H, m, *J* 7 Hz, Me_2CHCO), 5.22 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH_2), 5.90 (1 H, s, PhC=C*H*CO), 7.2—7.5 (5 H, m, ArH), and 9.84 and 10.90 (each 1 H, s, OH); *m*/*z* 392 (M^+, 35%), 349 (75), 337 (18), and 293 (100).

Mammea A/BA (**1e**). This was prepared from 5,7-dihydroxy-8-(3-methylbutyryl)-4-phenylcoumarin (**10a**) (0.75 g, 2.2 mmol) as white needles (200 mg, 22%), m.p. 123—125 °C from hexane (lit.,[2b] 125—126 °C) (Found: M^+, 406.1802. Calc. for $C_{25}H_{26}O_5$: *M*, 406.1780); $\nu_{max.}$($CHCl_3$) 3 500, 2 950, 1 730, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$ 294 and 333 (in base 260, 339, and 385infl.) nm; δ($CDCl_3$) 1.05 (6 H, d, *J* 7 Hz, Me_2CH), 1.60 and 1.68 (6 H, 2 × s, Me_2C=CH), 1.28 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 3.12 (2 H, d, *J* 7 Hz, $CHCH_2CO$), 3.24 (2 H, d, *J* 7 Hz, $ArCH_2CH$), 5.04 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH_2), 5.84 (1 H, s, PhC=C*H*CO), 5.98 (1 H, s, non-chelated OH), 7.2—7.5 (5 H, m, ArH), and 14.12 (1 H, s, chelated OH); *m*/*z* 406 (M^+, 83%), 363 (64), 351 (100), 349 (33), and 293 (100).

Mammea A/BB (**1f**). This was prepared from 5,7-dihydroxy-8-(2-methylbutyryl)-4-phenylcoumarin (**10b**) (1 g, 2.96 mmol) as white needles (250 mg; 21%), m.p. 111—112 °C from hexane (lit.,[2b] 124—125 °C) (Found: C, 73.95; H, 6.6%; M^+, 406.1796. Calc. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45%; *M*, 406.1780); $\nu_{max.}$($CHCl_3$) 3 500, 2 950, 1 740, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$ 293 and 331 (in base 256, 338, and 385infl.) nm; δ($CDCl_3$) 1.02 (3 H, t, *J* 7 Hz, $MeCH_2$), 1.28 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.0 (2 H, m, $MeCH_2CH$), 1.66 and 1.72 (6 H, 2 × s, Me_2C=CH), 3.34 (2 H, d, *J* 7 Hz, $ArCH_2CH$), 4.0 (1 H, m, CH_2CHCO), 5.18 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH_2), 6.04 (2 H, s, PhC=C*H*CO and non-chelated OH), 7.4—7.7 (5 H, m, ArH), and 14.6 (1 H, s, chelated OH); *m*/*z* 406 (M^+, 87%), 363 (20), 351 (43), 349 (100), and 294 (39).

Mammea A/BD (**1g**). This was prepared from 5,7-dihydroxy-8-(2-methylpropionyl)-4-phenylcoumarin (**10c**) (1.75 g, 5.4 mmol) by the general procedure but using 9 ml of 10% aqueous potassium hydroxide, as white needles (421 mg, 20%),

m.p. 169—171 °C from hexane–chloroform (lit.,[6a] 171 °C) (Found: C, 73.8; H, 6.45%; M^+, 392.1610. Calc. for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16%; *M*, 392.1623); $\nu_{max.}$(CHCl$_3$) 3 500, 1 730, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$ 294 and 333 (in base 260, 338, and 385infl.) nm; δ(CDCl$_3$) 1.26 (6 H, d, *J* 7 Hz, Me_2CH), 1.62 and 1.68 (6 H, 2 × s, Me_2C=CH), 3.22 (2 H, d, *J* 7 Hz, ArCH_2CH), 4.0 (1 H, m, *J* 7 Hz, Me_2C*H*CO), 5.0 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 5.92 (2 H, s, PhC=C*H*CO and non-chelated OH), 7.25—7.5 (5 H, m, ArH), and 14.4 (1 H, s, chelated OH); *m/z* 392 (M^+, 33%), 349 (80), 337 (20), and 293 (100).

Mammea B/AA (**1h**). This was prepared from 5,7-dihydroxy-6-(3-methylbutyryl)-4-propylcoumarin (**9d**) (1 g, 3.3 mmol) as yellow needles (270 mg, 22%), m.p. 119—120 °C from hexane (lit.,[2d] 119—121 °C) (Found: M^+, 372.1949. Calc. for $C_{22}H_{28}O_5$: *M*, 372.1937); $\nu_{max.}$(CHCl$_3$) 3 300, 2 950, 1 710, and 1 620 cm^{-1}; $\lambda_{max.}$ 285 and 325 (in base 239 and 301) nm; δ(CDCl$_3$) 0.98 (6 H, d, *J* 7 Hz, Me_2CH), 1.02 (3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.24—1.90 (2 H, m, MeCH_2CH$_2$), 1.80 and 1.88 (6 H, 2 × s, Me_2C=CH), 2.36 (1 H, m, Me_2C*H*CH$_2$), 2.96 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.0 (2 H, d, *J* 7 Hz, CHCH_2CO), 3.54 (2 H, d, *J* 7 Hz, ArCH_2CH), 5.16 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 5.90 (1 H, s, CH$_2$=C*H*CO), 7.2 (1 H, br, non-chelated OH), and 15.1 (1 H, s, chelated OH); *m/z* 372 (M^+, 80%), 329 (5), 317 (100), 315 (9), and 259 (11).

Mammea B/AB (**1i**). This was prepared from 5,7-dihydroxy-6-(2-methylbutyryl)-4-propylcoumarin (**9e**) (6.8 g, 22.4 mmol) as yellow needles (1.8 g, 22%), m.p. 97—100 °C (lit.,[2d] 98—100 °C) (Found: M^+, 372.1928. Calc. for $C_{22}H_{28}O_5$: *M*, 372.1937); $\nu_{max.}$(CHCl$_3$) 3 300, 3 000, 1 730, and 1 620 cm^{-1}; $\lambda_{max.}$ 285 and 324 (in base 239 and 302) nm; δ(CDCl$_3$) 0.96 and 1.04 (each 3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.20 (3 H, d, *J* 7 Hz, *Me*CH), 1.4—1.9 (4 H, m, MeCH_2CH$_2$ and MeCH_2CH), 1.84 and 1.92 (6 H, 2 × s, Me_2C=CH), 3.02 (2 H, t, *J* 7 Hz CH_2C=CHCO), 3.54 (2 H, d, *J* 8 Hz, ArCH_2CH), 3.9 (1 H, m, *J* 7 Hz, CH$_2$C*H*CO), 5.30 (1 H, t, *J* 8 Hz, Me_2C=C*H*CH$_2$), 6.04 (1 H, s, CH$_2$C=C*H*CO), 7.14 (1 H, s, non-chelated OH), and 15.2 (1 H, s, chelated OH); *m/z* 372 (M^+, 50%), 329 (6), 317 (35), 315 (100), and 259 (50).

Mammea B/AC (**1j**). This was prepared from 6-butyryl-5,7-dihydroxy-4-propylcoumarin (**9f**) (1 g, 3.45 mmol) as yellow needles (300 mg, 25%), m.p. 127—128 °C from hexane (lit.,[2d] 127—128.5 °C) (Found: M^+, 358.1800. Calc. for $C_{21}H_{26}O_5$: *M*, 358.1780); $\nu_{max.}$(CHCl$_3$) 3 500, 3 050, 1 720, 1 630, and 1 600 cm^{-1}; $\lambda_{max.}$ 284 and 325 (in base 239 and 300) nm; δ(CDCl$_3$) 1.0 (6 H, t, *J* 7 Hz, 2 × *Me*CH$_2$), 1.4—1.9 (4 H, m, 2 × MeCH_2CH$_2$), 1.76 and 1.84 (6 H, 2 × s, Me_2C=CH), 2.9 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.06 (2 H, t, *J* 7 Hz, CH$_2$CH_2CO), 3.48 (2 H, d, *J* 7 Hz, ArCH_2CH), 5.08 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 5.8 (1 H, s, CH$_2$=C*H*CO), 7.06 (1 H, s, non-chelated OH), and 14.8 (1 H, s, chelated OH); *m/z* 358 (M^+, 75%), 315 (22), 303 (100), and 259 (27).

Mammea B/AD (**1k**). This was prepared from 5,7-dihydroxy-6-(2-methylpropionyl)-4-propylcoumarin (**9g**) (1 g, 3.45 mmol) as yellow crystals (245 mg, 20%), m.p. 139—140 °C from hexane–chloroform (Found: C, 70.50; H, 7.6%; M^+, 358.1769. $C_{21}H_{26}O_5$ requires C, 70.37; H, 7.31%; *M*, 358.1780); $\nu_{max.}$ 3 300, 2 950, 1 710, and 1 620 cm^{-1}; $\lambda_{max.}$ 285 and 325 (in base 238 and 301) nm; δ(CDCl$_3$) 0.98 (3 H, t, *J* 7 Hz, *Me*CH$_2$) 1.16 (6 H, d, *J* 7 Hz, Me_2CH), 1.3—1.9 (2 H, m, MeCH_2CH$_2$), 1.74 and 1.8 (6 H, 2 × s, Me_2C=CH), 2.98 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.44 (2 H, d, *J* 7 Hz, ArCH_2CH), 3.8 (1 H, m, *J* 7 Hz, Me_2C*H*CO), 5.02 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 5.76 (1 H, s, CH$_2$=C*H*CO), 6.90 (1 H, s, non-chelated OH), and 14.7 (1 H, s, chelated OH); *m/z* 358 (M^+, 58%), 315 (100), 303 (46), and 259 (100).

Mammea B/BA (**1l**). This was prepared from 5,7-dihydroxy-8-(3-methylbutyryl)-4-propylcoumarin (**10d**) (1.8 g, 5.9 mmol) as white needles (0.5 g, 23%), m.p. 128—129 °C from hexane (lit.,[2a] 127 °C) (Found: M^+, 372.1950. Calc. for $C_{22}H_{28}O_5$: *M*, 372.1937); $\nu_{max.}$(CHCl$_3$) 3 350, 2 950, 1 720, and 1 610 cm^{-1}; $\lambda_{max.}$ 294 and 320infl. (in base 256 and 334) nm; δ(CDCl$_3$) 1.02 (3 H, t, *Me*CH$_2$), 1.06 (6 H, d, *J* 7 Hz, Me_2CH), 1.5—1.9 (2 H, m, MeCH_2CH$_2$), 1.86 and 1.92 (6 H, 2 × s, Me_2C=CH), 2.30 (1 H, m, Me_2C*H*CH$_2$), 2.98 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.20 (2 H, d, *J* 7 Hz, CHCH_2CO), 3.56 (2 H, d, *J* 7 Hz, ArCH_2CH), 5.34 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 6.10 (1 H, s, CH$_2$C=C*H*CO), 7.04 (1 H, br s, non-chelated OH), and 14.85 (1 H, s, chelated OH); *m/z* 372 (M^+, 100%), 329 (24), 317 (70), 315 (30), and 259 (37).

Mammea B/BB (**1m**). This was prepared from 5,7-dihydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) (4.15 g, 13.7 mmol) as white needles (1.48 g, 29%), m.p. 121—122 °C from hexane (lit.,[2a] 122 °C) (Found: M^+, 372.1927. Calc. for $C_{22}H_{28}O_5$: *M*, 372.1937); $\nu_{max.}$ 3 350, 2 950, 1 720, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$ 294 and 320infl. (in base 255 and 333) nm; δ(CDCl$_3$) 1.0 and 1.04 (each 3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.28 (3 H, d, *J* 7 Hz, *Me*CH), 1.4—2.0 (4 H, m, MeCH_2CH$_2$ and MeCH_2CH), 1.84 and 1.92 (6 H, 2 × s, Me_2C=CH), 3.0 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.56 (2 H, d, *J* 7 Hz, ArCH_2CH), 4.0 (1 H, m, *J* 7 Hz, CH$_2$C*H*CO), 5.30 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 6.10 (1 H, s, CH$_2$C=C*H*CO), 7.12 (1 H, s, non-chelated OH), and 14.7 (1 H, s, chelated OH); *m/z* 372 (M^+, 100%), 317 (24), 316 (75), 315 (100), and 259 (61).

On one occasion a yellow gum was isolated (1%), along with mammea B/BB, and identified as 5,7-*dihydroxy*-3,6-*bis*(3-*methylbut*-2-*enyl*)-8-(2-*methylbutyryl*)-4-*propylcoumarin* (**11**) (Found: M^+, 440.2575. $C_{27}H_{36}O_5$ requires *M*, 440.2563); $\nu_{max.}$ 3 350, 2 950, 1 700, and 1 600 cm^{-1}; $\lambda_{max.}$ 299 and 321infl. (in base 253 and 341) nm; δ(CDCl$_3$) 1.0 and 1.08 (each 3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.28 (3 H, d, *J* 7 Hz, *Me*CH), 1.3—1.9 (4 H, m, MeCH_2CH$_2$ and MeCH_2CH), 1.76, 1.84, and 1.92 (12 H, 3 × s, 2 × Me_2C=CH), 3.02 (2 H, t, *J* 7 Hz, CH_2C=CCO), 3.36 (2 H, d, *J* 7 Hz, CHCH_2CCO), 3.52 (2 H, d, *J* 7 Hz, ArCH_2CH), 3.96 (1 H, m, CH$_2$C*H*CO), and 5.0—5.2 (2 H m, 2 × Me_2C=C*H*CH$_2$); the hydroxy protons were not discernible; *m/z* 440 (M^+, 100%), 385 (27), 384 (22), 383 (40), 355 (7), 329 (12), and 327 (9).

Mammea B/BC (**1n**). This was prepared from 8-butyryl-5,7-dihydroxy-4-propylcoumarin (**10f**) (3.2 g, 11 mmol) as white needles (1.26 g, 32%), m.p. 132—134 °C from hexane (lit.,[2a] 132—133 °C) (Found: M^+, 358.1801. Calc. for $C_{21}H_{26}O_5$: *M*, 358.1780); $\nu_{max.}$(CHCl$_3$) 3 350, 2 950, 1 720, and 1 610 cm^{-1}; $\lambda_{max.}$ 294 and 321infl. (in base 256 and 333) nm; δ(CDCl$_3$) 0.96 and 0.98 (each 3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.35—1.9 (4 H, m, 2 × MeCH_2CH$_2$), 1.74 and 1.80 (6 H, 2 × s, Me_2C=CH), 2.82 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.14 (2 H, t, *J* 7 Hz, CH$_2$CH_2CO), 3.36 (2 H, d, *J* 7 Hz, ArCH_2CH), 5.04 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 6.0 (1 H, s, CH$_2$C=C*H*CO), 7.0 (1 H, br s, non-chelated OH), and 14.6 (1 H, s chelated OH); *m/z* (M^+, 85%), 315 (75), 303 (100), 302 (27), and 259 (60).

Mammea B/BD (**1o**). This was prepared from 5,7-dihydroxy-8-(2-methylpropionyl)-4-propylcoumarin (**10g**) (1 g, 3.45 mmol) as white crystals (245 mg, 20%), m.p. 119—120 °C from hexane–chloroform (Found: C, 70.45; H, 7.65%; M^+, 358.1766. $C_{21}H_{26}O_5$ requires C, 70.37; H, 7.31%; *M*, 358.1780); $\nu_{max.}$(CHCl$_3$) 3 300, 2 950, 1 720, and 1 600 cm^{-1}; $\lambda_{max.}$ 295 and 320 (in base 256 and 333) nm; δ(CDCl$_3$) 0.96 (3 H, t, *J* 7 Hz, *Me*CH$_2$), 1.22 (6 H, d, *J* 7 Hz, Me_2CH), 1.4—1.9 (2 H, m, MeCH_2CH$_2$), 1.76 and 1.82 (6 H, 2 × s, Me_2C=CH), 2.84 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.36 (2 H, d, *J* 7 Hz, ArCH_2CH), 4.02 (1 H, m, *J* 7 Hz, Me_2C*H*CO), 5.20 (1 H, t, *J* 7 Hz, Me_2C=C*H*CH$_2$), 6.0 (1 H, s, CH$_2$C=C*H*CO), 7.0 (1 H, s, non-chelated OH), and 14.0 (1 H, s, chelated OH); *m/z* 358 (M^+, 100%), 315 (100), 303 (55), 302 (30), and 257 (97).

Mammea C/BB (**1r**). This was prepared from 5,7-dihydroxy-8-(2-methylbutyryl)-4-pentylcoumarin (**10h**) (1 g, 3 mmol) as white needles (225 mg, 19%), m.p. 85—86 °C from hexane (lit.,[8]

81—83 °C,[2a] 100—101 °C) (Found: M^+, 400.2257. Calc. for $C_{24}H_{32}O_5$: M, 400.2250); $\nu_{max.}$($CHCl_3$) 3 300, 2 950, 1 710, and 1 600 cm^{-1}; $\lambda_{max.}$ 295 and 320infl. (in base 256 and 333) nm; δ($CDCl_3$) 0.98 (6 H, t, J 7 Hz, 2 × $MeCH_2$), 1.26 (3 H, d, J 7 Hz, $MeCH$), 1.2—1.8 (8 H, m, $MeCH_2CH_2CH_2$ and $MeCH_2CH$), 1.84 and 1.88 (6 H, 2 × s, Me_2C=CH), 2.96 (2 H, t, J 7 Hz, CH_2C=CHCO), 3.52 (2 H, d, J 7 Hz, $ArCH_2CH$), 3.94 (1 H, m, J 7 Hz, CH_2CHCO), 5.28 (1 H, t, J 7 Hz, Me_2C=$CHCH_2$), 6.06 (1 H, s, CH_2C=$CHCO$), 6.96 (1 H, s, non-chelated OH), and 14.7 (1 H, s, chelated OH); m/z 400 (M^+, 18%), 343 (100), 287 (20), and 259 (2).

Mammea C/AB (**1s**). This was prepared from 5,7-dihydroxy-6-(2-methylbutyryl)-4-pentylcoumarin (**9h**) (1 g, 3 mmol) as yellow crystals (225 mg, 19%), m.p. 78—80 °C from hexane (Found: C, 71.8; H, 8.3%; M^+, 400.2258. $C_{24}H_{32}O_5$ requires C, 72.00; H, 8.00%; M, 400.2250); $\nu_{max.}$($CHCl_3$) 3 300, 2 950, 1 720, and 1 620 cm^{-1}; $\lambda_{max.}$ 284 and 322 (in base 239 and 302) nm; δ($CDCl_3$) 0.90 (6 H, t, J 7 Hz, 2 × $MeCH_2$), 1.16 (3 H, d, J 7 Hz, $MeCH$), 1.2—1.8 (8 H, m, $MeCH_2CH_2CH_2$ and $MeCH_2CH$), 1.70 and 1.80 (6 H, 2 × s, Me_2C=CH), 2.88 (2 H, t, J 7 Hz, CH_2C=CHCO), 3.42 (2 H, d, J 7 Hz, $ArCH_2CH$), 3.66 (1 H, m, J 7 Hz, CH_2CHCO), 5.02 (1 H, t, J 7 Hz, Me_2C=$CHCH_2$), 5.72 (1 H, s, CH_2C=$CHCO$), 7.0 (1 H, br s, non-chelated OH), and 14.30 (1 H, s, chelated OH); m/z 400 (M^+, 75%), 343 (100), and 287 (33).

The gum eluted from the chromatography column before mammea C/AB was further separated by preparative t.l.c., developing with chloroform, to give a yellow gum (75 mg, 6%) identified as the *pyrone* (**12**) or its 5-hydroxy-7-keto tautomer (Found: M^+, 468.2851. $C_{29}H_{40}O_5$ requires M, 468.2876); $\nu_{max.}$($CHCl_3$) 1 740 and 1 660 cm^{-1}; $\lambda_{max.}$ 270 and 284 (in base 246, 253, and 308) nm; δ (250 MHz; $CDCl_3$) 0.95 (6 H, t, J 7 Hz, 2 × $MeCH_2$) 1.20 (3 H, dd, J 3 and 7 Hz, $MeCH$), 1.3—1.9 (8 H, m, $MeCH_2CH_2CH_2$ and $MeCH_2CH$), 1.55 (12 H, s, 2 × Me_2 C=CH), 2.7—3.1 (2 H, m, CH_2C=CHCO), 2.85 (4 H, d, J 7 Hz, 2 × MeC = $CHCH_2$), 3.95 (1 H, m, J 7 Hz, CH_2CHCO), 4.7 (2 H, t, J 7 Hz, 2 × Me_2C=$CHCH_2$), 6.05 (1 H, s, CH_2C=$CHCO$), and 18.5 (1 H, s, chelated OH); m/z 468 (M^+, 7%), 400 (100), 399 (55), 357 (40), 343 (45), and 287 (18).

C-Prenylation in 2,2,2-Trifluoroethanol.—Potassium hydroxide (400 mg, 6.9 mmol) in dry methanol was added to a stirred suspension of 6-butyryl-5,7-dihydroxy-4-propylcoumarin (**9f**) (1 g, 3.45 mmol) in dry methanol (10 ml) under nitrogen. The clear yellow solution was evaporated to dryness under reduced pressure (bath temperature 0 °C). To the residue in 2,2,2-trifluoroethanol (9 ml) at 0 °C and under nitrogen was added 3-methylbut-2-enyl bromide (0.51 g, 3.45 mmol), stirring was continued for 1.5 h, and the solution was then poured into dilute hydrochloric acid. The mixture was extracted with ether and the combined organic extracts were dried and evaporated to leave a residue that was chromatographed on a column of silica gel. Elution with light petroleum (b.p. 40—60 °C)–chloroform afforded mammea B/AC (**1j**) (250 mg; 20%), m.p. 127—129 °C, identical with other samples of synthetic mammea B/AC (see earlier).

Surangin A (**1p**).—A stirred solution of 5,7-hydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) (1 g, 33 mmol) in 10% aqueous potassium hydroxide (3.7 ml, 6.6 mmol) was maintained at 40—45 °C under nitrogen for 24 h, during which time (2*E*)-3,7-dimethylocta-2,6-dienyl chloride (0.57 g, 3.3 mmol) was added dropwise. The mixture was allowed to cool, poured into dilute hydrochloric acid–ice, and extracted with ether. The combined organic extracts were dried and evaporated to dryness. The residue was suspended in chloroform (10 ml) and filtered to remove unchanged starting material (**10e**) (0.5 g, 50%). The filtrate was evaporated and the residue chromatographed on a silica gel column eluting with light petroleum (b.p. 60—80 °C)–chloroform (1 : 1 v/v) to give the 6,6-*bis*(*geranylated*) *pyrone* (**13**) (100 mg, 5%) as a yellow gum (Found: M^+, 576.3797. $C_{37}H_{52}O_5$ requires M, 576.3814); $\nu_{max.}$($CHCl_3$) 2 950, 1 740, 1 660, and 1 600 cm^{-1}; $\lambda_{max.}$ 295, 299, and 347 (in base 240, 312, and 403) nm; δ (250 MHz; $CDCl_3$) 1.0 and 1.05 (each 3 H, t, $MeCH_2$), 1.25 (3 H, d, J 7 Hz, $MeCH$), 1.50, 1.55, and 1.60 (18 H, 3 × s, 2 × Me_2C and 2 × MeC=CH), 1.3—2.0 (12 H, m, $MeCH_2CH_2$, $MeCH_2CH$, and 2 × $CHCH_2CH_2CMe$), 2.75 (4 H, d, J 7 Hz, 2 × C=$CHCH_2$), 2.90 (2 H, t, J 7 Hz, CH_2C=CHCO), 3.75 (1 H, m, J 7 Hz, CH_2CHCO), 4.80 (2 H, t, J 7 Hz, 2 × CH_2CH=CMe), 4.95 (2 H, m, 2 × CH_2CH=CMe_2), 5.9 (1 H, s, CH_2=$CHCO$), and 19.0 (1 H, s, chelated OH); m/z 576 (M^+, 1%), 507 (1), 440 (80), 439 (100), 421 (2), 383 (19), 371 (81), and 317 (59). Later fractions gave, on evaporation, a yellow gum (200 mg) that was separated by reverse-phase h.p.l.c., eluting with methanol–water (4 : 1 v/v), to afford *surangin A* (**1p**) as a pale yellow gum that crystallised from hexane as a white solid (101 mg, 7%), m.p. 81—82 °C (lit.,[5] 85 °C) (Found: M^+, 440.2568. Calc. for $C_{27}H_{36}O_5$: M, 440.2562); $\nu_{max.}$($CHCl_3$) 3 325, 2 950, 1 720, and 1 600 cm^{-1}; $\lambda_{max.}$ 294 and 317 (in base 256 and 332) nm; δ (250 MHz; $CDCl_3$) 1.0 and 1.02 (each 3 H, t, J 7 Hz, $MeCH_2$), 1.25 (3 H, d, J 7 Hz, $MeCH$), 1.6 and 1.7 (6 H, 2 × s, Me_2C=CH), 1.85 (3 H, s, MeC=$CHCH_2Ar$), 1.4—2.0 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.15 (4 H, m, $CHCH_2CH_2C$=CH), 2.95 (2 H, t, J 7 Hz, CH_2C=CHCO), 3.55 (2 H, d, J 7 Hz, $ArCH_2CH$), 3.95 (1 H, m, J 7 Hz, CH_2CHCO), 5.05 (1 H, m, Me_2C=$CHCH_2$), 5.25 (1 H, t, J 7 Hz, CH_2C=$CHCH_2$), 6.05 (1 H, s, CH_2C=$CHCO$), 6.9 (1 H, s, non-chelated OH), and 14.65 (1 H, s, chelated OH); m/z 440 (M^+, 50%), 383 (100), 371 (25), 355 (30), 317 (90), and 259 (40). Synthetic surangin A was identical (mixed m.p., u.v., n.m.r., t.l.c.) with a sample of the natural material kindly supplied by Dr. T. Govindachari. Also isolated from the h.p.l.c. separation was 7-*hydroxy*-8-(2-*methylbutyryl*)-5-[(2E)-3,7-*dimethylocta*-2,6-*dienyloxy*]-4-*propylcoumarin* (**14**) which crystallised from hexane as white needles (85 mg, 6%), m.p. 54—55 °C (Found: C, 74.0; H, 8.05%; M^+, 440.2564. $C_{27}H_{36}O_5$ requires C, 73.61; H, 8.24%; M, 440.2562); $\nu_{max.}$($CHCl_3$) 2 950, 1730, and 1 620 cm^{-1}; $\lambda_{max.}$ 289 and 318 (in base 236 and 377) nm; δ (250 MHz; $CDCl_3$) 1.0 (6 H, t, J 7 Hz, $MeCH_2CH_2$ and $MeCH_2CH$), 1.25 (3 H, d, J 7 Hz, $MeCH$), 1.65, 1.70, and 1.75 (9 H, 3 × s, Me_2C=CH and CH_2CMe), 1.4—2.0 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.15 (4 H, s, $CHCH_2CH_2C$=CH), 2.90 (2 H, t, J 7 Hz, CH_2C=CHCO), 3.95 (1 H, m, J 7 Hz, CH_2CHCO), 4.65 (2 H, d, J 7 Hz, $CHCH_2O$), 5.1 (1 H, m, Me_2C=$CHCH_2$), 5.5 (1 H, t, J 7 Hz, C=$CHCH_2O$), 6.0 (1 H, s, CH_2C=$CHCO$), 6.35 (1 H, s, ArH), and 14.25 (1 H, s, chelated OH); m/z 440 (M^+, 3%), 334 (5), 304 (75), and 247 (100). Another reaction on the same scale as above was heated at 80—85 °C overnight before work-up to give a residue that was chromatographed on a silica gel column, eluting with hexane–chloroform (1 : 1 v/v) to afford bis(geranyl)pyrone (**13**) (153 mg, 8%), then a mixture (50 mg; 3%) of surangin A (**1p**) and the 5-*O*-geranyl isomer (**14**), and lastly unchanged starting material (0.43 g, 43%).

In a further experiment potassium hydroxide (370 mg, 6.6 mmol) in dry methanol was added to a stirred suspension of the 8-acylcoumarin (**10e**) (1 g, 3.3 mmol) in dry methanol (5 ml) under nitrogen. The solution was evaporated to dryness under reduced pressure (bath temperature <0 °C). To the residue in 2,2,2-trifluoroethanol (10 ml) stirred at 45 °C under nitrogen was added (2*E*)-3,7-dimethylocta-2,6-dienyl chloride (0.57 g, 3.3 mmol) in three equal portions over 18 h. The solution was evaporated to dryness and the residue partitioned between ether and dilute hydrochloric acid. The aqueous layer was further extracted with ether and the combined ether extracts were dried and evaporated. The residue was suspended in chloroform (10

ml) and filtered to remove unchanged starting material (0.5 g, 50%). The filtrate was evaporated and the residue chromatographed on a silica gel column eluting with light petroleum (b.p. 60—80 °C)–chloroform (1:1 v/v) to give a complex mixture of *O*- and *C*-alkylated coumarins as a pale yellow gum (240 mg). Further elution with chloroform–methanol (49:1 v/v) gave 5,7-dihydroxy-6-(2-methylbutyryl)-4-propylcoumarin (**9e**) (150 mg, 15%) identical to an authentic sample (see earlier).

O-Alkylation with 3-Chloro-3-methylbut-1-yne.—To 5,7-dihydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) (1 g, 3.3 mmol) in dry ethyl methyl ketone (20 ml) were added 3-chloro-3-methylbut-1-yne (0.34 g, 3.3 mmol), anhydrous potassium carbonate (0.48 g, 3.5 mmol), and potassium iodide (30 mg), and the mixture was heated at reflux overnight. The cooled solution was partitioned between dilute hydrochloric acid and ether, the aqueous layer was further extracted with ether, and the combined ether extracts were dried and evaporated to low volume. Unchanged starting material (0.64 g, 64%) was removed by filtration and the residue obtained on evaporation of the filtrate was separated by preparative t.l.c., developing with chloroform, into two crystalline components. The fraction with lower R_F was identified as further unchanged starting material, whilst that with higher R_F was mammea B/BB cyclo D (**3b**) (70 mg, 6%), m.p. 92—95 °C (lit.,[10] 93—95 °C), identical (mixed m.p., i.r., u.v., n.m.r.) with an authentic sample of mammea B/BB cyclo D. When dry acetone (40 ml) was substituted for ethyl methyl ketone as the reaction solvent, only unchanged starting material was isolated.

7-Hydroxy-8-(2-methylbutyryl)-5-(prop-2-enyloxy)-4-propylcoumarin (**15**).—To 5,7-dihydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) (0.5 g, 1.65 mmol) in dry acetone (30 ml) was added allyl bromide (0.2 g, 1.65 mmol), anhydrous potassium carbonate (2.5 mol equiv.), and a catalytic quantity of potassium iodide, and the mixture was heated at reflux overnight. The cooled solution was partitioned between dilute hydrochloric acid and ether, the aqueous layer was further extracted with ether, and the combined ether extracts were dried and evaporated. Column chromatography of the residue on silica, eluting with chloroform, gave *7-hydroxy-8-(2-methylbutyryl)-5-(prop-2-enyloxy)-4-propylcoumarin* (**15**) as white needles from hexane–chloroform, m.p. 95—96 °C (Found: C, 69.75; H, 7.15%; M^+, 344.1606. $C_{20}H_{24}O_5$ requires C, 69.77; H, 6.98%; *M*, 344.1624); $\nu_{max.}$($CHCl_3$) 1 730 and 1 620 cm^{-1}; $\lambda_{max.}$ 288 and 319 (in base 235 and 369) nm; δ($CDCl_3$) 1.05 (6 H, t, *J* 7 Hz, *Me*CH_2CH_2 and *Me*CH_2CH), 1.15 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.1 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 2.95 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.95 (1 H, m, *J* 7 Hz, CH_2CHCO), 4.70 (2 H, d, *J* 6 Hz, CHCH_2O), 5.5 (2 H, m, CH_2=CHCH_2O), 6.0 (1 H, s, CH_2C=CHCO), 5.9—6.3 (1 H, m, CH_2=CHCH_2O), 6.4 (1 H, s, ArH), and 14.20 (1 H, s, chelated OH); *m/z* 344 (M^+, 40%), 303 (62), 287 (100), and 259 (14).

2,3-Dihydro-4-hydroxy-2-methyl-5-(2-methylbutyryl)-9-propylfuro[2,3-f][1]*benzopyran-7-one* (**16a**).—7-Hydroxy-8-(2-methylbutyryl)-5-(prop-2-enyloxy)-4-propylcoumarin (**15**) (1 g, 2.9 mmol) was heated at reflux in *N,N*-dimethylaniline under nitrogen for 24 h. The cooled mixture was partitioned between ether and dilute hydrochloric acid, the aqueous layer was further extracted with ether, and the combined ether extracts were dried and evaporated. The residue crystallised from hexane–chloroform to afford *2,3-dihydro-4-hydroxy-2-methyl-5-(2-methylbutyryl)-9-propylfuro*[2,3-f][1]*benzopyran-7-one* (**16a**) (0.65 g, 65%) as white needles, m.p. 100—102 °C (Found: C, 69.75; H, 7.35%; M^+, 344.1624. $C_{20}H_{24}O_5$ requires C, 69.75; H, 7.02%; *M*, 344.1609); $\nu_{max.}$($CHCl_3$) 1 730, 1 630, and 1 600 cm^{-1}; $\lambda_{max.}$ 296 (in base 240 and 376) nm; (250 MHz; $CDCl_3$) 1.0 and 1.05 (each 3 H, t, *J* 7 Hz, *Me*CH_2), 1.25 (3 H, d, *J* 7 Hz, *Me*$CHCH_2$), 1.4—2.0 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 1.55 (3 H, d, *J* 6 Hz, *Me*CHO), 2.8 (1 H, dd, *J* 7 and 15 Hz, ArC*H*CHO), 2.8 (2 H, m, *J* 7 Hz, CH_2C=CHCO), 3.35 (1 H, dd, *J* 9 and 15 Hz, ArC*H*CHO), 3.9 (1 H, m, *J* 7 Hz, CH_2CHCO), 5.2 (1 H, m, CH_2CHO), 6.0 (1 H, s, CH_2C=CHCO), and 14.10 (1 H, s, chelated OH); *m/z* 344 (M^+, 62%), 287 (100), and 259 (20).

2,3-Dihydro-2,4-dihydroxy-5-(2-methylbutyryl)-9-propylfuro[2,3-f][1]*benzopyran-7-one* (**16b**).—Synthetic mammea B/BB (**1m**; see earlier) (0.75 g, 2.0 mmol), sodium periodate (1.28 g, 6 mmol), and osmium tetraoxide (100 mg) were stirred in tetrahydrofuran–water (3:1 v/v; 50 ml) at 0 °C for 30 min and then at room temperature for 1.5 h. The solution was extracted with ether and the combined extracts were dried and evaporated. Chromatography of the residue on a silica column, eluting with hexane–chloroform (1:1 v/v) and then increasing proportions of chloroform (to 100%), gave white crystals of *2,3-dihydro-2,4-dihydroxy-5-(2-methylbutyryl)-9-propylfuro*[2,3-f][1]*benzopyran-7-one* (**16b**) (300 mg, 43%), m.p. 125 °C (Found: C, 65.65; H, 6.70%; M^+, 346.1418. $C_{19}H_{22}O_6$ requires C, 65.88; H, 6.40%; *M*, 346.1416); $\nu_{max.}$($CHCl_3$) 2 950, 1 730, 1 640, and 1 610 cm^{-1}; $\lambda_{max.}$ 296 and 327 (in base 256 and 333) nm; δ (250 MHz; $CDCl_3$) 0.95 and 1.0 (each 3 H, t, *J* 7 Hz, *Me*CH_2), 1.25 (3 H, dd, *J* 7 and 9 Hz, *Me*CH), 1.35—2.0 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 2.85 (2 H, m, *J* 7 Hz, CH_2C=CHCO), 3.10 (1 H, dd, *J* 2 and 16 Hz, ArC*H*CHOH), 3.40 (1 H, dd, *J* 7 and 16 Hz, ArC*H*CHOH), 3.9 (1 H, m, *J* 7 Hz, CH_2CHCO), 4.15 (1 H, br s, CHO*H*), 6.0 (1 H, d, *J* 2 Hz, CH_2C=CHCO), 6.3 (1 H, m, OC*H*OH), and 14.15 (1 H, s, chelated OH); *m/z* 346 (M^+, 12%), 289 (100), and 261 (13).

Mammea B/AB Cyclo D (**2e**).—5,7-Dihydroxy-6-(2-methylbutyryl)-4-propylcoumarin (**9e**) (1.5 g, 4.9 mmol) and 1,1-dimethoxy-3-methylbutan-3-ol[21] (4 g, 27 mmol) were stirred and heated to 160 °C in dry pyridine (2 ml) for 2 days. The mixture was allowed to cool and then chromatographed on a silica column, eluting with light petroleum (b.p. 60—80 °C)–chloroform, to give mammea B/AB cyclo D (**2e**) as pale yellow crystals (0.95 g, 52%), m.p. 97—98 °C from hexane (lit.,[15] 97—98.5 °C); $\nu_{max.}$($CHCl_3$) 1 730 and 1 620 cm^{-1}; $\lambda_{max.}$ 227, 287, and 333 (in base 248, 311, and 417) nm; δ($CDCl_3$) 0.92 and 1.0 (each 3 H, t, *J* 7 Hz, *Me*CH_2), 1.18 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.0 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 1.56 (6 H, s, Me_2C), 2.88 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.68 (1 H, m, *J* 7 Hz, CH_2CHCO), 5.48 (1 H, d, *J* 10 Hz, ArCH=C*H*) 5.84 (1 H, s, CH_2C=CHCO), 6.70 (1 H, d, *J* 10 Hz, ArC*H*=CH), and 14.95 (1 H, s, OH).

Mammea C/AB Cyclo D (**2i**).—This was prepared similarly from 5,7-dihydroxy-6-(2-methylbutyryl)-4-pentylcoumarin (**9h**) (1 g, 3 mmol) and 1,1-dimethoxy-3-methylbutan-3-ol (2 g, 13.5 mmol) in dry pyridine (1 ml) as bright yellow crystals (0.9 g, 75%), m.p. 113—115 °C from hexane (Found: C, 72.35; H, 7.85%; M^+, 398.2087. $C_{24}H_{30}O_5$ requires C, 72.34; H, 7.59%; *M*, 398.2093); $\nu_{max.}$($CHCl_3$) 1 720 and 1 610 cm^{-1}; $\lambda_{max.}$ 229, 287, and 328 (in base 249 and 311) nm; δ($CDCl_3$) 0.92 (6 H, t, *J* 7 Hz, 2 × *Me*CH_2), 1.18 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.0 (8 H, m, MeCH_2CH_2 and MeC$H_2CH_2CH_2$), 1.57 (6 H, s, Me_2C), 2.9 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.7 (1 H, m, *J* 7 Hz, CH_2CHCO), 5.52 (1 H, d, *J* 10 Hz, ArCH=C*H*), 5.88 (1 H, s, CH_2C=CHCO), 6.76 (1 H, d, *J* 10 Hz, ArC*H*=CH), and 15.15 (1 H, s, OH); *m/z* 398 (M^+, 98%), 383 (100), and 341 (45).

Mammea A/BB Cyclo D (**3a**).—This was prepared similarly from 5,7-dihydroxy-8-(2-methylbutyryl)-4-phenylcoumarin (**10b**) (1.4 g, 4.1 mmol) and 1,1-dimethoxy-3-methylbutan-3-ol

(4 g, 27 mmol) in dry pyridine (2 ml) as yellow crystals (1.3 g, 78%), m.p. 127—129 °C from hexane–chloroform (lit.,[10] 128.5—130 °C); $\nu_{max.}$($CHCl_3$) 1 730, 1 640, and 1 600 cm^{-1}; $\lambda_{max.}$ 263, 271, 311, and 385 (in base 263, 323, and 402) nm; δ($CDCl_3$) 1.0 (6 H, s, Me_2C), 1.04 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.32 (3 H, d, *J* 7 Hz, *Me*CH), 1.3—2.1 (2 H, m, MeCH_2CH), 4.0 (1 H, m, CH_2CHCO), 5.52 (1 H, d, *J* 11 Hz, ArCH=C*H*), 6.16 (1 H, s, PhC=C*H*CO), 6.76 (1 H, d, *J* 11 Hz, ArC*H*=CH), 7.3—7.6 (5 H, m, ArH), and 14.90 (1 H, s, OH).

Mammea B/BB Cyclo D (**3b**).—This was prepared similarly from 5,7-dihydroxy-8-(2-methylbutyryl)-4-propylcoumarin (**10e**) (1 g, 3.3 mmol) and 1,1-dimethoxy-3-methylbutan-3-ol (2 g, 13.5 mmol) in dry pyridine (1 ml) as pale yellow crystals (0.91 g, 75%), m.p. 94—96 °C from hexane–chloroform (lit.,[10] 93.5—95 °C), $\nu_{max.}$(KBr) 1 720 and 1 610 cm^{-1}; $\lambda_{max.}$ 264, 271, 304, and 377 (in base 245 and 392) nm; δ($CDCl_3$) 0.96 and 1.04 (each 3 H, t, *J* 7 Hz, *Me*CH_2), 1.24 (3 H, d, *J* 7 Hz, *Me*CH), 1.4—2.0 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 1.54 (6 H, s, Me_2C), 2.85 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.90 (1 H, m, *J* 7 Hz, MeC*H*CO), 5.52 (1 H, d, *J* 10 Hz, ArCH=C*H*), 5.85 (1 H, s, CH_2C=C*H*CO), 6.62 (1 H, d, *J* 10 Hz, ArC*H*=CH), and 14.1 (1 H, s, OH).

Mammea C/BB Cyclo D (**3c**).—This was prepared similarly from 5,7-dihydroxy-8-(2-methylbutyryl)-4-pentylcoumarin (**10h**) (1 g, 3 mmol) and 1,1-dimethoxy-3-methylbutan-3-ol (2 g, 13.5 mmol) in dry pyridine (1 ml) as yellow crystals (0.85 g, 71%), m.p. 79—80 °C from hexane (Found: C, 72.40; H, 7.85%; M^+, 398.2113. $C_{24}H_{30}O_5$ requires C, 72.34; H, 7.59%; *M*, 398.2093); $\nu_{max.}$($CHCl_3$) 1 730 and 1 610 cm^{-1}; $\lambda_{max.}$ 265infl., 272, 307, and 361 (in base 245 and 388) nm; δ($CDCl_3$) 0.98 (6 H, t, *J* 7 Hz, 2 × *Me*CH_2), 1.24 (3 H, d, *J* 7 Hz, *Me*CH), 1.2—2.0 (8 H, m, MeCH_2CH and MeC$H_2CH_2CH_2$), 1.54 (6 H, s, Me_2C), 2.9 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.85 (1 H, m, *J* 7 Hz, CH_2CHCO), 5.5 (1 H, d, *J* 10 Hz, ArCH=C*H*), 5.92 (1 H, s, CH_2C=C*H*CO), 6.64 (1 H, d, *J* 10 Hz, ArC*H*=CH), and 14.3 (1 H, s, OH); *m*/*z* 398 (M^+, 95%), 383 (100), and 341 (100).

Preparation of Mammea Cyclo E Coumarins.—*m*-Chloroperbenzoic acid (1 mol equiv.) in chloroform (10 ml) was added to the uncyclised synthetic mammea coumarin (1 mol equiv.) and toluene-*p*-sulphonic acid (10 mg) in chloroform (10 ml). The mixture was stirred at room temperature for 24 h, washed with saturated aqueous sodium hydrogen carbonate (3 × 10 ml), and dried. The residue on evaporation was chromatographed on a silica column, eluting with chloroform–methanol (99:1 v/v), to give the cyclo E mammea. Using this method the following coumarins were prepared:

Mammea B/BA Cyclo E (**4a**). This was prepared from mammea B/BA (**1l**) (100 mg, 0.27 mmol) as white crystals (55 mg, 53%), m.p. 220—222 °C from chloroform–methanol (lit.,[2c] 209—212 °C) (Found: C, 68.08; H, 7.28%; M^+, 388.1884. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27%; *M*, 388.1886), $\nu_{max.}$(KBr) 3 300, 2 950, 1 700, and 1 600 cm^{-1}; $\lambda_{max.}$ 260 and 323 (in base 260, 330, and 389) nm; δ (250 MHz; C_5D_5N) 0.95 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.10 (6 H, dd, *J* 3 and 7 Hz, Me_2CH), 1.50 and 1.55 (6 H, 2 × s, Me_2CO), 1.6—1.8 (2 H, m, *J* 7 Hz, MeCH_2CH), 2.48 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 2.92 (2 H, d, *J* 7 Hz, CHCH_2CO), 3.05 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.10 (1 H, dd, *J* 8 and 16 Hz, ArC*H*CHOH), 3.40 (1 H, dd, *J* 6 and 16 Hz, ArC*H*CHOH), 5.12 (1 H, dd, *J* 6 and 8 Hz, CH_2CHOH), and 6.15 (1 H, s, CH_2C=C*H*CO); the hydroxy protons were not discernible; *m*/*z* (M^+, 15%), 331 (100), 313 (15), 259 (30), and 231 (6).

Mammea B/BB Cyclo E (**4b**). This was prepared from mammea B/BB (**1m**) (200 mg, 0.54 mmol) as white crystals (100 mg, 48%), m.p. 185—187 °C from hexane–chloroform (Found: C, 68.12; H, 7.43%; M^+, 388.1869. $C_{22}H_{28}O_6$ requires C, 68.02; H, 7.27%; *M*, 388.1886); $\nu_{max.}$($CHCl_3$) 3 400, 3 000, 1 700, and 1 610 cm^{-1}; $\lambda_{max.}$ 260 and 323 (in base 259, 329, and 388) nm; δ (250 MHz; $CDCl_3$) 0.95 (6 H, m, 2 × *Me*CH_2), 1.18 (3 H, dd, *J* 3 and 7 Hz, *Me*CH), 1.32 and 1.35 (6 H, 2 × s, Me_2CO), 1.25—1.9 (4 H, m, MeCH_2CH_2 and MeCH_2CH), 2.70 (1 H, dd, *J* 6 and 16 Hz, ArC*H*CHOH), 2.80 (2 H, m, *J* 7 Hz, CH_2C=CHCO), 2.95 (1 H, dd, *J* 5 and 16 Hz, ArC*H*CHOH), 4.05 (1 H, m, CH_2CHCO), 4.85 (1 H, t, *J* 5 Hz, CH_2CHOH), 4.15 (1 H, br s, CHO*H*), 5.85 (1 H, s, CH_2C=C*H*CO), and 8.25 (1 H, br s, ArOH); *m*/*z* 388 (M^+, 10%), 331 (100), 313 (27), 259 (54), and 231 (10).

Mammea B/BC Cyclo E (**4c**). This was prepared from mammea B/BC (**1n**) (200 mg, 0.56 mmol) as white crystals (100 mg, 48%), m.p. 210—211 °C from chloroform–methanol (Found: C, 67.7; H, 7.1%; M^+, 374.1703. $C_{21}H_{26}O_6$ requires C, 67.4; H, 7.0%; *M*, 374.1729); $\nu_{max.}$(KBr) 3 400, 2 950, 1 700, and 1 600 cm^{-1}; $\lambda_{max.}$ 260 and 323 (in base 259, 329, and 388) nm; δ (250 MHz; C_5D_5N) 0.95 and 1.05 (each 3 H, t, *J* 7 Hz, *Me*CH_2), 1.50 and 1.55 (6 H, 2 × s, Me_2CO), 1.65—1.95 (4 H, m, *J* 7 Hz, 2 × MeCH_2CH_2), 3.0 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 3.05 (2 H, t, *J* 7 Hz, CH_2C=CHCO), 3.12 (1 H, dd, *J* 8 and 16 Hz, ArC*H*CHOH), 3.4 (1 H, dd, *J* 6 and 16 Hz, ArC*H*CHOH), 4.15 (1 H, dd, *J* 6 and 8 Hz, CH_2CHOH), and 6.15 (1 H, s, CH_2C=C*H*CO), hydroxy protons not discernible; *m*/*z* 374 (M^+, 53%), 331 (100), 313 (25), 259 (55), and 231 (10).

Preparation of Mammea Cyclo F Coumarins.—The uncyclised synthetic mammea coumarin (1 mol equiv.) and *m*-chloroperbenzoic acid (1 mol equiv.) were stirred in dry dichloromethane (10 ml) at room temperature overnight. The solution was then washed successively with 10% aqueous sodium sulphite (2 × 10 ml) and 5% aqueous sodium hydrogen carbonate (2 × 10 ml), and dried. The residue on evaporation was chromatographed on a silica column, eluting with chloroform followed by methanol–chloroform (1:99 v/v), to give the cyclo F mammea. Using this method the following coumarins were prepared:

Mammea A/AA Cyclo F (**5a**) was prepared from mammea A/AA (**1a**) (200 mg, 0.49 mmol) as yellow crystals (120 mg, 58%), m.p. 131—132 °C from chloroform–hexane (lit.,[2d] 115—117 °C) (Found: C, 71.35; H, 6.45%; M^+, 422.1714. Calc. for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20%; *M*, 422.1729); $\nu_{max.}$($CHCl_3$) 3 050, 1 720, and 1 610 cm^{-1}; $\lambda_{max.}$ 280 and 347 (in base 247 and 313) nm; δ($CDCl_3$) 0.94 (6 H, d, *J* 7 Hz, Me_2CH), 1.28 and 1.40 (6 H, 2 × s, Me_2CCH), 2.04 (1 H, br s, Me_2CO*H*), 2.14 (1 H, m, Me_2CHCH_2), 2.84 (2 H, dd, *J* 5 and 7 Hz, CHCH_2CO), 3.24 (2 H, d, *J* 9 Hz, ArCH_2CH), 4.80 (1 H, t, *J* 9 Hz, Me_2CC*H*CH_2), 5.72 (1 H, s, PhC=C*H*CO), 7.0—7.2 (5 H, m, ArH), and 15.0 (1 H, s, chelated OH); *m*/*z* 422 (M^+, 22%), 365 (38), 364 (78), 363 (62), 347 (28), 307 (70), and 293 (100).

Mammea A/AB Cyclo F (**5b**). This was prepared from mammea A/AB (**1b**) (100 mg, 0.25 mmol) as yellow crystals (51 mg, 49%), m.p. 140—142 °C from chloroform–hexane (lit.,[2d] 115—117 °C) (Found: C, 70.75; H, 6.5%; M^+, 422.1705. Calc. for $C_{25}H_{26}O_6$: C, 71.04; H, 6.20%; *M*, 422.1729); $\nu_{max.}$($CHCl_3$) 2 950, 1 720, and 1 600 cm^{-1}; $\lambda_{max.}$ 281 and 350 (in base 246 and 315) nm; δ($CDCl_3$) 0.88 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.12 (3 H, dd, *J* 2 and 7 Hz, *Me*CH), 1.28 and 1.38 (6 H, 2 × s, Me_2CCH), 1.2—1.9 (2 H, m, MeCH_2CH), 1.80 (1 H, br s, Me_2CO*H*) 3.24 (2 H, d, *J* 9 Hz, ArCH_2CH), 3.54 (1 H, m, CH_2CHCO), 4.82 (1 H, t, *J* 9 Hz, Me_2CC*H*CH_2), 5.80 (1 H, s, PhC=C*H*CO), 7.0—7.4 (5 H, m, ArH), and 14.28 (1 H, s, chelated OH); *m*/*z* 422 (M^+, 100%), 365 (72), 364 (12), 363 (14), 347 (23), 307 (10), and 293 (72).

Mammea B/AA Cyclo F (**5e**). This was prepared from mammea B/AA (**1h**) (200 mg, 0.54 mmol) as yellow crystals (150 mg, 72%), m.p. 82—84 °C from hexane–chloroform (lit.,[2d] 72—77 °C) (Found: C, 68.35; H, 7.6%; M^+, 388.1891. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.3%; *M*, 388.1886); $\nu_{max.}$($CHCl_3$) 2 950, 1 710, and 1 600 cm^{-1}; $\lambda_{max.}$ 281 and 335 (in base 242, 287, and

414) nm; δ($CDCl_3$) 1.0 (9 H, m, $MeCH_2$ and Me_2CH), 1.26 and 1.40 (6 H, 2 × s, Me_2CCH), 1.3—1.8 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.20 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 2.46 (1 H, br s, Me_2COH), 2.65—3.0 (4 H, m, $CHCH_2CO$ and $CH_2C{=}CHCO$), 3.16 (2 H, m, $ArCH_2CH$), 4.74 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.6 (1 H, s, $CH_2C{=}CHCO$), and 14.65 (1 H, s, chelated OH); *m/z* 388 (M^+, 100%), 331 (7), 329 (14), 317 (40), 273 (10), and 259 (10).

Mammea B/AB Cyclo F (**5f**). This was prepared form mammea B/AB (**1i**) (200 mg, 0.54 mmol) as yellow crystals (111 mg, 53%), m.p. 119—120 °C from hexane–ether (lit.,[2d] 92—94 °C) (Found: C, 68.1; H, 7.6%; M^+, 388.1865. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.3%; *M*, 388.1886); $\nu_{max.}$($CHCl_3$) 2 950, 1 720, and 1 610 cm^{-1}; $\lambda_{max.}$ 281 and 334 (in base 242, 294, and 413) nm; δ($CDCl_3$) 0.92 (6 H, m, 2 × $MeCH_2$), 1.12 (3 H, dd, *J* 3 and 7 Hz, *Me*CH), 1.22 and 1.34 (6 H, 2 × s, Me_2CCH), 1.2—1.9 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.06 (1 H, br s, Me_2COH), 2.80 (2 H, t, *J* 7 Hz, $CH_2C{=}CHCO$), 3.14 (2 H, d, *J* 9 Hz, $ArCH_2CH$), 3.56 (1 H, m, CH_2CHCO), 4.76 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.68 (1 H, s, $CH_2C{=}CHCO$) and 14.8 (1 H, s, chelated OH); *m/z* 388 (M^+, 100%), 331 (46), 273 (21), and 259 (28).

Mammea B/AC Cyclo F (**5g**). This was prepared from mammea B/AC (**1j**) (200 mg, 0.56 mmol) as yellow crystals (125 mg, 60%), m.p. 117—120 °C from hexane–ether (lit.,[2d] 75—81 °C) (Found: C, 67.4; H, 7.25%; M^+, 374.1743. Calc. for $C_{21}H_{26}O_6$: C, 67.38; H, 7.0%; *M*, 374.1729); $\nu_{max.}$($CHCl_3$) 2 950, 1 720, and 1 610 cm^{-1}; $\nu_{max.}$ 281 and 334 (in base 241, 286, and 413) nm; δ($CDCl_3$) 1.00 (6 H, m, 2 × $MeCH_2$), 1.30 and 1.44 (6 H, 2 × s, Me_2CCH), 1.4—1.9 (4 H, m, 2 × $MeCH_2CH_2$), 2.56 (1 H, br s, Me_2COH), 2.80 (2 H, m, $CH_2C{=}CHCO$), 3.04 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 3.22 (2 H, dd, *J* 3 and 9 Hz, $ArCH_2CH$), 4.86 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.72 (1 H, s, $CH_2C{=}CHCO$), and 14.9 (1 H, s, chelated OH); *m/z* 374 (M^+, 100%), 315 (6), 303 (30), 273 (6), and 259 (6).

Mammea B/BA Cyclo F (**6a**). This was prepared from mammea B/BA (**1l**) (200 mg, 0.54 mmol) as white plates (140 mg, 67%), m.p. 126—127 °C from hexane–chloroform (lit.,[2c] 126—127 °C) (Found: C, 68.15; H, 7.6%; M^+, 388.1888. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27%; *M*, 388.1885); $\nu_{max.}$($CHCl_3$) 2 950, 1 720, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$ 232infl. and 298 (in base 240 and 378) nm; δ($CDCl_3$) 1.00 (9 H, m, $MeCH_2$ and Me_2CH), 1.24 and 1.40 (6 H, 2 × s, Me_2CCH), 1.3—1.8 (2 H, m, $MeCH_2CH_2$), 2.12 (1 H, m, *J* 7 Hz, Me_2CHCH_2), 2.5—2.8 (3 H, m, $CH_2C{=}CHCO$ and Me_2COH), 2.90 (2 H, dd, *J* 2 and 7 Hz, $CHCH_2CO$), 3.04 (2 H, dd, *J* 3 and 9 Hz, $ArCH_2CH$), 4.66 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.62 (1 H, s, $CH_2C{=}CHCO$), and 13.55 (1 H, s, chelated OH); *m/z* 388 (M^+, 60%), 373 (20), 331 (100), and 259 (23).

Mammea B/BB Cyclo F (**6b**). This was prepared from mammea B/BB (**1m**) (200 mg, 0.54 mmol) as white plates (140 mg, 67%), m.p. 119—121 °C from hexane–chloroform (lit.,[2c] 118—119.5 °C) (Found: C, 67.95; H, 7.4%; M^+, 388.1872. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27%; *M*, 388.1885); $\nu_{max.}$($CHCl_3$) 2 975, 1 730, 1 630, and 1 610 cm^{-1}; $\lambda_{max.}$ 233infl. and 298 (in base 240 and 378) nm; δ($CDCl_3$) 1.06 (6 H, t, 2 × $MeCH_2$), 1.24 (3 H, dd, *J* 2 and 7 Hz, *Me*CH), 1.32 and 1.46 (6 H, 2 × s, Me_2CCH), 1.3—2.0 (4 H, m, $MeCH_2CH_2$ and $MeCH_2CH$), 2.6—3.0 (3 H, m, $CH_2C{=}CHCO$ and Me_2COH), 3.20 (2 H, d, *J* 9 Hz, $ArCH_2CH$), 3.84 (1 H, m, CH_2CHCO), 4.90 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.94 (1 H, s, $CH_2C{=}CHCO$), and 14.2 (1 H, s, chelated OH); *m/z* 388 (M^+, 17%), 331 (100), and 259 (17).

Mammea B/BC Cyclo F (**6c**). This was prepared from mammea B/BC (**1n**) (200 mg, 0.56 mmol) as white plates (100 mg, 49%), m.p. 133—135 °C from hexane–chloroform (lit.,[2c] 129.5—131.5 °C) (Found: C, 67.55; H, 7.20%; M^+, 374.1739. Calc. for $C_{21}H_{26}O_6$: C, 67.38; H, 7.0%; *M*, 374.1729); $\nu_{max.}$($CHCl_3$) 3 000, 1 720, 1 630, and 1 600 cm^{-1}; $\lambda_{max.}$ 231infl. and 296 (in base 240 and 376) nm; δ($CDCl_3$) 0.98 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.22 and 1.38 (6 H, 2 × s, Me_2CCH), 1.4—1.9 (4 H, m, 2 × $MeCH_2CH_2$), 2.5—3.0 (2 H, m, $CH_2C{=}CHCO$), 2.76 (1 H, s, Me_2COH), 2.98 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 3.06 (2 H, dd, *J* 2 and 9 Hz, $ArCH_2CH$), 4.68 (1 H, t, *J* 9 Hz, Me_2CCHCH_2), 5.66 (1 H, s, $CH_2C{=}CHCO$), and 13.8 (1 H, s, chelated OH); *m/z* 374 (M^+, 68%), 331 (100), 315 (22), 273 (12), and 159 (12).

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