Chemical Constituents of Gentianaceae. Part 22.[1] Structures of New 1,3,5-Tri- and 1,3,5,6,7-Penta-oxygenated Xanthones of *Canscora decussata* Schult

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Two new xanthone glucosides and two free xanthones, isolated from *Canscora decussata*, have been identified as 1-glucosyloxy-3-hydroxy-5-methoxy- (1), 7-glucosyloxy-1,6-dihydroxy-3,5-dimethoxy- (2), 1.5.6-trihydroxy-3,7-dimethoxy- (4), and 1.5.7-trihydroxy-3,6-dimethoxy-xanthone (7) on the basis of chemical transformations and spectral evidence. On the basis of reassessment of the spectroscopic data and additional chemical evidence, it has been shown that the pentaoxygenated xanthones previously reported to be 1,3,7-trihydroxy-5,6-dimethoxy-xanthone (' Xanthone IV ') and 1,7-dihydroxy-3,5,6-trimethoxyxanthone (' Xanthone XII ') are in fact 1,3,5-trihydroxy-6,7-dimethoxy- (9) and 1,5-dihydroxy-3,6,7-trimethoxy-xanthone (10), respectively. The stucture of 1,6,7-trihydroxy-3,5-dimethoxyxanthone (' Xanthone XIII ') has been confirmed.

THE isolation of nearly two dozen polyoxygenated xanthones,[1,2] five triterpenes,[3] and loliolide[4] from *Canscora decussata* Schult (Gentianaceae) has been reported. Further investigation of the alcoholic extractives of the whole plant furnished two new xanthone glucosides (1) and (2) and two new free xanthones (4) and (7) whose structures have been established as follows.

Compound (1), $C_{20}H_{20}O_{10}$, showed u.v. absorption maxima characteristic of 1,3,5-trioxygenated xanthones[1,5] (Table 1). In the mass spectrum of the

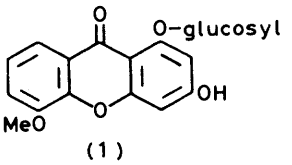
TABLE 1

U.v. data of xanthones of *C. decussata*

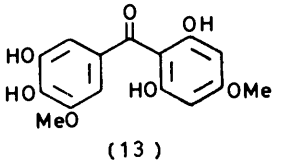
Xanthone	$\lambda_{max.}$/nm (log ε) (solvent MeOH)
(1)	248 (4.23), 253sh (4.09), 275sh (3.83), 310 (3.91)
(2)	244sh (4.37), 262 (4.42), 277sh (4.01), 315 (4.05)
(3)	258 (4.55), 285infl (3.96), 328 (4.16), 362 (3.50)
(4)	258 (4.58), 282infl (4.03), 325 (4.29), 360 (3.58)
(7)	255 (4.46), 285infl (4.12), 390 (4.25)
(9)	253 (4.54), 280infl (4.18), 335 (4.11), 355 (3.89)
(10)	253 (4.48), 280—282 (3.96), 318 (4.21), 328 (4.05)

acetate, there was no molecular ion peak, but significant fragment-ion peaks appeared due to a monoacetoxy-monohydroxy-monomethoxyxanthone (*m/e* 300) and glucose tetra-acetate (*m/e* 331). Hydrolysis of the xanthone glucoside (1) with emulsin furnished glucose and a xanthone (M^+ 258), m.p. 278—280°. The aglucone formed a diacetate and on methylation with ethereal diazomethane gave 1-hydroxy-3,5-dimethoxyxanthone.[5] The aglucone was, however, different from any of the previously reported 1,3,5-monomethoxydihydroxyxanthones. In the u.v. absorption spectrum of the glucoside, in ethanolic sodium acetate, there was a bathochromic shift of the longer wavelength maximum by 22 nm (310 ⟶ 332 nm) indicating the presence of a free 3-hydroxy-group. Permethylation of the glucoside and acidic hydrolysis of the product gave 1-hydroxy-3,5-dimethoxyxanthone; this shows that the glucoside linkage is at C-1.

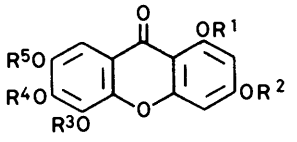
Compound (2), $C_{21}H_{22}O_{12}$, did not exhibit any molecular ion peak in its mass spectrum. It gave a hexa-acetate the mass spectrum of which showed monohydroxy-diacetoxy-dimethoxyxanthone (*m/e* 388) and glucose tetra-acetate (*m/e* 331) fragments. Hydrolysis of the glucoside with emulsin furnished glucose and the aglucone (3), which was identical with ' Xanthone XIII ', previously



(1)



(13)



(2) $R^1 = R^4 = H, R^2 = R^3 = Me, R^5 =$ β-D-glucosyl
(3) $R^1 = R^4 = R^5 = H, R^2 = R^3 = Me$
(4) $R^1 = R^3 = R^4 = H, R^2 = R^5 = Me$
(5) $R^1 = R^3 = H, R^4R^5 = CH_2, R^2 = Me$
(6) $R^1 = H, R^3R^4 = CH_2, R^2 = R^5 = Me$
(7) $R^1 = R^3 = R^5 = H, R^2 = R^4 = Me$
(8) $R^1 = R^2 = R^5 = H, R^3 = R^4 = Me$
(9) $R^1 = R^2 = R^3 = H, R^4 = R^5 = Me$
(10) $R^1 = R^3 = H, R^2 = R^4 = R^5 = Me$
(11) $R^1 = R^4 = H, R^2 = R^3 = R^5 = Me$
(12) $R^1 = R^2 = R^5 = H, R^3R^4 = CH_2$

reported from this plant.[5,6] The u.v. absorption spectrum of the glucoside showed a sodium acetate-induced bathochromic shift of the longer wavelength maximum (315 ⟶ 334 nm) thereby indicating the presence of free 3- and/or 6-hydroxy group. The absence of a sodium acetate–boric acid-induced shift eliminated the

[1] Part 21, S. Ghosal, R. B. P. S. Chauhan, K. Biswas, and R. K. Chaudhuri, *Phytochemistry*, 1976, **15**, 1041.
[2] S. Ghosal and R. K. Chaudhuri, *Phytochemistry*, 1973, **12**, 2035.
[3] S. Ghosal, R. K. Chaudhuri, and A. Nath, *Phytochemistry*, 1973, **12**, 1763.
[4] S. Ghosal, A. K. Singh, and R. K. Chaudhuri, *J. Pharm. Sci.*, 1976, **65**, 1549.
[5] R. K. Chaudhuri and S. Ghosal, *Phytochemistry*, 1971, **10**, 2425.
[6] S. Ghosal, R. K. Chaudhuri, and K. R. Markham, *J.C.S. Perkin I*, 1974, 2538.

possibility of an *ortho*-dihydroxy-system being present. Since ' Xanthone XIII ' contains a 3-methoxy group,[6] hence there must be a free 6-hydroxy group. In assigning the 1,6,7-trihydroxy-3,5-dimethoxyxanthone structure (3) to ' Xanthone XIII ', we relied primarily on the downfield shift of the 8-H signal in the ^{1}H n.m.r. spectrum of its triacetate.[6] The other possible structure, 1,5,6-trihydroxy-3,7-dimethoxyxanthone (4), for ' Xanthone XIII ' has new been examined by synthesis. Treatment of 1-hydroxy-3,5,6,7-tetramethoxyxanthone with sulphuric acid gave, by selective 5,6-bis-de-*O*-methylation,[7] the xanthone (4), which was different from respect to signals of acetoxy-groups at other positions (*e.g.* 1-, 3-, 6-, and 7-, which showed shifts of ⩽1—2 Hz). This phenomenon could be attributed to shielding by the pyrone ring of the 5-acetoxy protons.[10] In the hexa-acetate of the xanthone glucoside (2) the two aromatic acetoxy-signals appeared as a singlet at δ 2.45.

Compound (4), $C_{15}H_{12}O_7$, showed a close similarity in its u.v. absorption maxima (Table 1) to ' Xanthone XIII '.[5,6] The di- and tri-methyl ethers were identical with 1-hydroxy-3,5,6,7-tetramethoxy- and 1,3,5,6,7-pentamethoxy-xanthone respectively. Compound (4) responded positively to a Tollens test and showed

TABLE 2

60 MHz ^{1}H N.m.r. spectral data for the acetates of 1,3,5,6,7-pentaoxygenated xanthones *

	Acetate of xanthone							
Assignment	(2)	(3)	(4)	(12)	(7)	(9)	(10)	(11)
1-Subst.	2.45 (OAc)	2.45 (OAc)	2.43 (OAc)	2.46 (OAc)	2.45 (OAc)	2.45 (OAc)	2.45 (OAc)	2.41 (OAc)
2-H	6.65 †	6.65 †	6.65 †	6.60 †	6.65 †	6.72 †	6.65 †	6.64 †
3-Subst.	4.03 (OMe)	4.03 (OMe)	3.93 (OMe)	2.46 (OAc)	3.90 (OMe)	2.48 (OAc)	3.94 (OMe)	4.08 (OMe)
4-H	6.83 †	6.82 †	6.81 †	6.86 †	6.81 †	6.85 †	6.80 †	6.78 †
5-Subst.	3.98 (OMe)	3.96 (OMe)	2.36 (OAc) }	6.2	2.36 (OAc)	2.36 (OAc)	2.36 (OAc)	4.08 (OMe)
6-Subst.	2.45 (OAc)	2.48 (OAc)	2.45 (OAc) }	(O·CH_2·O)	3.96 (OMe)	3.96 (OMe)	3.94 (OMe)	2.41 (OAc)
7-Subst.	2.0—2.1 [$(OAc)_4$]	2.45 (OAc)	3.93 (OMe)	2.46 (OAc)	2.48 (OAc)	3.96 (OMe)	3.94 (OMe)	4.08 (OMe)
8-H	7.45	7.60	7.68	7.56	7.70	7.68	7.67	7.48

* δ Values; solvent $CDCl_3$; internal standard Me_4Si. † J 2 Hz.

' Xanthone XIII '. Further chemical evidence in favour of a 5- rather than a 7-methoxy-group in ' Xanthone XIII ' was obtained as follows. Treatment of the aglucone (3) with methylene iodide [8] in the presence of potassium carbonate afforded the 6,7-methylenedioxy-derivative (5) which responded to selective monodemethylation [9] in the presence of hydrochloric acid. This observation indicated that the only methoxy-group in ring B of the xanthone (3) was situated between two substituted oxygen functions, and was therefore at C-5.

In the ^{1}H n.m.r. spectrum of the hexa-acetate of the xanthone glucoside (2), the 8-H signal appeared at δ 7.45, which is normal for a 1,3,5,6,7-pentamethoxyxanthone. Thus there was no effect of the acetoxy-groups on this proton. The variation in chemical shift of 8-H in the acetate derivatives of a number of reference 1,3,5,6,7-pentaoxygenated xanthones, observed in this study, is now considered to enable location of the free hydroxy-group(s) in ring B of related pentaoxygenated xanthones. The 8-H signal shifts by *ca.* 0.23—0.25 p.p.m. downfield (relative to its position in the permethyl ether, δ 7.45) in the case of *p*-acetoxy- and *op*-diacetoxyxanthones, whereas *o*-acetoxy and *om*-diacetoxy-substituents caused a downfield shift of this signal by only 0.12—0.15 p.p.m. There is no shift of this signal in the case of a *m*-acetoxy-substituent (Table 2). Comparison of the acetoxy signals of these compounds has also offered a basis for locating free hydroxy-groups in the parent xanthones. The signal of an acetoxy-group at C-5 appeared at δ 2.36, 4—6 Hz upfield with bathochromic shifts of 43 and 77 nm in the 325 nm maximum in the presence of sodium acetate–boric acid and aluminium chloride, respectively. These properties indicated the presence of two *ortho*-hydroxy-groups. The aluminium chloride-induced shift was reduced to 26 nm in the presence of hydrochloric acid; hence there is a free 1-hydroxy-group. Of the two methoxy-groups, one must be at C-3 and the other at C-5 or C-7. Since the xanthone was different from the xanthone (3), it must be 1,5,6-trihydroxy-3,7-dimethoxyxanthone (4). Chemical evidence in favour of a 7- rather than a 5-methoxy-group was obtained as follows. The xanthone (4) was heated with methylene iodide in the presence of potassium carbonate to give the methylenedioxy-derivative (6) which did not undergo any change when refluxed with hydrochloric acid.[9] The ring B methoxy-group is thus not buttressed by two substituted oxygen functions and therefore at C-7. Finally, synthesis of this xanthone from 1-hydroxy-3,5,6,7-tetramethoxyxanthone by 5,6-bisde-*O*-methylation with sulphuric acid [7] established its structure (4).

Compound (7), $C_{15}H_{12}O_7$, gave 1-hydroxy-3,5,6,7-tetramethoxyxanthone on methylation with ethereal diazomethane and 1,3,5,6,7-pentamethoxyxanthone with dimethyl sulphate and alkali. It also gave a triacetate. The u.v. maxima of this compound remained unchanged in the presence of sodium acetate, indicating that the C-3 and C-6 oxygen functions are substituted. In the presence of aluminium chloride, there was a bathochromic shift of the longer wavelength maximum by 20 nm (390 ⟶ 410 nm) which remained unaffected on

[7] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2653.
[8] O. R. Gottlieb, M. Taveira Magalhães, M. Camey, A. A. Lins Mesquita, and D. de Barroscorrêa, *Tetrahedron*, 1966, **22**, 1777.
[9] A. Brossi and S. Teitel, *Org. Prep. Procedures*, 1969, **1**, 171.
[10] D. K. Holdsworth, *Phytochemistry*, 1973, **12**, 2011.

addition of hydrochloric acid. This indicated the presence of a 1-hydroxy group. The ^{1}H n.m.r. spectrum of the xanthone showed a one-proton signal at δ 13.03 due to a chelated hydroxy-group. The 2- and 4-H signals appeared as *meta*-split doublets at δ 6.33 and 6.61, respectively; the 8-H signal appeared as a singlet at δ 7.11. In the triacetate of the xanthone, the 8-H signal was shifted to δ 7.70 owing to the presence of *o*- and *p*-acetoxy-substituents. The 2- and 4-H signals in this derivative appeared at δ 6.65 and 6.81, respectively, which are normal positions for such protons in 1-acetoxy-3-methoxyxanthones.[11] Selective methylation [12] of the xanthone (3) with sodium hydrogen carbonate and dimethyl sulphate in acetone, followed by selective 5-de-*O*-methylation with hydrochloric acid [9] afforded 1,5,7-trihydroxy-3,6-dimethoxyxanthone, identical with the natural product.

'Xanthone IV' was previously identified,[5,6] as 1,3,7-trihydroxy-5,6-dimethoxyxanthone (8). This structure has now been revised to (9) on the basis of ^{1}H n.m.r. data of its triacetate, in which the 8-H signal appeared at δ 7.68 (due to *p*-acetoxy-shift), indicating the presence of a 5-hydroxy-group in the parent xanthone. In conformity with this assignment, one of the acetoxy-signals in the spectrum of the triacetate appeared at δ 2.36 (5-OAc).

Reassessment of the ^{1}H n.m.r. data of 'Xanthone XII' [5,6] and its diacetate (the latter showing 0.22 p.p.m. downfield shift in the 8-H signal relative to its position in the case of the permethyl ether) necessitates revision of its structure to (10). In support of this, the xanthone (4) was selectively 6-*O*-methylated with dimethyl sulphate and sodium hydrogen carbonate to give 'Xanthone XII'.[5,6]

In a recent paper on the structure of pentaoxygenated xanthones of *Mesua ferrea* L., Gunasekera *et al.* proposed [13] a 1,3,6,7,8-oxygenation pattern for their xanthones (VIIb) and (VIIc) on the basis of a correspondence in properties of these xanthones with two of those isolated from *Canscora decussata*.[5] In view of the revised oxygenation pattern (1,3,5,6,7-), subsequently reported for the xanthones of *C. decussata*,[6] the pentaoxygenated xanthones of *M. ferrea* also must have a 1,3,5,6,7-oxygenation pattern. Consequently, a reallocation of the hydroxy- and methoxy-groups in the xanthones of *M. ferrea* is warranted.

The complementary xanthones (3) and (4) have never been found to co-occur in the various batches of *C. decussata* plants investigated during the past seven years. This observation seems to have a bearing on the biogenesis of the pentaoxygenated xanthones of *C. decussata*. It would be difficult to explain, on the basis of a simple phenolic coupling [14] involving the benzophenone (13) (or equivalent), the complete absence of one xanthone (3) or (4) when the other compound is present in appreciable amount.

[11] G. H. Stout and W. J. Balkenhol, *Tetrahedron*, 1969, **25**, 1947.
[12] K. R. Markham, *Tetrahedron*, 1965, **21**, 1449.

EXPERIMENTAL

U.v. spectra were recorded with a Cary 14 or Spectromom 203 spectrophotometer, i.r. spectra with a Perkin-Elmer 621 or 257 instrument, mass spectra with an A.E.I. MS-9 spectrometer (at 70 eV), and 60 MHz ^{1}H n.m.r. spectra with a Varian A-60 spectrometer. T.l.c. was carried out on silica gel G (Merck) in the solvent systems (1) $CHCl_3$–HOAc (95 : 5), (2) C_6H_6–HOAc (99 : 1), (3) Bu^nOH–HOAc–H_2O (4 : 1 : 2), and (4) C_6H_6–HOAc (96 : 4). Spots were detected by u.v. fluorescence and staining with iodine vapour. Physical data relating to some of the xanthones were reported previously.[5,6]

Extraction Procedure.—In a typical experiment, the concentrated ethanolic extract of *C. decussata* (whole plant; *ca.* 1 kg), after removal of mangiferin by filtration, was poured into aqueous acetic acid (4%; 400 ml). The solution was kept overnight at room temperature, then extracted with ether (3 l) (fraction A) and ethyl acetate (3 l) (the processing of this fraction was reported previously [6]). The acidic layer was then basified (pH *ca.* 8) with ammonia; a sticky solid separated which was successively extracted with ether (3 l) and ethyl acetate (6 l) (fraction B).

Treatment of Fraction A.—The solvent was removed under reduced pressure and the brown gummy residue was triturated with benzene (200 ml) and chloroform (400 ml). The chloroform-insoluble solid on repeated crystallizations from methanol furnished either xanthone (4) or (7).

1,5,6-*Trihydroxy*-3,7-*dimethoxyxanthone* (4). This was obtained as a pale brown *solid* (0.148 g), sparingly soluble in methanol, m.p. 285°, R_F 0.4 (1) and 0.72 (3); $\lambda_{max.}$ (EtOH–NaOAc) 255 (log ε 4.54), 270—275sh (4.18), and 380 nm (4.25), $\lambda_{max.}$ (EtOH–NaOAc–H_3BO_3) 255 (4.42), 282infl. (4.27), and *ca.* 365sh nm (4.25); δ [$(CD_3)_2SO$] 7.11 (1 H, s), 6.65 (1 H, d, *J* 3 Hz), 6.43 (1 H, d, *J* 3 Hz), and 3.95 and 3.90 (6 H); *m/e* 304 (M^+, 100%), 289(20), 275(24), 274(14), 261(30), and 233(10) (Found: C, 58.75; H, 4.3. $C_{15}H_{12}O_7$ requires C, 59.2; H, 3.95%). The dimethyl ether, prepared with ethereal diazomethane, crystallized from ethanol as yellow needles, m.p. 171—173°, identical [m.p., mixed m.p., R_F value (2), and u.v. spectrum] with authentic 1-hydroxy-3,5,6,7-tetramethoxyxanthone. The permethyl ether, prepared with dimethyl sulphate and potassium carbonate in anhydrous acetone under reflux (46 h), crystallized from ethanol as yellow needles, m.p. 175°, identical (m.p., mixed m.p., R_F value, and u.v. spectrum) with 1,3,5,6,7-pentamethoxyxanthone.[6] The *triacetate* was prepared by warming the xanthone (4) (0.025 g) with acetic anhydride (5 ml) and pyridine (2 drops) on a steam-bath (4 h). The product crystallized from ethanol as needles (14 mg), m.p. 262°; R_F 0.6 (4); $\lambda_{max.}$ (EtOH) 245 (log ε 4.22), 302 (3.89), and 342 nm (3.56) (Found: C, 58.25; H, 4.45. $C_{21}H_{18}O_{10}$ requires C, 58.6; H, 4.5%).

1-*Hydroxy*-3,7-*dimethoxy*-5,6-*methylenedioxyxanthone* (6). To a mixture of the xanthone (4) (0.020 g) and potassium carbonate (0.5 g), in anhydrous acetone (15 ml), methylene iodide (0.5 ml) was added, and the mixture was refluxed on a steam-bath (14 h). After the usual work-up, the product crystallized from ethanol as pale brown *crystals* (0.02 g), m.p. 240—242°; R_F 0.71 (1); $\lambda_{max.}$ (MeOH) 235infl (log ε 4.46), 255 (4.51), 287infl (4.09), 325 (4.17), and 365sh (3.70) (Found: C, 61.1; H, 3.45. $C_{16}H_{12}O_7$ requires C, 60.75;

[13] S. P. Gunasekera, S. Ramachandran, S. Selliah, and M. S. Sultanbawa, *J.C.S. Perkin I*, 1975, 2447.
[14] J. E. Atkinson and J. R. Lewis, *J. Chem. Soc.* (*C*), 1969, 281.

H, 3.8%). The xanthone (6) remained unchanged when refluxed (16 h) with hydrochloric acid (30%).

Synthesis of the xanthone (4). 1-Hydroxy-3,5,6,7-tetramethoxyxanthone (0.092 g) was heated at 75 °C with concentrated sulphuric acid (s.g. 1.84; 1 ml) for 20 min and then kept at ambient temperature overnight. The mixture was poured on to crushed ice and the precipitate was filtered off. The solid showed two spots on t.l.c., R_F 0.65 and 0.78 (3) which were separated by preparative layer chromatography. The component of R_F 0.65 was identical with the xanthone (4). The acetate was identical (m.p., mixed m.p., and R_F value) with 1,5,6-triacetoxy-3,7-dimethoxyxanthone. The component of R_F 0.78 was a dihydroxytrimethoxyxanthone (11) (12 mg), m.p. 252—255°; *m/e* 318 (M^+). On acetylation (acetic anhydride–pyridine) it gave 1,6-*diacetoxy*-3,5,7-*trimethoxyxanthone* as straw coloured microcrystals, R_F 0.7 (4); *m/e* 402 (M^+) (Found: C, 59.25; H, 4.55. $C_{20}H_{18}O_9$ requires C, 59.7; H, 4.45%). Thus the demethylation yielded a mixture of mono- and bis-de-*O*-methylated products; the 6-methoxy-group was demethylated preferentially.

1,5,7-*Trihydroxy*-3,6-*dimethoxyxanthone* (7). This was obtained as a sparingly soluble (in methanol) snuff coloured *solid* (0.075 g), m.p. 280—282°; R_F 0.68 (1); $\lambda_{max.}$ (MeOH–NaOAc) 261 (log ε 4.48), 327sh (4.52), and 394nm (4.54); $\lambda_{max.}$ (MeOH–$AlCl_3$) 274 (log ε 4.53) and 410 nm (4.56); $\lambda_{max.}$ (MeOH–$AlCl_3$–HCl) 273 (log ε 4.53), 292infl (4.60), and 414 nm (4.62) (no shift in u.v. maxima with NaOAc–H_3BO_3); δ [$(CD_3)_2SO$] 13.13 (1 H), 7.11 (1 H, s), 6.63 (1 H, d, *J* 3 Hz), 6.35 (1 H, d, *J* 3 Hz), and 3.93 (6 H, s); *m/e* 304 (M^+, 100%), 289(15), 275(24), 261(51), 246(6), 245(5), 233(20), 218(6), 203(3.5), and 159(5) (Found: C, 58.85; H, 4.0. $C_{15}H_{12}O_7$ requires C, 59.2; H, 3.95%). The dimethyl ether, prepared with ethereal diazomethane, crystallized from ethanol as yellow needles, m.p. 171—173°, identical (m.p., mixed m.p., and R_F value) with 1-hydroxy-3,5,6,7-tetramethoxyxanthone.[6] The permethyl ether, prepared with dimethyl sulphate and potassium carbonate in acetone under reflux (46 h), crystallized from acetone as needles, m.p. and mixed m.p. 175°. The *triacetate* was prepared by warming the xanthone (7) (0.025 g) with acetic anhydride (5 ml) and pyridine (2 drops) on a steam-bath (4 h), and crystallized from ethanol as needles, m.p. 265—267°; R_F 0.62 (4); $\lambda_{max.}$ (MeOH) 242 (log ε 4.38), 305 (4.04), and 342 nm (3.74) (Found: C, 58.45; H, 4.55. $C_{21}H_{18}O_{10}$ requires C, 58.6; H, 4.2%).

Synthesis of the xanthone (7). 1,6,7-Trihydroxy-3,5-dimethoxyxanthone [6] (3) (0.014 g) was selectively 6-*O*-methylated by refluxing in acetone (10 ml) with sodium hydrogen carbonate (0.22 g) and dimethyl sulphate (0.04 ml) on a steam-bath (4 h). The solution was then filtered and the solvent removed. The residue was acidified with dilute sulphuric acid and kept overnight at ambient temperature; a pale brown solid separated, m.p. 220—225°; *m/e* 318 (M^+). This was selectively demethylated with hydrochloric acid (30%) at 170 °C for 14 h. The solid was filtered off and triturated with chloroform and methanol. The solid sparingly soluble in methanol (0.008 g), m.p. 279—281°; R_F 0.68 (1); $\lambda_{max.}$ (MeOH) 242sh (log ε 4.43), 256 (4.48), 285sh (4.13), and 390 nm (4.21), was identical with the naturally occurring xanthone (7). Acetylation of the compound (0.005 g) with acetic anhydride (1 ml) and pyridine (2 drops) on a steam-bath (4 h) furnished the triacetate, m.p. 265—267°, identical (mixed m.p., t.l.c., and u.v. spectrum) with the triacetate of the naturally occurring xanthone (7).

Treatment of Fraction B.—This fraction on concentration gave a brown solid (0.45 g), which was filtered off. The mother liquor on evaporation afforded a brown gum (0.22 g) (fraction C).

1-*Glucosyloxy*-3-*hydroxy*-5-*methoxyxanthone* (1). The brown gum crystallized from methanol as cream-coloured crystals, m.p. 210—212°; R_F 0.72 (3); $\lambda_{max.}$ (EtOH–NaOAc) 245 (log ε 4.24), 272 (4.01), 309infl (3.84), and 332 nm (3.87) (Found: C, 54.3; H, 5.05. $C_{20}H_{20}O_{10},H_2O$ requires C, 54.8; H, 5.0%). The penta-acetate was prepared by warming the glucoside (0.032 g) with acetic anhydride (5 ml) and pyridine (4 drops) on a steam-bath (4 h), and crystallized from ethanol; yield 22 mg, m.p. 158—161°; *m/e* 331 (50%), 300(100), 258(100), 257(45), 229(78), 228(50), 212(35), 169(98), 127(38), and 119(95). The permethyl ether, prepared by treatment of the glucoside with sodium hydride and methyl iodide in tetrahydrofuran at room temperature,[15] was obtained as a glassy solid. It was hydrolysed with sulphuric acid (3%) to give 1-hydroxy-3,5-dimethoxyxanthone and 2,3,4,6-tetra-*O*-methylglucose. Hydrolysis of the glucoside (0.035 g) with emulsin, according to a previously described procedure,[15] gave 1,3-dihydroxy-5-methoxyxanthone and glucose.

7-*Glucosyloxy*-1,6-*dihydroxy*-3,5-*dimethoxyxanthone* (2). The brown solid crystallized from ethanol; m.p. 220°; R_F 0.70 (3); $\lambda_{max.}$ (EtOH–NaOAc) 245 (log ε 4.41), 275 (4.60), and 334 nm (4.18) (no shift with NaOAc–H_3BO_3); δ [$(CD_3)_2SO$] 13.0 (1 H, s), 7.10 (1 H, s), 6.61 (1 H, d, *J* 3 Hz), 6.38 (1 H, d, *J* 3 Hz), 4.9—5.07 (1 H), and 3.90 (6 H, s) (Found: C, 51.75; H, 5.35. $C_{21}H_{22}O_{12},H_2O$ requires C, 52.05; H, 4.95%). The glucoside (0.025 g) on warming with acetic anhydride (5 ml) and pyridine (4 drops) on a steam-bath (4 h) followed by the usual work-up gave the hexa-acetate, which crystallized from ethanol; yield 0.014 g, m.p. 158—161°; *m/e* 338(100%), 346(80), 331(48), 304(98), 289(20), 275(24), 274(16), and 261(46). Hydrolysis of the glucoside (0.020 g) with emulsin gave 1,6,7-trihydroxy-3,5-dimethoxyxanthone (3) and glucose. The triacetate of the aglucone, prepared by warming with acetic anhydride and pyridine, crystallized from ethanol as needles, m.p. 203—205°; R_F 0.51 (4); $\lambda_{max.}$ (MeOH) 242 (log ε 4.35) and 305 nm (3.99) [properties identical with those recorded for the triacetate of the naturally occurring xanthone (3)].

1,5-*Dihydroxy*-3-*methoxy*-6,7-*methylenedioxyxanthone* (5). To a mixture of the xanthone (3) (0.022 g) and potassium carbonate (0.45 g) in anhydrous acetone (15 ml), methylene iodide (0.3 ml) was added. The mixture was refluxed (14 h) on a steam-bath. After the usual work-up, the product crystallized from ethanol as cream-coloured crystals, m.p. 189—190°; R_F 0.78 (1). Selective 5-de-*O*-methylation of the product was carried out by refluxing it (0.018 g) with hydrochloric acid (30%) for 16 h. After the usual work-up, the yellow 1,5-*dihydroxy*-3-*methoxy*-6,7-*methylenedioxyxanthone* (5) crystallized from methanol; yield 0.016 g; m.p. 170—172°; R_F 0.6 (1); $\lambda_{max.}$ (MeOH) 255 (log ε 4.52), 282infl (4.19), and 325 nm (4.31) (Found: C, 59.2; H, 3.45. $C_{15}H_{10}O_7$ requires C, 59.6; H, 3.3%).

1,3,5-*Trihydroxy*-6,7-*dimethoxyxanthone* (9). The isolation, physical, and spectral properties of this xanthone ('Xanthone IV') were reported previously.[5,6] The triacetate, prepared by warming it (0.020 g) with acetic anhydride (5 ml) and pyridine (2 drops) on a steam-bath (4 h), was obtained as a glassy *solid* on trituration with hexane–

[15] S. Ghosal, P. V. Sharma, and R. K. Chaudhuri, *Phytochemistry*, 1975, **14**, 2671.

methylene chloride; R_F 0.45 (4); *m/e* 430 (M^+) (Found: C, 58.4; H, 4.4. $C_{21}H_{18}O_{10}$ requires C, 58.6; H, 4.2%).

1,5-*Dihydroxy*-3,6,7-*trimethoxyxanthone* (10). The isolation, and physical and spectral properties of this xanthone ('Xanthone XII')[6] were reported previously.[5,6] The diacetate crystallized from ethanol as needles, m.p. 240—243°; R_F 0.52 (4); $\lambda_{max.}$ (MeOH) 245 (log ε 4.41), 270infl (3.98), 304 (4.06), and 342 nm (3.52); *m/e* 402 (M^+).

Transformation of the Xanthone (4) *into the Xanthone* (10). —Selective methylation of the xanthone (4) (0.05 g) was accomplished with dimethyl sulphate (0.016 ml) and sodium hydrogen carbonate (0.89 g) in anhydrous acetone (50 ml) under reflux (4 h). The solution was then filtered and evaporated. The residue was acidified and then extracted with ether. The ether-soluble solid (0.042 g) crystallized from methanol as pale yellow crystals, m.p. 239—241°, identical with the naturally occurring xanthone (10). The diacetate crystallized from ethanol as needles, identical (m.p., R_F value, and u.v. spectrum) with the diacetate of the xanthone (10).

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