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IDENTIFICATION OF NINE NEW 5,6-ANNULATED RELATIVES OF THE MAMMEA COUMARINS B/BA, B/BB & B/BC

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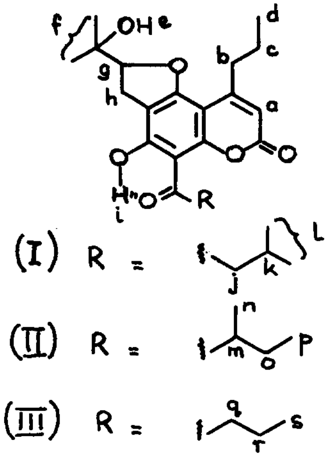
Biogenetically related phloroglucinol-coumarins have been isolated from seeds of *Mammea americana* L.[2-4] We now report the isolation of 9 new coumarins containing structure-elements not previously encountered: three are peroxides. The extractives were separated into groups of closely related congeners and identified spectrally. The structures deduced were then synthesised, or interconnected with known compounds, to verify conclusions.

Chromatography of the light-petroleum extract gave mixture L1, crystals, m.p. 130-131°, shown to be a mixture of (I), (II) and (III). It was optically active, and the highest M$^+$, indicated $C_{22}H_{28}O_6$. I.r. and u.v. data supported a 5,7-dioxygenated coumarin core[2,5] with an 8-acyl substituent[2]. N.m.r. data showed similarities to coumarins of the mammea B/B type and detailed interpreta-



a) 4.05(1)s.
b) 7.15(2)t. *J* 7Hz
c) 8.0-8.7(2)m.
d) 8.98(3)t. *J* 7Hz
e) 8.06(1)s.
f) 8.73(3)s.
   8.61(3)s.
g) 5.14(1)t. *J* 9Hz
h) 6.84(2)d. *J* 9Hz
i) -4.1(1)s. (variable)

(I)
j) 6.95(2)d. *J* 7Hz
k) 7.8(1)m.
l) 8.98(6)d. *J* 7Hz

(II)
m) 6.15(1)m.
n) 8.76(3)d. *J* 7Hz
o) 8.0-8.7(2)m.
p) 8.96(3)t. *J* 7Hz

(III)
q) 6.84(2)t. *J* 7Hz
r) 8.0-8.7(2)m.
s) 8.97(3)t. *J* 7Hz

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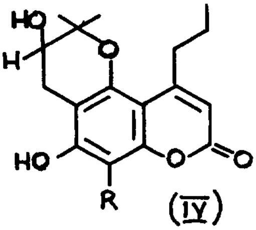
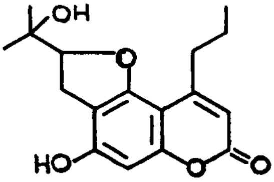
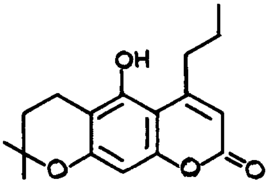
tion (above) revealed that L1 was a mixture having 8-acyl variation i.e. 3-methylbutyryl, 2-methylbutyryl and butyryl. The signals due to the 6-(3-methylbut-2-enyl) substituent of a mammea B/B type were, however, absent and an alcohol proton replaced one of the phenolic protons. In view of this an α-hydroxy-isopropyl-dihydrofuran (cf. I) or a 2,2-dimethyl-3-hydroxydihydropyran (cf. IV) was entertained, and model systems[6] supported the former. Mass-spectral fragmentations accord with (I) and (II) and an abundant ion m/e 59 (16) is in agreement with an α-hydroxy-isopropyl-dihydrofuran feature.[7] Some samples of L1 showed an ion m/e 374 of similar abundance to the molecular ion M^+388: this indicates the presence of (III) in the mixture, since loss of 14 mass units is unlikely. The diacetate of L1 showed a downfield shift of 0.27 ppm. for the methine proton in agreement with (I) rather than (IV). L1 underwent deacylation when treated with trifluoroacetic acid to give (V).



(IV)



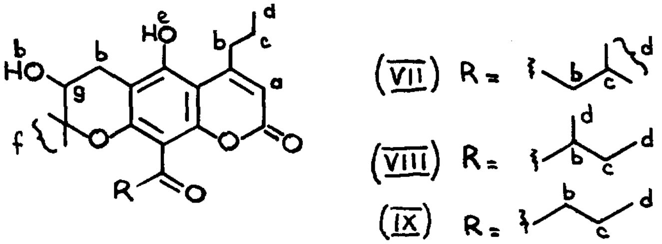
(V)



(VI)

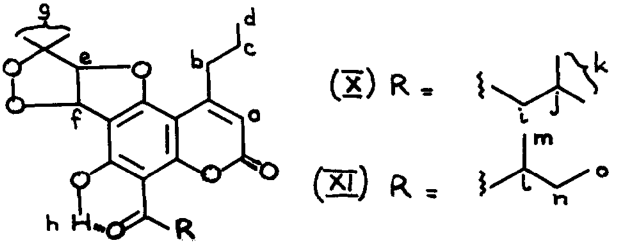
To confirm these conclusions, mammea B/BA, B/BB and B/BC[2] were individually treated with monoperphthalic or m-chloroperbenzoic acid to give (I), (II) and (III) in high yield. Spectral and t.l.c. comparison with L1 confirmed its nature, though different specimens possessed varying amounts of the three components.

A second crystalline isolate , M9, m.p. 213-217°, had main components $C_{22}H_{28}O_6$. I.r. and u.v. data supported a 5,7-dioxygenated coumarin structure and similarity to the linear 2,2-dimethyldihydropyran (VI) was noted. Analysis of n.m.r. data showed no chelated hydroxyl and, taken with other data, agreed with M9 being a mixture of (VII), (VIII) and (IX). Mass-spectral fragmentation was very similar to L1 and the occurrence of two M^+ peaks, 388 and 374 indicated the presence of (IX). A major difference between L1 and M9 is the low abundance of m/e 59, characteristic of the α-hydroxyisopropyldihydrofuran of the former. Loss of a 2-methylpropanal fragment has been predicted for a 2,2-dimethyl-3-hydroxypyran system[8] and this (m/e 331-259) is the major fragmentation for M9. Treatment of a mixture of mammea B/BA, B/BB and B/BC with m-chloroperbenzoic acid gave the mixture L1 as major product, but smaller amounts of a crystalline product very similar to M9 in spectroscopic and t.l.c. behaviour, were obtained.



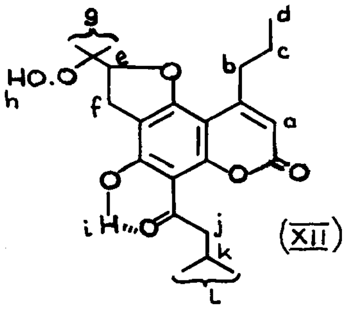
a) 4.07(1)s.
b) 6.9-7.6(6-7)m.
c) 8.10-8.65(4-5)m.
d) 8.88-9.20(9)m.
e) 4.65(1)s.
f) 8.70(3)s.
8.78(3)s.
g) 6.23(1)t. J 6.5Hz

The third crystalline mixture, L2, $M^+C_{22}H_{26}O_7$, m.p. 181-182°, optically active, gave a positive peroxide test. The u.v. and i.r. spectra were similar to those for (I), (II) and (III) but there was no hydroxyl absorption and the carbonyl vibration was shifted 35 cm^{-1} to higher frequency. N.m.r. and mass-spectral data are consistent with L2 being a mixture of (X) and (XI). Confirmation was provided by catalytic hydrogenolysis (10% Pd/C) to a mixture of (I) and (II).



a) 4.00(1)s.
b) 7.16(2)d. J 7Hz
c) 8.2-8.5(2)m.
d) 8.91(3)t. J 7Hz
e) 3.97(1)d. J 6Hz
f) 4.64(1)d. J 6Hz
g) 8.53(6)s.
h) -4.43(1)s.

Crystalline L, $C_{22}H_{28}O_7$, m.p. 133°, was optically active. The u.v. and i.r. data were similar to L1 except that hydroxyl absorption occurred at higher frequency, consistent with a hydroperoxide. N.m.r. assignments (XII) are similar to (I), the main difference being a downfield shift of the hydroperoxide proton and the nearby methine and methylene ring protons: data fall into line with other hydroperoxides.[9] Mass spectral data agree with (XII). The diacetate had ν_{max}



a) 4.01(1)s.
b) 7.16(2)t. J 7Hz
c) 8.2-8.5(2)m.
d) 8.96(3)t. J 7Hz
e) 4.82(1)t. J 9Hz
f) 6.82(2)d. J 9Hz
g) 8.66(3)s.
8.68(3)s.
h) 2.33(1)s.
i) -4.18(1)s.
j) 6.87(2)s. J 7Hz
k) 7.8(1)m.
l) 8.97(6)d. J 7Hz

(CCl_4) 1780 cm^{-1}, consistent with a peroxyester.[10]

Aerial oxidation of a mixture of mammea B/BA and B/BC, by keeping in chloroform in the light[11] for 10 weeks, has given mixture M, and t.l.c. shows the presence of the L1 and L2 mixtures. Whether certain products we report are formed intracellularly or extracellularly is not established.

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