Two New Xanthones, Calozeyloxanthone and Zeyloxanthonone, from Calophyllum zeylanicum (Guttiferae)

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Two new xanthones, calozeyloxanthone (1) and zeyloxanthonone (4), have been isolated from the bark of *C. zeylanicum* as well as betulinic acid, friedelan-3β-ol, calabaxanthone, taraxerone, friedelin, taraxerol, and β-sitosterol. Zeyloxanthonone (4) is identical with wightianone and the structure of the latter is revised. The timber of *C. zeylanicum* yielded 6-deoxyjacareubin (11), 1,6-dihydroxy-5-methoxyxanthone, 1,5-dihydroxyxanthone, 1,7-dihydroxyxanthone, 2-hydroxyxanthone, and jacareubin.

Calophyllum zeylanicum Kosterm † is endemic to Sri Lanka. Its morphological characteristics are similar to those of *Calophyllum trapezifolium*.[1] However, we found that their extractives were chemically different and herein we report the isolation, from the bark of *C. zeylanicum*, of two new xanthones, calozeyloxanthone and zeyloxanthonone,[2] which have been identified as 3,4,4a,14c-tetrahydro-11,13-dihydroxy-2,5,5-trimethyl-5*H*-[2]-benzopyrano[3,4-*a*]xanthen-14-one (1) and 1,2,3,4-tetra-

(2)   (3)

(4)

(5)

(6)   (7)

R = 3-methylbut-2-enyl

hydro-6,8-dihydroxy-1,1,7-tris(3-methylbut-2-enyl)-xanthen-2,9-dione (4), respectively.

RESULTS AND DISCUSSION

The percentages of the compounds isolated are given in Table 1. Calabaxanthone, an isoprenylated xanthone,

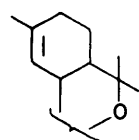† *Calophyllum zeylanicum* Kosterm has now been renamed as *Calophyllum lankaensis* Kosterm.

has been isolated as the major xanthone from the bark of *C. zeylanicum*. This xanthone has been previously isolated from several other endemic *Calophyllum* species.[3-5] Calozeyloxanthone (1), $C_{23}H_{22}O_5$ (M^+ 378.1467), was obtained as a yellow powder by chromatography (silica gel) of the benzene extract of the bark.
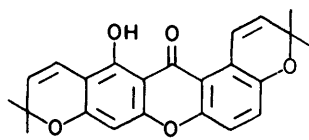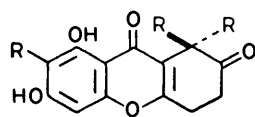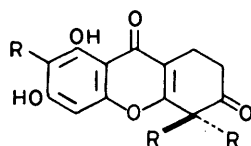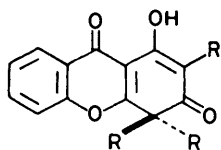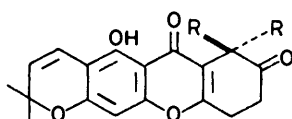
TABLE 1

Xanthones and terpenes isolated from
Calophyllum zeylanicum (%) [a]

Compounds	Bark	Timber
Betulinic Acid	0.1	
Friedelan-3β-ol	0.02	
Calabaxanthone	0.3	
Taraxerone	0.01	
β-Sitosterol	0.04	
Friedelin	0.01	
Tarazerol	0.03	
Zeyloxanthonone (4)	0.05	
Calozeyloxanthone (1)	0.024	
6-Deoxyjacareubin (11)		0.01
1,6-Dihydroxy-5-methoxyxanthone		0.4
1,5-Dihydroxyxanthone		0.02
1,7-Dihydroxyxanthone		0.02
2-Hydroxyxanthone		0.01
Jacareubin		0.01

[a] Percentage of the dry-plant weight.

The u.v. and i.r. spectra were suggestive of a xanthone. The molecular formula is thus compatible with a xanthone nucleus having either two C_5 units or one C_{10} unit attached.

Calozeyloxanthone, on methylation with diazomethane, gave a dimethyl ether and acetylation with Ac_2O–pyridine gave a diacetate. This indicates the presence of two hydroxy-groups. The $AlCl_3$-shift in the u.v. spectrum and the low-field singlet (δ 13.25) in the [1]H n.m.r. spectrum of the parent compound, which disappeared with D_2O, confirmed that one of the OH groups was chelated with the xanthone carbonyl group. The two OH groups were shown to be *meta*-oriented by the [1]H n.m.r. spectra of the xanthone and its derivatives. The [1]H n.m.r. spectrum of calozeyloxanthone also showed the presence of two additional aromatic protons at δ 7.25 as did [5] the [1]H n.m.r. spectrum of thwaitesixanthone (3) whose C-5 and C-6 aromatic protons appeared at δ 7.14. Evidence for the presence of a 2,2-dimethylchroman moiety and a MeC= group in calozeyloxanthone was also obtained from its n.m.r. spectrum.

The u.v. spectra of tetrahydrothwaitesixanthone,[5] calozeyloxanthone, and dihydrocalozeyloxanthone were similar, showing that the double bond in calozeyloxanthone is not conjugated with the aromatic ring and that calozeyloxanthone has oxygenation and ring-substitution patterns similar to tetrahydrothwaitesixanthone.

The [13]C n.m.r. spectrum coupled with the off-resonance decoupled spectrum of the new xanthone confirmed the presence of four unsubstituted aromatic carbon atoms, one substituted olefinic carbon atom at δ 134.5, one unsubstituted olefinic carbon atom at δ 117.7, eight aliphatic carbon atoms, including three Me groups, at δ 29.1 (two overlapping signals) and δ 22.2, and one fully substituted carbon atom at δ 77.4 The complete [13]C n.m.r. chemical shift assignments are given in the Figure.

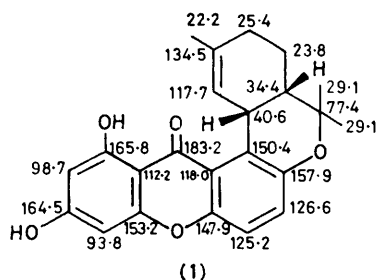FIGURE [13]C N.m.r. (CDCl$_3$, 25.15 MHz), δ (p.p.m.) for calozeyloxanthone

Calozeyloxanthone did not give any signals in the range δ 3.6—3.2 in its [1]H n.m.r. spectrum, indicating the absence of the usual benzylic protons in xanthones containing side-chains. From the above it is clear that the ten-carbon skeleton linked to the xanthone molecule cannot be of the normal, open-chain type, but is cyclised as shown in (2). Further evidence for such a system was also provided by the n.m.r. spectrum which had a one-proton, broad multiplet at δ 4.72 which shifted to δ 4.2 in the [1]H n.m.r. spectrum of dihydrocalozeyloxanthone. This can be attributed to a deshielded, benzylic proton resulting from the linkage of the chain (2) to the xanthone moiety, giving structure (1), which has been assigned for calozeyloxanthone.

The mass spectrum of calozeyloxanthone did not contain fragments due to allylic or benzylic cleavage of the molecular ion. The characteristic $(M^+ - \text{Me})$ peak, observed at m/e 363, is in keeping with a structure possessing the dimethylchroman moiety. A positive Gibbs test [2] gave further proof that (1) is the structure of calozeyloxanthone.

The quinone dehydrogenation of hydroaromatic compounds has been used [6] to assign the stereochemistry of the pyranotetrahydrobenzene ring-fusions in tetrahydrocannabinols. Calozeyloxanthone remained almost unchanged when treated with chloranil in benzene, even after 20 h. The inability of calozeyloxanthone to undergo quinone dehydrogenation is attributed [6] to the *cis*-fusion of the dihydropyranotetrahydrobenzene system, as shown in structure (1).

Calozeyloxanthone can be biogenetically derived as follows: geranylation of 1,3,7-trihydroxyxanthone (9) gives the geranylxanthone (10) which, on oxidation and cyclisation (Scheme 1) could give calozeyloxanthone (1).
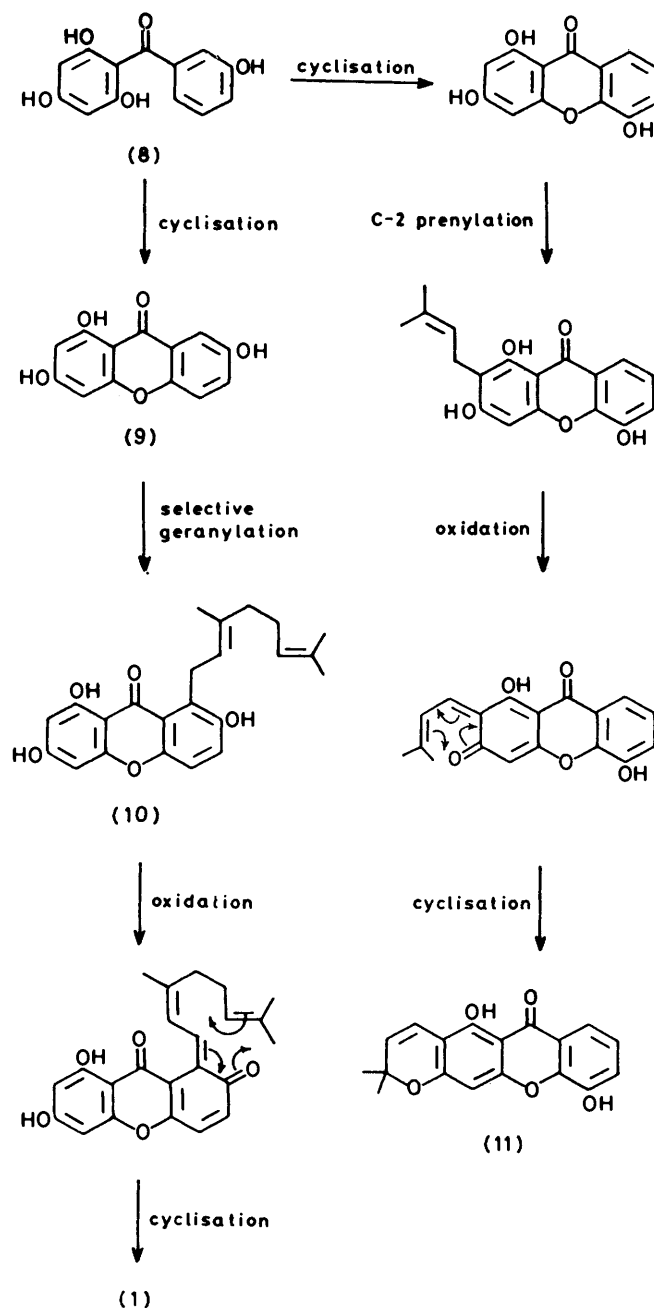
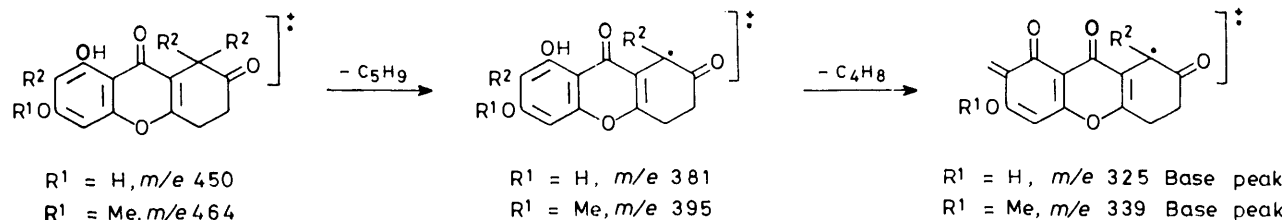SCHEME 1 Biogenesis of calozeyloxanthone (1) and 6-deoxyjacareubin (11) from the same benzophenone precursor

The benzophenone precursor (8) (Scheme 1) of 1,3,7-trihydroxyxanthone (9) can also yield 6-deoxyjacareubin (11), which was also isolated, in 0.01% yield (see the Table), from the timber of *C. zeylanicum*.

Xanthones with geranyl side-chains are common in species of the genus *Garcinia* L. of the family Guttiferae.

To date, *Calophyllum* species have yielded only iso-prenylated xanthones. The isolation of the unique, geranyl side-chain-cyclised calozeyloxanthone, with its structural similarities to the cannabinols, from the endemic *C. zeylanicum* is of interest in chemical taxonomy.

Zeyloxanthonone (4) is the other new xanthone iso-lated from the benzene extract of the bark of *C. zeylanicum*. In a preliminary communication,[2] we assigned the structure (4) to zeyloxanthonone. Further evidence is presented in this paper supporting this structure. The mass spectrum of zeyloxanthonone and its methyl ether showed a prominent loss of 69 mass units from the molecular ion and then a further loss of 56 mass units giving rise to the base peak in each case. Scheme 2

as a palmitic acid clathrate from *Calophyllum wightianum* T. Anders, to which they have assigned the structure (5) from benzene-induced n.m.r. chemical-shift data. However, they failed to note Helboe and Arends' results[7] and they also ignored the widely different chemical shifts for the two pairs of isoprenyl allylic protons. Direct comparison of zeyloxanthonone and wightianone showed that both pigments were, indeed, identical.[9]

It is noteworthy that both the new xanthones calo-zeyloxanthone (1) and zeyloxanthonone (4) from *C. zeylanicum* have similar oxygenation patterns. The timber extracts of *C. zeylanicum* gave six xanthones (see the Table) including jacareubin which is generally regarded as the chemical taxonomic marker[10] for the *Calophyllum* species.

$R^1 = H, m/e\ 450$
$R^1 = Me, m/e\ 464$

$-C_5H_9$

$R^1 = H, m/e\ 381$
$R^1 = Me, m/e\ 395$

$-C_4H_8$

$R^1 = H, m/e\ 325$ Base peak
$R^1 = Me, m/e\ 339$ Base peak

$R^2 = 3$-methylbut-2-enyl

SCHEME 2

illustrates the fragmentation pattern. The dichlorodi-cyanoquinodimethane (DDQ)-cyclised product (7) of zeyloxanthonone, in which the loss of the C_4H_8 group cannot take place, gave the fragment arising from the loss of a C_5H_9 group from its parent ion as the base peak, as shown in Scheme 2.

The [1]H n.m.r. spectrum of zeyloxanthonone showed two types of allylic, two-proton doublets at different chemical shifts (δ 3.05 and 2.70). The splitting patterns and double-irradiation experiments show that each two-proton doublet consists of one resonance from different methylene groups, indicating two $CH_A H_B CH_X=C$ systems, confirming the assignment of two isoprenyl groups at same sp^3 carbon atom. Two structures, (4) and (5), are the possible for zeyloxanthonone. Inspection of Dreiding models shows that in (4) the xanthone carbonyl group bisects the angle between two isoprenyl groups and that the two inner allylic protons of the chain are within the deshielding region of the xanthone carbonyl group, hence explaining the different chemical shifts of these allylic protons. Structure (5) does not explain the difference in the chemical shifts observed for the side-chain allylic protons of zeyloxanthonone. Besides, Helboe and Arends[7] have found that the allylic protons of the isoprenyl chains attached to the sp^3 carbon atom in the synthetic compound (6) had identical chemical-shifts and that the four allylic protons appeared at δ 2.79 as a four-proton doublet (J 7 Hz). Zeyloxanthonone therefore has structure (4). Dean and his co-workers recently reported[8] the isolation of wightianone

Bark and timber of *Calophyllum zeylanicum* were collected at Madugoda, Sri Lanka. U.v. spectra were recorded with a Unicam SP 8000B spectrophotometer, i.r. spectra with a Perkin-Elmer 257 spectrophotometer, and n.m.r. spectra with a Varian T60A spectrometer. Silica gel G (Merck) was used for analytical and preparative t.l.c. and silica gel (Merck, 30—70 mesh) was used for column chromatography. M.p.s were determined with a Kofler hot-stage apparatus. Elemental analyses were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne, Australia.

The dried, powdered bark (4.6 kg) was extracted with benzene and methanol. The benzene extract was separated into acidic and non-acidic fractions by washing with NaOH. The NaOH-soluble fraction was triturated with light petroleum and the filtrate, after being concentrated, gave betulinic acid, m.p. 298 °C (lit.,[11] 306—310 °C). The NaOH-insoluble fraction was separated by column chromatography over silica gel. Elution with benzene–light petroleum gave calabaxanthone, m.p. 176 °C (lit.,[3] 172 °C); taraxerone, m.p. 238 °C (lit.,[12] 245—249 °C); friedelan-3β-ol, m.p. 280 °C (lit., 283—285 °C); friedelin, m.p. 260 °C (lit.,[13] 264—265 °C); and taraxerol, m.p. 278 °C (lit.,[14] 279—282 °C). Elution of the column with benzene gave two new natural products, calozeyloxanthone and zeyl-oxanthonone.

Calozeyloxanthone.—This was obtained as a yellow powder which was crystallised from $CHCl_3$–light petroleum to give pure 3,4,4a,14c-*tetrahydro*-11,13-*dihydroxy*-2,5,5-*trimethyl*-5H-[2]*benzopyrano*[3,4-a]*xanthen*-14-*one* (*calozeyloxanthone*) (1), m.p. 236 °C (Found: *M* 378.1467. Calc. for $C_{23}H_{22}O_4$: 378.1467); *m/e* 378 (100%), 363 (80), 349 (32), 335 (88), and

69 (52); $\lambda_{max.}$ (EtOH) 241 (log ε 4.34), 265 (4.40), 320 (4.02), and 360 nm (3.91); $\lambda_{max.}$ (EtOH–AlCl₃) 280 (4.46) and 332 nm (4.20); $\lambda_{max.}$ (EtOH–NaOAc) 267 (4.29) and 352 nm (4.11); $\nu_{max.}$ (KBr) 3 240, 2 900, 1 650, 1 600, 1 575, 1 440, 1 270, 1 150, 1 025, 920, 830, and 695 cm⁻¹; δ (CD₃COCD₃) 13.25 (1 H, s, chelated OH), 7.25 (2 H, br s, aromatic), 6.4 (1 H, d, J 2 Hz, aromatic), 6.25 (1 H, d, J 2 Hz, aromatic), 5.8 (1 H, br, olefinic), 4.72 (1 H, br m, deshielded benzylic proton), 1.6 (3 H, br s, Me–C), 1.4 (6 H, Me₂C–O), and 1.55—1.2 (5 H, m, methylene).

Diacetoxycalozeyloxanthone.—Calozeyloxanthone (0.04 g) was dissolved in pyridine (2 ml) and acetic anhydride (2 ml) was then added. The mixture was left at room temperature for 24 h. The acetylated product was worked up in the usual manner and was then recrystallised from CH₂Cl₂–light petroleum to give, as yellow crystals, 11,13-*diacetoxy*-3,4,4a,14c-*tetrahydro*-2,5,5-*trimethyl*-5H-[2]benzopyrano-[3,4-a]xanthen-14-one, m.p. 134—135 °C, [α]_D 0° (CHCl₃); m/e 462 (M⁺, 95%) 447 (10), 420 (100), 377 (35), and 335 (48); $\lambda_{max.}$ (MeOH) 249 (log ε 4.65), 265 (4.54), 280 (4.39), and 306 nm (4.09), no shifts with AlCl₃, NaOAc, or NaOAc–H₃BO₃; $\nu_{max.}$ (KBr) 2 945, 2 910, 1 750, 1 655, 1 610, 1 585, 1 450, 1 425, 1 350, 1 282, 1 260, 1 160, 1 110, 1 050, 1 010, 885, 834, 807, 790, 678, and 655 cm⁻¹; δ (CCl₄), no low-field signals, 7.15 (1 H, d, J 2 Hz), 7.15 (1 H, d, J 8 Hz, aromatic), 7.05 (1 H, d, J 8 Hz, aromatic), 6.65 (1 H, d, J 2 Hz, aromatic), 5.6 (1 H, br m, olefinic), 4.55 (1 H, br m, deshielded benzylic), 2.4 (3 H, s, MeC–O–), 2.22 (3 H, s, MeC–O–), 1.8 (2 H, allylic), 1.6 (3 H, br s, Me–C=), 1.4 (3 H, s, Me), 2—1.35 (3 H, s, Me), and 2—1.4 (3 H, m, methylene).

Acetoxycalozeyloxanthone.—The minor product of the above acetylation was separated by preparative t.l.c. to give the *acetoxycalozeyloxanthone*, m.p. 129—131 °C; δ (CCl₄) 12.98 (1 H, s, chelated OH), 7.15 (2 H, s, aromatic), 6.6 (1 H, d, J 2 Hz, aromatic), 6.4 (1 H, d, J 2 Hz, aromatic), 5.7 (1 H, br m, olefinic), 4.6 (1 H, br m, deshielded benzylic), 2.25 (3 H, s, MeC–O–), 1.9 (2 H, m, methylene), 1.6 (3 H, br s, Me–C=), 1.4 (3 H, s, Me), 1.3 (3 H, s, Me), and 2.0—1.0 (m, methylene).

Methoxycalozeyloxanthone.—Calozeyloxanthone (0.03 g) was dissolved in ether (5 ml) and a few drops of methanol were added. Diazomethane in ether (5 ml) was added and, after 3 h, the solvent was evaporated to give the *methoxy-derivative* which was recrystallised from CH₂Cl₂–light petroleum as yellow crystals, m.p. 166—168 °C (Found: M 392.1623. Calc. for C₂₄H₂₄O₅: 392.1623); m/e 392 (100%), 377 (71), 373 (65), 349 (95), and 309 (74); $\lambda_{max.}$ (EtOH) 265 (log ε 4.34), 312 (3.93), and 382 nm (3.58); $\lambda_{max.}$ (EtOH–NaOH) 275 (4.28), 331 (3.86), and 392 nm (3.70); $\lambda_{max.}$ (EtOH–AlCl₃) 280 (4.15), 329 (3.82), and 412 nm (3.20); $\nu_{max.}$ (CHCl₃) 2 910, 1 655, 1 640, 1 590, 1 450, 1 375, 1 305, 1 270, 1 180, 1 150, 1 080, and 820 cm⁻¹; δ (CCl₄) 13.18 (1 H, s, chelated OH), 7.1 (2 H, s, aromatic), 6.28 (1 H, d, J 1 Hz, aromatic), 6.23 (1 H, d, J 1 Hz, aromatic), 5.70 (1 H, br m, olefinic), 4.7 (1 H, br m, deshielded benzylic), 3.9 (3 H, s, OMe), 1.95 (2 H, m, methylene), 1.6 (3 H, br s, Me–C=), 1.4 (6 H, s, 2 × Me), and 2—1.2 (m, methylene).

Dimethoxycalozeyloxanthone.—The above methylation using diazomethane was repeated with an excess of the reagent and in an ether–methanol (1 : 1) solution and after 6 h the pure 3,4,4a,14c-*tetrahydro*-11,13-*dimethoxy*-2,5,5-*trimethyl*-5H-[2]benzenopyrano]3,4-a]xanthen-14-one (*dimethoxycalozeyloxanthone*), m.p. 172—174 °C, was isolated in the usual manner; $\lambda_{max.}$ (EtOH) 257 (log ε 4.68), 305 (4.16), and 370 nm (3.86), no change with added NaOH and

added AlCl₃; $\nu_{max.}$ (KBr) 2 920, 1 650, 1 610, 1 590, 1 460, 1 425, 1 295, 1 270, 1 200, 1 150, 1 110, 845, and 820 cm⁻¹; δ (CCl₄) 7.0 (1 H, br s, aromatic), 6.35 (1 H, d, J 2 Hz, aromatic), 6.2 (1 H, d, J 2 Hz, aromatic), 5.75 (1 H, br m, olefinic), 4.6 (1 H, br m, deshielded benzylic), 5.96 (3 H, s, OMe), 5.9 (3 H, s, OMe), 1.9 (2 H, m, methylene), 1.62 (3 H, br s, Me–C=), 1.4 (6 H, s, 2 × Me), and 2.0—1.2 (3 H, m, methylene).

Dihydrocalozeyloxanthone.—Calozeyloxanthone (0.039 g) was dissolved in ethanol and a catalyst (Pd–CaCO₃) was then added. Hydrogen was passed through the solution for 2—3 d to complete the reaction. The solvent was evaporated and the residue was then crystallised from benzene–light petroleum to give the *dihydrocalozeyloxanthone*, m.p. 238 °C (Found: M 380.1623. Calculated for C₂₃H₂₄O₅: 380.1623); m/e 380(91%), 365(33), 337(100), 311(60), 295(55), 281(55), and 269(72); $\lambda_{max.}$ (EtOH) 242 (log ε 4.40), 264 (4.45), 317 (4.04), and 370 nm (3.81); $\lambda_{max.}$ (EtOH–AlCl₃) 239 (4.30), 278 (4.34), 330 (4.06), and 414 nm (3.27); δ (CD₃COCD₃) 12.61 (1 H, s, chelated OH), 7.22 (2 H, br s, aromatic), 6.35 (1 H, br s, aromatic), 6.25 (1 H, br s, aromatic), 4.2 (1 H, br m, deshielded benzylic), 1.4 (3 H, s, Me), 1.28 (3 H, s, Me), and 1.4—0.6 (12 H, Me and methylenes).

Zeyloxanthonone.— 1,2,3,4-*Tetrahydro*-6,8-*dihydroxy*-1,1,7-*tris*-(3-*methylbut*-2-*enyl*)xanthen-2,9-dione (*zeyloxanthonone*) was crystallised from light petroleum as a bright yellow solid, m.p. 137 °C (Found: M 450.2433. Calc. for C₂₈H₃₄O₅: 450.2461); m/e 450 (33%), 382 (13), 381 (41), 326 (31), 325 (100), and 323 (23); $\lambda_{max.}$ (EtOH) 234 (log ε 3.39), 292 (3.00) 326sh (3.00), and 360 nm (2.28); $\nu_{max.}$ (KBr) 3 200, 1 645, 1 600, 1 580, 1 470, 1 450, 1 380, 1 350, 1 310, 1 290, 1 220, 1 190, 1 175, 1 080, 1075, 1060, 890, and 870 cm⁻¹; δ [(CD₃)₂CO, 100 MHz] 13.2 (1 H, s, chelated OH), 6.5 (1 H, s, aromatic), 5.3 (1 H, t, vinylic H), 4.9 (2 H, t, vinylic), 3.4 (2 H, d, benzylic CH₂), 3.05 (2 H, methylene), 3.0—2.70 (6 H, m, methylene), and 1.8—1.5 (18 H, 3 s, Me of side-chains).

Methylzeyloxanthonone.—Zeyloxanthonone (0.04 g) was dissolved in methanol (1 ml) and was then treated with an excess of diazomethane in ether. After 2 d, the solvent was evaporated under reduced pressure and the product was crystallised from CHCl₃–light petroleum to give the *methylzeyloxanthonone*, m.p. 118 °C (Found: M 464.2564. Calc. for C₂₉H₃₆O₅: 464.2562); m/e 464 (50%), 394 (78), 395 (58), 340 (67), 339 (100), and 69 (28); $\lambda_{max.}$ (EtOH) 260 (log ε 4.18) and 295 nm (3.97); $\lambda_{max.}$ (EtOH–NaOH) 274 nm (4.21); $\nu_{max.}$ (CHCl₃) 1 705, 1 645, 1 610, 1 585, 1 435, 1 372, 1 300, 1 170, and 1 085 cm⁻¹; δ (CDCl₃, 100 MHz), 13.14 (1 H, s, chelated OH), 6.36 (1 H, s, aromatic), 5.25 (1 H, t, olefinic), 4.82 (2 H, t, olefinic), 2.9 (3 H, s, OMe), 3.3—2.5 (m, methylene), 3.36 (2 H, d, benzylic methylene), 2.83 (2 H, dd, allylic), 2.6 (2 H, d, allylic), 1.8 (3 H, s, Me), 1.7 (3 H, s, Me), 1.56 (6 H, s, 2 × Me), and 1.48 (6 H, s, 2 × Me).

Diacetoxyzeyloxanthonone.—Zeyloxanthonone (0.05 g) was dissolved in pyridine (2 ml) and was then treated with acetic anhydride (2 ml). The mixture was heated at 100 °C (bath temp.) for 4 h, and was then left at room temperature for 20 h. The product was worked up in the usual manner to give 6,8-diacetoxy-1,2,3,4-tetrahydro-1,1,7-tris-(3-methylbut-2-enyl)xanthen-2,9-dione, m.p. 120 °C (crystallised from CHCl₃–light petroleum); m/e 534, 506, 492, 474, 464, 450, 381, 325, 297, 283, and 271; δ (CCl₄) 7.1 (1 H, s, aromatic), 4.8 (3 H, m, olefinic), 3.2 (2 H, d, benzylic), 3.1—2 (m, methylene), 2.35 (3 H, s, OCOMe), 2.28 (3 H, s, OCOMe),

1.62 (6 H, 2 × Me), 1.6 (6 H, s, 2 × Me), and 1.4 (6 H, s, 2 × Me).

Acetoxyzeyloxanthonone.—Zeyloxanthonone (0.05 g) was dissolved in pyridine (2 ml) and was then treated with acetic anhydride (2 ml). The mixture was left overnight and the product was isolated in the usual manner; the acetate was crystallised from $CHCl_3$–light petroleum as a yellow powder, m.p. 115 °C (Found: M 492.2514. Calc. for $C_{30}H_{36}O_6$: 492.2511); m/e 492 (57%), 450 (17), 423 (83), 381 (47), 367 (66), 325 (100), and 69 (60); $\lambda_{max.}$ (EtOH) 245 (log ε 4.36) and 335 nm (3.60); $\lambda_{max.}$ (EtOH–NaOH) 271 (4.25) and 347 nm (4.12); δ (CDCl$_3$, 100 MHz) 13.31 (1 H, s, chelated OH), 6.64 (1 H, s, aromatic), 5.16 (1 H, t, olefinic), 4.8 (2 H, t, olefinic), 3.33 (2 H, d, benzylic), 3.2—2.5 (m, methylene), 2.84 (2 H, d, allylic), 2.6 (2 H, d, allylic), 2.34 (3 H, s, OCOMe), 1.78 (3 H, s, Me), 1.7 (3 H, s, Me), 1.56 (6 H, s, 2 × Me), and 1.49 (6 H, s, 2 × Me).

Hexahydrozeyloxanthonone.—Zeyloxanthonone (0.04 g) was dissolved in absolute ethanol (4 ml) and a catalyst, Pd–CaCO$_3$, was then added. Hydrogen was passed through the solution for *ca.* 2 d. Evaporation of the solvent and crystallisation from $CHCl_3$–light petroleum gave hexahydro-zeyloxanthonone as a yellow powder, m.p. 153 °C (Found: M 456.2877. Calc. for $C_{28}H_{40}O_5$: 456.2875); m/e 456 (87%), 441 (50), 428 (53), 430 (58), 400 (88), 386 (80), 371 (98), 367 (82), 343 (62), 329 (100), 315 (78), 301 (82), 287 (70), 271 (78), 257 (65), 243 (68), 231 (57), 223 (58), 217 (35), 189 (35), 165 (68), 149 (43), and 123 (57); $\nu_{max.}$ (KBr) 3 300, 2 900, 2 860, 1 700, 1 650, 1 600, 1 460, 1 410, 1 380, 1 360, 1 320, 1 270, 1 200, 1 100, 1 050, 1 000, 815, and 760 cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (log ε 4.37), 256 (4.44), 269 (4.44), and 300 nm (3.83); δ (CDCl$_3$, 100 MHz), 13.3 (1 H, s, chelated OH), 6.35 (1 H, s, aromatic), 2.95 (2 H, d, benzylic), 2.9—1.2 (m, methylene), 1.00 (6 H, d, 2 × Me), 0.85 (6 H, d, 2 × Me), and 0.88 (6 H, d, 2 × Me).

DDQ Cyclisation of Zeyloxanthonone.—Zeyloxanthonone (0.046 g) was dissolved in dry benzene (20 ml), DDQ (0.0325 g) was then added, and the mixture was heated under reflux. After *ca.* 3 h, examination by t.l.c. showed that the reaction was complete. The precipitate was filtered, washed with benzene, and the solvent evaporated from the filtrate. The residue was purified by preparative t.l.c. and yellow crystals of 1,2,3,4-*tetrahydro*-11-*hydroxy*-8,8-*dimethyl*-1,1-*bis*-(3-*methylbut*-2-*enyl*)-8H-*pyrano*[3,2-i]-*xanthen*-2,12-*dione* (7) were obtained, m.p. 78 °C (Found: M 448.2248. Calc. for $C_{28}H_{32}O_5$: 448.2249); m/e 448 (73%), 433 (37), 430 (33), 420 (35), 405 (37), and 379 (100); $\lambda_{max.}$ (EtOH) 279 nm (log ε 4.31); $\lambda_{max.}$ (EtOH–NaOH) 288 (4.62) and 380 nm (3.95); $\nu_{max.}$ (CHCl$_3$) 3 000, 1 640, 1 615, 1 580, 1 430, 1 375, 1 290, 1 220, 1 140, 1 080, 1 040, and 920 cm^{-1}; δ (CDCl$_3$) 13.25 (1 H, s, chelated OH), 6.75 (1 H, d, J 10 Hz, olefinic), 6.25 (1 H, s, aromatic), 5.55 (1 H, d, J 10 Hz, olefinic), 5.12 (2 H, t, olefinic), 3.05—2.00 (8 H, m, allylic), and 1.6—1.2 (18 H, 6 × Me).

Dried, powdered timber (2.25 kg) was exhaustively extracted with hot benzene and methanol, successively, to give the benzene extract (58 g) and the methanol extract (350 g). The benzene extract, on trituration with acetone, gave 1,6-dihydroxy-5-methoxyxanthone, m.p. 246 °C (lit.,[15] 243—246 °C). The mixture, after separating 1,6-dihydroxy-5-methoxyanthone, was chromatographed over silica gel and the following compounds were separated and characterised: 5,9,10-trihydroxy-2,2-dimethyl-2H,6H-pyrano-[3,2-i]xanthen (6-deoxyjacareubin) (11), m.p. 210 °C (lit.,[16] 211—213 °C); β-sitosterol, m.p. 136 °C; 1,5-dihydroxy-xanthen-9-one, m.p. 265 °C (lit.,[15] 268—270 °C); 1,7-di-hydroxyxanthen-9-one, m.p. 238 °C (lit.,[17] 238—240 °C); 2-hydroxyxanthen-9-one, m.p. 239 °C (lit.,[18] 240—242 °C); and 5,9,10-trihydroxy-2,2-dimethyl-2H,6H-pyrano[3,2-i]-xanthen-6-one (jacareubin), m.p. 254 °C (lit.,[19] 254—256 °C).

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