Extractives from Guttiferae. Part XXIX.[1] Synthesis of Celebixanthone Methyl Ether and Related 1,5,6,7-Tetraoxygenated Xanthones †

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The total synthesis of celebixanthone methyl ether [1,5-dihydroxy-6,7-dimethoxy-8-(3-methylbut-2-enyl)xanthen-9-one] (2) is described. The route involves preparation of 2-hydroxy-2',3,4,5,6'-pentamethoxybenzophenone (8) and subsequent base catalysed cyclisation to give 1,5,6,7-tetramethoxyxanthen-9-one (4). Selective demethylation and methylation gives 1,5-dihydroxy-6,7-dimethoxyxanthen-9-one (3). Preparation of the 5-(3-methyl-2-butenyloxy)xanthen-9-one (10) followed by a Claisen rearrangement gives celebixanthone methyl ether.

CELEBIXANTHONE is a yellow, optically inactive phenol, isolated from the bark of *Cratoxylon celebicum* Blume (Guttiferae) by Stout *et al.* and assigned structure (1) on the basis of spectroscopic and *X*-ray analyses.[2] This metabolite was the only known 1,5,6,7-tetraoxygenated xanthone until the recent isolation of 1,5-dihydroxy-6,7-dimethoxyxanthone (3) in Brazil.[3] We now report the total synthesis of this latter metabolite and related compounds, including celebixanthone methyl ether.

† Part of this work was first presented at the Autumn meeting of the Chemical Society, University of Nottingham, September 1972.

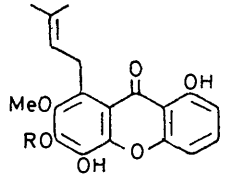
The synthetic strategy first required the synthesis of 1,5,6,7-tetraoxygenated xanthones, and then appropriate interconversions by selective methylation and demethylation, and in the case of the celebixanthone derivatives (1) and (2), isoprenylation at the crowded C-8 position.

[1] Part XXVIII, P. J. Cotterill, P. J. Owen, and F. Scheinmann, *J.C.S. Perkin I*, 1974, 2423.

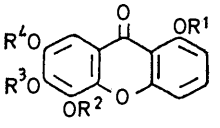
[2] G. H. Stout, V. F. Stout, and M. F. Welsh, *Tetrahedron*, 1963, **19**, 667.

[3] R. Alves de Lima, O. R. Gottlieb, and A. A. Lins Mesquita, *Phytochemistry*, 1972, **11**, 2307.

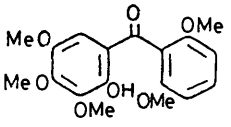
Our previous work [4] leads to a simple synthesis of 1,5,6,7-tetraoxygenated xanthones whereas attempts to prepare such xanthones by the method of Grover *et al.*[5]



(1) R = H
(2) R = Me



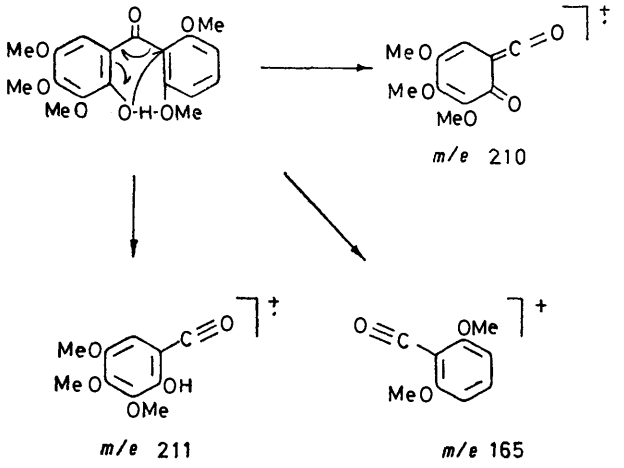
(3) $R^1 = R^2 = H$, $R^3 = R^4 = Me$
(4) $R^1 = R^2 = R^3 = R^4 = Me$
(5) $R^1 = H$, $R^2 = R^3 = R^4 = Me$
(6) $R^1 = R^2 = R^3 = H$, $R^4 = Me$
(7) $R^1 = R^2 = R^3 = R^4 = H$



(8)

were unsuccessful. 2,6-Dimethoxybenzoyl chloride and 1,2,3,4-tetramethoxybenzene [4] in the presence of ethereal aluminium chloride gave 2-hydroxy-2',3,4,5,6'-pentamethoxybenzophenone (8). Alkaline cyclisation of this benzophenone (8) is slow and incomplete in the presence of sodium methoxide in anhydrous methanol, but addition of water to the reaction mixture results in quantitative formation of 1,5,6,7-tetramethoxyxanthone (4). The structure of the benzophenone (8) was confirmed by spectral data: in particular the mass spectral fragmentation with ions at *m/e* 165, 210, and 211, consistent with the Scheme, confirmed that selective demethylation had occurred at C-2 and not at C-2'.

Selective demethylation and methylation experiments on 1,5,6,7-tetraoxygenated xanthones were carried out to provide suitable intermediates for isoprenylation studies. Thus boron trichloride in methylene chloride caused demethylation exclusively at the site adjacent to the carbonyl group [6] to give 1-hydroxy-5,6,7-trimethoxyxanthone (5). This product (5) or the tetramethoxyxanthone (4) on reaction with hydrogen bromide in acetic acid under controlled conditions gave 1,5,6-trihydroxy-7-methoxyxanthone (6). Under more vigorous conditions total demethylation of both (4) and (5) gave 1,5,6,7-tetrahydroxyxanthone (7).



SCHEME

A mixture of zinc chloride and phosphoryl chloride demethylates the tetramethoxyxanthone (4) to give the mono- (5), di- (3), tri- (6), and tetra-hydroxyxanthones (7). The structures of the demethylation products follow from n.m.r. analyses (Table 1) and in the case of the di- (3) and tri-hydroxyxanthones (5) the u.v. spectra (Table 2) were of diagnostic value. Thus the u.v.

TABLE 1

^{1}H N.m.r. spectra of the benzophenone (8) [a] and xanthones at 60 MHz (τ values; solutions in $CDCl_3$; Me_4Si as internal reference)

Compound	H-2 H-3' [a]	H-3 H-4' [a]	H-4 H-5' [a]	H-8 H-6' [a]	OH	MeO	$-CH_2-$	$-CH=$	$=CMe_2$
(8) [a]	3·34d	2·59q	3·34d	2·44s	−2·41s	5·95s, 6·01s, 6·24s			
(4)	3·15q	2·35t	2·82q	2·45s		5·88s, 5·91s, 5·95s, 6·02s			
(5)	3·15d	2·36t	2·95d	2·50s	−2·79s	5·80s, 5·90s, 6·10s			
(3) [b,c]	3·35d	2·58t	3·10d	2·88s	−2·61s	6·08s, 6·15s			
(9)	3·13d	2·33t	2·93d	2·49s		5·99s	5·20d	4·35t	8·21s, 8·21s
(10) [c]	3·32d	2·55t	3·14d	2·69s	−2·59s	6·02s, 6·14s	5·40d	4·46t	8·39s, 8·41s
(2) [c]	3·35d	2·59t	3·20d			6·01s, 6·29s	6·04d	4·88t	8·21s, 8·38s

[a] Benzophenone numbering referred to. [b] In $(CD_3)_2CO$. [c] At 100 mHz.

TABLE 2

U.v. spectra of xanthones and benzophenones measured in methanol

Compound	$\lambda_{max.}$/nm ($\varepsilon \times 10^{-3}$)							
(8)	245 (5·8)				286 (13·5)			360 (5·5)
(4)	247sh (28·4)	253 (35·2)			298 (12·4)			361 (9·5)
(5)	249sh (25·8)	258 (32·0)			273inf (16·9)	299 (12·3)		380 (8·6)
(3)	237sh (20·2)	256 (31·7)			275sh (11·1)	311 (9·8)		278 (5·6)
(6)	230 (21·5)	250 (25·6)		261sh (11·5)	270sh (8·2)	313 (10·2)		371 (9·8)
(9)	236 (24·8)	249sh (24·8)		256 (29·4)	271inf (14·4)	299 (12·2)	350sh (4·4)	377 (8·2)
(10)	236 (22·7)	249sh (23·7)		256 (26·6)	271sh (12·4)	298 (10·1)	351sh (4·0)	376 (7·4)
(12)	212 (26·6)	240sh (27·1)		257 (30·2)		325 (13·5)	350sh (8·2)	370sh (5·8)

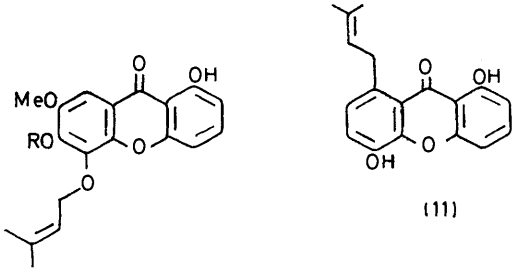
[4] A. J. Quillinan and F. Scheinmann, *J.C.S. Perkin I*, 1973, 1329.

[5] P. K. Grover, G. D. Shah, and R. C. Shah, *J. Chem. Soc.*, 1955, 3982.

[6] F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, B. Parton, A. W. Price, and N. Somvichien, *Tetrahedron Letters*, 1966, 4153.

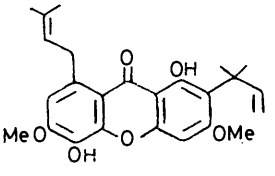
spectrum of 1,5,6-trihydroxy-7-methoxyxanthone (6) showed very pronounced hypsochromic and bathochromic effects in the presence of sodium acetate which were not observed with the 6-methoxy-derivative (3).[7]

The acidity of the 6-hydroxy-group allowed selective methylation at that position in the presence of sodium hydrogen carbonate and 1 equiv. of dimethyl sulphate. The synthetic 1,5-dihydroxy-6,7-dimethoxyxanthone (3) was identical with the metabolite isolated by Gottlieb *et al.*[3]



(9) R = $CH_2CH{:}CMe_2$
(10) R = Me

(11)



(12)

The first attempt to introduce an isoprenyl side chain at C-8 involved preparation and rearrangement studies on 1-hydroxy-7-methoxy-5,6-bis-(3-methylbut-2-enyloxy)xanthone (9). Heating the ether (9) under various conditions led only to ether cleavage to give 1,5,6-trihydroxy-7-methoxyxanthone (6). This result was inexplicable especially since isoguanandin (11)[8] and alvaxanthone dimethyl ether (12)[9] had been synthesised by *para*-Claisen rearrangements of 5-(3-methylbut-2-enyloxy)xanthones. However, related studies[10] on the synthesis of the morellin ring-structure showed the favoured nature of 6 ⟶ 5 allyl migration in a 5,6-diallylxanthone system. To avoid complications caused by adjacent allyl ether groups the 5-isoprenyl ether (10) of 1,5-dihydroxy-6,7-dimethoxyxanthone (3) was prepared. Heating the product (10) in *NN*-dimethylaniline gave celebixanthone methyl ether (2) by rearrangement, and also some 1,5-dihydroxy-6,7-dimethoxyxanthone (3) by elimination of the side chain. The m.p. of celebixanthone methyl ether (2) is in good agreement with that reported by Stout *et al.*[2] and the spectral data compare well with those recorded for celebixanthone (1).

EXPERIMENTAL

Microanalyses were performed by Mr. J. Jordan, Salford. U.v. spectra were measured for solutions in methanol with a Unicam SP 800 recording spectrophotometer, and i.r. spectra for Nujol mulls with a Perkin-Elmer 257 grating spectrophotometer; n.m.r. spectra were measured with Varian A60 and HA100 instruments. Analytical and preparative t.l.c. were carried out on silica G (Merck nach Stahl) with thicknesses of 0·3 and 1·0 mm, respectively; column chromatography was performed on silica gel MFC (Hopkin and Williams). Mass spectra were obtained with an A.E.I. MS 12 (single focusing) or MS 9 (double focusing) instrument operated at 70 eV.

2-Hydroxy-2′,3,4,5,6′-pentamethoxybenzophenone (8).—Powdered aluminium chloride (10·5 g) was added with stirring to a cooled solution of 2,6-dimethoxybenzoyl chloride (5·1 g) and 1,2,3,4-tetramethoxybenzene (5·1 g) in dry ether (200 ml), and the mixture was stirred for 30 h. The solvent was evaporated off under reduced pressure and the residue poured onto water (700 ml) to give a pale yellow solid. The aqueous suspension was acidified with hydrochloric acid, and extracted with benzene (400 ml). The organic layer was washed with 2N-hydrochloric acid and water, and evaporation of the dried ($MgSO_4$) benzene solution gave a brown oil which slowly crystallised as yellow needles (8·8 g). *2-Hydroxy-2′,3,4,5,6′-pentamethoxybenzophenone* gave bright yellow needles, m.p. 142—143° (from ethanol) (8·8 g), R_F 0·60 (benzene–ethyl acetate; 17 : 3), $\nu_{max.}$ 1630, 1615, 1600, 960, 830, 800, and 750 cm^{-1} (Found: C, 62·2; H, 5·6%; M^+, 348. $C_{18}H_{20}O_7$ requires C, 62·05; H, 5·8%; *M*, 348).

1,5,6,7-Tetramethoxyxanthen-9-one (4).—(*a*) The benzophenone (8) (12·4 g) in pyridine (160 ml), water (150 ml), and tetramethylammonium hydroxide (5 ml; 25% solution) was refluxed overnight. The cooled reaction mixture was diluted with water (450 ml) and acidified with hydrochloric acid. Evaporation of the dried ($MgSO_4$) dichloromethane extract (2 × 200 ml) gave a pale brown oil which rapidly solidified. Recrystallisation from chloroform–cyclohexane gave *1,5,6,7-tetramethoxyxanthen-9-one* (9·5 g), as radial aggregates of white needles, m.p. 160—162°, $\nu_{max.}$ 1662, 1621, 1605, 1305, 1132, 1090, and 805 cm^{-1} (Found: C, 64·5; H, 5·15%; M^+, 316. $C_{17}H_{16}O_6$ requires C, 64·55; H, 5·1%; *M*, 316).

(*b*) The benzophenone (8) (1·0 g) in absolute methanol (20 ml) containing dissolved sodium (2·5 g) was stirred under reflux for 10 days. After 48 h, no further change was observed (t.l.c.) to take place in the reaction mixture. The mixture was poured onto water (70 ml) and acidified with hydrochloric acid, before extraction with dichloromethane (100 ml). The extract was washed with 10% sodium hydroxide solution, and with water, and the alkaline extract retained. The dried ($MgSO_4$) organic phase was evaporated and the residue purified by preparative t.l.c. (p.l.c.), eluting with benzene–ethyl acetate (78 : 22). The main band (white fluorescence under u.v. light) at R_F *ca.* 0·25 gave 1,5,6,7-tetramethoxyxanthen-9-one (0·31 g), as needles (from chloroform–ethyl acetate–cyclohexane), m.p. 160—162°, identical with an authentic sample from the previous preparation.

Neutralisation of the alkaline extract with hydrochloric acid and extraction with dichloromethane afforded unchanged 2-hydroxy-2′,3-4,5,6′-pentamethoxybenzophenone (472 mg) as lustrous yellow needles, m.p. 142° (from ethanol), identical with an authentic sample.

[7] B. Jackson, H. D. Locklsey, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1968, 2579.

[8] A. J. Quillinan and F. Scheinmann, *J.C.S. Perkin I*, 1972, 1382.

[9] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2653.

[10] A. J. Quillinan and F. Scheinmann, *Chem. Comm.*, 1971, 966.

When this experiment was repeated in the presence of water (7 ml) as well as the previous cyclisation reagents (methanol, sodium methoxide), no benzophenone survived, and cyclisation to the xanthone (4) was complete.

Selective Demethylation Experiments.—1-*Hydroxy*-5,6,7-*trimethoxyxanthen*-9-*one* (5). A solution of the tetramethoxyxanthone (4) (7·4 g) in dichloromethane (140 ml) was treated with boron trichloride in dichloromethane (35 ml; 4 ml ≡ 1 g BCl_3) at room temperature. The red complex was stirred for 20 min, after which the mixture was poured onto water (180 ml) containing dichloromethane (150 ml) and stirred for 2 h. Evaporation of the solvent from the dried organic layer gave an oil which rapidly solidified. 1-*Hydroxy*-5,6,7-*trimethoxyxanthen*-9-*one* (6·75 g) formed matted, silky needles from ethanol, m.p. 135·5—136°, $\nu_{max.}$ 1648, 1620, 1610, 1590, 1140, 810, and 712 cm^{-1} (Found: C, 63·6; H, 4·65%; M^+, 302. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·7%; *M*, 302).

Phosphoryl chloride–zinc chloride demethylation of 1,5,6,7-*tetramethoxyxanthen*-9-*one*. The tetramethoxyxanthone (4) (1·5 g) in phosphoryl chloride (25 ml) containing freshly fused and powdered zinc chloride (8·0 g) was stirred at 60—65° for 2 h, and the cooled viscous liquid poured onto crushed ice (400 ml). The suspension, after standing overnight, was filtered, and the filtrate discarded. The dried residue was a brown powder (1·1 g) containing several components (t.l.c.). The acetone-soluble fraction of this solid was applied to 12 silica plates (20 × 20 × 0·1 cm) and eluted with benzene–ethyl acetate (5 : 2) to give three compounds: 1-hydroxy-5,6,7-trimethoxyxanthen-9-one, R_F *ca.* 0·9, m.p. 135°, crystallised from ethanol as yellow needles (78 mg), identical with an authentic sample; 1,5-*dihydroxy*-6,7-*dimethoxyxanthen*-9-*one*, R_F *ca.* 0·6 (deep red fluorescence under u.v. light), crystallised as matted, pale yellow needles from ethyl acetate–light petroleum (b.p. 100—120°), m.p. 251° (175 mg), $\nu_{max.}$ 3300, 1660, 1620, 1595, 1510, 1140, and 807 cm^{-1} (Found: C, 62·6; H, 4·1%; M^+, 288. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%; *M*, 288); and 1,5,6-*trihydroxy*-7-*methoxyxanthen*-9-*one*, R_F *ca.* 0·4 (red-brown fluorescence under u.v. light), crystallised from ethyl acetate–light petroleum (b.p. 100—120°) as pale yellow, matted needles (0·41 g), m.p. 241°, $\nu_{max.}$ 3250, 1662, 1620, 1585, 1445, 1315, 1245, 1070, and 818 cm^{-1} (Found: C, 61·2; H, 3·6%; M^+, 274. $C_{14}H_{10}O_6$ requires C, 61·3; H, 3·7%; *M*, 274).

1,5,6-*Trihydroxy*-7-*methoxyxanthen*-9-*one* (6). The tetramethoxyxanthone (4) (11·0 g) in glacial acetic acid containing hydrogen bromide (45% w/v; 150 ml) was refluxed for 0·5 h. Solvents were largely removed under reduced pressure, and the residue (45 ml; partly solid) was poured onto water (300 ml). The granular yellow precipitate gave 1,5,6-trihydroxy-7-methoxyxanthen-9-one (6·2 g) as bright yellow needles, m.p. 241° (from methanol), identical with this compound obtained by the previous method.

Selective methylation of 1,5,6-trihydroxy-7-methoxyxanthen-9-one (3·2 g) occurred with dimethyl sulphate (1·642 g) in acetone (110 ml) containing an excess of potassium hydrogen carbonate on refluxing overnight. Evaporation of the filtered solution gave a yellow solid which on crystallisation from methanol gave 1,5-dihydroxy-6,7-dimethoxyxanthen-9-one (2·5 g) as matted, yellow needles, m.p. 251°, identical with an authentic sample obtained from the phosphoryl chloride–zinc chloride demethylation reaction.

1,5,6,7-*Tetrahydroxyxanthen*-9-*one* (7). (*a*) The tetramethoxyxanthone (4) (0·5 g) in acetic acid containing hydrogen bromide (45% w/v; 20 ml) was refluxed for 18 h, and the cooled reaction mixture poured onto water. The yellow solid gave 1,5,6,7-*tetrahydroxyxanthen*-9-*one* as yellow needles, m.p. >300° (decomp.) (from methanol), τ [$(CD_3)_2CO$, 100 MHz] −3·02 (s, 1-OH), 0·8—1·2br (3 × OH), 2·49 (t, *J* 9 Hz, H-3), 2·90 (s, H-8), and 3·11 and 3·40 (both d, *J* 9 Hz, H-2 and -4), $\nu_{max.}$ (Nujol) 3420, 3180, 1650, 1620, 1597, 1267, 1091, 1047, 962, 741, and 708 cm^{-1} (Found: C, 59·85; H, 2·85%; M^+, 260. $C_{13}H_8O_6$ requires C, 60·0; H, 3·1%; *M*, 260).

(*b*) The following conditions for the reaction of Grover *et al.*[5] were attempted. 2,3-Dihydroxycyclohex-5-ene-1,4-dione (2·8 g) (tautomeric with 1,2,3,4-tetrahydroxybenzene) and 2,6-dihydroxybenzoic acid (3 g) in phosphoryl chloride (30 ml) containing freshly fused, powdered zinc chloride (12 g) at 60° for 3 h gave no precipitate after 12 h when poured onto water (750 ml). Extraction gave a purple oil (2·5 g) devoid of 1,5,6,7-tetrahydroxyxanthone. Even after methylation of the oil with dimethyl sulphate no methoxyxanthone could be detected.

1-*Hydroxy*-7-*methoxy*-5,6-*bis*-(3-*methylbut*-2-*enyloxy*)-*xanthen*-9-*one* (9). 1,5,6-Trihydroxy-7-methoxyxanthen-9-one (5·0 g) in acetone (250 ml) containing potassium carbonate (10·0 g) was refluxed with an excess of 3-methylbut-2-enyl bromide (8 g) until reaction to the monohydroxyxanthone (9) was complete (55 min, t.l.c. control). Evaporation of the filtered solution and recrystallisation of the residue from light petroleum (b.p. 60—80°) gave 1-*hydroxy*-7-*methoxy*-5,6-*bis*-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (4·7 g) as matted needles, m.p. 90—92°, $\nu_{max.}$ 1650, 1623, 1610, 1586, 1302, 1250, 1150, 1080, 809, and 761 cm^{-1} (Found: C, 70·1; H, 6·5. $C_{23}H_{26}O_6$ requires C, 70·2; H, 6·4%).

1-*Hydroxy*-6,7-*dimethoxy*-5-(3-*methylbut*-2-*enyloxy*)-*xanthen*-9-*one* (10).—1,5-Dihydroxy-6,7-dimethoxyxanthone (2·5 g) in acetone (75 ml) containing potassium carbonate (4·0 g) and 3-methylbut-2-enyl bromide (3·0 g) was refluxed until only a monohydroxyxanthone remained (37 min, t.l.c. control). Evaporation of the filtrate gave an oil which solidified on scratching. Recrystallisation from light petroleum (b.p. 80—100°) gave 1-*hydroxy*-6,7-*dimethoxy*-5-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (2·1 g) as pale yellow, matted needles, m.p. 123—125°, $\nu_{max.}$ 1650, 1610, 1587, 1301, 1250, 1145, 808, and 757 cm^{-1} (Found: C, 67·15; H, 5·6. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%).

Claisen Rearrangement Studies.—(a) *With* 1-*hydroxy*-7-*methoxy*-5,6-*bis*-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (9). A solution of the xanthone (9) (1·5 g) in *NN*-dimethylaniline (50 ml) was refluxed for 4·25 h, and the cooled mixture poured onto an excess of 2N-hydrochloric acid. The beige precipitate gave 1,5,6-trihydroxy-7-methoxyxanthen-9-one (0·9 g) as yellow needles, m.p. 241° (from methanol), identical with an authentic sample. T.l.c. on the mother liquors from the above crystallisation showed that this compound was virtually the entire reaction product. Methylation of the crude reaction product gave 1,5,6,7-tetramethoxyxanthen-9-one, m.p. 160—162°, identical with an authentic sample. When the Claisen rearrangement was attempted in refluxing decalin similar results were obtained.

(b) *With* 1-*hydroxy*-6,7-*dimethoxy*-5-(3-*methylbut*-2-*enyloxy*)*xanthone* (10). (i) A solution in decalin (10 ml) of the xanthone (10) (0·5 g) was heated in an air-bath at 190° for 2·5 h, and the mixture allowed to cool. The pale

yellow crystalline precipitate was identical with an authentic sample of starting material, m.p. 123—125°. The remainder of the precipitate was then redissolved and the solution heated under reflux for 6 h, and allowed to cool. The precipitate gave needles (0·23 g), m.p. 251° (from methanol), identical with an authentic sample of 1,5-dihydroxy-6,7-dimethoxyxanthone.

The mother liquors from the recrystallisation were evaporated and the residue combined with that from evaporation of the decalin, and the resulting solid was recrystallised from methanol to give more 1,5-dihydroxy-6,7-dimethoxyxanthone (0·08 g), m.p. 250—253°, identical with the previous fraction. Examination of the methanol filtrate showed that rearrangement products were absent.

(ii) A solution of the xanthone (10) (125 mg) in *NN*-dimethylaniline (8 ml) was refluxed for 7·5 h, and the cooled mixture poured onto dilute hydrochloric acid. The resulting suspension was extracted with chloroform (100 ml), and the organic extract washed with further dilute hydrochloric acid (50 ml) and water (50 ml), dried ($MgSO_4$), and evaporated to a yellow-brown oil. P.l.c. on silica gel, eluting with benzene–ethyl acetate (17 : 3) gave two components: 1,5-dihydroxy-6,7-dimethoxyxanthen-9-one (45 mg), R_F *ca.* 0·60 (red fluorescence under u.v. light), m.p. 251° [from ethyl acetate–light petroleum (b.p. 100—120°)], identical with an authentic sample; and *1,5-dihydroxy-6,7-dimethoxy-8-(3-methylbut-2-enyl)xanthen-9-one* (*celebixanthone methyl ether*) (25 mg), R_F *ca.* 0·65 (black fluorescence under u.v. light), pale yellow plates, m.p. 162—164° (lit.,[2] 164—169°) [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 67·2; H, 5·6. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%).

[4/1640 *Received, 5th August,* 1974]