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# Extractives from Guttiferae. Part XVI.[1] Biogenetic-type Synthesis of Xanthones from their Benzophenone Precursors

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A general synthesis of polyhydroxybenzophenones is described. 2,3',4',6-Tetrahydroxy- 2,2',3',6-tetrahydroxy-, and 2,3,3',4',6-pentahydroxybenzophenones were prepared and oxidised to 1,6,7-trihydroxy-, 1,2,8-trihydroxy-, and 1,2,6,7- (or 1,4,6,7-) tetrahydroxyxanthones, respectively, by oxidative coupling.

It has been suggested [2] that shikimate–acetate derived benzophenones are the immediate precursors of xanthones found in higher plants, and in two cases these metabolites have been found to co-occur.[2c,3a] Furthermore, labelling experiments show that 2,3',4,6-tetrahydroxybenzophenone (I) is incorporated to a considerable extent into the 1,3,7-trioxygenated xanthones of *Gentiana lutea* (Gentianaceae).[3] Polyhydroxybenzophenones may co-occur commonly with xanthones, but if the former are present in trace amounts their detection could be difficult without the assistance of reference samples for t.l.c. comparison.

We have reported the isolation of buchanaxanthone (1,6-dihydroxy-5-methoxyxanthone) (II), 1,5,6-trihydroxyxanthone (III), and a 1,2,8-trioxygenated xanthone as its dimethyl ether (IV) from *Calophyllum fragrans* Ridley (Gutteriferae).[4] The preparation of the postulated benzophenone precursors (V) and (VI) of these xanthones has not been reported previously, so a method for their synthesis was devised. The benzophenones both require the carbonyl group to be in the 2-position of a resorcinol nucleus, but existing methods of synthesis do not provide easy access to benzophenones with this structural feature. For example, 2-carboxyresorcinol and its derivatives tend to undergo self condensation or decarboxylation rather than reaction with another phenol.[5] Alternatively, introduction of a carbonyl function into a resorcinol nucleus favours 4- rather than 2-substitution.

Lithiation of resorcinol dimethyl ether has been shown [6] to occur almost exclusively at the 2-position. 2,6-Dimethoxyphenyl-lithium was therefore prepared from resorcinol dimethyl ether and n-butyl-lithium in ether, and added to 3,4-dimethoxybenzoyl chloride in ether to give 2,3',4',6-tetramethoxybenzophenone (VII) (46%). No appreciable reaction of the benzophenone occurs with the organolithium reagent; this is attributed to steric hindrance around the carbonyl group. Under milder conditions, at −70°, the same reagents gave predominantly αα-dibutyl-3,4-dimethoxybenzyl alcohol (VIII), resulting from direct reaction between n-butyllithium and the acid chloride, thus demonstrating that only slight lithiation of the resorcinol nucleus occurs at this temperature. 2,2',3',6-Tetramethoxybenzophenone (IX) was prepared in a similar manner from 2,6-dimethoxyphenyl-lithium and 2,3-dimethoxybenzoyl chloride; and 2,3,3',4',6-pentamethoxybenzophenone (X) from 2,3,6-trimethoxyphenyl-lithium and 3,4-di-

[1] Part XV, B. Jackson, G. A. Herbin, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, *Phytochemistry*, 1969, in the press.

[2] (*a*) M. L. Wolfrom, F. Komitsky, G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, A. Thompson, P. M. Mundell, and O. M. Windrath, *J. Org. Chem.*, 1964, **29**, 692; (*b*) J. R. Lewis and R. H. Warrington, *J. Chem. Soc.*, 1964, 5074; (*c*) H. D. Locksley, I. Moore, and F. Scheinmann, *Tetrahedron*, 1967, **23**, 2229; (*d*) I. Carpenter, H. D. Locksley, and F. Scheinmann, *Phytochemistry*, 1969, **8**, 2013; (*e*) K. R. Markham, *Tetrahedron*, 1965, **21**, 3687.

[3] (*a*) J. E. Atkinson, P. Gupta, and J. R. Lewis, *Chem. Comm.*, 1968, 1386; (*b*) J. E. Atkinson and J. R. Lewis, *J. Chem. Soc.* (*C*), 1969, 281; (*c*) J. E. Atkinson, P. Gupta, and J. R. Lewis, *Tetrahedron*, 1969, **25**, 1507.

[4] H. D. Locksley and I. G. Murray, *J. Chem. Soc.* (*C*), 1969, 1567.

[5] H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 430; B. Jackson, Ph.D. Thesis, University of Salford, 1967.

[6] G. Wittig and U. Pockels, *Ber.*, 1939, **72***B*, 89.

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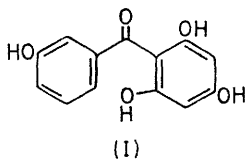
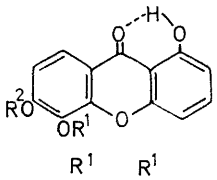
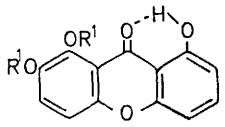


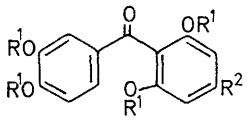
(I)



| | $R^1$ | $R^1$ |
|---|---|---|
| (II) | Me | H |
| (III) | H | H |

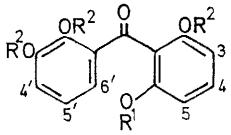


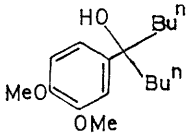
| | $R^1$ |
|---|---|
| (IV) | Me |
| (XXIII) | H |



| | $R^1$ | $R^2$ |
|---|---|---|
| (V) | H | H |
| (VII) | Me | H |
| (XIX) | H | OH |

| | $R^1$ | $R^2$ |
|---|---|---|
| (VI) | H | H |
| (IX) | Me | Me |
| (XV) | Me | H |
| (XVIII) | Me | $CO_2Et$ |





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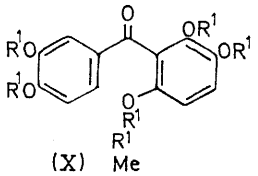
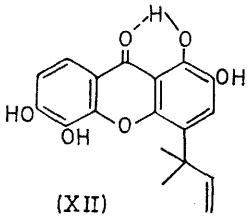
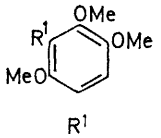


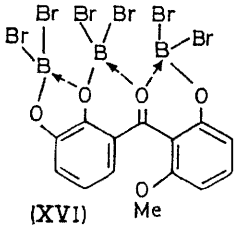
| | $R^1$ |
|---|---|
| (X) | Me |
| (XI) | H |



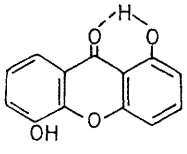
(XII)



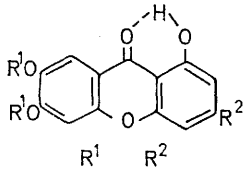
| | $R^1$ |
|---|---|
| (XIII) | Li |
| (XIV) | Me |



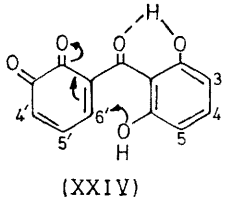
(XVI)



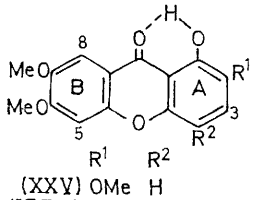
(XVII)



| | $R^1$ | $R^2$ |
|---|---|---|
| (XX) | H | OH |
| (XXI) | H | H |
| (XXII) | Me | H |



(XXIV)



| | $R^1$ | $R^2$ |
|---|---|---|
| (XXV) | OMe | H |
| (XXVI) | H | OMe |

methoxybenzoyl chloride. The latter benzophenone, as its free phenol (XI), should be the immediate precursor of 1,2,5,6-, 1,2,6,7-, 1,4,5,6-, and 1,4,6,7-tetrahydroxyxanthones, the first of which has been isolated from the heartwood of *Symphonia globulifera* L., as the isoprenyl derivative (XII).[7] At room temperature, lithiation of 1,2,4-trimethoxybenzene occurs violently; the reaction was therefore carried out at −70° to achieve smooth formation of 2,3,6-trimethoxyphenyl-lithium (XIII). The site and the percentage of metallation (86%) in this product were determined by its conversion into 2,3,6-trimethoxytoluene (XIV), by treatment with dimethyl sulphate, followed by n.m.r. analysis of the reaction mixture.

Use of powerful reagents for demethylation of polymethoxybenzophenones, *e.g.* hydrogen bromide in acetic acid, may produce deacylation or cyclodehydration of the resulting polyhydroxybenzophenones, the latter giving xanthones.[8] However, the milder reagent boron tribromide,[9] in dry methylene chloride or benzene, smoothly demethylated 2,3′,4′,6-tetramethoxybenzophenone (VII) at room temperature to give the corresponding tetrahydroxybenzophenone (V); likewise, 2,3,3′,4′,6-pentamethoxybenzophenone (X) gave the pentahydroxybenzophenone (XI).

Unanticipated difficulties were encountered in the boron tribromide demethylation of 2,2′,3′,6-tetramethoxybenzophenone (IX): the desired product was formed in only 16% yield, the major product (76%) being the monomethyl ether (XV) of the latter. The methoxy-group of the benzophenone (XV) was tentatively located in the resorcinol nucleus on the basis of mechanistic considerations for boron tribromide demethylations,[9] because formation of the planar complex (XVI) would leave a methoxy-group sterically inaccessible to further attack by the reagent.

Comparison of the n.m.r. spectra of the tetrahydroxybenzophenone (VI) and its monomethyl ether (XV) confirmed the location of the methoxy-group in the latter. The hydroxy-groups of the tetrahydroxybenzophenone (VI) gave rise to three signals, at τ −2·10 (1H, s), 1·59 (2H, s), and 2·94 (1H, s): the two equivalent protons are assigned to the resorcinol hydroxy-groups. In the spectrum of the monomethyl ether (XV), a signal for only one proton appears in the same region [τ −2·38 (1H, s), 1·30 (1H, s), and 2·20 (1H, s). Structure (XV), 2,2′,3′-trihydroxy-6-methoxybenzophenone, is consistent with these data.

No further demethylation of the monomethoxybenzophenone (XV) occurred in the presence of eight equivalents of boron tribromide, and reaction with hydrogen bromide in acetic acid gave 1,5-dihydroxyxanthone (XVII).[8] To prevent the formation of a planar boron complex of the type (XVI), the tris-ethyl carbonate

[7] H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 2186.

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

[9] J. F. W. McOmie, M. L. Watts, and D. E. West, *Tetrahedron*, 1968, **24**, 2289.

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derivative (XVIII) was first prepared [10] from the monomethyl ether (XV). In this derivative (XVIII) free rotation about the carbonyl group permits the boron agent to gain access to and demethylate readily the remaining methoxy-group, after which removal of the protective groups by rapid hydrolysis with alkali under nitrogen gives 2,2',3',6-tetrahydroxybenzophenone (VI) (61% overall).

Several oxidants were used to convert the polyhydroxybenzophenones described into their respective xanthones by oxidative cyclisation, but no generally applicable method was developed to produce consistently high yields.

Firstly, in view of the successful conversion of maclurin (2,3',4,4',6-pentahydroxybenzophenone) (XIX) into 1,3,6,7-tetrahydroxyxanthone (XX) by photochemical oxidation,[11] irradiation of 2,3',4',6-tetrahydroxybenzophenone (V) under similar conditions yielded exclusively the *para*-coupled product, 1,6,7-trihydroxyxanthone (XXI) * which, to facilitate isolation and purification, was converted into the dimethyl ether (XXII). T.l.c. comparison of the reaction mixture with 1,5,6-trihydroxyxanthone (III) (from *Calophyllum fragrans* Ridley) [4] showed that none of this *ortho*-coupled isomer had formed. This result parallels that found for maclurin (XIX).[11] Surprisingly, under the same conditions, 2,2',3',6-tetrahydroxy- and 2,3,3',4',6-pentahydroxy-benzophenones (VI) and (XI) failed to cyclise oxidatively to the corresponding xanthones. In the former case failure of the coupling reaction was attributed to hydrogen bonding by the C-3' hydroxy-group to the adjacent C-2' oxygen function, which could prevent abstraction of hydrogen from the former. Addition of photosensitisers (such as benzophenone and Methylene Blue) failed to induce coupling.

However, treatment of the benzophenone (VI) with active manganese dioxide in chloroform successfully gave 1,2,8-trihydroxyxanthone (XXIII) (33%), characterised as the dimethyl ether (IV). A mechanism involving the prior formation of an *ortho*-quinone intermediate (XXIV) and its subsequent cyclisation by intramolecular nucleophilic attack of the C-6 hydroxy-group at C-6' provides an attractive explanation for the success of this reaction. Quinone intermediates of this type have been suggested on several previous occasions.[14] With the same reagent 2,3',4',6-tetrahydroxybenzophenone (V) gave 1,6,7-trihydroxyxanthone (XXI) in high yield (65%): the conversion was also effected with the recently reported reagent manganese(III) tris(acetonylacetonate),[15] but in poorer yield (25%). Neither irradiation in the presence of oxygen, nor treatment with the manganese reagents cyclised 2,3,3',4',6-pentahydroxybenzophenone (XI), but use of a benzene solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant, produced material with an $R_F$ value corresponding with that expected for a tetrahydroxyxanthone. To suppress aerial oxidation, the reaction mixture was methylated with diazomethane, after which t.l.c. purification afforded a yellow solid (3%) with i.r. and u.v. spectral characteristics typical of a xanthone. The mass spectrum ($M^+$ 302, $C_{16}H_{14}O_6$) and the n.m.r. spectrum (ring A, two *ortho*-coupled aromatic protons, one hydrogen bonded hydroxyl at C-1; ring B, two aromatic protons with no detectable coupling at 60 MHz) were compatible with a xanthone nucleus having either a 1,2,6,7- or a 1,4,6,7-tetraoxygenation pattern, as in (XXV) and (XXVI), respectively; the small quantity of xanthone available precluded a more definitive structural assignment. The desired 1,2,5,6-tetraoxygenated xanthone [7] was not detected.

The oxidant DDQ also gave good yields of 1,6,7-trihydroxyxanthone (XXI) and 1,2,8-trihydroxyxanthone (XXIII) (50%) from the respective benzophenones (V) and (VI). Use of chloranil gave the trihydroxyxanthones (XXI) and (XXIII) in poorer yields but this reagent did not react with the pentahydroxybenzophenone (XI); use of the lower potential quinone, 2,5-dimethyl-1,4-benzoquinone, however, was unsuccessful in all reactions with the polyhydroxybenzophenones (V), (VI), and (XI).

Although the polyhydroxybenzophenones (V) and (VI) have not been found to co-occur with their corresponding xanthones (XXI) and (XXIII) in the heartwood of *Calophyllum fragrans* Ridley,[4] their ready *in vitro* conversion into the natural xanthones demonstrates that they are very likely the true precursors in Nature.

The n.m.r. spectrum of the polymethoxybenzophenone (IX) was examined at 60 and at 100 MHz but first-order analysis was not possible at either frequency, and double irradiation experiments at 100 MHz provided no further clarification. The other polymethoxybenzophenones (VII) and (X) also gave complex spectra at 60 MHz. At 220 MHz, however, the spectra of all three polymethoxybenzophenones readily responded to first-order analysis in carbon tetrachloride and in hexadeuteriobenzene. Comparison of the results obtained in these two solvents (see Table) shows that the solvent shifts [$\Delta = \tau(C_6D_6) - \tau(CCl_4)$] [16] are considerable at this high level of dispersion,[17] their sign and magnitude providing useful verification for the assignment of the proton signals.

All the aromatic protons experience a positive solvent

* 1,6,7-Trihydroxyxanthone (XXI) has recently been isolated as a natural product from *Garcinia eugeniifolia* Wall and *Mammea africana* G. Don (both Guttiferae).[12,13]

[10] L. F. Fieser, J. E. Herz, M. W. Klohs, M. A. Romero, and T. Utne, *J. Amer. Chem. Soc.*, 1952, **74**, 3309.
[11] A. Jefferson and F. Scheinmann, *J. Chem. Soc.* (C), 1966, 175.
[12] I. Carpenter, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (C), 1969, 2421.
[13] B. Jackson, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (C), 1969, 2201.
[14] (*a*) R. C. Ellis, W. B. Whalley, and K. Ball, *Chem. Comm.* 1967, 803; (*b*) H. Musso in 'Oxidative Coupling of Phenols,' ed. W. I. Taylor and A. R. Battersby, Edward Arnold Ltd., London, 1967, p. 78; (*c*) A. R. Battersby in ref. 14*b*, pp. 122, 158.
[15] M. J. S. Dewer and Tadao Nakaya, *J. Amer. Chem. Soc.*, 1968, **90**, 7134.
[16] J. Ronayne and D. H. Williams, *J. Chem. Soc.* (B), 1967, 540, and references cited therein.
[17] J. K. Becconsall and M. C. McIvor, *Chem. in Britain*, 1969, **5**, 147.

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shift influence with the exception of those situated at C-2′ and C-6′ *ortho* to the carbonyl group, which always show a negative shift. In accordance with the theory of Ronayne and Williams,[16] these negative values suggest that for the benzophenones (VII), (IX), and (X), the most heavily populated conformations are those in which ring A and the carbonyl group are coplanar. Ring B, for steric reasons, will then prefer to adopt the staggered conformation, lying in a plane at right angles to the carbonyl group.

Methoxy-groups flanked by certain *ortho*-substituents fail to produce the positive upfield solvent shift normally expected; explanations for this phenomenon have been advanced.[18] Our solvent shift studies on the polymethoxybenzophenones (VII), (IX), and (X) (see Table) tend to confirm these findings: in hexadeuteriobenzene the benzophenones (IX) and (X) show a lone methoxy-signal, well downfield from the remainder, which can be attributed in each case to the methoxy-groups at C-2′ and C-2, respectively. In accord with theory,[18] the four methoxy-groups of the tetramethoxybenzophenone (VII), none of which is flanked by *two ortho*-substituents, *all* experience a marked upfield shift in hexadeuteriobenzene relative to carbon tetrachloride.

$^1$H N.m.r. spectral data (220 MHz) for some polymethoxybenzophenones

| | | C-2 | C-3 | C-4 | C-5 | C-6 | C-2′ | C-3′ | C-4′ | C-5′ | C-6′ | OMe * |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3′,4′,6-Tetramethoxybenzophenone (VII) | τ($C_6D_6$) | OMe | 3·71 (1H,d) [a] | 2·92 (1H,t) [a] | 3·71 (1H,d) [a] | OMe | 2·20 (1H,d) [b] | OMe | OMe | 3·68 (1H,q) [c] | 2·60 (1H,q) [b,d] | 6·71, 6·78, 6·80 (6H) |
| | τ($CCl_4$) | OMe | 3·51 (d) | 2·83 (t) | 3·51 (d) | OMe | 2·58 (d) | OMe | OMe | 3·35 (q) | 2·97 (q) | 6·13, 6·16, 6·28 (6H) |
| | Δ | | +0·20 | +0·09 | +0·20 | | −0·38 | | | +0·33 | −0·37 | |
| 2,2′,3′,6-Tetramethoxybenzophenone (IX) | τ($C_6D_6$) | OMe | 3·76 (1H,d) [d] | 3·00 (1H,t) [d] | 3·76 (1H,d) [a] | OMe | OMe | OMe | 3·48 (1H,d) [d] | 3·24 (1H,t) [d] | 2·29 (1H,q) [e] | 6·41, 6·80, 6·82 (6H) |
| | τ($CCl_4$) | OMe | 3·57 (d) | 2·91 (t) | 3·57 (d) | OMe | OMe | OMe | 3·10 (d) | 3·11 (t) | 2·80 (q) | 6·21, 6·61, 6·40 (6H) |
| | Δ | | +0·19 | +0·09 | +0·19 | | | | +0·38 | +0·13 | −0·51 | |
| 2,3,3′,4′,6-Pentamethoxybenzophenone (X) | τ($C_6D_6$) | OMe | OMe | 3·38 (1H,d) [f] | 3·68 (1H,d) [f] | OMe | 2·18 (1H,d) [b] | OMe | OMe | 3·68 (1H,d) [d] | 2·57 (1H,q) [b,d] | 6·20, 6·60, 6·70, 6·77, 6·78 |
| | τ($CCl_4$) | OMe | OMe | 3·28 (d) | 3·55 (d) | OMe | 2·61 (d) | OMe | OMe | 3·38 (d) | 2·99 (q) | 6·17, 6·20, 6·22, 6·37, 6·40 |
| | Δ | | | +0·10 | +0·13 | | −0·43 | | | +0·30 | −0·42 | |

* Each 3H, s, unless otherwise stated; no correlation of signal with ring position has been made. [a] *J* 8·2 Hz; [b] *J* 2·0 Hz; *J* 8·2 and 0·5 Hz; [d] *J* 8·0 Hz; [e] *J* 8·0 and 1·5 Hz; [f] *J* 9·0 Hz.

For spectra of solutions in perdeuteriobenzene, chemical shift (τ), coupling constant, and proton count are given. For the spectra of solutions in carbon tetrachloride, only the chemical shift is given.

Solvent shift Δ (p.p.m.) = τ($C_6D_6$) − τ($CCl_4$) (see ref. 16).

**Internal reference:** tetramethylsilane.

## EXPERIMENTAL

U.v. spectra (solutions in methanol) were measured with a Unicam SP 800 recording spectrophotometer and i.r. spectra (Nujol mulls) with either a Unicam SP 200 or a Perkin-Elmer 257 grating instrument. N.m.r. spectra were determined with Varian A60, HA100, and HR220 instruments, and mass spectra with A.E.I. MS12 (single focusing) and MS9 (double focusing) instruments. Analytical and preparative t.l.c. were performed with silica gel (Merck Kieselgel G); column chromatography was performed with Hopkin and Williams silica gel MFC and B.D.H. alumina.

*Synthesis of Polymethoxybenzophenones.*—(a) *2,3′,4′,6-Tetramethoxybenzophenone* (VII). 3,4-Dimethoxybenzoyl chloride [b.p. 124°/0·5 mm., m.p. 70° (lit.,[19] 70°)] (31·5 g., 91%) was prepared from the acid (31·4 g.), oxalyl chloride (16·2 ml.), and dimethylformamide (10 drops) in dry benzene (150 ml.) at room temperature (12 hr.).

Resorcinol dimethyl ether (12 g.) in dry ether (50 ml.) under nitrogen was treated with n-butyl-lithium in hexane (0·0025 mole/ml.; 35 ml.) and the mixture was heated under reflux for 2 hr. 2,6-Dimethoxyphenyl-lithium, which crystallised from the ether solution, was transferred as a slurry to a dropping funnel fitted with a by-pass arm to permit passage of a continuous counter-current of nitrogen. The aryl-lithium was added to a vigorously stirred solution of 3,4-dimethoxybenzoyl chloride (18 g.) in ether (100 ml.) during 30 min., at 0° under nitrogen. After 15 min., water (100 ml.) was added and an orange solid which appeared at the interface was dissolved by addition of benzene (150 ml.). The organic phase was separated and washed successively with water, 2N-sodium hydroxide, 2N-hydrochloric acid, and water, and then dried ($MgSO_4$) and evaporated to give a brown oil. Addition of ether precipitated *2,3′,4′,6-tetramethoxybenzophenone* (VII) (11·9 g., 46%), which gave colourless cubes, m.p. 130—131° [from benzene–light petroleum (b.p. 60—80°) (1 : 1)], $R_F$ 0·45 [ethyl acetate–benzene (1 : 9)], $\nu_{max.}$ 1655 cm.$^{-1}$ (C=O) $\lambda_{max.}$ 227 (ε 18,400), 278 (11,800), and 308 (9450) nm. [Found: C, 67·95; H, 5·85%; *M* (mass spectrometry), 302. $C_{17}H_{18}O_5$ requires C, 67·55; H, 6·0%; *M*, 302].

At −70° the same reactants gave a yellow oil which was isolated as before (extraction with hydrochloric acid was omitted) and chromatographed on an alumina column (made up with benzene) to give a solid [eluted with ethyl acetate–benzene (1 : 19)]. After trituration with light petroleum (b.p. 60—80°) and filtration, the solid gave *αα-dibutyl-3,4-dimethoxybenzyl alcohol* (1·05 g., 30%) as colourless cubes, m.p. 79—80° [from light petroleum (b.p. 60—80°)], $R_F$ 0·45 [ethyl acetate–benzene (1 : 9)], $\nu_{max.}$ 3500 (OH) and 1250 (C–O–C stretch) cm.$^{-1}$, $\lambda_{max.}$ 229 (ε 5110) and 227 (1820) nm., τ($C_6D_6$) 2·86 (1H, d, *J* 2 Hz, 2-H), 3·05 (1H, q, *J* 8·5 and 2 Hz, 6-H), 3·29 (1H, d, *J* 8·5 Hz, 5-H), 6·41 (3H, s), 6·48 (3H, s, 2× OMe), 8·23 (4H, t, 2 × α-$CH_2$), 8·52 (1H, exchangeable s, OH), 8·77 (8H, m, 2× $CH_2$·$CH_2$),

[18] J. H. Bowie, J. Ronayne, and D. H. Williams, *J. Chem. Soc.* (*B*), 1967, 535.

[19] St. v. Kostanecki and J. Tambor, *Ber.*, 1906, **39**, 4022.

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and 9·15 (6H, t, 2 × Me) [Found: C, 73·05; H, 10·1%; *M* (mass spectrum), 280. $C_{17}H_{28}O_3$ requires C, 72·85; H, 10·05%; *M*, 280].

(b) 2,2′,3′,6-*Tetramethoxybenzophenone* (IX). This was prepared in improved yield [8] from 2,3-dimethoxybenzoyl chloride (synthesised from the acid and oxalyl chloride in 91% yield) and 2,6-dimethoxyphenyl-lithium (molar ratio 1 : 1) as described in (a). Trituration three times with ether and crystallisation of the insoluble material from cyclohexane gave the benzophenone (IX) as colourless needles, m.p. 107° (lit.,[8] 104—106°), $R_F$ 0·5 [ethyl acetate–benzene (1 : 9)], $\nu_{max.}$ 1655 (C=O) and 1255 (C–O–C stretch) cm.$^{-1}$, $\lambda_{max.}$ 219 (ε 26,800), 258 (9900), and 295sh (3350) nm. [Found: C, 67·55; H, 6·2%; *M* (mass spectrometry), 302. Calc. for $C_{17}H_{18}O_5$: C, 67·55; H, 6·0%; *M*, 302].

Filtrates from the trituration were chromatographed on alumina. Elution with ethyl acetate–benzene (1 : 19) afforded more 2,2′,3′,6-tetramethoxybenzophenone (IX) (total yield 48%).

(c) *Lithiation of* 1,2,4-*trimethoxybenzene*. 1,2,4-Trimethoxybenzene [b.p. 98°/1 mm. (lit.,[20] 247°/760 mm.)] was prepared from 1,2,4-triacetoxybenzene by the method of Govindachari and his co-workers [20] in 90% yield. Metallation of the trimethyl ether (1·68 g.) in ether (20 ml.) with n-butyl-lithium (0·0033 mole/ml. in hexane; 3·5 ml.) under nitrogen occurred vigorously at room temperature. After 1 hr. stirring, the aryl-lithium was treated with an excess of dimethyl sulphate (5 ml.) in ether (10 ml.) and stirring was continued for 30 min. Aqueous sodium hydroxide (50%) was then added and the reaction was continued overnight. After work-up, the ethereal phase gave a colourless oil, τ($CDCl_3$) 3·36 (d, *J* 9 Hz, 5-H), 3·60 (d, *J* 9 Hz, 4-H), 6·24(s), 6·28(s), and 6·32(s) (9H, 2-, 3-, and 6-OMe), and 7·85 (3H, s, 1-Me), showing the presence of 2,3,6-trimethoxytoluene (XIV). Integration indicated that the product contained 86% of the trimethoxytoluene (XIV).

(d) 2,3,3′,4′,6-*Pentamethoxybenzophenone* (X). 2,3,6-Trimethoxyphenyl-lithium (XIII), prepared under nitrogen at −70° by slow addition of n-butyl-lithium (0·0033 mole/ml. in hexane; 27 ml.) to a stirred solution of 1,2,4-trimethoxybenzene (14·1 g.) in dry ether (100 ml.), was allowed to warm to room temperature (2 hr.). The crystalline slurry which formed was added *via* a dropping funnel as described in (a) to an ethereal solution of 3,4-dimethoxybenzoyl chloride (16·8 g.) at room temperature. After 1·5 hr. stirring, the mixture was worked up as in (a) to yield 2,3,3′,4′,6-*pentamethoxybenzophenone* (X) (18·5 g., 67%) which gave colourless cubes, m.p. 147—149° [from cyclohexane (charcoal)], $R_F$ 0·4 [ethyl acetate–benzene (1 : 9)], $\nu_{max.}$ 1665 (C=O) and 1275 (C–O–C stretch) cm.$^{-1}$, $\lambda_{max.}$ 230 (ε 21,900), 280 (13,700), and 308 (11,100) nm. [Found: C, 64·95; H, 6·05%; *M* (mass spectrometry), 332. $C_{18}H_{20}O_6$ requires C, 65·1; H, 6·05%; *M*, 332].

*Demethylation of Polymethoxybenzophenones*.[9]—(a) 2,3′,4′,6-*Tetrahydroxybenzophenone* (V). Boron tribromide in dry methylene chloride (0·13 g./ml.; 256 ml., 5 equiv.) was added dropwise during 1 hr., to a stirred solution of 2,3′,4′,6-tetramethoxybenzophenone (8 g.) in methylene chloride (400 ml.) at room temperature. The reaction, which produced an orange precipitate dissolving to give a deep red solution, was monitored by t.l.c. After 12 hr., more (100 ml.) of the boron reagent was added, and the mixture was stirred for a further 12 hr. Water (400 ml.) was then carefully added at 0° with stirring. The aqueous layer was separated and extracted with ether (4 × 250 ml.). The organic phase was washed with water and the washings were then extracted with ether (2 × 250 ml.). The combined extracts were dried ($MgSO_4$) and evaporated to leave a red oil, which solidified (5·4 g., 84%) only after removal of residual water by azeotropic distillation from benzene. Purification by column chromatography over silica gel gave a fraction [eluted with acetone–chloroform (1 : 4)] which furnished the product as a pale yellow amorphous solid (3·3 g.). Purification by preparative t.l.c. [band at $R_F$ 0·4 (acetic acid–chloroform, 3 : 7)] afforded 2,3′,4′,6-*tetrahydroxybenzophenone* (V) as pale yellow cubes, m.p. 113—119° (decomp.), after repeated azeotropic distillation and crystallisation from toluene; $\nu_{max.}$ 3520, 3460, 3300, and 3200 (OH) and 1645 (C=O) cm.$^{-1}$, $\lambda_{max.}$ 229 (ε 16,000), 281 (11,000), and 313 (9500) nm., $\lambda_{max.}$ (with added NaOH) 245 (ε 14,300), 297 (5200), and 347 (16,950) nm. No change occurred to the u.v. spectrum on addition of sodium acetate. N.m.r. signals [$(CD_3)_2CO$] τ 2·55—3·60(m). After addition of deuterium oxide the proton count fell from 10 to 6 in accord with a ratio of aromatic to hydroxylic protons of 3 : 2 [Found: *M* (mass spectrometry), 246·052817. $C_{13}H_{10}O_5$ requires 246·052817].

(b) 2,2′,3′,6-*Tetrahydroxybenzophenone* (VI) *and* 2,2′,3′-*trihydroxy*-6-*methoxybenzophenone* (XV). 2,2′,3′,6-Tetramethoxybenzophenone (IX) (10·2 g.) in dry benzene (150 ml.) was added dropwise with stirring to boron tribromide in benzene (0·178 g./ml.; 190 ml., 4 equiv.) during 30 min., at room temperature. After a further 4·5 hr., t.l.c. analysis showed the reaction to be complete, and water (200 ml.) was slowly added (30 min.) with vigorous stirring; a yellow solid then appeared at the interface. The reaction yielded two products, *A* and *B*.

(i) *Isolation of* A. The solid was collected and chromatographed on a silica column (made up with chloroform). Elution with acetone–chloroform (1 : 19) gave 2,2′,3′-*trihydroxy*-6-*methoxybenzophenone* (XV) (2·21 g.). The organic phase on evaporation afforded more of the benzophenone (XV) (2·22 g.) (total yield 76%) as yellow needles from benzene, m.p. 147—150°, $R_F$ 0·56 [acetic acid–chloroform (2 : 23)], $\nu_{max.}$ 3360 (H-bonded OH), 1620 (H-bonded C=O) cm.$^{-1}$, $\lambda_{max.}$ 219 (ε 24,400), 270 (14,600), and 347 (3250) nm., $\lambda_{max.}$ (with added NaOH) 240 (ε 26,800), 285 (13,400), and 380 (3350) nm. No change occurred to the u.v. spectrum on addition of sodium acetate. N.m.r. signals [$(CD_3)_2CO$] τ −2·38 (1H, s, 2′-OH), 1·3 (1H, s, 2-OH), 2·20 (1H, s, 3′-OH), 2·55—3·50 (6H, m, aromatic), and 6·30 (3H, s, 6-OMe). The three OH signals disappeared after addition of deuterium oxide [Found: C, 64·25; H, 4·6%; *M* (mass spectrometry), 260. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%; *M*, 260].

(ii) *Isolation of* B. The aqueous phase from the separation described in (b) was extracted first with benzene (250 ml.), then with ethyl acetate (2 × 250 ml.). The latter extract furnished a red solid (1·32 g.), which gave 2,2′,3′,6-*tetrahydroxybenzophenone* (VI) as yellow cubes (16%), m.p. 173—174° (from benzene), $R_F$ 0·65 [acetic acid–chloroform (3 : 7)], $\nu_{max.}$ 3520 (OH), 3360 (H-bonded OH), and 1610 (H-bonded C=O) cm.$^{-1}$, $\lambda_{max.}$ 221 (ε 23,800), 270 (14,800), and 344 (3350) nm., $\lambda_{max.}$ (with added NaOH) 241 (ε 24,200), 285 (12,300), and 382 (3200) nm. No change occurred to the u.v. spectrum on addition of sodium acetate. N.m.r. signals [$(CD_3)_2CO$–$CDCl_3$] τ −2·10 (1H, s, 2′-OH), 1·59 (2H, s, 2- and 6-OH), 2·94br (1H, s, 3′-OH),

[20] T. R. Govindachari, K. Nagarajan, and P. C. Parthasarathy, *J. Chem. Soc.*, 1957, 548.

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and 2·45—3·60 (6H, m, aromatic). After addition of deuterium oxide the OH signals disappeared [Found: C, 63·2; H, 4·3%; *M* (mass spectrometry), 246. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%; *M*, 246].

(c) *Demethylation of 2,2′,3′-trihydroxy-6-methoxybenzophenone* (XV). 2,2′,3′-Trihydroxy-6-methoxybenzophenone (3·0 g.), ethyl chloroformate (3·5 ml.), and potassium carbonate (8·0 g.) in dry acetone (50 ml.) were heated under reflux for 30 min.; more ethyl chloroformate (3·5 ml.) was then added and refluxing was continued for 5 hr. The acetone-soluble material, worked up in the usual manner, furnished an oil which crystallised when dried under high vacuum. Trituration with light petroleum (b.p. 60—80°) and isolation of the residue gave *2,2′,3′-trisethoxycarbonyloxy-6-methoxybenzophenone* (XVIII) (5·03 g., 91%) which gave colourless cubes, m.p. 89—91° [from light petroleum (b.p. 100—120°)–benzene, 3 : 1 (with charcoal)], $R_F$ 0·75 [acetone–benzene (1 : 9)], $\nu_{max.}$ 1770, 1765, and 1755 (ester C=O), 1665 (benzophenone C=O), and 1250 (C–O–C stretch) cm.$^{-1}$, $\lambda_{max.}$ 220 (ε 9600), 247 (11,000), and 290sh (2850) nm., τ($CDCl_3$) 2·35—2·78 (3H, m, ring A 4′-, 5′-, and 6′-H), 2·57 (1H, t, *J* 8·5, Hz, 4-H), 3·12 (1H, q, *J* 8·5 and 1 Hz) and 3·17 (1H, q, *J* 8·5 and 1 Hz) (3- and 5-H), 5·69 (2H, q, *J* 7 Hz), and 5·80 (4H, q, *J* 7 Hz) (3 × $CH_2$), 6·37 (3H, s, 2-OMe), and 8·67, 8·72, and 8·77 (each 3H, t, *J* 7 Hz, Me) [Found: C, 58·1; H, 5·0%; *M* (mass spectrometry), 476. $C_{23}H_{24}O_{11}$ requires C, 57·95; H, 5·1%; *M*, 476].

2,2′,3′-Trisethoxycarbonyloxy-6-methoxybenzophenone (XVIII) (5·4 g.) in methylene chloride (65 ml.) was treated under nitrogen with boron tribromide (0·13 g./ml. solution in methylene chloride; 125 ml., 5 equiv.) added dropwise during 30 min. The mixture was stirred at room temperature for 4·5 hr., then hydrolysed at 0° by addition of water (200 ml.). Still under nitrogen, the mixture was basified with 4N-sodium hydroxide (colour change from red to green) then acidified after 1 min., with 4N-hydrochloric acid. From the aqueous phase, repeated extraction with ether gave, on work-up, a red oil which crystallised (following azeotropic removal of residual water) from benzene to give 2,2′,3′,6-tetrahydroxybenzophenone (VI) as yellow cubes (1·71 g., 61%), m.p. 173—174°, $R_F$ 0·65 [acetic acid–chloroform (3 : 7)], identical (mixed m.p. and i.r. spectrum) with the sample isolated in (b) (ii).

No demethylation of 2,2′,3′-trihydroxy-6-methoxybenzophenone (XV) occurred when 8 equiv. of boron tribromide reagent were used: the parent compound was recovered unchanged (95%). When heated with hydrogen bromide in acetic acid, the methoxybenzophenone (XV) gave 1,5-dihydroxyxanthone (XVII), m.p. 263—265° (lit.,[8] 266—267°) (38%), identical (mixed m.p. and i.r. spectra) with an authentic sample.

(d) *2,3,3′,4′,6-Pentahydroxybenzophenone* (XI). This was prepared from the pentamethyl ether (X) and boron tribromide (6 equiv.) in methylene chloride as described in (a). After 8 hr., the mixture was worked up in the usual way. The product, following chromatography on silica gel [made up in chloroform; fraction eluted with acetone–chloroform (3 : 7)], was triturated with acetone–chloroform (1 : 2) to give *2,3,3′,4′,6-pentahydroxybenzophenone* (XI) as an amorphous powder (5·55 g., 70%), m.p. 131—135°, $R_F$ 0·4 [acetic acid–chloroform (2 : 3)], $\nu_{max.}$ 3300 (OH), 1695 (acetone C=O; solvent of crystallisation), and 1650 (benzophenone C=O) cm.$^{-1}$, $\lambda_{max.}$ 232 (ε 14,200), 283 (11,000), and 314 (9300) nm., $\lambda_{max.}$ (with added NaOH) 252 (ε 20,800) and 350 (22,800) nm., $\lambda_{max.}$ (with added NaOAc) 230sh (ε 16,050), 275 (9750), and 318 (8450) nm., τ[$(CD_3)_2CO$] 2·55—3·22 (3H, m, 2′, 5′-, and 6′-H), 3·12 (1H, d, *J* 8·5 Hz, 3-H), and 3·66 (1H, d, *J* 8·5 Hz, 4-H) [Found: *M* (mass spectrometry), 262·046953. $C_{13}H_{10}O_6$ requires *M*, 262·047731].

*Oxidations of Polyhydroxybenzophenones.*—(a) *2,3′,4′,6-Tetrahydroxybenzophenone* (V). (i) *Photochemical oxidation.*[11] A continuous stream of oxygen was passed into a solution of the benzophenone (V) (2·0 g.) in dry ethanol (100 ml.) heated under gentle reflux in a Hanovia medium pressure u.v. reactor for 11 hr. The solvent was then evaporated off to leave a brown solid (1·9 g.), part of which was purified by preparative t.l.c. The band at $R_F$ 0·7 [methanol–chloroform (3 : 17); streaking occurred] yielded slightly impure *1,6,7-trihydroxyxanthone* (XXI) (8 mg.), m.p. 230—235° (decomp.), the t.l.c. and spectroscopic properties of which were the same as those of the pure material prepared in (a) (ii).

The remaining crude mixture (1·6 g.) in methanol (15 ml.) was methylated with an excess of diazomethane in ether. *1-Hydroxy-6,7-dimethoxyxanthone* (XXII) (200 mg., 11%), isolated by preparative t.l.c. [band with $R_F$ 0·5 in ethyl acetate–benzene (1 : 9)], gave yellow needles from acetone (charcoal), m.p. 186—190° (lit.,[12] 187—189°), identical (mixed m.p. and i.r. spectra) with a sample prepared from 1,6,7-trihydroxyxanthone (*ex Mammea africana* G. Don, Guttiferae),[12] $\nu_{max.}$ 1650 (C=O and 1230 (C–O–C stretch) cm.$^{-1}$, $\lambda_{max.}$ 219 (ε 23,000), 251 (34,000), 269 (18,850), 289 (12,600), 308sh (7700), and 370 (11,000) nm., τ($CDCl_3$) —2·90 (1H, s, 1-OH, exchangeable), 2·44 (1H, s, 8-H), 2·44 (1H, t, *J* 8 Hz, 3-H), 3·11 (1H, s, 5-H), 3·12 (1H, q, *J* 8 and 1 Hz, 2-H), 3·22 (1H, q, *J* 8 and 1 Hz, 4-H), and 5·97 (3H, s) and 6·00 (3H, s) (6- and 7-OMe) [Found: *M* (mass spectrometry), 272·0683. $C_{15}H_{12}O_5$ requires *M*, 272·0685].

T.l.c. of the reaction mixture indicated that 1,5,6-trihydroxyxanthone (III) was absent.

(ii) *Oxidation with manganese dioxide.* The benzophenone (V) (375 mg.) in dry acetone (200 ml.) was stirred at room temperature for 2 hr. with manganese dioxide (3·75 g.; prepared by pyrolysis of manganese carbonate at 250° for 2 hr.). The mixture was then percolated through a short column of t.l.c. Kieselgel G. The filtrate yielded a brown oil which, as a solution in chloroform, was chromatographed on a silica column. The fractions eluted with acetic acid–chloroform (1 : 39 and 1 : 19) were collected and the solvent was removed. To induce crystallisation, the residue was repeatedly evaporated from toluene to give 1,6,7-trihydroxyxanthone (XXI) (241 mg., total yield 65%). After being heated with charcoal in ethyl acetate this product had m.p. 258—268° (decomp.) [lit.,[12] 258° (decomp.)], $R_F$ 0·55 [acetic acid–chloroform (1 : 4)], $\nu_{max.}$ 3520 (free OH), 3160 (H-bonded OH), and 1640 (C=O) cm.$^{-1}$, $\lambda_{max.}$ 221 (ε 22,850), 251 (28,200), 269 (10,700), 312sh (7800), and 374 (10,300) nm., $\lambda_{max.}$ (with added NaOAc) 230 (ε 34,400), 242 (26,100), 290 (4000), and 380 (21,500) nm., $\lambda_{max.}$ (with added NaOH) 230 (ε 48,800), 242 (39,500), and 380 (26,000) nm., τ[$(CD_3)_2SO$] —3·08 (1H, s, 1-OH, exchangeable), 2·33 (1H, t, *J* 8 Hz, 3-H), 2·51 (1H, s, 8-H), 2·96 (1H, q, *J* 8 and 1 Hz, 4-H), 3·04 (1H, s, 5-H), 3·25 (1H, q, *J* 8 and 1 Hz, 2-H) [Found: *M* (mass spectrometry), 244. $C_{13}H_8O_5$ requires *M*, 244].

(iii) *Oxidation with manganese*(III) *tris*(*acetonylacetonate*).[15] The manganese complex (2 equiv.) in acetonitrile was used as described by Dewer and his co-workers [15] to oxidise the benzophenone (V) (25 mg.). 1,6,7-Trihydroxyxanthone

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(XXI) was isolated (25%), identical with an authentic sample prepared as in (a) (ii).

(iv) *Oxidation with quinones.* 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (6·1 mg.) in benzene (10 ml.) was added dropwise with stirring to a solution of the benzophenone (V) (6 mg.) in methanol (5 ml.) and maintained at room temperature for 12 hr. The reaction was monitored by t.l.c. Material corresponding to authentic 1,6,7-trihydroxyxanthone (XXI), $R_F$ 0·56 [acetic acid–chloroform (1 : 4)] was formed in highest yield after 30 min.

Under similar reaction conditions, chloroanil and the benzophenone (V) gave 1,6,7-trihydroxyxanthone (XXI); reaction with 2,5-dimethyl-1,4-benzoquinone left unchanged starting material (t.l.c.).

(b) 2,2′,3′,6-*Tetrahydroxybenzophenone* (VI).—(i) *Oxidation with manganese dioxide.* The benzophenone (VI) (200 mg.) and manganese dioxide (2 g.) in chloroform (75 ml.) were stirred for 2 hr. at room temperature then worked up as in (a) (ii). Impure 1,2,8-trihydroxyxanthone (XXIII) [21] (65 mg., 33%) was obtained as dark yellow cubes from benzene. Further purification proved difficult so the product was first methylated with diazomethane in ether, and the derivative, 1,2-dimethoxy-8-hydroxyxanthone (IV), isolated by preparative t.l.c. [$R_F$ 0·6 in acetone–benzene (1 : 19)] as yellow needles (16 mg.), m.p. 171—173° (lit.,[4] 171—173°) (from ethanol), was identical with a sample isolated from *Calophyllum fragrans* Ridley [4] (mixed m.p. and i.r. spectra).

(ii) *Oxidations with quinones.* DDQ (400 mg.) in benzene (30 ml.) was added dropwise to the benzophenone (VI) (400 mg.) in methanol (35 ml.) during 15 min., and the mixture was stirred at room temperature for 1 hr. The crude product (800 mg.) was chromatographed on silica; the fraction eluted with benzene furnished 1,2,8-trihydroxyxanthone (XXIII) (200 mg., 50%), which gave yellow needles, m.p. 237—238° (lit.,[21] 234—237°), from light petroleum (b.p. 100—120°) after treatment with charcoal in benzene; $R_F$ 0·75 [acetone–benzene (1 : 4)], $\nu_{max.}$ 3500 (OH), 1655 (H-bonded C=O), and 1630 (H-bonded C=O) cm.$^{-1}$, $\lambda_{max.}$ 239 (ε 25,000), 264 (31,500), 287sh (6100), 337 (7200), and 406 (3300) nm., $\lambda_{max.}$ (with added NaOH) 253 (ε 26,900), 264 (26,900), 276sh (19,700), 336 (7200), and 438 (3900) nm., τ[$(CD_3)_2SO$] 2·27 (1H, t, *J* 8 Hz, 6-H), 2·62 (1H, d, *J* 9 Hz, 3-H), 3·04 (1H, q, *J* 8 and 1 Hz, 5-H), 3·07 (1H, d, *J* 9 Hz, 4-H), and 3·21 (1H, q, *J* 8 and 1 Hz, 7-H) [Found: C, 63·55; H, 3·3%; *M* (mass spectrometry), 244. $C_{13}H_8O_5$ requires C, 63·95; H, 3·3%; *M*, 244].

In a similar reaction with chloranil [see (a) (iv)], the benzophenone (VI) gave 1,2,8-trihydroxyxanthone (XXIII) in maximum yield (t.l.c. monitoring) after 30 min. at room temperature.

No change into the benzophenone (VI) occurred on reaction with 2,5-dimethyl-1,4-benzoquinone (t.l.c.).

(iii) *Oxidation with other reagents.* Neither photochemical oxidation [see (a) (i)] nor oxidation with alkaline potassium ferricyanide of benzophenone (VI) gave any 1,2,8-trihydroxyxanthone (XXIII).

(c) 2,3,3′,4′,6-*Pentahydroxybenzophenone* (XI). (i) *Oxidations with quinones.* DDQ (950 mg.) in benzene (100 ml.) was added dropwise during 15 min. to a solution of the benzophenone (XI) (1 g.) in methanol (100 ml.) and the mixture was stirred for 1 hr. Evaporation under reduced pressure gave a brown solid (1·9 g.) which, in chloroform, was chromatographed on a silica column. Elution with acetone–chloroform (1 : 4 and 3 : 7) gave two fractions, *A* and *B*, respectively; both gave a green colour with iron(III) chloride, and the major constituent of each had nearly the same $R_F$ value on t.l.c.

Fraction *A* gave a yellow solid (672 mg.) which was methylated with an excess of ethereal diazomethane. The product was triturated with methanol (10 ml.) and the residue crystallised from acetone to give 2,3-*dichloro*-5,6-*dicyano*-1,4-*dimethoxybenzene* (140 mg.) as colourless cubes, m.p. 193—195°, $R_F$ 0·6 (benzene), $\nu_{max.}$ 2240 (C≡N) and 1245 (C–O–C stretch) cm.$^{-1}$, τ($CDCl_3$) 5·87(s) [Found: C, 46·7; H, 2·4; N, 10·85%; *M* (mass spectrometry), 256 for $^{35}Cl$. $C_{10}H_6Cl_2N_2O_2$ requires C, 46·75; H, 2·35; N, 10·9%; *M*, 256 for $^{35}Cl$].

Fraction *B* gave a yellow solid (284 mg.) which was treated in methanol with ethereal diazomethane for 1 hr. The product, purified by preparative t.l.c. ($R_F$ 0·75 in chloroform), furnished 1-hydroxy-2,6,7-(or 4,6,7-)-trimethoxyxanthone, (XXV) or (XXVI) (25 mg., 3%), as a yellow solid, m.p. 197—202°, $\nu_{max.}$ 3360 (H-bonded OH), and 1650 (C=O) cm.$^{-1}$, $\lambda_{max.}$ 256 (ε 13,700), 280 (18,400), 321 (4500), and 384 (4700) nm.; $\lambda_{max.}$ (with added NaOH) 256 (18,150), 280 (21,900), 319 (6250), and 385 (5900) nm. τ($CDCl_3$) −2·68 (1H, s, 1-OH, exchangeable), 2·37 (1H, s, 8-H), 2·72 (1H, d, *J* 9 Hz, 3-H), 2·93 (1H, s, 5-H), 3·24 (1H, d, *J* 9 Hz, 2- or 4-H), and 5·95, 5·97, and 5·99 (each 3H, s) [2- (or 4-), 6-, and 7-OMe] [Found: *M* (mass spectrometry), 302·079839. $C_{16}H_{14}O_6$ requires *M*, 302·079034].

(ii) *Oxidations with other reagents.* Photochemical oxidation and others using manganese dioxide, manganese(III) tris(acetonylacetonate), and potassium ferricyanide under the conditions previously described [see (a) (i), (ii), (iii); (b) (iii)] gave unidentifiable products, none of which possessed the t.l.c. characteristics of a tetrahydroxyxanthone. Chloranil and 2,5-dimethyl-1,4-benzoquinone did not react at all with the benzophenone (XI).

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