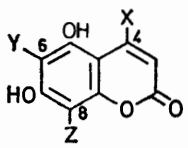
Extractives of *Mammea americana* L. Part III.[1a] Identification of New Coumarin Relatives of Mammea B/BA, B/BB, and B/BC having 5,6-Annulation and Higher Oxidation Levels

By **L. Crombie,*† D. E. Games, N. J. Haskins,** and **G. F. Reed,** Department of Chemistry, University College (University of Wales), Cardiff CF1 1XL

Six new 4-n-propylcoumarins, all having 5,6-annulation and a higher oxidation level than the mammeas B/BA, B/BB, and B/BC, to which they are related, have been identified in the seed-extract from *Mammea americana* L. A group of three ((VIa—c) all contain an α-(hydroxyisopropyl)dihydrofuran ring and are differentiated by 3-methylbutyryl, 2-methylbutyryl, and butyryl substituents at the coumarin C-8. They have been deacylated to a common product (VIIIa), which has been synthesised. Compounds (VIa—c) have been obtained by partial synthesis from mammea B/BA, B/BB, and B/BC, respectively. Two further compounds are similar but contain a cyclic peroxide feature (XVa and b). The sixth compound is a hydroperoxide (XVI). Structural evidence is based on a combination of spectral information, the results of chemical degradation, and partial synthesis.

THE seeds of the West Indian tree *Mammea americana* L. are insecticidal and contain an array of phloroglucinol coumarins having structure (I) as the core. This nucleus carries a 4-alkyl or 4-phenyl substituent X; Y and Z are usually 3-methylbut-2-enyl, butyryl, 3-methylbutyryl, or 2-methylbutyryl residues. Structures (III)—(V) are typical 4-alkyl members. None of the nine crystalline coumarins isolated in our earlier work,[1,2] or of the other compounds mentioned there, possessed the insecticidal properties of the crude light petroleum extract from which they were separated; the investigation of this extract has therefore been continued. Six new coumarins [(VIa—c), (XVa and b),



(I)

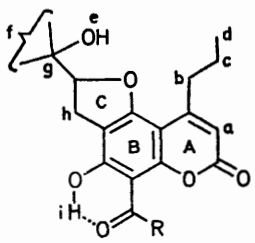
X = Pr^n, Y = $Me_2C{:}CH{\cdot}CH_2$

(II) B/B Z = H
(III) B/BA Z = $Me_2CH{\cdot}CH_2{\cdot}CO$
(IV) B/BB Z = $MeCH_2{\cdot}CHMe{\cdot}CO$
(V) B/BC Z = $MeCH_2{\cdot}CH_2{\cdot}CO$

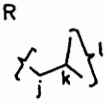
and (XVI)] containing structural features not previously found in this group are now reported; none of these are insecticidally active.‡

Separation of the closely related compounds proved difficult; the problem of identification was approached by resolution of the extractives into small groups of congeners. The structures of the members were then deduced from spectral data and the compounds identified were synthesised or related to known compounds by chemical conversions.

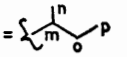
Chromatography of the fractions of the light petroleum extract of *M. americana* seeds gave a crystalline mixture designated L1, m.p. 130—131°, which by further preparative layer chromatography was resolved into two sub-fractions, L1a, m.p. 126°, and L1b, m.p. 120—123°. Sub-fraction L1a was optically active (r.d. curve) and the results of combustion analysis and mass measurement supported $C_{22}H_{28}O_6$ as the molecular formula. Sub-fraction L1b, however, did not give satisfactory analytical figures for $C_{22}H_{28}O_6$, and the



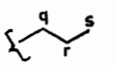
(VI) a; R =



b; R =



c; R =



τ Values

a 4·05 (1H, s)
b 7·15 (2H, t, *J* 7 Hz)
c 8·0—8·7 (2H, m)
d 8·98 (3H, t, *J* 7 Hz)
e 8·06 (1H, s, exchanged by D_2O)
f 8·73, 8·61 (both 3H, s)
g 5·14 (1H, t *J* 9 Hz)
h 6·84 (2H, d, *J* 9 Hz)
i *ca.* −4·1 (1H, s, exchanged by D_2O)

(VIa) j 6·95 (2H, d, *J* 7 Hz)
k 7·8 (1H, m)
l 8·98 (6H, d, *J* 7 Hz)

(VIb) m 6·15 (1H, m)
n 8·76 (3H, d, *J* 7 Hz)
o 8·0—8·7 (2H, m)
p 8·96 (3H, t, *J* 7 Hz)

(VIc) q 6·84 (2H, t, *J* 7 Hz)
r 8·0—8·7 (2H, m)
s 8·97 (3H, t, *J* 7 Hz)

N.m.r. data for partially synthetic specimens. In this and similar n.m.r. presentations, data for the 'core' differ little among the relatives and represent average values.

mass spectrum examination showed an additional molecular ion in substantial amount [*m/e* 374, $C_{21}H_{26}O_6$ (accurate mass)]. U.v. data (Table) suggest classification of L1a and L1b as acylated, 5,7-dioxygenated coumarins: their i.r. data are also consistent with a coumarin core of the mammea type. N.m.r. data (VIa—c) showed certain similarities to mammea B/B coumarins [*cf.* (II)] and this relationship was established by synthesis (see later). Detailed n.m.r. interpretation showed that L1a was a mixture of 8-(3-methylbutyryl) and 8-(2-methylbutyryl) compounds (VIa and b). The mixture L1b contained both components (VIa and b) but the major 8-acyl contributor was in this case

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‡ For conjoint preliminary reports of the work described in this paper and the following, see L. Crombie, D. E. Games, N. J. Haskins, G. F. Reed, R. A. Finnegan, and K. E. Merkel, *Tetrahedron Letters*, 1970, 3975, 3979. The independent work of Professor Finnegan's group will be reported elsewhere. The independent investigation of *Mammae africana* bark, reported adjacently to our communication (I. Carpenter, E. J. McGarry, and F. Scheinmann, *Tetrahedron Letters*, 1970, 3983) is also relevant. We appreciate the exchange of information with Professor Finnegan and Dr. Scheinmann.

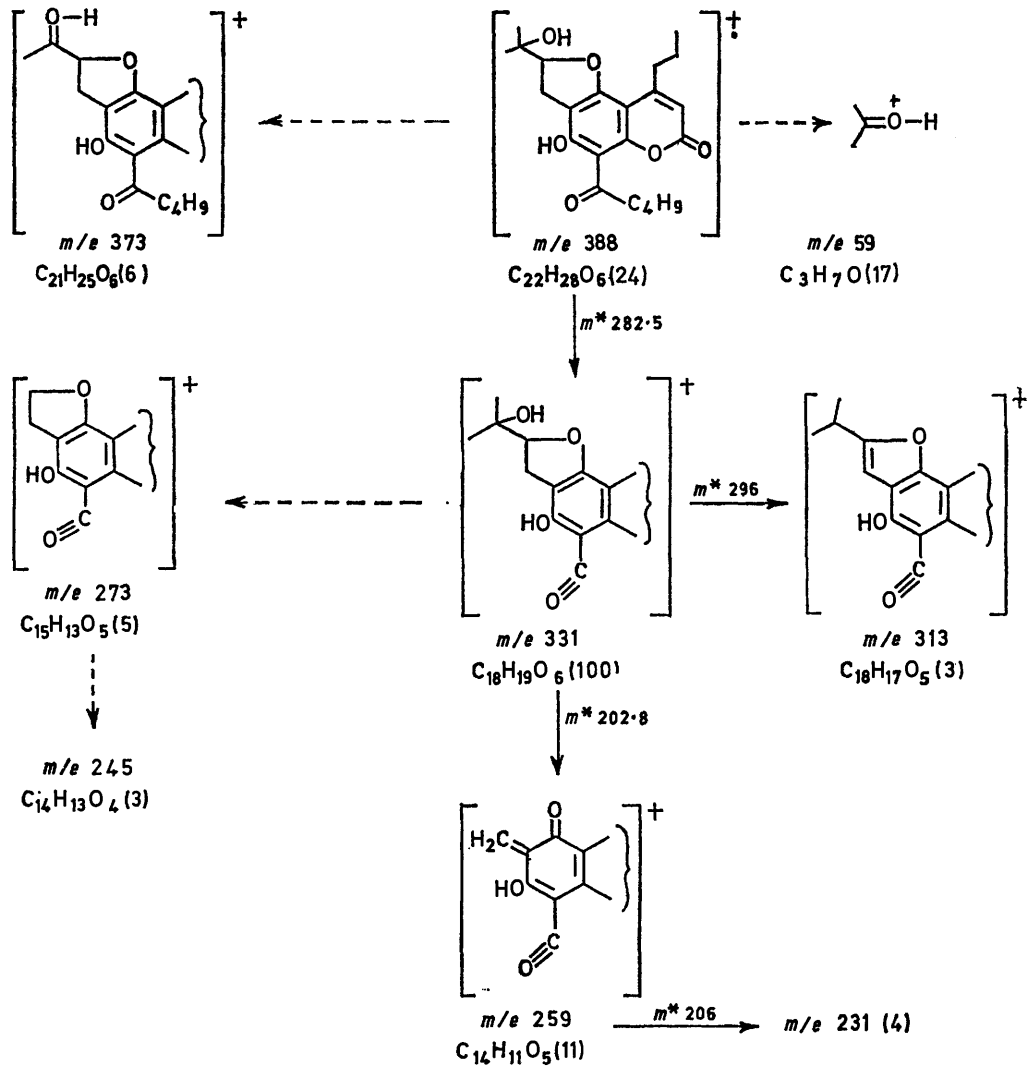
[1] (*a*) Part II, L. Crombie, D. E. Games, and A. McCormick, *J. Chem. Soc.* (*C*), 1967, 2553; (*b*) *Tetrahedron Letters*, 1966, 145.

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

the 8-butyryl compound (VIc). The presence of the chelated 7,8-system was shown by the low field proton signal (τ *ca.* −4·1) and by i.r. data.

Important differences in the n.m.r. data relative to those for compounds (III)—(V) show that the substituent Y has been substantially modified, the signals assigned to the 3-methylbut-2-enyl group being absent. In their place are resonances at τ 8·73 (3H, s), 8·61 (3H, s) 6·84 (2H, d, J 9 Hz), and 5·14 (1H, t, J 9 Hz). The phenolic 5-OH signal at τ *ca.* 2·9 has disappeared, but a new OH signal at τ 8·06 is now presemt. This led us to consider an α-(hydroxyisopropyl)dihydrofuran structure [see (VI)] or a 3-hydroxy-2,2-dimethyldihydropyran system [see (VII)] fused at the coumarin 5- and 6-positions. Comparison with model systems[3] led us to prefer the former.

Mass spectral fragmentation of the mixture L1a (Scheme 1) supports the presence of compounds (VIa and b). Loss of a butyl radical (M − 57) is characteristic of a 2-methylbutyryl or a 3-methylbutyryl substituent in this series, and the presence of an abundant ion at *m/e* 59 (17) is in agreement with an α-(hydroxyisopropyl)dihydrofuran feature.[4] Further confirmation is provided by the ion at *m/e* 273 (accurate mass), probably originating from *m/e* 331 by acetone loss. The latter loses water to give the species *m/e* 313. The presence of a metastable ion at *m/e* 202·8 indicates that the ion at *m/e* 259 is derived from the M − 57 ion by loss of C_4H_8O, and it has been suggested that such ions arise from the α-(hydroxyisopropyl)dihydro-



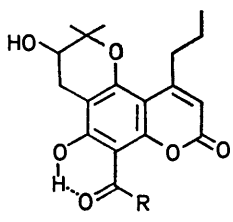
SCHEME 1 Mass spectral fragmentation of 5,6-annulated mammea compounds

[3] R. M. Brooker, J. N. Eble, and N. A. Starkovsky, *Lloydia*, 1967, **30**, 73; B. E. Nielsen and J. Lemmich, *Acta Chem. Scand.*, 1964, **18**, 1379; T. O. Soine and F. H. Jawad, *J. Pharm. Sci.*, 1964, **53**, 990; S. N. Shanbag, C. K. Mesta, M. L. Mahesurari, S. K. Panikar, and S. C. Battacharja, *Tetrahedron*, 1964, **20**, 2605; 'N.m.r. Spectra Catalogue,' Varian Associates, Palo Alto, 1962, Spectrum No. 310.

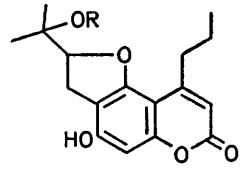
[4] F. M. Abdel-Hay, E. A. Abu-Mustafa, B. A. H. El-Tarvil, M. B. E. Fayez, C. S. Barnes, and J. L. Occolowitz, *Indian J. Chem.*, 1967, **5**, 89; M. Shipchandler and T. O. Soine, *J. Pharm. Sci.*, 1968, **57**, 741.

furan by rearrangement followed by elimination of isobutene epoxide:[5] the cleavage has been noted in hop extractives.[6] Mass spectral fragmentation of the mixture L1b was similar to that for L1a except for the presence of an abundant ion at *m/e* 374 ($C_{21}H_{26}O_6$) and a metastable ion at *m/e* 293, indicating loss of a propyl radical from *m/e* 374 to give *m/e* 331. Such fragmentation, and the presence of an ion at *m/e* 359, agrees with the presence of (VIc), the remaining fragmentations yielding the same ions as (VIa) and (VIb).

Mixture L1a gave a monoacetate and a diacetate, the n.m.r. spectrum of the latter being helpful[7] in distinguishing between the ring C types exemplified by structures (VI) and (VII). Thus the methine proton

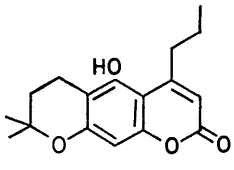


(VII)

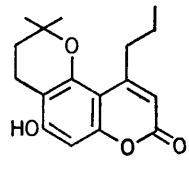


(VIII) a; R = H
b; R = HCO

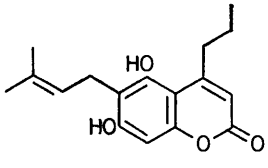
showed a downfield shift of 0·27 p.p.m., in agreement with (VI), a much larger shift being expected[8] for the proton of the secondary alcohol in (VII). On treatment with trifluoroacetic acid, the mixture L1 underwent deacylation, giving the homogeneous coumarin (VIIIa). The structure of the latter is supported by n.m.r. and mass spectral data (Experimental section). It gave a negative Gibbs colour (photometric). Confirmation of the structure of compound (VIIIa) was



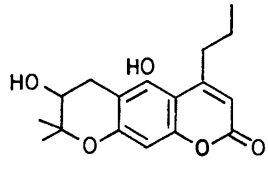
(IX)



(X)



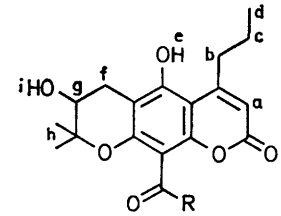
(XI)



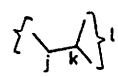
(XII)

provided by comparison with a sample synthesised from the coumarin (XI)[9] by treatment with *m*-chloroperbenzoic acid. Treatment of the coumarin (XI) with *m*-chloroperbenzoic acid containing a trace of toluene-*p*-sulphonic acid,[10] however, gave the linear chroman (XII). This orientation was assigned on the basis of a Gibbs reaction (photometric); spectral comparison with compounds (IX) and (X) supports the structure. The deacylation of the natural mixture L1a could also be accomplished with formic acid, but in this case the formate (VIIIb) was isolated.

By application of the epoxidation reaction the three compounds (VIa—c) were synthesised from the natural coumarins isolated in our earlier study. Individual treatment of mammea B/BA (III), B/BB (IV), and B/BC (V) with monoperphthalic or *m*-chloroperbenzoic acid gave compounds (VIa), (VIb), and (VIc) in high yield. The spectral and t.l.c. properties of the pure compounds or of appropriate mixtures, confirmed the deductions as to the nature of L1a and L1b. Finnegan and Merkel[7] have identified the mixture (XIIIa—c) in *M. americana*. For comparison, the hydroxydihydropyran (XIIIa) was therefore made from mammea B/BA (III) by use of the *m*-chloroperbenzoic acid–



(XIII) a; R =



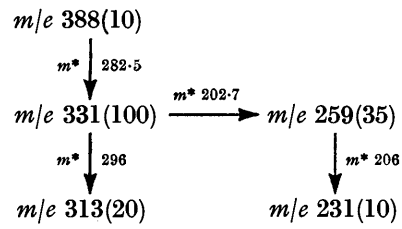
b; R =

c; R =

τ Values

a 4·13 (1H, s)
b 7·05 (2H, t, *J* 7 Hz)
c 8·1—8·5 (2H, m)
d 9·0 (3H, t, *J* 7 Hz)
e 0·90 (1H, s, exchanged by D_2O)
f 7·0—7·5 (2H, m)
g 6·28 (1H, m)
h 8·67, 8·75 (both 3H, s)
i 5·40 (1H, s, exchanged by D_2O)
j 7·10 (2H, d, *J* 7 Hz)
k 7·80 (1H, m)
l 9·04 (6H, d, *J* 7 Hz)

toluene-*p*-sulphonic acid reagent. Its structure, and linear ring-C orientation, are in agreement with n.m.r. data. No chelated 7,8-system is in evidence. The main mass spectral fragmentation of (XIIIa) was as follows:

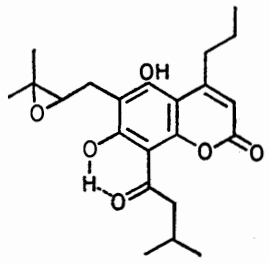


The major and important difference from (VIa) was the absence of a strong *m/e* 59 peak, though the two spectra were less different than had been expected from published data for 3-hydroxy-2,2-dimethylpyran-fused coumarins[11]

[5] I. Carpenter, E. J. McGarry, and F. Scheinmann, *Tetrahedron Letters*, 1970, 3983.
[6] S. J. Shaw and P. V. R. Shannon, *Org. Mass Spectrometry*, 1970, **3**, 941.
[7] K. E. Merkel, Ph.D. Thesis, University of New York, Buffalo, 1970.
[8] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 176.
[9] D. E. Games and N. J. Haskins, *Chem. Comm.*, 1971, 1005.
[10] W. Steck, *Canad. J. Chem.*, 1971, **49**, 1197.
[11] M. Shipchandler and T. O. Soine, *J. Pharm. Sci.*, 1968, **57**, 2062.

and those having the α-(hydroxyisopropyl)dihydrofuran feature.[4]

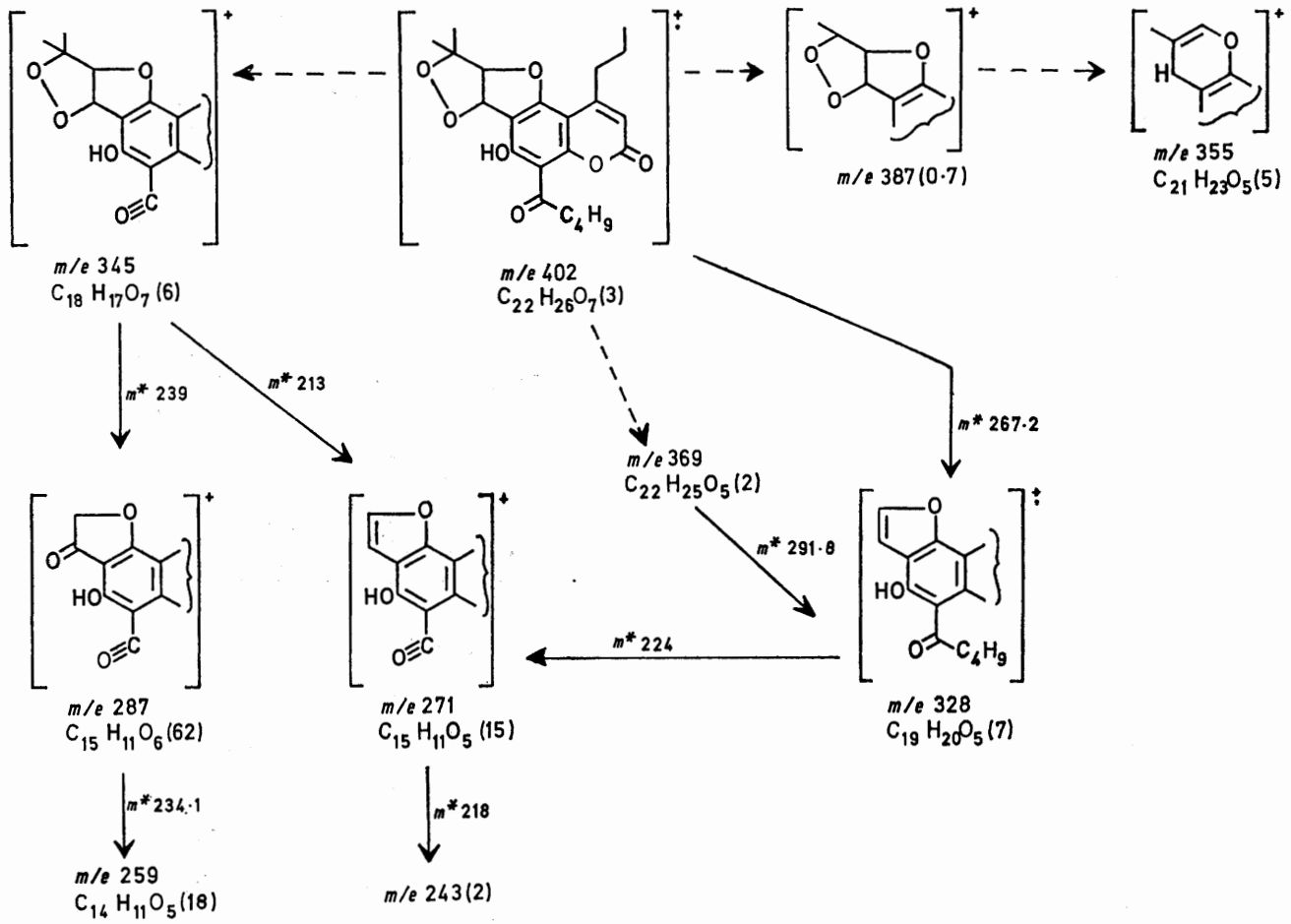
When n.m.r. spectra were run immediately after work up of the *m*-chloroperbenzoic acid reaction with



(XIV)

mammea B/BA (III), the characteristic signals due to the α-(hydroxyisopropyl)dihydrofuran were replaced by signals at τ 8·58 (3H, s), 8·39 (3H, s), and 6·3—6·8 (3H, m), indicating the presence of the epoxide (XIV). When kept at room temperature the epoxide cyclised to the coumarin (VIa). Structure (XIV) was confirmed by the identity of its diacetate with the diacetate obtained by epoxidation of the diacetate of mammea B/BA with *m*-chloroperbenzoic acid.

A further fraction (L2) obtained chromatographically from the light petroleum extract of *M. americana* seeds had m.p. 170—171° and was optically active (r.d. curve). It reacted positively in a peroxide test [12] and the results of combustion analysis and mass measurement agreed with the molecular formula $C_{22}H_{26}O_7$. U.v. data were similar to those for compounds (VIa—c). I.r. data were also similar, but there was no unchelated hydroxy-absorption. The n.m.r. spectrum of L2 (XVa and b) showed similarity to those of the coumarins of the L1a and b group, and detailed interpretation revealed the presence of 8-(3-methylbutyryl) and 8-(2-methylbutyryl) groups. The n.m.r. signals for an intact α-(hydroxyisopropyl)dihydrofuran feature were not in evidence; in their place were signals at τ 8·53 (6H, s), 4·64 (1H, d, *J* 6 Hz) and 3·97 (1H, d, *J* 6 Hz). The cyclic peroxide structure (XV) was therefore assigned to L2: n.m.r. assignments resemble those reported in connection with a related cyclic peroxide.[13]

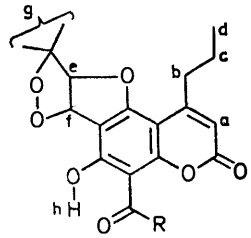


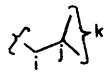
SCHEME 2 Mass spectra fragmentation of cyclic peroxides (XVa and b)

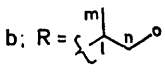
[12] A. G. Davies, 'Organic Peroxides,' Butterworth, London, 1961, p. 193.

[13] R. K. Razdan and V. V. Kane, *J. Amer. Chem. Soc.*, 1969, **91**, 5190.

Mass spectral fragmentations (Scheme 2) are consistent with the formulation (XVa and b) for L2. Losses of butyl radicals ($M - 57$ and $M - 74 - 57$) are indicative of the presence of 3-methylbutyryl or 2-methylbutyryl substituents, and the other fragmentations



(XV) a; R = 

b; R = 

τ Values

a 4·00 (1H, s)
b 7·16 (2H, d, *J* 7 Hz)
c 8·2—8·5 (2H, m)
d 8·91 (3H, t, *J* 7 Hz)
e 3·97 (1H, d, *J* 6 Hz)
f 4·64 (1H, d, *J* 6 Hz)
g 8·53 (6H, s)
h −4·43 (1H, s, exchanged by D_2O)

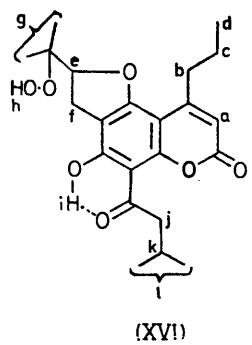
(XVa) i 6·87 (d, *J* 7 Hz)
j 7·8 (m)
k 8·90 (d, *J* 7 Hz)

(XVb) l 6·2 (m)
m 8·72 (d, *J* 7 Hz)
n 8·2—8·5 (m)
o 8·91 (t, *J* 7 Hz)

N.m.r. data for natural mixtures.

are readily intelligible on the basis of the peroxide structure (XV). Finnegan and Merkel [7] have neatly confirmed the nature of L2 by catalytic hydrogenolysis to a mixture containing (VIa and VIb).

The third crystalline material (L) isolated from the *M. americana* extract was pure (m.p. 133°) and optically active (r.d. curve). It had the molecular formula $C_{22}H_{28}O_7$ and its u.v. data (Table 1) were similar to those of L1 and L2. I.r. data [$\nu_{max.}$ ($CHCl_3$) **1730, 1635,** and **1610** cm^{-1}] resembled those for the coumarins (VIa—c), and a **3540** cm^{-1} vibration is consistent with a hydroperoxide.[14] N.m.r. assignments (XVI) are similar to those of (VIa), the main difference being a downfield shift (to τ 2·33) of the hydroperoxide proton signal and the nearby methine and methylene ring protons: data fall into line with those for other hydroperoxides.[15] The mass spectral fragmentations (Scheme 3) are consistent with formulation (XVI). In contrast with L1a, treatment of the hydroperoxide L with acetic anhydride and pyridine at 20° gave a diacetate with $\nu_{max.}$ (CCl_4) 1780 cm^{-1}, consistent with the presence of a peroxyester.[16]



(XVI)

τ Values

a 4·01 (1H, s)
b 7·16 (2H, t, *J* 7 Hz)
c 8·2—8·5 (2H, m)
d 8·96 (3H, t, *J* 7 Hz)
e 4·82 (1H, t, *J* 9 Hz)
f 6·82 (2H, d, *J* 9 Hz)
g 8·66, 8·68 (both 3H, s)
h 2·33 (1H, s, exchanged by D_2O)
i −4·18 (1H, s, exchanged by D_2O)
j 6·87 (2H, d, *J* 7 Hz)
k 7·8 (1H, m)
l 8·97 (6H, d, *J* 7 Hz)

N.m.r. data for natural compound.

In view of the oxidation levels of the new compounds described in this paper the aerial oxidation of a mixture of mammea B/BA, B/BB, and B/BC was examined by keeping it in chloroform in light [17] and air for 10 weeks. The crystalline mixture isolated contained the mixture (XIIIa—c) and t.l.c. showed the presence of the L1 and L2 mixtures, together with unchanged and unidentified material. Whether these products originate from metabolism within the seed, are formed during the isolation, or come from both sources, remains undetermined.

EXPERIMENTAL

For general experimental conditions and the meaning of symbols, see Part I.[2] Unless otherwise stated n.m.r. spectra were measured at 100 MHz for solutions in deuteriochloroform, and i.r. spectra for solutions in chloroform. Detailed n.m.r. and mass spectral data for compounds marked with an asterisk are deposited with the N.L.L. as Supplementary Publication No. SUP 20426 (13 pp., 1 microfiche).†

Isolation of Fractions L, L1, and L2.—The mother liquors from which the white crystalline mammea compounds had been obtained (see Part I [2]) after several months in the refrigerator deposited white crystals of 2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroperoxy*-1-*methylethyl*)-5-(3-*methylbutyryl*)-9-*propylfuro*[2,3-f][1]*benzopyran*-7-*one* (compound L) (XVI),* m.p. 127—129° [133° after crystallisation from chloroform–light petroleum (b.p. 60—80°)]. T.l.c. [methylene chloride and benzene–ethyl acetate (8 : 2)] indicated that the material was homogeneous. It showed a blue fluorescence under u.v. light and gave a brown-purple colouration with ethanolic iron(III) chloride solution [Found: C, 65·55; H, 6·95%; *M* (mass spec.), 404·1823 ± 15. $C_{22}H_{28}O_7$ requires C, 65·35; H, 7·0%; *M*, 404·1835], $\nu_{max.}$ 3540, 1730, 1635, and 1610 cm^{-1}; $\nu_{max.}$ (mull) 3310, 1710, 1630, and 1600 cm^{-1}, o.r.d. (*c* 0·05 in MeOH, 25°) $[\phi]_{297}$ +1620°, $[\phi]_{270}$ −440°.

The *diacetate* * had m.p. 87° (Found: C, 63·75; H, 6·65. $C_{26}H_{32}O_9$ requires C, 63·9; H, 6·6%), $\nu_{max.}$ (CCl_4) 1780, 1740, 1620, and 1605 cm^{-1}, $\nu_{max.}$ (mull) 1775, 1730, 1715, 1685, 1625, and 1590 cm^{-1}, $\lambda_{max.}$ 230 and 295 nm (log ε 3·85 and 4·16).

Chromatography [column and preparative layer (p.l.c.)] [ethyl acetate–benzene (2 : 8)] of the mother liquors yielded small quantities of three crystalline materials in the following order of decreasing R_F value: L2 (m.p. 170—171°), more L, and L1. Mixture L2 * appeared homogeneous on t.l.c. [methylene chloride and ethyl acetate–benzene (1 : 4)] [Found: *M* (mass spec.), 402·1670 ± 12. Calc. for $C_{22}H_{26}O_7$: *M*, 402·1678], $\nu_{max.}$ 1730, 1630, and 1610 cm^{-1}, $\nu_{max.}$ (mull) 1750, 1630, and 1605 cm^{-1}, o.r.d. (*c* 0·05 in MeOH, 25°) $[\phi]_{330}$ −285°, $[\phi]_{299}$ +1990°, $[\phi]_{286}$ +2360°. The n.m.r. data showed that the 2-methylbutyryl and 3-methylbutyryl components were present in the ratio *ca.* 1 : 3.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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[16] W. H. T. Davison, *J. Chem. Soc.*, 1951, 2456.

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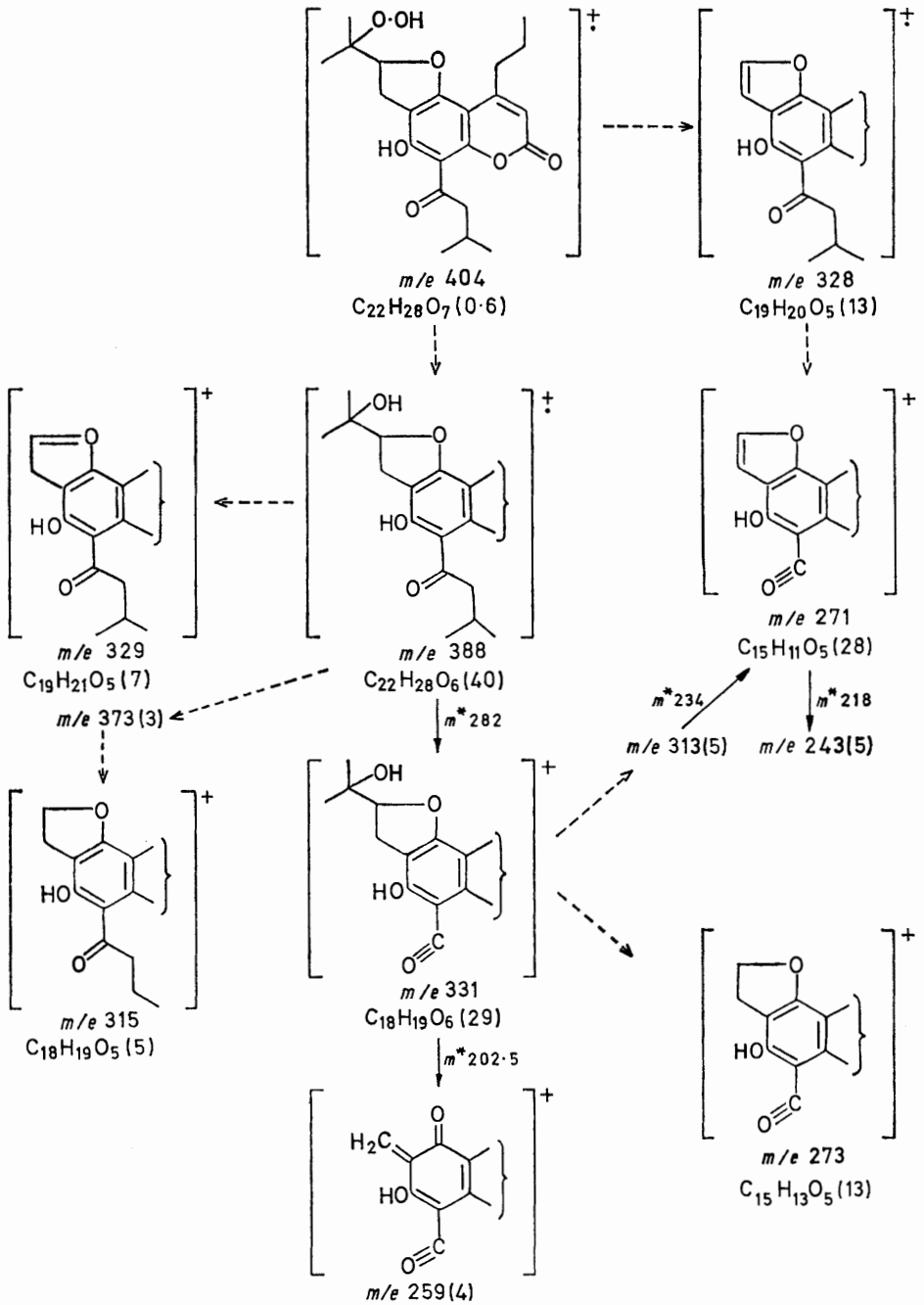
Compound L1,* m.p. 130—131°, on t.l.c. [(ethyl acetate–benzene (2 : 8)] proved to be resolvable into two groups; the higher R_F component (L1a) was separated by p.l.c. It was not further separable by t.l.c., gave a purple-brown colouration with ethanolic iron(III) chloride, and had m.p. and similar i.r. and u.v. spectra to L1a. Integration (n.m.r.) suggested that the butyryl compound (VIc) was the major component.

Mammea B/BA (Mammein) Diacetate.—Treatment of mammea B/BA (III) with pyridine–acetic anhydride



SCHEME 3 Mass spectral fragmentation of the hydroperoxide (XVI)

126° [Found: C, 68·05; H, 7·0%; *M* (mass spec.), 388·1884 ± 5. Calc. for $C_{22}H_{28}O_6$: C, 68·0; H, 7·25%; *M*, 388·1886], $\nu_{max.}$ 1725, 1630, and 1605 cm^{-1}, $\nu_{max.}$ (mull) 3480, 1715, 1705, 1630, and 1600 cm^{-1}, o.r.d. (*c* 0·043 in MeOH, 25°) $[\phi]_{333}$ −640°, $[\phi]_{303}$ +3400°, $[\phi]_{265}$ −690°.

The lower R_F component (L1b) * had m.p. 120—123° overnight gave the *diacetate*,* m.p. 118—120° (from ether–carbon tetrachloride) (Found: C, 68·25; H, 7·05. $C_{26}H_{32}O_7$ requires C, 68·4; H, 7·05%), $\nu_{max.}$ (CCl_4) 1780, 1750, 1700, 1600, 1580 cm^{-1}, $\nu_{max.}$ (mull) 1775, 1730, 1710, 1615, 1590, and 1570 cm^{-1}, $\lambda_{max.}$ 282 and 320 nm (log ε 4·03 and 3·75).

m-*Chloroperbenzoic Acid Epoxidation of Mammea B/BA Diacetate*.—A solution of mammea B/BA diacetate (100 mg) and *m*-chloroperbenzoic acid (65 mg) in chloroform (5 ml) was kept at 25 °C for 2 days, then extracted successively with 10% sodium sulphite solution (2 × 5 ml), 5% sodium hydrogen carbonate solution (2 × 5 ml), water (2 × 5 ml), and sodium chloride solution (2 × 5 ml), and dried. Removal of the solvent left 5,7-*diacetoxy*-6-(2,3-*epoxy*-3-*methylbutyl*)-8-(3-*methylbutyryl*)-4-*propylcoumarin* * (91 mg), m.p. 98—101° (from carbon tetrachloride–hexane) [Found: C, 65·9; H, 6·8%; *M* (mass spec.) 472·2097 ± 24. $C_{26}H_{32}O_8$ requires C, 66·1; H, 6·85%; *M*, 472·2097], $\nu_{max.}$ 1780, 1740, 1615, 1595, and 1570 cm^{-1}, $\lambda_{max.}$ 280 and 318 nm (log ε 4·02 and 3·80).

acid treatment was carried out in dioxan, the product contained little epoxide.

m-*Chloroperbenzoic Acid Oxidation of Mammea B/BB*.—Mammea B/BB (IV) was similarly treated with *m*-chloroperbenzoic acid to give 2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-5-(2-*methylbutyryl*)-9-*propylfuro*[2,3-*f*][1]*benzopyran*-7-*one* (V1b), m.p. 118—119·5° (from chloroform–hexane) [Found: C, 68·2; H, 7·4%; *M* (mass spec.), 388·1886 ± 19. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·25%; *M*, 388·1886], $\nu_{max.}$ 1730, 1632, and 1608 cm^{-1}, $\nu_{max.}$ (mull) 3480, 1713, 1633, and 1603 cm^{-1}.

m-*Chloroperbenzoic Acid Oxidation of Mammea B/BC*.—Mammea B/BC (V) (contaminated with a little B/BA and B/BB) was treated similarly with *m*-chloroperbenzoic acid

U.v. data for natural and synthetic 4-alkylcoumarins in ethanol

		$\lambda_{max.}$/nm (log ε)					
Mixture L1a [a]	0·01N-HCl	222 (4·36)	232 * (4·21)		297 (4·43)		
	0·01N-KOH		241 (4·35)			315 * (3·75)	374 (4·25)
Coumarin (VIa)	0·01N-HCl	222 (4·40)	234 * (4·29)		297 (4·45)		
	0·01N-KOH		241 (4·35)			320 * (3·86)	374 (4·30)
Coumarin (VIb)	0·01N-HCl	222 (4·41)	232 * (4·26)		297 (4·46)		
	0·01N-KOH		240 (4·40)			320 * (3·85)	375 (4·32)
Coumarin (VIc)	0·01N-HCl	223 (4·37)	236 * (4·22)		295 (4·42)		
	0·01N-KOH		239 (4·37)			320 * (3·77)	375 (4·27)
Mixture L2	0·01N-HCl	221 (4·40)	229 * (4·26)		288 (4·32)	311 (4·18)	
	0·01N-KOH		235 (4·32)		280 * (3·71)		370 (4·28)
Coumarin (VIIIa)	0·01N-HCl	229 * (4·15)		260 (3·77)		322 (4·20)	
	0·01N-KOH		236 (4·24)	271 (3·81)			372 (4·30)
Compound L (XVI)	0·01N-HCl	220 (4·34)	232 * (4·19)		297 (4·39)		370 (4·28)
	0·01N-KOH		240 (4·19)	251 (4·02)		315 (3·65)	374 (4·25)
Coumarin (XIIIa)	0·01N-HCl	225 (4·32)		260 (3·85)		320 (4·21)	
	0·01N-KOH			258 (4·10)		328 (4·31)	388 (3·92)
Coumarin (IX)	0·01N-HCl		249 (3·80)	259 (3·80)		327 (4·29)	
	0·01N-KOH			275 (4·18)		333 (4·07)	396 (4·02)
Coumarin (X)	0·01N-HCl		249 (3·76)	257 (3·75)		331 (4·23)	
	0·01N-KOH		238 (4·19)	273 (3·84)			384 (4·28)
Coumarin (III)	0·01N-HCl	223 (4·57)		252 (4·03)	293 (4·39)	322·5 (4·23)	
	0·01N-KOH	225 (4·50)		253·5 (4·24)		322·5 (4·25)	

* Inflection. [a] Data for L1b closely similar.

m-*Chloroperbenzoic Acid Oxidation of Mammea B/BA* (*Mammein*) (III).—A solution of mammea B/BA (100 mg) and *m*-chloroperbenzoic acid (60 mg) in methylene chloride (5 ml) was stirred at 25° overnight. The solution was worked up as in the previous experiment to give white crystalline 2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-5-(3-*methylbutyryl*)-9-*propylfuro*[2,3-f][1]*benzopyran*-7-*one* (VIa), m.p. 126—127° (from chloroform–hexane) [Found: C, 68·1; H, 7·1%; *M* (mass spec.), 388·1886 ± 19. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·25%; *M*, 388·1886], $\nu_{max.}$ 1725, 1630, and 1605 cm^{-1}.

Treatment of (VIa) with pyridine–acetic anhydride overnight gave a 4-*monoacetate*,* m.p. 126—129° (from chloroform–hexane) [Found: C, 67·0; H, 6·95%; *M* (mass spec.), 430·1991 ± 22. $C_{24}H_{30}O_7$ requires C, 66·9; H, 6·95%; *M*, 430·1991], $\nu_{max.}$ 1770, 1730, 1695, 1625, and 1610 cm^{-1}, $\lambda_{max.}$ 228, 261infl, and 294 nm (log ε 4·16, 4·00, and 4·15).

Rapid and careful work-up of the epoxidation experiment resulted in the isolation of the unstable epoxide * (XIV), which was readily converted into the dihydrofuran. The epoxide had $\nu_{max.}$ 1725, 1608, and 1560 cm^{-1}, $\nu_{max.}$ (mull) 1733, 1600, and 1563 cm^{-1}, $\lambda_{max.}$ 222, 233, and 296 nm; its identity was confirmed by treatment with pyridine–acetic anhydride at room temperature for 3 h, which yielded a diacetate identical with the epoxide of mammea B/BA diacetate already prepared (i.r., t.l.c., and n.m.r. comparison). When the *m*-chloroperbenzoic acid treatment was carried out in dioxan, the product contained little epoxide.

m-*Chloroperbenzoic Acid Oxidation of Mammea B/BB*.—Mammea B/BB (IV) was similarly treated with *m*-chloroperbenzoic acid to give 2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-5-(2-*methylbutyryl*)-9-*propylfuro*[2,3-*f*][1]*benzopyran*-7-*one* (V1b), m.p. 118—119·5° (from chloroform–hexane) [Found: C, 68·2; H, 7·4%; *M* (mass spec.), 388·1886 ± 19. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·25%; *M*, 388·1886], $\nu_{max.}$ 1730, 1632, and 1608 cm^{-1}, $\nu_{max.}$ (mull) 3480, 1713, 1633, and 1603 cm^{-1}.

m-*Chloroperbenzoic Acid Oxidation of Mammea B/BC*.—Mammea B/BC (V) (contaminated with a little B/BA and B/BB) was treated similarly with *m*-chloroperbenzoic acid to give *5-butyryl*-2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-9-*propylfuro*[2,3-f][1]*benzopyran*-7-*one* * (VIc), m.p. 129·5—131·5° (from chloroform–hexane) [Found: *M* (mass spec.), 374·1729 ± 18. $C_{21}H_{26}O_6$ requires *M*, 374·1729], $\nu_{max.}$ 1730, 1635, and 1610 cm^{-1}, $\nu_{max.}$ (mull) 3420, 1718, 1635, and 1600 cm^{-1}. The n.m.r. spectrum gave evidence of the 3-methylbutyryl and 2-methylbutyryl contaminants.

Treatment of Mammea B/BA with m-*Chloroperbenzoic Acid–Toluene*-p-*sulphonic Acid*.—A solution of *m*-chloroperbenzoic acid (100 mg) in chloroform (5 ml) was added to a solution of mammea B/BA (III) (95 mg) and toluene-*p*-sulphonic acid (5 mg) in chloroform (5 ml). The mixture was stirred at room temperature for 18 h, washed with saturated aqueous sodium hydrogen carbonate solution (3 × 10 ml) and saturated aqueous sodium chloride (1 × 10 ml), and then dried. Removal of solvent yielded a yellow gum (90 mg) which on treatment with chloroform–light petroleum (b.p. 60—80°) gave 6,7-*dihydro*-5,7-*dihydroxy*-10-(3-*methylbutyryl*)-4-*propyl*-2H,8H-*benzo*-[1,2-b:5,4-b']*dipyran*-2-*one* (XIIIa), m.p. 209—212° [Found: *M* (mass spec.), 388·1884 ± 19. $C_{22}H_{28}O_6$ requires *M*, 388·1886], $\nu_{max.}$ 3420, 3360, 1710, 1603, and 1570 cm^{-1}.

Trifluoroacetic Acid Treatment of the α-(*Hydroxyisopropyl*)*dihydrofurans* (VIa—c) (*Mixture L1*).—Treatment of the mixture of α-(hydroxyisopropyl)dihydrofurans (VIa—c) (L1) with trifluoroacetic acid, as described in

Part V, gave 2,3-*dihydro*-4-*hydroxy*-2-(1-*hydroxy*-1-*methylethyl*)-9-*propylfuro*[2,3-f][1]*benzopyran*-7-*one* (VIIIa),* white needles, m.p. 219—219·5° (from ethanol) [Found: *M* (mass spec.), 304·1311 ± 15. $C_{17}H_{20}O_5$ requires *M*, 304·1311], $\nu_{max.}$ 1705, 1690, and 1610 cm^{-1}, $\nu_{max.}$ (mull) 3440, 3340, 1680, and 1615 cm^{-1}. Similar trifluoroacetic acid treatment of mixture L1a gave an identical compound (i.r. spectrum, mixed m.p., and t.l.c.). Treatment of the deacylated coumarin (VIIIa) with acetic anhydride–pyridine at room temperature gave a crystalline *monoacetate*,* m.p. 134—135° (from chloroform–hexane) [Found: *M* (mass spec.), 346·1416 ± 17. $C_{19}H_{22}O_6$ requires *M*, 346·1416], $\nu_{max.}$ 1780, 1715, and 1625 cm^{-1}, $\nu_{max.}$ (mull) 3470, 1770, 1700, and 1620 cm^{-1}, $\lambda_{max.}$ 224, 254, and 295 nm (log ε 4·07, 3·94, and 4·13).

Reaction between Formic Acid (98%) *and the* α-(*Hydroxyisopropyl*)*dihydrofurans* (VIa—c).—A mixture of α-(hydroxyisopropyl)dihydrofurans (VIa—c) (L1) was treated with formic acid as described in Part V to give the crystalline 2-(1-*formyloxy*-1-*methylethyl*)-2,3-*dihydro*-4-*hydroxy*-9-*propylfuro*[2,3-f][1]*benzopyran*-7-*one* (VIIIb),* m.p. 189—195° (from chloroform–hexane), [Found: C, 65·2; H, 6·15%; *M* (mass spec.), 332·1259 ± 15; $C_{18}H_{20}O_6$ requires C, 65·05; H, 6·05%; *M*, 332·1260], $\nu_{max.}$ 1730, 1715, and 1625 cm^{-1}, $\nu_{max.}$ (mull) 3350, 1725, 1690, 1620, and 1605 cm^{-1}, $\lambda_{max.}$ (0·01N ethanolic HCl) 248, 257, 275, and 321 nm (log ε 3·56, 3·65, 3·64, and 3·80), $\lambda_{max.}$ (0·01N ethanolic KOH) 225, 273, 325, and 388 nm. Compound (VIIIb) on treatment with pyridine–acetic anhydride at room temperature for 12 h gave a *monoacetate*,* m.p. 171—173·5°.

Reaction of m-*Chloroperbenzoic Acid with* 5,7-*Dihydroxy*-6-(3-*methylbut*-2-*enyl*)-4-n-*propylcoumarin* (XI).—Treatment of the coumarin (XI) (92 mg) with *m*-chloroperbenzoic acid as before gave white crystals of the coumarin (VIIIa), m.p. 211—214° (65 mg), identical (t.l.c., i.r. spectrum, and mixed m.p.) with the sample prepared by the action of trifluoroacetic acid on the mixture of coumarins (VIa—c).

Reaction of m-*Chloroperbenzoic Acid–Toluene*-p-*sulphonic Acid with* 5,7-*Dihydroxy*-6-(3-*methylbut*-2-*enyl*)-4-n-*propylcoumarin* (XI).—Treatment of the coumarin (XI) (98 mg) with *m*-chloroperbenzoic acid–toluene-*p*-sulphonic acid as before gave tan needles of 6,7-*dihydro*-5,7-*dihydroxy*-4-*propyl*-2H,8H-*benzo*[1,2-b:5,4-b′]*dipyran*-2-*one* * (XII) m.p. 269—271° (30 mg) [Found: C, 67·2; H, 6·75%; *M* (mass spec.), 304·1311 ± 15. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%; *M*, 304·1311], $\nu_{max.}$ (mull) 3370, 1725, 1625, 1610, and 1570 cm^{-1}, $\lambda_{max.}$ 248, 258, and 326 nm (log ε 3·56, 3·56, and 4·02). The compound gave a positive Gibbs test (photometric).

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