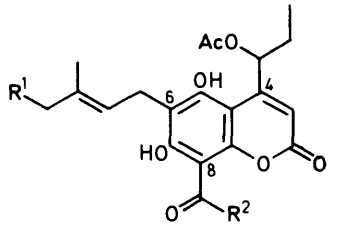
# Synthesis of the *Mammea* Coumarins. Part 3.[1] The Insecticidal Coumarins of the Mammea E Series, Mammea D/BB, and a Dihydrocoumarin of the Mammea C Series

**Leslie Crombie,* Raymond C. F. Jones,* and Christopher J. Palmer**
*Department of Chemistry, The University, Nottingham, NG7 2RD*

A dihydrocoumarin metabolite of *Mammea africana* has been prepared by Lewis acid-mediated acylation of 5,7-dihydroxy-4-pentyl-3,4-dihydrocoumarin (available by hydrogenation of the corresponding coumarin). Acylation of 4-(1-methylpropyl)- and 4-(1-acetoxypropyl)-5,7-dihydroxycoumarin, each prepared by Pechmann condensation of phloroglucinol with the appropriate β-keto ester, gave 8-acylcoumarins that have been *C*-alkylated with 3-methylbut-2-enyl bromide to provide, respectively, mammea D/BB (ferruol A), and the natural insecticidal 4-(1-acetoxypropyl)coumarins of *M.americana*, mammea E/BA and E/BB; *C*-alkylation with 3,7-dimethylocta-2,6-dienyl chloride of 4-(1-acetoxypropyl)-5,7-dihydroxy-8-(2-methylbutyryl)coumarin afforded surangin B, an insecticidal component of *M.longifolia*.

A group of some twenty 4-alkyl- and 4-aryl-5,7-dioxygenated coumarins have been isolated from various parts of the insecticidal tree *Mammea americana*; this group of *Mammea* coumarins is expanded to nearly fifty compounds by inclusion of coumarins of the same type isolated from *M.africana* and *M.longifolia*, as well as from *Mesua ferrea* and *Mesua thwaitesii*.[2] Important members of the group are the 4-(1-acetoxypropyl) coumarins mammea E/BA (**1a**), E/BB (**1b**), and either E/BC (**1c**) or E/BD (**1d**), the insecticidal components of the seeds of *Mammea americana*, and surangin B (**1e**), an insecticidal component of *M.longifolia*.



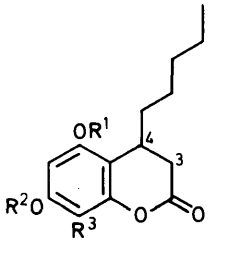

(**1**) **a**; $R^1$ = H, $R^2$ = $CH_2CHMe_2$
**b**; $R^1$ = H, $R^2$ = $CHMeCH_2Me$
**c**; $R^1$ = H, $R^2$ = $CH_2CH_2Me$
**d**; $R^1$ = H, $R^2$ = $CHMe_2$
**e**; $R^1$ = $CH_2CH{=}CMe_2$, $R^2$ = $CHMeCH_2Me$

In the preceding papers[1] we have described the total synthesis of the 4-phenyl (mammea A), 4-propyl (mammea B), and 4-pentyl (mammea C) coumarins, and our initial attempts to synthesise the mammea E series; these latter investigations culminated in the synthesis of mammea E/AC, the 6-acyl isomer of the naturally-occurring 8-acyl insecticidal coumarin mammea E/BC (**1c**). In the present paper we describe a further successful approach to the mammea E coumarins that has resulted in the total synthesis of the insecticidal compounds mammea E/BA (**1a**), E/BB (**1b**), and surangin B (**1e**). In addition we report synthesis of the 3,4-dihydrocoumarin (**2a**), isolated from *M.africana*, and the 4-(1-methylpropyl)coumarin (**3a**; ferruol A), a natural product from *Mesua ferrea*.

## Results and Discussion

Our earlier reported synthesis of the mammea A, B, and C coumarins was based on Pechmann condensation of acylphloroglucinols with appropriate β-keto esters to give separable mixtures of 6- and 8-acylcoumarins that could be *C*-alkylated to insert a prenyl (3-methylbut-2-enyl) or geranyl (3,7-dimethylocta-2,6-dienyl) group.[1a] Attempts to extend this approach to the 4-(1-acetoxypropyl) mammea E coumarins by use of the γ-functionalised β-keto ester, ethyl 4-acetoxy-3-oxohexanoate (**4a**), or the corresponding 4-halo-3-oxohexanoates (**4b,c**), in a Pechmann condensation with an acylphloroglucinol were unsuccessful.[1b] Functionalisation of the 4-propyl substituent in an acylcoumarin after Pechmann condensation was successfully employed as a route to 6-acyl mammea E coumarins but proved to be unsuitable for synthesis of the natural insecticidal 8-acyl mammea E compounds (**1a**—**e**).[1b]

The solution to this problem was suggested by our findings during the synthesis of the 3,4-dihydrocoumarin (**2a**), a metabolite of *Mammea africana*. We initially attempted reduction of the 3,4-double bond by hydrogenation of the 8-acyl-4-pentylcoumarin (**5a**), itself a natural product from *M.africana*, that had been prepared earlier from condensation between (2-methylbutyryl)phloroglucinol and ethyl 3-oxo-octanoate;[1a] in contrast to recent reports of hydrogenation of simple coumarins under mild conditions,[3] treatment of (**5a**) at hydrogen pressures from 1—35 atm and with various catalysts (Adams catalyst, 10% palladium-on-charcoal, T-1 Raney nickel) in ethanol or ethyl acetate gave no reduction, and recovery of unchanged coumarin. Eventually reduction was observed under 50 atm of hydrogen using 10% palladium-on-charcoal in ethanol at 100 °C, to afford the 3,4-dihydrocoumarin (**2b**), characterised also as its diacetate (**2c**), in which the carbonyl of the acyl group



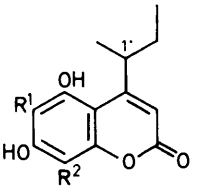

(**2**) **a**; $R^1$ = $R^2$ = H, $R^3$ = $COCHMeCH_2Me$
**b**; $R^1$ = $R^2$ = H, $R^3$ = $CH_2CHMeCH_2Me$
**c**; $R^1$ = $R^2$ = Ac, $R^3$ = $CH_2CHMeCH_2Me$
**d**; $R^1$ = $R^2$ = $R^3$ = H
**e**; $R^1$ = $R^2$ = $COCHMeCH_2Me$, $R^3$ = H
**f**; $R^1$ = H, $R^2$ = $COCHMeCH_2Me$, $R^3$ = H
**g**; $R^1$ = $COCHMeCH_2Me$, $R^2$ = $R^3$ = H

had also been reduced. Condensation of (2-methylbutyryl)-phloroglucinol and ethyl 3-hydroxyoctanoate, obtained from sodium borohydride reduction of ethyl 3-oxo-octanoate, in 5% sulphuric acid in acetic acid did not yield any dihydrocoumarin product.

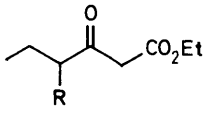
Attention was next directed to the hydrogenation of the non-acylated coumarin (**5b**), with introduction of the acyl group as a next stage. 5,7-Dihydroxy-4-pentylcoumarin (**5b**) was prepared by condensation between phloroglucinol and ethyl 3-oxo-octanoate in 75% sulphuric acid; hydrogenation in ethanol under 50 atm hydrogen pressure in the presence of 10% palladium-on-charcoal afforded the dihydrocoumarin (**2d**) in good yield. The i.r. spectrum of (**2d**) showed a carbonyl absorption at 1 760 $cm^{-1}$; and in the $^1H$ n.m.r. spectrum a two-proton doublet at δ 2.7 (3-H) and a one-proton multiplet at δ 3.3 (4-H) had replaced the one-proton singlet at δ 5.85 corresponding to 3-H in the spectrum of (**5b**).

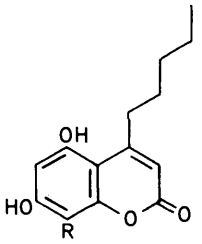
Friedel-Crafts acylation of (**2d**) with 2-methylbutyryl chloride and aluminium trichloride in nitrobenzene, when terminated after only 15 min, gave a mixture of *O*- and *C*-acyl products that could be separated by column chromatography on silica gel. First eluted was the 5,7-bis-(*O*-acyl)-3,4-dihydrocoumarin (**2e**) (14%), followed by the 7-*O*-acyl dihydrocoumarin (**2f**) which proved to be the major product (53%); a positive Gibbs test confirmed that the acyloxy group was located at C-7 rather than C-5. Next, the desired 8-*C*-acyl dihydrocoumarin (**2a**) was obtained, in only 1% yield, followed finally by the 5-*O*-acyl dihydrocoumarin (**2g**) (12%); both (**2a**) and (**2g**) gave a negative Gibbs test as expected. The synthetic dihydrocoumarin (**2a**) was identical with a sample of the natural material, the structure of which had been assigned on the basis of chemical and spectroscopic studies, and an *X*-ray crystal structure determination.[4] When the acylation was allowed to proceed overnight before chromatography, the yield of the 8-*C*-acyl dihydrocoumarin (**2a**) was increased to 27%, with the mono-*O*-acyl isomers (**2f** and **g**) being obtained in 37% and 7% yields, respectively. The mono-*O*-acyl dihydrocoumarins (**2f** and **g**) were separately subjected to Fries rearrangement with aluminium trichloride in nitrobenzene to afford further 8-*C*-acyl material (**2a**) [27% and 35% from (**2f** and **g**), respectively] along with deacylated dihydrocoumarin (**2d**). These experiments suggest that the acylation of (**2d**) proceeds *via* *O*-acylation and subsequent Fries rearrangement to the 8-*C*-acyl dihydrocoumarin; there was no evidence of the 6-*C*-acyl dihydrocoumarin in any of these reactions. The success of this acylation suggested a route to the so far elusive 8-acyl mammea E coumarins.

As a further test of the acylation reaction, this time with a 5,7-dihydroxycoumarin rather than dihydrocoumarin, we undertook synthesis of mammea D/BB (**3a**), the single member of the 4-(1-methylpropyl) mammea D series of natural products. We have earlier reported that no coumarin material could be isolated from reaction between (2-methylbutyryl)-phloroglucinol and ethyl 4-methyl-3-oxohexanoate (**4d**),[1a] but in contrast, Pechmann condensation of (**4d**) with phloroglucinol in 75% sulphuric acid did produce the non-acylated 5,7-



(**3**) **a**; $R^1 = CH_2CH{=}CMe_2$, $R^2 = COCHMeCH_2Me$
**b**; $R^1 = R^2 = H$
**c**; $R^1 = H$, $R^2 = COCHMeCH_2Me$



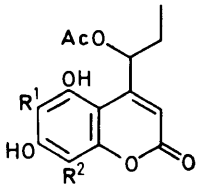


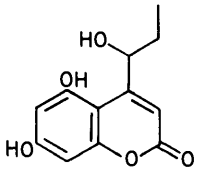
(**4**) **a**; R = OAc
**b**; R = Br
**c**; R = Cl
**d**; R = Me

(**5**) **a**; R = $COCHMeCH_2Me$
**b**; R = H

dihydroxy-4-(1-methylpropyl)coumarin (**3b**), albeit in modest yield; γ-substitution in β-keto esters is known to have an inhibitory effect on such condensations.[5] Acylation of (**3b**) with 2-methylbutyryl chloride and aluminium trichloride allowing the reaction to proceed for 6 days, afforded the 8-*C*-acyl-coumarin (**3c**) in 43% yield along with recovered starting material (**3b**) (34%); again no trace of 6-acyl isomer was observed. *C*-Prenylation by the usual method (prenyl bromide in 10% aqueous potassium hydroxide) gave mammea D/BB (**3a**) in 22% yield. Synthetic (**3a**) had a $^1H$ n.m.r. spectrum superimposable on that reproduced in the report of the isolation of ferruol A (mammea D/BB),[6] and other spectral and analytical data are in agreement with the assigned structure. The m.p. is *ca.* 8 °C below that reported for the natural material as our synthetic product is a mixture of closely similar diastereoisomers because of the chiral centres at C-1′ and C-2″.

These successful acylations encouraged us to apply this strategy of *C*-acylation after coumarin formation to the mammea E series. Although condensation between ethyl 4-acetoxy-3-oxo-hexanoate (**4a**) and acylphloroglucinols was known not to produce coumarins,[1b] treatment of (**4a**) with the more reactive phloroglucinol in trifluoroacetic acid did produce the required 4-(1-acetoxypropyl)-5,7-dihydroxycoumarin (**6a**)





(**6**) **a**; $R^1 = R^2 = H$
**b**; $R^1 = H$, $R^2 = COCH_2CHMe_2$
**c**; $R^1 = COCH_2CHMe_2$, $R^2 = H$
**d**; $R^1 = H$, $R^2 = COCHMeCH_2Me$

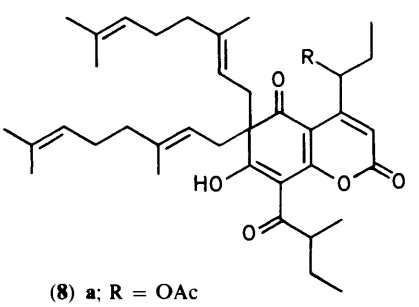
(**7**)

(53%) along with some of the 4-(1-hydroxypropyl) analogue (**7**). Acylation of (**6a**) with 3-methylbutyryl chloride did indeed afford the desired 8-*C*-acylcoumarin (**6b**) in 33% yield along with a small amount of the 6-acyl isomer (**6c**); similarly acylation of (**6a**) with 2-methylbutyryl chloride gave the corresponding 8-acylcoumarin (**6d**) (44%), some unchanged starting material (**6a**) (37%), and some trihydroxycoumarin (**7**). The u.v. spectra of the 8-acylcoumarins (**6b** and **d**) were very similar to those of other 8-acyl-5,7-dihydroxycoumarins prepared by us, and the $^1H$ n.m.r. spectra of both coumarins exhibited a three-proton signal at *ca.* δ 2.3 indicative of the acetoxy group. In addition the $^1H$ n.m.r. spectrum of the 8-(2-methylbutyryl)-coumarin (**6d**) showed two singlets, each *ca.* 0.5 protons, for the signal from the proton at C-3, two singlets for the acetoxy methyl group, and two separate doublets for the 2-methyl group

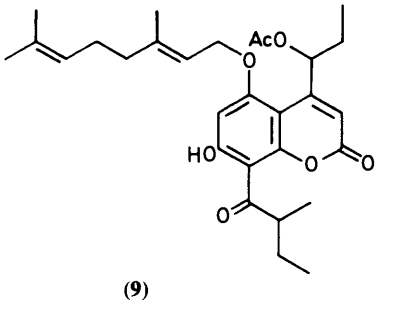
of the 8-acyl substituent, indicating that the compound had been obtained, as expected, as a mixture of diastereoisomers because of the two chiral centres present.

Treatment of the 8-(3-methylbutyryl)coumarin (**6b**) with prenyl bromide and 5% aqueous potassium hydroxide (two equiv.) gave crystalline mammea E/BA (**1a**) in 20% yield along with recovered starting material (**6b**) (50%) suitable for recycling. Direct comparison of synthetic (**1a**) with natural material was not possible as mammea E/BA (**1a**) and E/BB (**1b**) had been obtained as an inseparable mixture,[7] but the spectroscopic and analytical data for synthetic (**1a**) were fully consistent with the assigned structure. Similar treatment of the 8-(2-methylbutyryl)coumarin (**6d**) gave the crystalline *C*-alkyl product (**1b**) (20%) as a 1:1 mixture of mammea E/BB and its diastereoisomer, along with recovered starting material (**6d**) (40%); again direct comparison with natural material was not possible, but spectroscopic and analytical data confirmed the gross structure (**1b**). The presence of a diastereoisomeric mixture was indicated in the $^1$H n.m.r. spectrum by just discernible doubling of the signals at δ 6.3 for the C-3 proton, at δ 1.25 for the 2-methyl group of the acyl substituent, and at δ 1.00 and 1.05 for the two terminal methyl groups of the acyl and 4-(1-acetoxypropyl) side-chains. The signal due to the methylene protons of the prenyl group in both (**1a** and **b**) appeared as an eight line multiplet, collapsing to a doublet of doublets on irradiation of the adjacent vinyl proton, suggesting non-equivalence due to restricted rotation.

The 8-(2-methylbutyryl)coumarin (**6d**) was next geranylated with geranyl chloride in 5% aqueous potassium hydroxide (two equiv.) at 45 °C for 24 h, to afford, after column chromatography, three alkylation products. The first of these was the bis-(*C*-geranyl)pyrone (**8a**), which had a nearly identical u.v. spectrum to the bis(*C*-geranyl) pyrone (**8b**) prepared in our earlier work on surangin A. The remaining material was a 1:1




(**8**) **a**; R = OAc
**b**; R = H




(**9**)

mixture of the *C*-geranylated coumarin (**1e**) and its 5-*O*-geranyl isomer (**9**), that was finally separated by h.p.l.c. on a silica column; first eluted was (**9**) followed by (**1e**) as a mixture of surangin B and a diastereoisomer. Synthetic (**1e**) gave satisfactory analytical data and had virtually identical spectroscopic properties to those reported for natural surangin B;[8] the mass spectral fragmentation pattern and $^1$H n.m.r. spectrum of (**1e**) agreed closely with those depicted for natural surangin B in the report of its isolation, with the exception of some doubling of peaks in the $^1$H n.m.r. spectrum of synthetic (**1e**) due to the presence of the diastereoisomer.

We were unable to further separate synthetic mammea E/BB (**1b**) or surangin B (**1e**) from the diastereoisomers produced in the synthesis. Three of the natural *Mammea* coumarins, mammea B/BB, surangin A, and surangin B (**1e**), have been reported to possess optical rotations but the configurations of the chiral centres in the 2-methylbutyryl and/or 4-(1-acetoxypropyl) substituents have not been determined. Our efforts to determine the relative and absolute stereochemistry of the *Mammea* coumarins are described in the following paper. The experiments described herein comprise the first synthesis of the insecticidal 8-acyl *Mammea* coumarins, mammea E/BA (**1a**), E/BB (**1b**), and surangin B (**1e**), though separation of the natural stereoisomers remains to be attained.

## Experimental

General directions are in Parts 1 and 2.[1]

*Hydrogenation of 5,7-Dihydroxy-8-(2-methylbutyryl)-4-pentylcoumarin* (**5a**).—5,7-Dihydroxy-8-(2-methylbutyryl)-4-pentylcoumarin (**5a**) (332 mg, 1 mmol) in dry ethanol (25 ml) was stirred under hydrogen (50 atm) at 100 °C overnight in the presence of 10% palladium-on-carbon (250 mg). The cooled suspension was filtered through Kieselguhr, and the filtrate evaporated to leave a residue that was chromatographed on silica. Elution with chloroform gave a small amount of starting material followed by 5,7-*dihydroxy*-8-(2-*methylbutyl*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2b**) as a yellow gum (214 mg, 74%) (Found: $M^+$, 320.1973. $C_{19}H_{28}O_4$ requires *M*, 320.1987); $\nu_{max.}$(CHCl$_3$) 3 550, 2 925, 1 760, and 1 620 cm$^{-1}$; $\lambda_{max.}$ 288 (in base 301) nm; δ(CDCl$_3$) 0.8—1.0 (9 H, m, 2 × *Me*CH$_2$ and *Me*CH), 1.0—1.8 (11 H, m, MeC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$ and MeC*H*$_2$C*H*), 2.3—3.0 (4 H, m, ArC*H*$_2$CH and CHC*H*$_2$CO), 3.2—3.4 (1 H, m, ArC*H*CH$_2$CO), 6.1 (1 H, br s, OH), 6.4 (1 H, s, ArH), and 6.7 (1 H, br s, OH); *m/z* 320 ($M^+$, 9%), 263 (100), and 249 (20). Attempted reductions of coumarin (**5a**) under the following conditions gave only recovered starting material: (*i*) in dry ethanol under 1 atm of hydrogen in the presence of Adams catalyst, or of 10% palladium-on-charcoal, (*ii*) in dry ethanol under 20 atm of hydrogen, or dry ethyl acetate under 35 atm of hydrogen, both in the presence of 10% palladium-on-charcoal, and (*iii*) with T-1 Raney nickel in ethanol at 60 °C under 10 atm of hydrogen.

5,7-*Diacetoxy*-8-(2-*methylbutyl*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2c**).—5,7-Dihydroxy-8-(2-methylbutyl)-4-pentyl-3,4-dihydrocoumarin (**2b**) (200 mg) and acetic anhydride (2 ml) in dry pyridine (10 ml) were left at 20 °C for 2 days, and the mixture was then poured into ice–water containing dilute hydrochloric acid and extracted with ether. The organic layer was washed with dilute hydrochloric acid, dried, and evaporated to leave a residue that was chromatographed on silica, eluting with chloroform to afford 5,7-*diacetoxy*-8-(2-*methylbutyl*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2c**) as a yellow gum (170 mg, 68%) (Found: $M^+$, 404.2180. $C_{23}H_{32}O_6$ requires *M*, 404.2198); $\nu_{max.}$(CHCl$_3$) 2 950 and 1 760 cm$^{-1}$; $\lambda_{max.}$ 267 nm; δ (90 MHz; CDCl$_3$) 0.8—1.0 (9 H, m, 2 × *Me*CH$_2$ and *Me*CH), 1.2—1.7 (11 H, m, MeC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$ and MeC*H*$_2$C*H*), 2.3 (6 H, s, 2 × MeCO), 2.5 (2 H, t, *J* 7 Hz, ArC*H*$_2$CH), 2.6—2.8 (2 H, m, CHC*H*$_2$CO), 2.9—3.2 (1 H, m, C*H*CH$_2$CO), and 6.8 (1 H, s, ArH); *m/z* 404 ($M^+$, 10%), 362 (75), 320 (65), 305 (6), 263 (100), and 249 (25).

5,7-*Dihydroxy*-4-*pentylcoumarin* (**5b**).—To phloroglucinol (6.85 g, 54 mmol) in 75% sulphuric acid (100 ml) was added ethyl 3-oxo-octanoate (10 g, 54 mmol), and the mixture stirred for 24 h at room temperature. The mixture was poured into ice–water, and the yellow solid collected by filtration and washed with water. Crystallisation from aqueous ethanol gave 5,7-*dihydroxy*-4-*pentylcoumarin* (**5b**) as a yellow solid (8.65 g, 64%), m.p. 224—226 °C (lit.,[9] 235—237 °C) (Found: $M^+$, 248.1050. $C_{14}H_{16}O_4$ requires $M$, 248.1049); $\nu_{max.}$(KBr) 3 150, 1 660, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 251, 258, and 326 (in base 279 and 395) nm; δ [90 MHz; $(CD_3)_2SO$] 0.9 (3 H, t, $J$ 7 Hz, $MeCH_2$), 1.1—1.8 (6 H, m, $MeCH_2CH_2CH_2$), 2.9 (2 H, t, $J$ 7 Hz, $CH_2C{\equiv}CH$), 5.85 (1 H, s, $CH_2C{\equiv}CHCO$), 6.25 and 6.35 (each 1 H, d, $J$ 2 Hz, ArH), 10.2 (1 H, br s, OH), and 10.5 (1 H, s, OH).

5,7-*Dihydroxy*-4-*pentyl*-3,4-*dihydrocoumarin* (**2d**).—5,7-Dihydroxy-4-pentylcoumarin (**5b**) (0.5 g, 2 mmol) in dry ethanol (25 ml) was stirred under hydrogen (50 atm) at 20 °C overnight in the presence of 10% palladium-on-carbon (250 mg). The solution was filtered through Kieselguhr and the filtrate evaporated to leave a residue that was chromatographed on a silica column. Elution was light petroleum (b.p. 60—80 °C)–chloroform (1:1 v/v) followed by chloroform gave some gum; further elution with chloroform–methanol (49:1 v/v) gave 5,7-*dihydroxy*-4-*pentyl*-3,4-*dihydrocoumarin* (**2d**) as white needles (310 mg, 62%), m.p. 102—104 °C from hexane–chloroform (Found: C, 67.55; H, 7.45%; $M^+$, 250.1218. $C_{14}H_{18}O_4$ requires C, 67.20; H, 7.20%; $M$, 250.1205); $\nu_{max.}$($CHCl_3$) 3 600, 1 760, 1 630, and 1 620 $cm^{-1}$; $\lambda_{max.}$ 283 (in base 297) nm; δ [90 MHz; $(CD_3)_2CO$], 0.85 (3 H, t, $J$ 7 Hz, $MeCH_2$), 1.1—1.6 (8 H, m, $MeCH_2CH_2CH_2CH_2$), 2.7 (2 H, d, $J$ 4 Hz, $CHCH_2CO$), 3.3 (1 H, m, $CH_2CHCH_2$), 6.05 and 6.25 (each 1 H, d, $J$ 2 Hz, ArH), and 8.4 (2 H, br, 2 × OH); $m/z$ 250 ($M^+$, 42%), 179 (100), and 135 (40).

*Acylation of* 5,7-*Dihydroxy*-4-*pentyl*-3,4-*dihydrocoumarin* (**2d**).—To a suspension of 5,7-dihydroxy-4-pentyl-3,4-dihydrocoumarin (**2d**) (1 g, 4 mmol) and aluminium trichloride (2.135 g, 16 mmol) in carbon disulphide (8 ml) was added nitrobenzene (4 ml) and the mixture was stirred for 15 min, after which time 2-methylbutyryl chloride (0.48 g, 4 mmol) was added and stirring continued for a further 15 min. The mixture was poured onto ice–water and the solvents removed by steam distillation. The remaining solution was cooled and extracted with ether, the ether extracts were combined, dried, and evaporated, and the residue was chromatographed on a silica column. Elution with light petroleum (b.p. 60—80 °C)–chloroform (1:1 v/v) gave 5,7-*bis*(2-*methylbutyryloxy*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2e**) as a yellow gum (231 mg, 14%) (Found: $M^+$, 418.2348. $C_{24}H_{34}O_6$ requires $M$, 418.2355); $\nu_{max.}$($CHCl_3$) 2 925, 1 760, 1 620, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 267 nm; δ (90 MHz; $CDCl_3$) 0.85 (3 H, t, $J$ 7 Hz, $MeCH_2CH_2$), 1.0 and 1.02 (each 3 H, t, $J$ 7 Hz, $MeCH_2CH$), 1.25 and 1.32 (each 3 H, d, $J$ 7 Hz, $MeCH$), 1.2—2.0 (12 H, m, $MeCH_2CH_2CH_2CH_2$ and 2 × $MeCH_2CH$), 2.5—2.75 (2 H, m, 2 × $CH_2CHCO$), 2.80 (2 H, m, $CHCH_2CO$), 2.9—3.2 (1 H, m, $CH_2CHCH_2$), and 6.75 (2 H, s, ArH); $m/z$ 418 ($M^+$, 3%), 334 (40), 250 (100), and 179 (55). Continued elution with light petroleum (b.p. 60—80 °C)–chloroform (1:4 v/v) gave 5-*hydroxy*-7-(2-*methylbutyryloxy*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2f**) as a yellow gum (710 mg, 53%) (Found: $M^+$, 334.1788. $C_{19}H_{26}O_5$ requires $M$, 334.1780); $\nu_{max.}$($CHCl_3$) 3 600, 3 375, 2 950, 1 760 and 1 610 $cm^{-1}$; $\lambda_{max.}$ 277 and 280 (in base 299) nm; δ($CDCl_3$) 0.86 (3 H, t, $MeCH_2CH_2$), 1.0 (3 H, t, $J$ 7 Hz, $MeCH_2CH$), 1.28 (3 H, d, $MeCH$), 1.2—1.9 (10 H, m, $MeCH_2CH_2CH_2CH_2$ and $MeCH_2CH$), 2.5—2.9 (3 H, m, $CH_2CHCO$ and $CHCH_2CO$), 3.3 (1 H, m, $CH_2CHCH_2$), 6.40 and 6.46 (each 1 H, d, ArH), and 7.4 (1 H, s, OH); $m/z$ 334 ($M^+$, 4%), 250 (35), and 179 (100). Further elution with chloroform gave 5,7-*dihydroxy*-8-(2-*methylbutyryl*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2a**) as white crystals (15 mg, 1%), m.p. 132—134 °C (lit.,[4] 125 °C) (Found: C, 68.2; H, 8.15%; $M^+$, 334.1768. Calc. for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84%; $M$, 334.1780); $\nu_{max.}$($CHCl_3$) 3 600, 3 300, 2 950, 1 780, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 236, 286, and 321 (in base 247 and 336) nm; δ (90 MHz; $CDCl_3$) 0.85 and 0.95 (each 3 H, t, $J$ 7 Hz, $MeCH_2$), 1.15 (3 H, d, $J$ 7 Hz, $MeCH$), 1.25—2.05 (10 H, m, $MeCH_2CH_2CH_2CH_2$ and $MeCH_2CH_2$), 2.75 (2 H, m, $CHCH_2CO$), 3.35 (1 H, m, $CH_2CHCH_2$), 3.7 (1 H, m, $J$ 7 Hz, $CH_2CHCO$), 6.3 (1 H, s, ArH), 6.7 (1 H, br s, non-chelated OH), and 13.65 (1 H, s, chelated OH); $m/z$ 334 ($M^+$, 14%) and 277 (100). This compound was identical (u.v., n.m.r., t.l.c.) with a sample of natural material, mixed m.p. 127 °C. Elution with chloroform–methanol (50:1 v/v) afforded 7-*hydroxy*-5-(2-*methylbutyryloxy*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2g**) as a brown grum (160 mg, 12%) (Found: $M^+$, 334.1785. $C_{19}H_{26}O_5$ requires $M$, 334.1780); $\nu_{max.}$ 3 600, 3 325, 2 950, 1 760, 1 730, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 277infl and 282 (in base 293) nm; δ (90 MHz; $CDCl_3$) 0.85 and 1.05 (each 3 H, t, $MeCH_2$), 1.3 (3 H, d, $MeCH$), 1.2—2.0 (10 H, m, $MeCH_2CH_2CH_2CH_2$ and $MeCH_2CH$), 2.5—3.1 (4 H, m, $CHCH_2CO$, $CH_2CHCO$, and $CH_2CHCH_2$), 6.45 (2 H, s, ArH), and 7.25 (1 H, br s, OH); $m/z$ 334 ($M^+$, 17%), 250 (55), and 179 (100).

When the reaction was repeated, but stirring was continued overnight after the addition of the 2-methylbutyryl chloride, work-up as above gave the 7-*O*-acyldihydrocoumarin (**2f**) (614 mg, 37%), the 8-*C*-acyldihydrocoumarin (**2a**) (450 mg, 27%), and the 5-*O*-acyldihydrocoumarin (**2g**) (115 mg, 7%).

*Rearrangement of* 5-*Hydroxy*-7-(2-*methylbutyryloxy*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2f**).—A mixture of 5-hydroxy-7-(2-methylbutyryloxy)-4-pentyl-3,4-dihydrocoumarin (**2f**) (750 mg, 2.25 mmol), aluminium trichloride (1.2 g, 9 mmol), carbon disulphide (10 ml), and nitrobenzene (20 ml) was stirred for 6 days at 20 °C. The solution was poured into ice–water, the solvents were removed by steam distillation, and the remaining solution was cooled and extracted with ether. The combined ether extracts were dried and evaporated to leave a residue that was chromatographed on a silica column as above to afford the 8-*C*-acyldihydrocoumarin (**2a**) (200 mg, 27%) and 5,7-dihydroxy-4-pentyl-3,4-dihydrocoumarin (**2d**) (300 mg, 53%).

*Rearrangement of* 7-*Hydroxy*-5-(2-*methylbutyryloxy*)-4-*pentyl*-3,4-*dihydrocoumarin* (**2g**) was performed as above using 7-hydroxy-5-(2-methylbutyryloxy)-4-pentyl-3,4-dihydrocoumarin (**2g**) (115 mg, 0.35 mmol), aluminium trichloride (0.2 g, 1.5 mmol), carbon disulphide (10 ml), and nitrobenzene (10 ml). Work-up as above gave the 8-*C*-acyldihydrocoumarin (**2a**) (40 mg, 35%) and a small amount of 5,7-dihydroxy-4-pentyl-3,4-dihydrocoumarin (**2d**).

5,7-*Dihydroxy*-4-(1-*methylpropyl*)*coumarin* (**3b**).—To phloroglucinol (6.85 g, 54 mmol) in 75% sulphuric acid (80 ml) was added ethyl 4-methyl-3-oxohexanoate (**4d**) (9.3 g, 54 mmol), and the mixture was stirred for 24 h at room temperature. The solution was poured onto ice–water and the mixture extracted with ether. The combined ether extracts were dried and evaporated to leave a residue that was chromatographed on silica, eluting with chloroform followed by chloroform–methanol (50:1 v/v), to give 5,7-*dihydroxy*-4-(1-*methylpropyl*)*coumarin* (**3b**) as a yellow-brown solid (3.6 g, 28%), m.p. 216—218 °C from aqueous ethanol (Found: C, 66.75; H, 6.3%; $M^+$, 234.0888. $C_{13}H_{14}O_4$ requires C, 66.66; H, 6.02%; $M$, 234.0892); $\nu_{max.}$(KBr) 3 200, 1 650, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 251, 258, and 326 (in base 276 and 380) nm; δ [90 MHz; $(CD_3)_2SO$] 0.95 (3 H, t, $J$ 7 Hz, $MeCH_2$), 1.2 (3 H, d, $J$ 7 Hz, $MeCH$), 1.3—1.9 (2 H, m, $MeCH_2CH$), 3.95 (1 H, m, $CH_2CHCO$), 5.95 (1 H, s, C=CHCO), 6.3 and 6.4 (each 1 H, d, $J$ 2 Hz, ArH), and 10.3 (2 H,

br s, 2 × OH); *m/z* 234 ($M^+$, 40%), 219 (20), 206 (70), and 177 (100).

*Acylation of 5,7-Dihydroxy-4-(1-methylpropyl)coumarin* (**3b**).—To a stirred suspension of 5,7-dihydroxy-4-(1-methylpropyl)coumarin (**3b**) (2.34 g, 10 mmol) and aluminium trichloride (5.4 g, 40 mmol) in carbon disulphide (25 ml) was added nitrobenzene (25 ml). After 30 min, 2-methylbutyryl chloride (1.2 g, 10 mmol) was added and stirring continued for 6 days. The mixture was poured into ice–water, the solvents were removed by steam distillation, and the cooled remaining solution was extracted with ether. The combined ether extracts were dried and evaporated to afford a residue that was chromatographed on a silica column, eluting with chloroform followed by chloroform–methanol (49:1 v/v), to give 5,7-*dihydroxy*-8-(2-*methylbutyryl*)-4-(1-*methylpropyl*)*coumarin* (**3c**) as white needles (1.375 g, 43%), m.p. 182—184 °C from chloroform–methanol (Found: C, 67.75; H, 7.35%; $M^+$, 318.1467. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.97%; *M*, 318.1467); $\nu_{max.}$(KBr) 3 250, 1 690, and 1 630 cm$^{-1}$; $\lambda_{max.}$ 291 and 317 (in base 253 and 331) nm; δ [90 MHz; $(CD_3)_2CO$] 1.0 (6 H, t, *J* 7 Hz, 2 × *Me*$CH_2$CH), 1.20 and 1.25 (each 3 H, d, *J* 7 Hz, *Me*CH), 1.3—2.0 (4 H, m, 2 × MeC$H_2$CH), 3.90 (2 H, m, *J* 7 Hz, $CH_2CH$CO and CHC=CHCO), 6.05 (1 H, s, C=CHCO), 6.35 (1 H, s, ArH), 10.6 (1 H, br s, non-chelated OH), and 13.8 (1 H, br, chelated OH); *m/z* 318 ($M^+$, 23%), 261 (100), and 233 (22). Further elution with chloroform–methanol (19:1 v/v) gave some unchanged starting material (**3b**) (0.8 g, 34%).

*Mammea D/BB* (**3a**).—To 5,7-dihydroxy-8-(2-methylbutyryl)-4-(1-methylpropyl)coumarin (**3c**) (1 g, 3.1 mmol) in 10% aqueous potassium hydroxide (5 ml) stirred at 0 °C under nitrogen was added 3-methylbut-2-enyl bromide (462 mg, 3.1 mmol) dropwise over 1.5 h. The mixture was then poured into dilute hydrochloric acid and extracted with ether. The ether extracts were combined, dried, and evaporated to afford a residue that was chromatographed on a silica column, eluting with chloroform, to give mammea D/BB (**3a**) as white needles (265 mg, 22%), m.p. 117—119 °C from hexane (lit.,[6] 126.5 °C) (Found: C, 71.4; H, 8.0%; $M^+$, 386.2085. Calc. for $C_{23}H_{20}O_5$: C, 71.48; H, 7.82%; *M*, 386.2093); $\nu_{max.}$($CHCl_3$) 1 730 and 1 600 cm$^{-1}$; $\lambda_{max.}$ 294 and 318 (in base 256 and 333) nm; δ (90 MHz; $CDCl_3$) 1.0 (6 H, t, *J* 7 Hz, 2 × *Me*$CH_2$CH), 1.15 and 1.2 (each, 3 H, d, *J* 7 Hz, *Me*CH), 1.3—2.0 (4 H, m, 2 × MeC$H_2$CH), 1.75 and 1.80 (6 H, 2 × s, $Me_2$C=CH), 3.45 (2 H, d, *J* 7 Hz, ArC$H_2$CH), 3.95 (2 H, m, *J* 7 Hz, $CH_2CH$CO and CHC=CHCO), 5.3 (1 H, t, *J* 7 Hz, $Me_2C$=C*H*$CH_2$), 6.2 (1 H, s, C=CHCO), 7.2 (1 H, s, non-chelated OH), and 14.55 (1 H, s, chelated OH); *m/z* 386 ($M^+$, 63%), 329 (100), and 273 (31). Further elution with chloroform–methanol (20:1 v/v) gave some starting material.

4-(1-*Acetoxypropyl*)-5,7-*dihydroxycoumarin* (**6a**).—Phloroglucinol (5.8 g, 46 mmol) and ethyl 4-acetoxy-3-oxohexanoate (**4a**) (9.95 g, 46 mmol) in trifluoroacetic acid (60 ml) were heated at reflux for 2 h, and the mixture then poured into ice–water and extracted with ether. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate followed by water, dried and evaporated. Chromatography of the residue on a silica column, eluting with chloroform–methanol (49:1 v/v), gave 4-(1-*acetoxypropyl*)-5,7-*dihydroxycoumarin* (**6a**) as white needles (6.8 g, 53%), m.p. 238—242 °C (Found: $M^+$, 278.0811. $C_{14}H_{14}O_6$ requires *M*, 278.0790), $\nu_{max.}$(KBr) 3 100, 1 680, and 1 620 cm$^{-1}$; $\lambda_{max.}$ 251, 259, and 327 (in base 280 and 402) nm; δ (90 MHz; $C_5D_5N$) 1.10 (3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.6—2.5 (2 H, m, MeC$H_2$CH), 2.15 (3 H, s, MeCO), 6.5 (1 H, s, CHC=C*H*CO), 6.7 (2 H, s, ArH), 7.1 (1 H, dd, *J* 3 and 8 Hz, $CH_2CH$O), and 12.3 (2 H, br s, 2 × OH); *m/z* 278 ($M^+$, 25%), 236 (3), 218 (79), 203 (100), and 190 (40). Further elution with chloroform–methanol (19:1 v/v) afforded 5,7-*dihydroxy*-4-(1-*hydroxypropyl*)*coumarin* (**7**) as a white solid (1.3 g, 11%), m.p. 227—230 °C (Found: $M^+$, 236.0683. $C_{12}H_{12}O_5$ requires *M*, 236.0685), $\nu_{max.}$(KBr) 3 350, 3 200, 1 650, and 1 600 cm$^{-1}$; $\lambda_{max.}$ 250, 258, and 324 (in base 278 and 392) nm; δ (90 MHz; $C_5D_5N$) 1.25 (3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.6—2.4 (2 H, m, MeC$H_2$CH), 3.55 (1 H, s, CHO*H*), 5.85 (1 H, dd, *J* 3 and 7 Hz, $CH_2CH$OH), 6.7 (2 H, s, ArH), 7.0 (1 H, s, CHC=C*H*CO), and 10.0 (2 H, br, 2 × OH); *m/z* 236 ($M^+$, 60%), 218 (30), 203 (100), and 190 (35).

4-(1-*Acetoxypropyl*)-5,7-*dihydroxy*-8- *and* 6-(3-*methylbutyryl*)*coumarins* (**6b** *and* **c**).—To a stirred suspension of 4-(1-acetoxypropyl)-5,7-dihydroxycoumarin (**6a**) (1.62 g, 5.83 mmol) and aluminium trichloride (3.89 g, 29.15 mmol) in carbon disulphide (25 ml) was added nitrobenzene (15 ml). After 30 min, 3-methylbutyryl chloride (0.7 g, 5.83 mmol) was added and stirring was continued for a further 6 days before the mixture was poured onto ice–water. The solvents were removed by steam distillation and the remaining solution was cooled and extracted with ether. The combined ether extracts were dried and evaporated to leave a residue that was chromatographed on a silica column, eluting with chloroform followed by chloroform–methanol (99:1 v/v), to give a mixture of 6- and 8-acylcoumarins (1.11 g, 53%) shown by u.v. spectra to be predominantly the 8-acyl isomer. Crystallisation of the mixture from hexane–chloroform afforded 4-(1-*acetoxypropyl*)-5,7-*dihydroxy*-8-(3-*methylbutyryl*)*coumarin* (**6b**) as a white solid (445 mg, 21%), m.p. 210—212 °C (Found: C, 63.3; H, 6.5%; $M^+$, 362.1360. $C_{19}H_{22}O_7$ requires C, 62.98; H, 6.12%; *M*, 362.1365); $\nu_{max.}$($CHCl_3$) 1 730, 1 630, and 1 600 cm$^{-1}$; $\lambda_{max.}$ 290 and 323 (in base 246 and 331) nm; δ (90 MHz; $CDCl_3$) 1.05 (6 H, d, *J* 7 Hz, $Me_2$CH, 1.10 (3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.5—2.4 (3 H, m, $Me_2CHCH_2$ and MeC$H_2$CH), 2.30 (3 H, s, MeCO), 3.05 (2 H, t, *J* 7 Hz, $CHCH_2$CO), 6.05 (1 H, s, CHC=C*H*CO), 6.30 (1 H, s, ArH), 6.55 (1 H, dd, *J* 3 and 7 Hz, $CH_2CH$O), 9.1 (1 H, br s, non-chelated OH), and 14.1 (1 H, s, chelated OH); *m/z* 362 ($M^+$, 5%), 305 (2), 302 (19), 287 (24), 245 (100), and 217 (6). The remaining mixture was separated on reverse-phase h.p.l.c., eluting with methanol–water (4:1 v/v), to afford further 8-acylcoumarin (**6b**) (250 mg, 12%) and 4-(1-*acetoxypropyl*)-5,7-*dihydroxy*-6-(3-*methylbutyryl*)*coumarin* (**6c**) as yellow needles (300 mg, 14%), m.p. 213—214 °C from hexane–chloroform (Found: C, 62.8; H, 6.26%; $M^+$, 362.1363. $C_{19}H_{22}O_7$ requires C, 62.98; H, 6.12%; *M*, 362.1365); $\nu_{max.}$($CHCl_3$) 1 730, 1 710, and 1 620 cm$^{-1}$; $\lambda_{max.}$ 282 and 330 (in base 237, 298, and 413) nm; δ (90 MHz; $CDCl_3$) 1.00 (6 H, d, *J* 7 Hz, $Me_2$CH), 1.05 (3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.4—2.4 (3 H, m, MeC$H_2$CH and $Me_2CHCH_2$), 2.35 (3 H, s, MeCO), 3.05 (2 H, d, *J* 7 Hz, $CHCH_2$CO), 6.2 (1 H, s, CHC=C*H*CO), 6.6 (1 H, dd, *J* 2 and 7 Hz, $CH_2CH$O), 6.65 (1 H, s, ArH), 9.2 (1 H, br s, non-chelated OH), and 16.0 (1 H, s, chelated OH); *m/z* 362 ($M^+$, 7%), 320 (8), 302 (44), 287 (49), 245 (100), and 217 (18).

4-(1-*Acetoxypropyl*)-5,7-*dihydroxy*-8-(2-*methylbutyryl*)-*coumarin* (**6d**) was prepared as above from 4-(1-acetoxypropyl)-5,7-dihydroxycoumarin (**6a**) (1.5 g, 5.4 mmol), aluminium trichloride (3.6 g, 27 mmol), carbon disulphide (25 ml), nitrobenzene (15 ml), and 2-methylbutyryl chloride (0.65 g, 5.4 mmol). Work-up after 4 days and chromatography on silica, eluting with chloroform followed by chloroform–methanol (99:1 v/v), afforded 8-acylcoumarin contaminated with a trace of the 6-acyl isomer. Further purification of this fraction by reverse-phase h.p.l.c., eluting with methanol–water (4:1 v/v), gave pure 4-(1-*acetoxypropyl*)-5,7-*dihydroxy*-8-(2-*methylbutyryl*)*coumarin* (**6d**) as white needles (866 mg, 44%), m.p. 182—184 °C from hexane–chloroform (Found: C, 63.25; H, 6.45%; $M^+$, 362.1378. $C_{19}H_{22}O_7$ requires C, 62.98; H, 6.12%; *M*, 362.1365), $\nu_{max.}$($CHCl_3$) 1 730, 1 720, 1 630, and 1 600 cm$^{-1}$;

$\lambda_{max.}$ 290 and 322 (in base 246 and 330) nm; δ (90 MHz; $CDCl_3$) 0.95 and 1.10 (each 3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.25 (3 H, 2 × d, *J* 7 Hz, *Me*CH), 1.3—2.2 (4 H, m, MeC$H_2$CH and MeC$H_2$CHO), 2.3 (3 H, 2 × s, MeCO), 3.8 (1 H, m, *J* 7 Hz, $CH_2CH$CO), 6.15 and 6.20 (1 H, 2 × s, CHC=C*H*CO), 6.35 (1 H, s, ArH), 6.65 (1 H, m, $CH_2CH$O), 9.4 (1 H, br s, non-chelated OH), and 14.05 (1 H, br s, chelated OH) (extra signals in the $^1$H n.m.r. spectrum are due to the presence of a mixture of diastereoisomers; *m/z* 362 ($M^+$, 8%), 305 (29), 302 (45), 245 (100), and 217 (37). Further elution of the original silica column with chloroform–methanol (49:1 v/v) afforded unchanged starting material (**6a**) (0.55 g, 37%) followed by trihydroxycoumarin (**7**) (0.175 g, 14%).

*Mammea E/BA* (**1a**).—To 4-(1-acetoxypropyl)-5,7-dihydroxy-8-(3-methylbutyryl)coumarin (**6b**) (562 mg, 1.55 mmol) in 5% aqueous potassium hydroxide (3.5 ml, 3.1 mmol of KOH) stirred at 0 °C under nitrogen was added 3-methylbut-2-enyl bromide (0.23 g, 1.55 mmol) dropwise over 1.5 h. The solution was acidified with dilute hydrochloric acid and extracted with ether and chloroform. The combined organic extracts were dried and evaporated, and the residue was chromatographed on a silica column, eluting with chloroform–hexane (13:7 v/v) to give some initial gum followed by *mammea E/BA* (**1a**) as white needles (130 mg, 20%), m.p. 130—132 °C from hexane–chloroform (Found: C, 67.25; H, 7.3%; $M^+$, 430.1985. $C_{24}H_{30}O_7$ requires C, 66.96; H, 7.02%; *M*, 430.1991); $\nu_{max.}$($CHCl_3$) 3 300, 2 950, 1 720, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 294 and 328 (in base 256 and 333) nm; δ (250 MHz; $CDCl_3$) 1.05 (6 H, d, *J* 7 Hz, $Me_2$CH), 1.05 (3 H, t, *Me*$CH_2$), 1.6—2.0 (2 H, m, MeC$H_2$CH), 1.85 and 1.90 (6 H, 2 × s, $Me_2$C=CH), 2.2 (3 H, s, MeCO), 2.3 (1 H, m, *J* 7 Hz, $Me_2CHCH_2$), 3.15 (2 H, dd, *J* 3 and 7 Hz, CHC$H_2$CO), 3.50 (2 H, m, *J* 7 and 16 Hz, $Me_2$C=CHC$H_2$), 5.25 (1 H, t, *J* 7 Hz, $Me_2$C=C*H*$CH_2$), 6.3 (1 H, s, CHC=C*H*CO), 6.5 (1 H, dd, *J* 3 and 7 Hz, $CH_2CH$O), 7.15 (1 H, s, non-chelated OH), and 14.7 (1 H, s, chelated OH); *m/z* 430 ($M^+$, 7%), 388 (5), 370 (54), 355 (100), 327 (35), 315 (70), 313 (15), 299 (15), 257 (38), and 229 (10). Further elution with chloroform–methanol (49:1 v/v) led to recovery of starting material (**6b**) (283 mg, 50%).

*Mammea E/BB* (**1b**). This was prepared as above from 4-(1-acetoxypropyl)-5,7-dihydroxy-8-(2-methylbutyryl)coumarin (**6d**) (0.5 g, 1.38 mmol), 5% aqueous potassium hydroxide (3.1 ml; 2.76 mmol of KOH), and 3-methylbut-2-enyl bromide (0.2 g, 1.38 mmol). Work-up as above, but extracting only with chloroform, led to a residue that was chromatographed on a silica column, eluting with chloroform–hexane (13:7 v/v), to give some initial oil followed by *mammea E/BB* (**1b**) as a yellow gum (120 mg, 20%) that crystallised from hexane–chloroform as white needles, m.p. 114—116 °C (Found: C, 67.15; H, 7.2%; $M^+$, 430.1980. $C_{24}H_{30}O_7$ requires C, 66.96; H, 7.02%; *M*, 430.1991); $\nu_{max.}$($CHCl_3$), 3 300, 2 950, 1 730, 1 720, and 1 610 $cm^{-1}$; $\lambda_{max.}$ 294 and 333 (in base 257 and 333) nm; δ (250 MHz; $CDCl_3$), 1.00 and 1.05 (each 3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.25 (3 H, d, *J* 7 Hz, *Me*CH), 1.35—2.0 (4 H, m, 2 × MeC$H_2$CH), 1.85 and 1.90 (6 H, 2 × s, $Me_2$C=CH), 2.20 (3 H, s, MeCO), 3.50 (2 H, m, *J* 7 and 16 Hz, $Me_2$C=CHC$H_2$), 3.9 (1 H, m, *J* 7 Hz, $CH_2CH$CO), 5.25 (1 H, t, *J* 7 Hz, $Me_2$C=C*H*$CH_2$), 6.3 (1 H, s, CHC=C*H*CO), 6.5 (1 H, dd, *J* 3 and 7 Hz, $CH_2CH$O), 7.15 (1 H, s, non-chelated OH), and 14.65 (1 H, s, chelated OH); *m/z* 430 ($M^+$, 8%), 388 (4), 370 (42), 355 (33), 327 (21), 315 (42), 313 (42), 299 (12), 257 (100), and 299 (17). Further elution with chloroform–methanol (49:1 v/v) led to recovery of starting material (**6d**) (200 mg, 40%).

*Surangin B* (**1e**).—To 4-(1-acetoxypropyl)-5,7-dihydroxy-8-(2-methylbutyryl)coumarin (**6d**) (1 g, 2.76 mmol) in 5% aqueous potassium hydroxide (6 ml, 5.52 mmol of KOH) stirred at 45 °C under nitrogen was added (2*E*)-3,7-dimethylocta-2,6-dienyl chloride (0.48 g, 2.78 mmol) dropwise over 24 h. The cooled mixture was then poured onto ice–dilute hydrochloric acid and extracted with ether. The combined organic extracts were dried and evaporated to leave a residue that was chromatographed on a silica column, eluting with light petroleum (b.p. 60—80 °C)–chloroform (1:1 v/v) to give the *bisgeranyl pyrone* (**8a**) as a yellow gum (70 mg, 4%) (Found: $M^+$, 634.3889. $C_{39}H_{54}O_7$ requires *M*, 634.3869); $\nu_{max.}$($CHCl_3$) 2 950, 1 740, 1 660, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 296, 299, and 359 (in base 240, 312, and 408) nm; δ (90 MHz; $CDCl_3$) 0.9 and 1.05 (each 3 H, t, *J* 7 Hz, *Me*$CH_2$CH), 1.25 (3 H, d, *J* 7 Hz, *Me*CH), 1.50 and 1.60 (12 H, 2 × s, 2 × $Me_2$C and 2 × *Me*C=CH), 1.3—1.9 (4 H, m, 2 × MeC$H_2$CH), 1.85 (8 H, s, 2 × CHC$H_2$C$H_2$CMe), 2.1 (3 H, s MeCO), 2.75 (4 H, m, 2 × C=CHC$H_2$), 3.75 (1 H, m, *J* 7 Hz, $CH_2CH$CO), 4.7—5.1 (4 H, m, 2 × $Me_2$C=C*H* and 2 × C*H*=CMe), 6.1 (1 H, s, CHC=C*H*CO), 6.5 (1 H, m, C*H*OCOMe), and 19.2 (1 H, s, chelated OH) (some of these signals are twinned due to the presence of a mixture of diastereoisomers). Further elution afforded a 1:1 mixture (200 mg, 15%) of surangin B (**1e**) and the 5-*O*-geranyl isomer (**9**) that was separated by h.p.l.c. on a silica column, eluting with ethyl acetate–hexane (3:37 v/v), to give 4-(1-*acetoxypropyl*)-7-*hydroxy*-8-(2-*methylbutyryl*)-5-[(2E)-3,7-*dimethylocta*-2,6-*dienyloxy*]*coumarin* (**9**) as a white solid, m.p. 88—89 °C from hexane–ether (Found: C, 69.75; H, 7.8%; $M^+$,498.2620. $C_{29}H_{38}O_7$ requires C, 69.85; H, 7.7%; *M*, 498.2617); $\nu_{max.}$($CHCl_3$) 2 950, 1 730, and 1 620 $cm^{-1}$; $\lambda_{max.}$ 289 and 321 (in base 237 and 383) nm; δ (250 MHz; $CDCl_3$) 1.0 and 1.05 (each 3 H, t, *J* 7 Hz, *Me*$CH_2$CH), 1.25 (3 H, d, *J* 7 Hz, *Me*CH), 1.4—1.6 (2 H, m, MeC$H_2$CH), 1.60, 1.70, and 1.80 (9 H, 3 × s, $Me_2$C=CH and *Me*C=CH), 1.8—2.0 (2 H, m, MeC$H_2$CHO), 2.15 (4 H, s, CHC$H_2$C$H_2$CMe), 2.20 (3 H, s, MeCO), 3.9 (1 H, m, *J* 7 Hz, $CH_2CH$CO), 4.7 (2 H, d, *J* 8 Hz, CHC$H_2$O), 5.1 (1 H, m, $Me_2$C=C*H*$CH_2$), 5.5 (1 H, t, *J* 8 Hz, C*H*$CH_2$O), 6.3 (1 H, s, OCHC=C*H*CO), 6.37 (1 H, s, ArH), 6.45 (1 H, dd, *J* 3 and 7 Hz, C*H*OCOMe), and 14.25 (1 H, s, chelated OH) (some of these signals are twinned due to the presence of a mixture of diastereoisomers). This was followed by *surangin B* (**1e**) and a diastereoisomer as a gum (Found: C, 69.65; H, 7.8%; $M^+$, 498.2605. $C_{29}H_{38}O_7$ requires C, 69.85; H, 7.68%; *M*, 498.2617); $\nu_{max.}$($CHCl_3$) 3 300, 2 950, 1 740, 1 730, 1 610, and 1 600 $cm^{-1}$; $\lambda_{max.}$ 294 and 328 (in base 253 and 333) nm; δ (250 MHz; $CDCl_3$) 0.9 and 0.95 (each 3 H, t, *J* 7 Hz, *Me*$CH_2$CH), 1.2 (3 H, d, *J* 7 Hz, *Me*CH), 1.3—2.0 (4 H, m, 2 × MeC$H_2$CH), 1.50, 1.60, and 1.80 (9 H, 3 × s, $Me_2$C=CH and *Me*C=CH), 2.05 (4 H, s, CHC$H_2$C$H_2$CMe), 2.10 (3 H, s, MeCO), 3.45 (2 H, d, *J* 6 Hz, ArC$H_2$CH), 3.80 (1 H, m, *J* 7 Hz, $CH_2CH$CO), 5.0 (1 H, m, $Me_2$C=C*H*), 5.15 (1 H, t, *J* 6 Hz, ArC$H_2$C*H*=C), 6.2 (1 H, s, OCHC=C*H*CO), 6.4 (1 H, dd, *J* 3 and 7 Hz, C*H*OCOMe), 7.2 (1 H, br s, non-chelated OH), and 14.5 (1 H, s, chelated OH) (some of these signals are twinned due to the presence of a mixture of diastereoisomers).

## Acknowledgements

We thank Wellcome Research Laboratories (Berkhamsted) and the S.E.R.C. for a CASE studentship (to C. J. P.).

## References

1 (*a*) Part 1; (*b*) Part 2: L. Crombie, R. C. F. Jones, and C. J. Palmer, preceding papers. For a preliminary account of parts of this work, see: L. Crombie, R. C. F. Jones, and C. J. Palmer, *Tetrahedron Lett.*, 1985, **26**, 2929, 2933. For some model studies on simpler systems see C. W. Bird, H. I. Butler, and A. Hawi, *Chem. Ind.* (*London*), 1984, 154.

2 See Ref. 1(*a*) for a survey of *Mammea* coumarins.

3 P. Cannone, D. Belanger, and G. Lemay, *Synthesis*, 1980, 301; F. D. Mills, *J. Heterocycl. Chem.*, 1980, **17**, 1597.

4 E. G. Crichton and P. G. Waterman, *Phytochemistry*, 1978, **17**, 1783; C. H. Schwalbe, P. G. Waterman, and E. G. Crichton, work presented at the Chemical Crystallography Group of the Royal Society of Chemistry, Leeds, September 1981. We thank Dr. P. G. Waterman for a sample of natural (**2a**).
5 S. Sethna and R. Phoelka, *Org. React.*, 1953, **7**, 1.
6 T. R. Govindachari, B. R. Pai, P. S. Subramanian, U. Ramdas Rao, and N. Muthukumaraswamy, *Tetrahedron*, 1967, **23**, 4161.
7 L. Crombie, D. E. Games, N. J. Haskins, and G. F. Reed, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2255.
8 B. S. Joshi, V. N. Kamat, T. R. Govindachari, and A. K. Ganguly, *Tetrahedron*, 1969, **25**, 1453.
9 G. H. Stout and K. D. Sears, *J. Org. Chem.*, 1968, **33**, 4185.

*Received* 3*rd January* 1986; *Paper* 6/021