Extractives from Guttiferae. Part 33.† Synthesis of the Ozonolysis Product from Dimethylmangostin, 1-Hydroxy-3,6,7-trimethoxy-2,8-bis-(2-oxoethyl)xanthone; Some ^{13}C Nuclear Magnetic Resonance Spectra of Xanthones

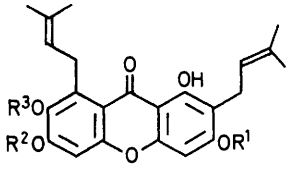
By **M. Sum b. Hj. Idris, Alan Jefferson,** and **Feodor Scheinmann,*** Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

The synthesis of the dialdehyde 1-hydroxy-3,6,7-trimethoxy-2,8-bis-(2-oxoethyl)xanthone, first obtained from ozonolysis of dimethylmangostin, is described. Xanthone formation by cyclisation of a benzophenone intermediate is followed by selective demethylations, allylation, and Claisen rearrangement. Oxidative cleavage of the allyl side chains in 2,8-diallyl-1,3,6,7-tetramethoxyxanthone, followed by demethylation with boron trichloride, gave the required dialdehyde (5). Some ^{13}C n.m.r. spectra of xanthones are discussed.

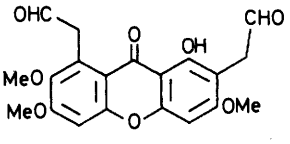
THE bark, fruit hulls, and dried latex of the mangosteen tree, *Garcinia mangostana* L. (family Guttiferae) contain the yellow pigments, mangostin, β-mangostin, and γ-mangostin, to which the xanthone structures (1)—(3) have been assigned.[1-4]

As part of a synthetic approach to natural isoprenylated 1,3,6,7-tetra-oxygenated xanthones we now report a preparation of the dialdehyde (5), previously obtained by ozonolysis of dimethylmangostin (4).[1,5]

1-Hydroxy-3,6,7-trimethoxyxanthone (6) was obtained either by oxidative cyclisation of maclurin (13) followed by methylation of the resulting 1,3,6,7-tetrahydroxyxanthone (7) with diazomethane,[6] or (in larger quantities) by cyclisation of 2-hydroxy-2′,4,4′,5,6′-pentamethoxybenzophenone (14) with aqueous methanolic sodium hydroxide followed by selective demethylation of the resulting 1,3,6,7-tetramethoxyxanthone (8) with boron trichloride.[7,8] Attempts to prepare dimethylmangostin

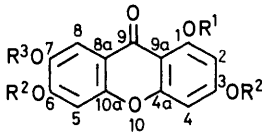


(1) $R^1 = R^2 = H, R^3 = Me$
(2) $R^1 = R^3 = Me, R^2 = H$
(3) $R^1 = R^2 = R^3 = H$
(4) $R^1 = R^2 = R^3 = Me$



(5)

(4) by isoprenylation of 1-hydroxy-3,6,7-trimethoxyxanthone (6) with 3-methylbut-2-enyl bromide in dioxan in the presence of silver oxide were unsuccessful: only the phloroglucinol ring was allylated. Three products were isolated in low yield and identified as 1-hydroxy-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)xanthone (15), 1-hydroxy-3,6,7-trimethoxy-4-(3-methylbut-2-enyl)xanthone (16), and 1-hydroxy-3,6,7-trimethoxy-2,4-bis-(3-methylbut-2-enyl)xanthone (17).



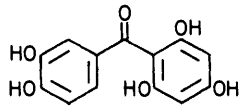
(6) $R^1 = H, R^2 = R^3 = Me$
(7) $R^1 = R^2 = R^3 = H$
(8) $R^1 = R^2 = R^3 = Me$
(9) $R^1 = R^3 = H, R^2 = Me$
(10) $R^1 = H, R^2 = Me, R^3 = CH_2{\cdot}CH{:}CH_2$
(11) $R^1 = R^3 = CH_2{\cdot}CH{:}CH_2, R^2 = Me$
(12) $R^1 = R^3 = H, R^2 = Me$
and $CH_2{\cdot}CH{:}CH_2$ at C-8

Failure to allylate C-8 of the xanthone nucleus by an intermolecular reaction led us to consider the Claisen rearrangement for introduction of a substituent at this hindered position.[9] 1-Hydroxy-3,6,7-trimethoxyxanthone (6) was converted into 1,7-dihydroxy-3,6-dimethoxyxanthone (9) by selective demethylation with concentrated sulphuric acid. The structure (9) was confirmed by unambiguous synthesis from 2,5-dihydroxy-4-methoxybenzoic acid [1] and phloroglucinol monomethyl ether in the presence of phosphoryl chloride and fused zinc chloride.[10] Attempts to prepare the 1,1-dimethylprop-2-ynyl ether (18) in good yield by the reaction of 3,3-dimethylprop-2-ynyl chloride with 1,7-dihydroxy-3,6-dimethoxyxanthone were frustrated by the slow formation of the desired ether (18) [11] in admixture with the pyranoxanthone (19),[7] formed by Claisen rearrangement.[11] Allyl groups were readily introduced at C-8 and at C-2 by Claisen rearrangements of 7-allyloxy-1-hydroxy- and 1,7-bisallyloxy-3,6-dimethoxy-xanthone,

† Part 32, P. J. Cotterill, F. Scheinmann, and G. S. Puranik, *Phytochemistry*, 1977, **16**, 148.

[1] P. Yates and G. H. Stout, *J. Amer. Chem. Soc.*, 1958, **80**, 1691.
[2] G. H. Stout, M. M. Krahn, P. Yates, and H. B. Bhat, *Chem. Comm.*, 1968, 211.
[3] P. Yates and H. B. Bhat, *Canad. J. Chem.*, 1968, **46**, 3770.
[4] A. Jefferson, A. J. Quillinan, F. Scheinmann, and K. Y. Sim, *Austral. J. Chem.*, 1970, **23**, 2539.
[5] O. Dragendorff, *Annalen*, 1931, **487**, 62.
[6] A. Jefferson and F. Scheinmann, *Nature*, 1965, **207**, 1193.
[7] A. J. Quillinan and F. Scheinmann, *J.C.S. Perkin I*, 1973, 1329.
[8] F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, A. W. Price, and N. Somvichien, *Tetrahedron Letters*, 1966, 4153.
[9] A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.
[10] P. K. Grover, G. D. Shah, and R. C. Shah, *J. Chem. Soc.*, 1955, 3982.
[11] P. J. Cotterill and F. Scheinmann, *J.C.S. Chem. Comm.*, 1975, 665.

(10) and (11). These ethers [(10) and (11)] were prepared by reactions of 1,7-dihydroxy-3,6-dimethoxyxanthone (9) with the appropriate amount of allyl bromide and in each case rearrangement gave only one product



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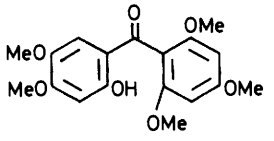

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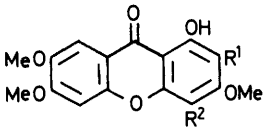
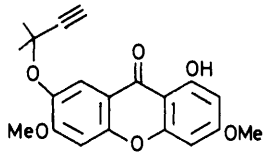


(15) $R^1 = CH_2{\cdot}CH{:}CMe_2$, $R^2 = H$
(16) $R^2 = CH_2{\cdot}CH{:}CMe_2$, $R^1 = H$
(17) $R^1 = R^2 = CH_2{\cdot}CH{:}CMe_2$



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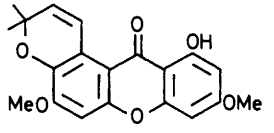
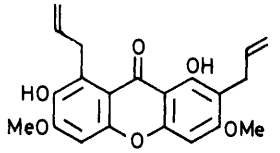


(19)



(20)

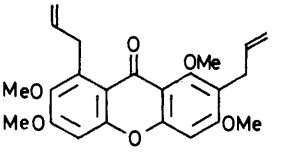
[(12) or (20)]. The structures (12) and (20) follow from analysis and ^1H n.m.r. spectra: rearrangement to C-8 is particularly easy to follow by observing the disappearance of the aromatic proton signal at lowest field (δ *ca.* 7.6). Rearrangement to C-2 is indicated by removal of a signal due to an aromatic proton which shows *meta*-coupling (J *ca.* 2 Hz) to leave the H-4 signal as a singlet.

As expected the ^1H n.m.r. spectrum of 2,8-diallyl-1,7-dihydroxy-3,6-dimethoxyxanthone (20) closely resembles that of dimethylmangostin (4) in the aromatic region and also in the benzylic methylene resonances (doublet, δ *ca.* 3.4 and 4.2).[12]

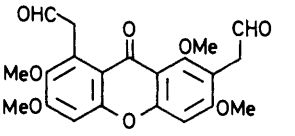
The ^{13}C n.m.r. spectra of the diallyl ether (11) and the diallylxanthone (20) are also of diagnostic value (Table 3). Thus, as expected, the doublets in the off-resonance decoupled spectrum of the diallyl ether (11) assigned to C-2 (93 p.p.m.) and C-8 (107.8 p.p.m.) are no longer present after rearrangement to the *C*-allyl derivative (20). The methylene carbon nuclei of the allyl side chain when attached to oxygen resonate in the region 70—80 p.p.m., whereas after rearrangement the *C*-methylene signals are at much higher field (26—30 p.p.m.).[13]

Methylation of 2,8-diallyl-1,7-dihydroxy-3,6-dimethoxyxanthone (20) with dimethyl sulphate gave 2,8-diallyl-1,3,6,7-tetramethoxyxanthone (21), which on oxidation with sodium periodate and osmium tetraoxide afforded the dialdehyde (22). Selective demethylation with boron trichloride[8] gave 1-hydroxy-3,6,7-trimethoxy-2,8-bis-(2-oxoethyl)xanthone (5), identical with the ozonolysis product from dimethylmangostin.[1]

We have previously demonstrated that a 2-oxoethylxanthone can be converted into a 3-methylbut-2-enylxanthone by a Wittig reaction.[14] Thus the synthesis of the dialdehyde (5) derived from dimethylmangostin not only provides confirmation of the xanthone substitution pattern of mangostin [1,2] but in addition suggests a pathway for the total synthesis of isoprenyl-1,3,6,7-tetrahydroxyxanthones found in *Garcinia* [1-4] and *Tovomita* species.[15] In addition, direct fusion of a 2,2-dimethyl-2*H*-pyran ring to a xanthone nucleus in an angular position at C-7 and C-8 as in structure (19) by a Claisen



(21)



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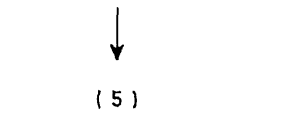

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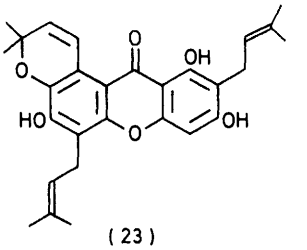
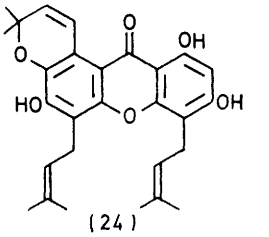
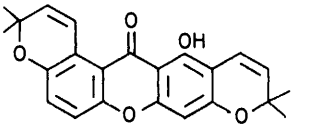


(23)



(24)



(25)

rearrangement provides an approach to the natural pyranoxanthones, *e.g.* tovophyllin-A (23),[15] pentadesmaxanthone (24),[16] and thwaitesixanthone (25).[17]

[12] F. Scheinmann, *Chem. Comm.*, 1967, 1015.
[13] K. K. Chexal, C. Fouweather, J. S. E. Holker, T. J. Simpson, and K. Young, *J.C.S. Perkin I*, 1974, 158.
[14] H. D. Locksley, A. J. Quillinan, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1971, 3804.
[15] W. G. De Oliveiria, O. R. Gottlieb, and A. A. Lins Mesquita, *Phytochemistry*, 1972, **11**, 3323; 1975, **14**, 1103.
[16] S. P. Gunasekera, K. Silvapalan, M. U. S. Sultanbawa, and W. D. Ollis, *J.C.S. Perkin I*, 1977, 11.
[17] M. Dahanayake, I. Kitagawa, R. Somanathan, and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1974, 2510.

The ^{13}C n.m.r. spectra of xanthones are of diagnostic value in assigning their structures. Chemical shift assignments of individual carbon atoms follow from comparison of experimental and calculated chemical shifts (Table 2). The calculated values for the aromatic carbon atoms can be obtained from data for either xanthone or benzene (δ 129 p.p.m.) by assuming additivity of substituent effects (Table 1). Thus for xanthone itself the incremental values for benzoyl and phenoxy (Table 1) are used as approximations to account for the influence of carbonyl and ether functions on the chemical shifts of the aromatic carbon atoms. Agreement between calculated and experimental values was good for C-2 and C-3, but at other positions where the discrepancy was more than 2 p.p.m. the assignments were confirmed by other methods. Thus the signals arising from the ring junction carbon atoms C-4a (156.2 p.p.m.) and C-9a (122.0 p.p.m.) were readily assigned from their appearance as singlets in the single frequency off-resonance decoupled spectrum. Although there is considerable discrepancy between the calculated chemical shift (132.3 p.p.m.) and the experimental value (126.7 p.p.m.) for C-1, addition of the shift reagent $Eu(fod)_3$ to xanthone in deuteriochloroform confirmed the assignment. Thus on addition of $Eu(fod)_3$ all the ^{13}C n.m.r. signals move downfield, the induced shift from use of an excess of the reagent being greatest at C-1 and C-9a (Table 2). The assignment of the signal at δ 126.7 p.p.m. to C-1 was also confirmed by comparison with reported data for C-1 in anthraquinone (127.0 p.p.m.) and anthrone (127.1 p.p.m.); as expected the *meta*-substituent at C-10 does not appreciably influence C-1.[18,19]

TABLE 1

^{13}C N.m.r. substituent effects [a] in substituted benzenes

	Position			
Substituent	C-1	*ortho*	*meta*	*para*
OH	+26.9	−12.7	+1.4	−7.3
OMe	+31.4	−14.4	+1.0	−7.7
COPh	+9.4	+1.7	−0.2	+3.6
Me	+8.9	0.7	−0.1	−2.9
OPh [b]	+29.2	−9.4	+1.6	−5.1

[a] In p.p.m. relative to internal benzene; positive shifts downfield; 10% solutions in carbon tetrachloride (G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972, p. 81). [b] Data for neat liquid (J. B. Stothers, 'Carbon–13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 197.

TABLE 2

Comparison of experimental and calculated ^{13}C n.m.r. chemical shifts (p.p.m.) for xanthone; effect of addition of $Eu(fod)_3$ on chemical shifts (p.p.m.) of xanthone in deuteriochloroform

Wt (mg) of $Eu(fod)_3$ added to a saturated solution of xanthone in $CDCl_3$ (2 ml)	C-1	C-2	C-3	C-4	C-4a	C-9a	C-9
0	126.7	123.8	134.6	117.9	156.2	122.0	176.8
51.4	126.9	123.9	134.7	117.95	156.3	122.3	177.0
100	127.3	124.0	134.8	118.0	156.6	122.7	177.2
200	128.2	124.3	135.2	118.3	157.2	123.8	177.8
400 (excess)	129.3	124.6	135.5	118.5	157.7	125.0	178.0
Δ = δ(xanthone) − δ[xanthone + excess $Eu(fod)_3$]	−2.6	−0.8	−0.9	−0.6	−1.5	−3.0	−1.2
Calc. δ values for xanthone	132.3	123.7	134.2	119.4	159.9	129.0	

TABLE 3

^{13}C N.m.r. chemical shifts (p.p.m. from Me_4Si) of 1,3,6,7-tetraoxygenated xanthones; comparison with calculated values for the aromatic carbon atoms

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-4a	C-8a	C-9a	C-10a	CH_2	−CH=	$=CH_2$	OMe
(8)	Calc.	159.1	95.0	167.0	95.8	104.5	153.1	140.8	113.3		158.2	115.7	99.9	151.5				56.7
	Found	161.6	92.6	164.1	94.9	98.8	150.6	145.6	105.7	174.0	159.9	115.8		146.4				56.1, 55.5
(6)	Calc.	154.6	96.7	167.4	96.2	104.9	153.3	136.3	115.0		158.6	115.7	101.6	149.5				
	Found	157.2	96.6	165.7	92.3	99.8	155.3	144.5	107.7	179.2	162.5	112.8	102.6	151.0				56.3, 56.0
(11)	Calc.*	159.1	95.0	167.0	95.8	104.5	153.1	140.8	113.3		158.2	115.7	99.9	151.5				
	Found	160.7	93.0	164.2	96.4	99.1	154.9	145.5	107.8	174.4	159.8	116.1	151.0	151.0	80.2	132.6	118.5	56.3
															70.0	132.9	117.8	55.0
(20)	Calc.†	155.3	105.6	168.1	96.1	102.0	153.3	137.0	123.9		155.7	116.4	101.5	149.8				
	Found	155.5		163.5	88.6	97.2	151.6		125.5	182.2	160.0	109.6		140.6	30.3	136.8	114.8	56.3,
															26.4	136.3	114.3	55.8

* Calculations from the fundamental parameters for xanthone given in Table 2 and the incremental values for hydroxy, methoxy, and methyl substituents given in Table 1. † For these calculations the incremental values for the methyl group are used as an approximation for the effect of the allyl group.

The chemical shifts of the substituted xanthones in Table 3 are computed from the experimental chemical shifts of xanthone and the incremental values of the substituents shown in Table 1. The agreement between calculated and found chemical shifts is close enough in

[18] L. R. Isbrandt, R. K. Jensen, and L. Petrakis, *J. Magnetic Resonance*, 1973, **12**, 143.

[19] J. F. Castelão, jun., O. R. Gottlieb, R. A. De Lima, A. A. L. Mesquita, H. E. Gottlieb, and E. Wenkert, *Phytochemistry*, 1977, **16**, 735.

most cases to allow unambiguous assignments. No attempt is made in Table 3 to take account of anomalies which may arise when substituents are adjacent, or to allow for the effect of hydrogen bonding.[20] Thus the xanthone carbonyl group resonates in the range 174—182.2 p.p.m. Within this range the presence of a hydrogen-bonded 1-hydroxy-group gives rise to absorptions at *ca.* 179—182 p.p.m., whereas loss of intramolecular hydrogen bonding on *O*-methylation or *O*-allylation causes the carbonyl resonance to move upfield by 5 p.p.m.*

EXPERIMENTAL

I.r. spectra (for Nujol mulls unless otherwise stated), were determined with a Perkin-Elmer Infracord 257 instrument. ^{1}H N.m.r. spectra were measured with a Varian A-60 or HA100 or a Perkin-Elmer R 32 spectrometer for solutions in deuteriochloroform unless otherwise stated (Me_4Si as internal reference), and ^{13}C n.m.r. spectra with a Varian CFT 20 instrument. Mass spectra were recorded with an A.E.I. MS902 or MS12 spectrometer at 70 eV. Analytical and preparative t.l.c. were carried out on silica gel G (Merck); column chromatography was performed on silica gel MFC (Hopkin and Williams).

Isoprenylation of 1-*Hydroxy*-3,6,7-*trimethoxyxanthone* (6).—3-Methylbut-2-enyl bromide (1.5 g) was added to a suspension of silver oxide (2 g) and 1-hydroxy-3,6,7-trimethoxyxanthone (6) (1 g) in dry dioxan (100 ml). The flask was enclosed in aluminium foil and the mixture was stirred. More 3-methylbut-2-enyl bromide (1.5 g) and silver oxide (2 g) were added at intervals until no starting materials remained (*ca.* 65 h). The silver oxide was filtered off, and the dioxan was removed. The residue was dissolved in benzene and shaken with Claisen's alkali to yield yellow insoluble sodium salts, which were dried and acidified with 2N-hydrochloric acid. The beige solid was dried, and applied to preparative t.l.c. plates, which were developed with chloroform–cyclohexane (70 : 30).

Fraction 1. A black band when viewed under u.v. illumination (R_F 0.80), fraction 1 crystallised from light petroleum (b.p. 60—80 °C) to give yellow needles of 1-*hydroxy*-3,6,7-*trimethoxy*-2,4-*bis*-(3-*methylbut*-2-*enyl*)*xanthone* (17) (80 mg), m.p. 152—153° (Found: C, 71.4; H, 7.3. $C_{26}H_{30}O_6$ requires C, 71.1; H, 7.0%), δ_H ($CDCl_3$; 100 MHz) 13.1 (1 H, s, OH at C-1), 7.54 (1 H, s, H-8), 6.81 (1 H, s, H-5), 5.24 (2 H, m, 2 × CH=), 3.93 (3 H, s, OMe), 3.97 (3 H, s, OMe), 3.76 (3 H, s, OMe), 3.48 (2 H, d, *J* 7 Hz, ArCH_2), 3.38 (2 H, d, *J* 8 Hz, ArCH_2), 1.86 (3 H, s, =CMe), 1.78 (3 H, s, =CMe), and 1.68 (6 H, s, 2 =CMe).

Fraction 2. A black band when viewed under u.v. illumination (R_F 0.65), fraction 2 crystallised from light petroleum (b.p. 100—120 °C) to yield yellow needles of 1-*hydroxy*-3,6,7-*trimethoxy*-2-(3-*methylbut*-2-*enyl*)*xanthone* (15) (40 mg), m.p. 161° (Found: C, 67.9; H, 6.15. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.15%); δ_H ($CDCl_3$; 100 MHz) 13.02 (1 H, s, H-1), 7.54 (1 H, s, H-8), 6.79 (1 H, s, H-5), 6.34 (1 H, s, H-4), 5.18 (1 H, m, CH=), 3.94 (3 H, s, OMe), 3.92 (3 H, s, OMe), 3.86 (3 H, s, OMe), 3.32 (2 H, d, *J* 7 Hz, ArCH_2), 1.78 and 1.66 (each 3 H, s, =CMe_2). The product readily cyclised on heating in the presence of acids (blue-white fluorescent t.l.c. spot under u.v.).

* ^{13}C N.m.r. spectral data of xanthones was also reported recently in a study of xanthonolignoids from Guttiferae.[19]

Fraction 3. An orange band when viewed under u.v. illumination (R_F 0.50), fraction 3 crystallised from light petroleum (b.p. 100—120°) to yield yellow needles of 1-*hydroxy*-3,6,7-*trimethoxy*-4-(3-*methylbut*-2-*enyl*)*xanthone* (16) (40 mg), m.p. 185° (Found: C, 68.6; H, 5.9. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.15%); δ_H ($CDCl_3$; 100 MHz) 13.05 (1 H, s, OH at C-1), 7.50 (1 H, s, H-8), 6.79 (1 H, s, H-5), 6.31 (1 H, s, H-4), 5.17 (1 H, m, CH=), 3.94, 3.92, and 3.85 (3 × OMe), 3.42 (2 H, d, *J* 7 Hz, ArCH_2), and 1.82 and 1.66 (each 3 H, s, =CMe_2).

Attempts to isoprenylate 1,7-dihydroxy-3,6-dimethoxyxanthone under similar conditions were unsuccessful.

1,7-*Dihydroxy*-3,6-*dimethoxyxanthone* (9) *from* 1-*Hydroxy*-3,6,7-*trimethoxyxanthone* (6).—1-Hydroxy-3,6,7-trimethoxyxanthone (1 g) in concentrated sulphuric acid (20 ml) was heated at 60 °C (oil-bath) for 4 days. The solution was poured into water and the aqueous solution was boiled for 30 min. The yellow precipitate was filtered off, dried, and purified by column chromatography on silica gel. The fraction eluted with toluene–ethyl acetate (17 : 3) gave 1,7-dihydroxy-3,6-dimethoxyxanthone (0.5 g) as yellow needles (from methanol), m.p. 237—240° (lit.,[12] 235—237°), $\nu_{max.}$ (Nujol) 3 400—3 200br (OH), 1 655, 1 600, 1 570, and 1 500 cm^{-1} (Found: C, 62,3; H, 4.2%; M^+, 288.063 0. $C_{15}H_{12}O_6$ requires C, 62.5; H, 4.2%; *M*, 288.063 3); δ [$(CD_3)_2CO$–$(CD_3)_2SO$; 90 MHz] 9.35 (1 H, s, OH at C-1), 7.45 (1 H, s, H-8), 6.94 (1 H, s, H-5), 6.35 (1 H, d, *J* 3 Hz, H-2), 6.25 (1 H, d, *J* 3 Hz, H-4), 4.00 (3 H, s, OMe at C-6), 3.90 (3 H, s, OMe at C-3), and 3.10 (s, 1 H, OH at C-7).

1,7-Dihydroxy-3,6-dimethoxyxanthone, identical (mixed m.p. and i.r. spectrum) with the sample prepared by selective demethylation, was also synthesised by the Grover–Shah method,[10] by condensation of 2,5-dihydroxy-4-methoxybenzoic acid (1.2 g) with phloroglucinol monomethylether (1.2 g) in the presence of phosphoryl chloride (15 ml) and fused zinc chloride (6.8 g). After 1.75 h at 75 °C the mixture was poured onto ice–water and 1,7-dihydroxy-3,6-dimethoxyxanthone was isolated by preparative t.l.c.

1,7-*Dihydroxy*-3,6-*dimethoxyxanthone from* 1,3,6,7-*Tetramethoxyxanthone*.—1,3,6,7-Tetramethoxyxanthone (2.5 g) in glacial acetic acid (50 ml) containing hydrogen bromide (45% w/w) was heated under reflux for 6 h. Glacial acetic acid (10 ml) containing hydrogen bromide was added every 1.5 h during the reaction. Removal of the solvent (30 ml) under reduced pressure followed by pouring the residue onto ice-cold water gave a yellow precipitate of a mixture of 1-hydroxy-3,6,7-trimethoxyxanthone and 1,7-dihydroxy-3,6-dimethoxyxanthone (2.2 g), m.p. 160—167°. Column chromatography on silica gel [elution with toluene–ethyl acetate (17 : 3)] gave pure 1,7-dihydroxy-3,6-dimethoxyxanthone (0.5 g), identical with the samples prepared previously.

Reaction of 1,7-*Dihydroxy*-3,6-*dimethoxyxanthone with* 3-*Chloro*-3-*methylbut*-1-*yne*.—A mixture of 1,7-dihydroxy-3,6-dimethoxyxanthone (1 g), potassium carbonate (2.5 g), and 3-chloro-3-methylbut-1-yne (1.2 g) in aqueous acetone (10% v/v; 75 ml) was heated under reflux and stirred for 10 days with further daily additions of 3-chloro-3-methylbut-1-yne (1.5 g) and potassium carbonate (1 g). The mixture was poured onto water (100 ml) and the solution was extracted with ethyl acetate (3 × 50 ml). Evaporation of the dried ($MgSO_4$) solution gave an oil, which was purified

[20] A. Pelter, R. S. Ward, and T. I. Gray, *J.C.S. Perkin I*, 1976, 2475.

by preparative t.l.c. A pale yellow band and a deep yellow band, R_F 0.77 and 0.80 (toluene-ethyl acetate, 17 : 3), respectively, were removed and the compounds were eluted from the silica with chloroform. Both products crystallised from acetone, giving the pyranoxanthone (19) and the butynyloxyxanthone (18), m.p. 232° (lit.,[21] 234°), as yellow crystals, identical with authentic samples.

7-Allyloxy-1-hydroxy-3,6-dimethoxyxanthone (10).—1,7-Dihydroxy-3,6-dimethoxyxanthone (560 mg), allyl bromide (260 mg), and potassium carbonate (6 g) were heated under reflux for 9 h in acetone (100 ml). The mixture was filtered and the filtrate evaporated to give a yellow solid which was crystallised from light petroleum (b.p. 100—120 °C)–ethyl acetate (2 : 1) to yield *7-allyloxy-1-hydroxy-3,6-dimethoxyxanthone* as yellow needles (300 mg), m.p. 183—184°; $\nu_{max.}$ 3 500—3 300br, 1 665, 1 610, and 1 580 cm^{-1}; δ_H ($CDCl_3$; 90 MHz) 12.95 (1 H, s, OH at C-1), 7.55 (1 H, s, H-8), 6.82 (1 H, s, H-5), 6.36 (1 H, d, *J* 2 Hz, H-2), 6.34 (1 H, d, *J* 2 Hz, H-4), 6.15 (1 H, m, CH=), 5.40 (2 H, m, $=CH_2$), 4.70 (2 H, d, *J* 1.8 Hz, O·CH_2), 3.99 (3 H, s, OMe at C-6), and 3.86 (3 H, s, OMe at C-3) (Found: C, 65.4; H, 4.9%; M^+, 328. $C_{18}H_{16}O_6$ requires C, 65.8; H, 4.9%; *M*, 328).

1,7-Bisallyloxy-3,6-dimethoxyxanthone (11).—1,7-Dihydroxy-3,6-dimethoxyxanthone (560 mg), allyl bromide (540 mg, 2.2 equiv.), and potassium carbonate (12 g) in acetone (100 ml) were heated under reflux for 2 days. The solution was filtered and evaporated off to give a pale yellow solid mixture of 7-allyloxy-1-hydroxy-3,6-dimethoxyxanthone and 1,7-bisallyloxy-3,6-dimethoxyxanthone (500 mg). The mixture was separated by preparative t.l.c.; a violet fluorescent band at R_F 0.18 (toluene–ethyl acetate, 85 : 15) was removed and the product eluted with chloroform. Evaporation gave a white solid which crystallised from light petroleum (b.p. 100—120 °C)–ethyl acetate to yield *1,7-bisallyloxy-3,6-dimethoxyxanthone* (11) as white needles (300 mg), m.p. 135—137°; δ_H ($CDCl_3$, 90 MHz) 7.65 (1 H, s, H-8), 6.72 (1 H, s, H-5), 6.38 (1 H, d, *J* 3 Hz, H-2), 6.30 (1 H, d, *J* 3 Hz, H-4), 6.05 (2 H, m, 2 CH=), 5.40 (4 H, m, 2 $=CH_2$), 4.70 (4 H, m, 2 O·CH_2), 3.98 (3 H, s, OMe at C-6), and 3.89 (3 H, s, OMe at C-3) (Found: C, 68.2; H, 5.4%; M^+, 368. $C_{21}H_{20}O_6$ requires C, 67.7; H, 5.4%; *M*, 368).

8-Allyl-1,7-dihydroxy-3,6-dimethoxyxanthone (12).—7-Allyloxy-1-hydroxy-3,6-dimethoxyxanthone (300 mg) was heated under reflux with *NN*-dimethylaniline (20 ml) for 3 h under nitrogen. The solution was acidified with 2M-hydrochloric acid. The precipitate was filtered off and washed with water. Recrystallization from ethyl acetate gave *8-allyl-1,7-dihydroxy-3,6-dimethoxyxanthone* (12) (200 mg) as yellow needles, m.p. 187—188°; $\nu_{max.}$ 3 500, 1 695, 1 600, and 1 590 cm^{-1}; δ_H [$CDCl_3$–$(CD_3)_2SO$; 60 MHz] 13.48 (1 H, s, OH at C-1), 8.49 (1 H, s, OH at C-7), 6.84 (1 H, s, H-5), 6.32 (1 H, d, *J* 2.5 Hz, H-2), 6.22 (1 H, d, *J* 2.5 Hz, H-4), 6.00 (1 H, m, CH=), 4.98 (2 H, m, $=CH_2$), 4.15 (2 H, d, *J* 1.8 Hz, ArCH_2), 4.00 (3 H, s, OMe at C-6), and 3.90 (3 H, s, OMe at C-3) (Found: C, 65.95; H, 4.9%; M^+, 328. $C_{18}H_{16}O_6$ requires C, 65.9; H, 4.9%; *M*, 328).

2,8-Diallyl-1,7-dihydroxy-3,6-dimethoxyxanthone (20).—1,7-Bisallyloxy-3,6-dimethoxyxanthone (400 mg) was heated under reflux with *NN*-dimethylaniline (22 ml) for 3.5 h under nitrogen. The solution was poured onto aqueous 10% hydrochloric acid. The precipitate was filtered off and washed with water. Recrystallisation from ethyl acetate gave *2,8-diallyl-1,7-dihydroxy-3,6-dimethoxyxanthone* (20) (200 mg) as yellow needles, m.p. 197—198°, R_F 0.43 (toluene–ethyl acetate, 17 : 3); $\nu_{max.}$ 2 900, 1 650, 1 600, and 1 550 cm^{-1}; δ_H 13.48 (1 H, s, OH at C-1), 6.65 (1 H, s, H-5), 6.27 (1 H, s, H-4), 6.00 (2 H, m, 2 CH=), 5.60 (1 H, s, OH at C-7), 5.05 (4 H, m, 2 $=CH_2$), 4.18 and 3.40 (4 H, d, *J* 1.8 Hz, 2 ArCH_2), 3.98 (3 H, s, OMe at C-6), and 3.88 (3 H, s, OMe at C-3) (Found: C, 68.35; H, 5.5. $C_{21}H_{20}O_6$ requires C, 67.7; H, 5.4%).

2,8-Diallyl-1,3,6,7-tetramethoxyxanthone (21).—2,8-Diallyl-1,7-dihydroxy-3,6-dimethoxyxanthone (200 mg), dimethyl sulphate (1.5 ml), and potassium carbonate (3 g) in acetone (75 ml) were heated under reflux for 24 h. The mixture was filtered and evaporated to leave an oil, which was applied to preparative t.l.c. plates. A blue fluorescent band under u.v. light at R_F 0.47 (toluene–ethyl acetate, 90 : 10) was removed and the compound was eluted with chloroform. The solvent was removed and the product set aside for 1 h to give, as a yellow solid, *2,8-diallyl-1,3,6,7-tetramethoxyxanthone* (21) (150 mg), m.p. 123—124°, $\nu_{max.}$ 1 630, 1 600, 1 560, and 1 550 cm^{-1}; δ_H ($CDCl_3$; 90 MHz) 6.73 (1 H, s, H-5), 6.59 (1 H, s, H-4), 6.00 (2 H, m, 2 CH=), 5.05 (4 H, m, 2 $=CH_2$), 4.25 and 3.48 (4 H, d, *J* 1.8 Hz, 2 ArCH_2), 3.98, 3.96, 3.92, and 3.82 (all 3 H, s, OMe) (Found: C, 69.6; H, 6.1. $C_{23}H_{24}O_6$ requires C, 69.7; H, 6.1%).

1,3,6,7-Tetramethoxy-2,8-bis-(2-oxoethyl)xanthone (22).—2,8-Diallyl-1,3,6,7-tetramethoxyxanthone (200 mg) in tetrahydrofuran (6 ml), sodium periodate (400 mg) in water (1.5 ml), and t-butyl alcohol (4 ml) were treated with osmium tetraoxide (2 mg, 1 crystal). The mixture was stirred under nitrogen at room temperature for 2 h. The suspension was poured into water (25 ml) and extracted with dichloromethane (3 × 25 ml). Evaporation of the dried ($MgSO_4$) solution gave a crude product which was purified by preparative t.l.c. in ethyl acetate–toluene (80 : 20); R_F 0.76. A blue fluorescent band was removed and the compound was eluted with chloroform. Removal of the solvent left yellow crystals of *3,6,7-tetramethoxy-2,8-bis-(2-oxoethyl)-xanthone* (20 mg), m.p. 128—130°; $\nu_{max.}$ ($CHCl_3$) 2 995, 2 900, and 1 730 cm^{-1}; *m/e* 400 (M^+), 370 (100%), 358 (73), 330 (78), 314 (26), and 300 (15); δ_H ($CDCl_3$; 90 MHz) 9.98 and 9.70 (each 1 H, t, *J* 1 Hz, CHO), 6.80 (1 H, s, H-5), 6.62 (1 H, s, H-4), 4.46 and 3.44 (each 2 H, d, *J* 1 Hz, ArCH_2), and 3.96, 3.88, 3.78, and 3.76 (all 3 H, s, OMe) (Found: M^+, 400.115 7. $C_{21}H_{20}O_8$ requires *M*, 400.115 8).

1-Hydroxy-3,6,7-trimethoxy-2,8-bis-(2-oxoethyl)xanthone (5).—The foregoing dialdehyde (30 mg) in dichloromethane (10 ml) was treated with boron trichloride [2 ml of a solution in dichloromethane (250 ml) containing 50 g], and the mixture was stirred at room temperature for 2 h. The mixture was decomposed with water (20 ml) and stirred for 1 h. Extraction with dichloromethane (3 × 25 ml) and evaporation of the dried ($MgSO_4$) extracts gave a mixture which was subjected to preparative t.l.c. Elution with ethyl acetate–toluene (70 : 30) gave a yellow band at R_F 0.71, which was removed, and the compound was eluted from the silica with chloroform. Removal of the solvent gave the dialdehyde (5) as a yellow powder, identical with the degradation product from natural mangostin.

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[21] P. J. Cotterill, Ph.D. Thesis, University of Salford, 1975.