# Chemical Investigation of Ceylonese Plants. Part XVII.[1] Isolation and Structures of the Xanthones in the Extractives of *Mesua ferrea* L. (Form *M. salicina* Pl. and Tr.) (Guttiferae)

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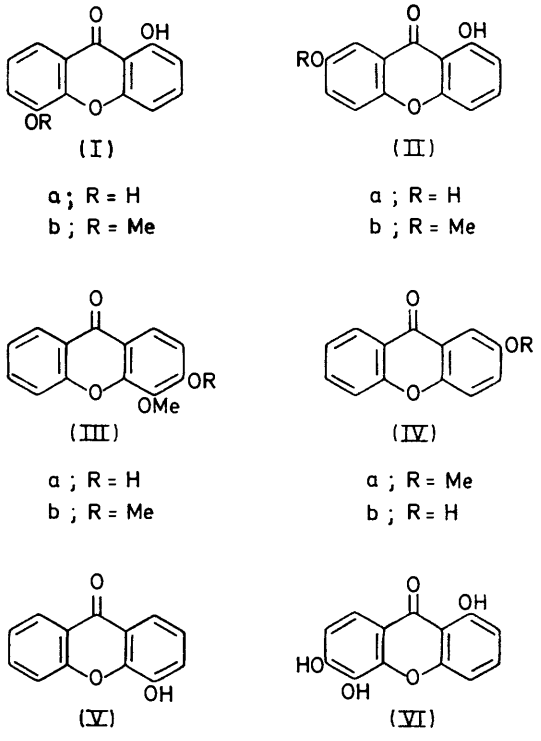
From the timber extractives of *Mesua ferrea* L. (form *M. salicina* Pl. and Tr.) nine known xanthones (2-hydroxy-, 2-methoxy-, 4-hydroxy-, 1,5-dihydroxy-, 1,7-dihydroxy-, 1-hydroxy-5-methoxy-, 1-hydroxy-7-methoxy, 3-hydroxy-4-methoxy-, and 1,5,6-trihydroxy-) and two new xanthones (1,3,6-trihydroxy-7,8-dimethoxy- and 3,6-dihydroxy-1,7,8-trimethoxy-) have been isolated and characterised. Taxonomic and biogenetic correlations are discussed.

As a continuation of our studies on Ceylonese Guttiferae species, the extractives obtained from the timber of *Mesua ferrea* L. (form *M. salicina* Pl. and Tr.) have been investigated, and the results compared with those obtained previously.[2]

The light petroleum extract on concentration gave a yellow solid and a gum. The solid was separated into three yellow pigments by chromatography on a silica gel column, followed by preparative t.l.c. These were identified as 1,5-dihydroxy-[3] (Ia), 1,7-dihydroxy-[3] (IIa), and 3-hydroxy-4-methoxy-xanthone[4] (IIIa) by comparison with authentic samples. The gum was separated on a column of silica gel and four xanthones and β-sitosterol were isolated. The xanthones were identified as 1-hydroxy-5-methoxy-[5] (Ib), 2-methoxy-[6] (IVa), 4-hydroxy-[7] (V), and 1-hydroxy-7-methoxy-xanthone[8] (IIb) by comparison with authentic samples.

The solid obtained from the benzene extract, on separaton on a silica gel column, gave 1,5-dihydroxy- (Ia), 1,7-dihydroxy- (IIa), 2-hydroxy-[7] (IVb), and 1,5,6-trihydroxy-xanthone[3] (VI), again identified by comparison with authentic samples.

The methanol extract was re-extracted with chloroform and the latter extract was separated into borax-soluble and insoluble fractions. From the borax-soluble fraction, three xanthanes were isolated. The least polar was 2-hydroxyxanthone (IVb), also isolated from the benzene extract. The second xanthone (VIIb) was a new natural product, $C_{15}H_{12}O_7$. Its n.m.r. spectrum (Table 1) showed a low-field signal at $\tau$ — 2.91 (chelated OH) and signals at $\tau$ 6.12 and 6.14 for two OMe groups. The aromatic signals appeared as a singlet (5-H) and two singlets showing *meta*-coupling (2- and 4-H). Acetylation gave a white crystalline product (VIIIb) showng n.m.r. signals at $\tau$ 7.63 and 7.68 for three acetate groups and at $\tau$ 6.09 and 6.10 for two OMe groups. The absence of signals for chelated OH indicated that the compound was fully acetylated; hence the natural material was considered to be a pentaoxygenated xanthone. The u.v. data were similar to those for 1,3,6,7,8-pentaoxygenated xanthones reported earlier[9] (Table 2). An aluminium chloride-induced shift[10] in the u.v. maxima confirmed the presence of chelated OH and a




sodium acetate-induced shift[11] in the higher wavelength region indicated the presence of 3-OH or 6-OH or both. The absence of a shift induced by NaOAc–$H_3BO_3$[3] indicated the absence of an *ortho*-dihydroxy-system. Methylation with diazomethane gave 1-hydroxy-3,6,7,8-tetramethoxyxanthone (VIIIa), showing the same m.p. and

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[2] (*a*) T. R. Govindachari, B. R. Pai, P. S. Subramaniam, U. R. Rao, and N. Muthukumaraswamy, *Tetrahedron*, 1967, **23**, 243; (*b*) Y. L. Chow and H. H. Quon, *Phytochemistry*, 1967, **7**, 1871.

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[6] R. A. Finnigan, J.K. Patel, and P. L. Backman, *Tetrahedron Letters*, 1966, 6087.

[7] R. A. Finnigan and J. K. Patel, *J.C.S. Perkin I*, 1972, 1896.

[8] D. De Barros Correa, O. R. Gottlieb, and M. Taveira Magalhaes, *Anais Acad. brasil. Cienc.*, 1966, **38**, 296.

[9] R. K. Chandhuri and S. Ghosal, *Phytochemistry*, 1971, **10**, 2425.

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[11] O. R. Gottlieb, M. Taveira Magalhaes, M. Ottoni de Silva Pereira, A. Lins Mesquita, D. De Barros Correa, and G. G. de Oliveira, *Tetrahedron*, 1968, **24**, 1601.

u.v. data as reported.[9] This indicated that the 8-OH is methylated and the 1-OH not methylated in the original compound, and confirms the oxygenation pattern. From the above arguments only two structures (VIIa and b) appear likely. In structure (VIIb) but not in (VIIa) there is a hydroxy-group *ortho* to 5-H. Hence the shift of the 5-H n.m.r. signal on acetylation should clearly distinguish between the two structures. The shifts [12] of the 2-, 4-, and 5-H signals for the acetylated compound (VIIIb) can be obtained from Table 1. Since the value for 5-H is −0.44 p.p.m., the natural compound is 1,3,6-trihydroxy-7,8-dimethoxyxanthone (VIIb).

TABLE 1

$^1$H N.m.r. data (τ values; 100 MHz)

| Xanthone | C-1 (1 H, s or 3 H, s) | C-2 (1 H, s) | C-3 (3 H, s) | C-4 (1 H, s) | C-5 (1 H, s) | C-6 (3 H, s) | C-7 (3 H, s) | C-8 (3 H, s) |
|---|---|---|---|---|---|---|---|---|
| (VIIb) [$(CD_3)_2SO$] | −2.91 | 3.82 | | 3.42 | 2.94 | | 6.14 (OMe) | 6.12 (OMe) |
| (VIIIb) [$(CD_3)_2SO$] | 7.51 (OAc) | 2.94 | 7.63 (OAc) | 2.51 | 2.50 | 7.68 (OAc) | 6.10 (OMe) | 6.07 (OMe) |
| (VIIIb) ($CDCl_3$) | 7.55 (OAc) | 3.19 | 7.55 (OAc) | 2.76 | 2.47 | 7.69 (OAc) | 6.06 (OMe) | 6.02 (OMe) |
| (VIIc) [$(CD_3)_2SO$] | 6.14 (OMe) | 3.64 | | 3.53 | 2.96 | | 6.16 (OMe) | 6.16 (OMe) |
| (VIIId) ($CDCl_3$) | 6.01 (OMe) | 3.43 | 7.54 (OAc) | 3.12 | 2.38 | 7.66 (OAc) | 6.03 (OMe) | 6.03 (OMe) |
| (VIIId) [$(CD_3)_2SO$] | 6.07 (OMe) | 3.18 | 7.53 (OAc) | 2.98 | 2.56 | 7.68 (OAc) | 6.12 (OMe) | 6.07 (OMe) |
| (VIIIc) [$(CD_3)_2SO$] | 6.02 (OMe) | 3.52 | 6.09 (OMe) | 3.30 | 2.73 | 6.09 (OMe) | 6.13 (OMe) | 6.09 (OMe) |

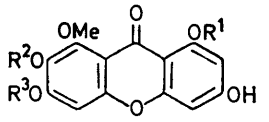
TABLE 2

U.v. data [$\lambda_{max.}$/nm (log ε)]

| Xanthone | | | | | | |
|---|---|---|---|---|---|---|
| 1,3,8-$(OH)_3$ [9] | | 255 | 280 | 320 | 335 | |
| (6,7-$(OMe)_2$ [9] | | (4.53) | (4.01) | (4.32) | (4.18) | |
| 1,8-$(OH)_2$-3,6,7- | | 253 | 280 | 318 | 330 | |
| $(OMe)_3$ [9] | | (4.48) | | (4.21) | (4.18) | |
| 1-OH-3,6,7,8- | 240 | 260 | | 308 | 355 | |
| $(OMe)_4$ [9] | (4.06) | (4.62) | | (3.90) | (3.84) | |
| 1,3,6,7,8-$(OH)_5$ [9] | | 255 | 283 | 320—325 | | |
| | | (4.47) | (3.97) | (4.22) | | |
| (VIIb) | 239 | 260 | 270sh | 325 | 345 | |
| | (4.24) | (4.33) | (4.18) | (4.14) | (4.01) | |
| (VIIIb) | 237 | 247 | 255 | 297 | 365 | |
| | (4.30) | (4.33) | (4.39) | (4.65) | (3.85) | |
| (VIIIa) | 240 | 259 | | 311 | 360 | |
| | (4.44) | (4.63) | | (4.35) | (3.99) | |
| (VIIc) | 244 | 253 | 283sh | 311 | 332 | 358 |
| | (4.52) | (4.59) | (4.15) | (4.15) | (4.21) | (4.08) |
| (VIIId) | 244 | 252 | 287 | | 354 | |
| | (4.45) | (4.49) | (4.15) | | (3.98) | |
| (VIIIc) | 244 | 254 | 303 | | 348 | |
| | (4.58) | (4.67) | (4.34) | | (3.77) | |

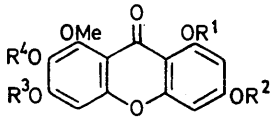
The third xanthone (VIIc) was also a new natural product, $C_{16}H_{14}O_7$. The u.v. data were similar to those for a 1,3,6,7,8-pentaoxygenated system [9] (Table 2). The n.m.r. spectrum showed signals at τ 6.14 (3H) and 6.16 (6H) for three OMe groups. The absence of low-field signals and the absence of an aluminium chloride-induced u.v. shift indicated that positions 1 and 8 carry OMe groups. Methylation with diazomethane gave a pentamethoxyxanthone identical with that (VIIIc) prepared from 1,3,6-trihydroxy-7,8-dimethoxyxanthone (VIIb). A sodium acetate-induced shift [11] in the u.v. maxima in the longer wavelength region indicated the presence of a 3- or 6-OH group or both. The absence of a shift induced by NaOAc–$H_3BO_3$ in the u.v. maxima indicated the absence of *ortho*-dihydroxy-groups. On the basis of the above data two possible structures (VIIc and d) were considered. Acetylation gave a diacetate (VIIId). The n.m.r. spectrum showed a shift of −0.40 p.p.m. for the 5-H signal on acetylation (Table 1), indicating the presence of a 6-hydroxy-group. Hence the compound is 3,6-dihydroxy-1,7,8-trimethoxyxanthone (VIIc).

Table 3 summarises the occurrence of xanthones in *M. ferrea* L. and related species.[2,13] 1,5- and 1,7-Dihydroxyxanthones and 1,5,6-trihydroxyxanthones are common to the three species. Although a 1,3,5-trioxygenated system occurs in the first two species, we have not isolated such a constituent in the present case. However *M. ferrea* L. (*M. salicina* Pl. and Tr.) is unique in the *Mesua* genus in having three mono-oxygenated and two pentaoxygenated xanthones. Besides the mono-oxygenated xanthones, the corresponding dioxygenated xanthones with a 1-hydroxy-group have also been isolated from the same plant.



(VII)

a; $R^1$ = $R^2$ = H, $R^3$ = Me
b; $R^1$ = $R^3$ = H, $R^2$ = Me
c; $R^1$ = $R^2$ = Me, $R^3$ = H
d; $R^1$ = $R^3$ = Me, $R^2$ = H



(VIII)

a; $R^1$ = H, $R^2$ = $R^3$ = $R^4$ = Me
b; $R^1$ = $R^2$ = $R^3$ = Ac, $R^4$ = Me
c; $R^1$ = $R^2$ = $R^3$ = $R^4$ = Me
d; $R^2$ = $R^3$ = Ac, $R^1$ = $R^4$ = Me

Mono-oxygenated xanthones (2- or 4-hydroxy or 2-

[12] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *J. Chem. Soc.* (*C*), 1971, 804.

[13] W. M. Bandaranayake, S. S. Selliah, and M. U. S. Sultanbawa, *Phytochemistry*, 1975, **14**, 265.

methoxy) have been reported from five *Kielmeyera* [14-18] species and *Calophyllum brasiliense* Camb.[19] Hitherto only from the seeds of *Mammea americana* L.[5,6] have 2- and 4-hydroxyxanthones and 2-methoxyxanthone been

TABLE 3

Occurrence of xanthones in *M. ferrea* L. and *M. thwaitesii*

| Xanthone | *M. ferrea* L.[2] | *M. thwaitesii* (Pl. & Tr.)[13] | *M. ferrea* L. (form *M. salicina* Pl. & Tr.) (%) |
|---|---|---|---|
| 2-Hydroxy | — | — | 0.02 |
| 2-Methoxy | — | — | 0.002 |
| 4-Hydroxy | — | — | 0.0005 |
| 1,5-Dihydroxy | √ | √ | 0.31 |
| 1,7-Dihydroxy | √ | √ | 0.23 |
| 1-Hydroxy-5-methoxy | — | — | 0.0004 |
| 1-Hydroxy-7-methoxy | — | √ | 0.002 |
| 3-Hydroxy-4-methoxy | — | — | 0.001 |
| 1,5-Dihydroxy-3-methoxy | √ | — | — |
| 5-Hydroxy-1,3-dimethoxy | — | √ | — |
| 1,5,6-trihydroxy | √ | √ | 0.013 |
| 1,3,6-trihydroxy-7,8-dimethoxy | — | — | 0.01 |
| 3,6-Dihydroxy-1,7,8-trimethoxy | — | — | 0.005 |

isolated. The presence of 2- and 4-hydroxy- and 2-methoxy-xanthone in the plant studied here thus shows its greater affinity to the *Mammea* genus. Lewis [20] proposed that certain naturally occurring xanthones are formed from hydroxybenzophenones. This was supported by Scheinmann *et al.*[21] who reported the occurrence of corresponding 5- and 7-hydroxylated xanthones in *Mammea americana* L. (two pairs) and in *M. africana* Don. (three pairs). Although the presence of two such pairs in the present case (2- and 4-hydroxyxanthones and 1,5- and 1,7-dihydroxyxanthones) may be considered as further support, the presence of xanthones without a 1-hydroxy-group along with the corresponding 1-hydroxylated compound can be interpreted in an alternative manner as follows. Both 2- and 4-hydroxyxanthones could be obtained from 2,3′-dihydroxybenzophenone, and for the formation of 1,5- and 1,7-dihydroxyxanthones, the presence of 2,3′,6-trihydroxybenzophenone would be required. Similar considerations apply to other compounds present. However if removal of a 1-hydroxy-group is readily accomplished by a specific enzyme system in certain plant species, the presence of only the hydroxybenzophenone corresponding to the 1-oxygenated xanthones would be sufficient to account for the presence of the various xanthones. The relative yields of the constituents seem to support this suggestion.

## EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. and u.v. spectra were determined with a Perkin-Elmer 257 grating and a Unicam SP 8000B spectrophotometer, respectively. Optical rotations were recorded with a Bellingham and Stanley polarimeter. T.l.c. was carried out on Merck silica gel G (0.25 mm thickness). Merck silica gel (30—70 mesh) was used for column chromatography. Light petroleum refers to the fraction of b.p. 60—80°. Spectroscopic data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21463 (8 pp.)*

*Extraction Procedure.*—The powdered timber (5.50 kg) was extracted in turn with hot light petroleum, hot benzene, and hot methanol. Concentration of the light petroleum extract gave a yellow solid (A) (15.0 g, 0.28%) and a mother liquor (B) (5.0 g, 0.09%). Similarly, concentration of the benzene extract gave a solid (C) (50.0 g, 0.90%) and a brown mother liquor (D) (95.0 g, 1.9%). The methanol extract on concentration gave a tarry mass E (850.0 g, 15.4%).

*Isolation of* 1,5-*dihydroxyxanthone* (Ia). The solid (A) (2.0 g) was separated on a column of silica gel (60 g). Elution with light petroleum–diethyl ether (17:3) gave 1,5-dihydroxyxanthone as pale yellow crystals (0.75 g), m.p. 264—266° (from acetone) (lit.,[3] 266—267°), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

*Isolation of* 1,7-*dihydroxyxanthone* (IIa). Further elution with light petroleum–diethyl ether (4:1) gave a yellow solid. This was separated on a preparative silica gel plate (30 g) with chloroform into 1,5-dihydroxyxanthone (Ia) (0.020 g) and 1,7-dihydroxyxanthone (IIa) (0.030 g), m.p. 234—234° (from acetone) (lit.,[3] 237—238°), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

*Isolation of* 3-*hydroxy*-4-*methoxyxanthone* (IIIa). Further elution with light petroleum–diethyl ether (3:1) gave 3-hydroxy-4-methoxyxanthone* (IIIa) (0.30 g), m.p. 218—220° (from acetone) (lit.,[4] 220—221°), t.l.c. $R_F$ 0.76 (chloroform–methanol 40:1), $M^+$ 242, identical with an authentic sample (mixed m.p., i.r. and t.l.c. comparison).

Methylation of 3-hydroxy-4-methoxyxanthone (0.005 g) with an excess of diazomethane in ether gave 3,4-dimethoxyxanthone (0.004 g) (IIIb), m.p. 158—159° (from light petroleum) (lit.,[3] 158—159°), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

*Isolation of* 1-*hydroxy*-7-*methoxyxanthone* (IIb). The mother liquor (B) (2.0 g) was separated on a column of silica gel (60 g). Elution with light petroleum–diethyl ether (19:1) gave 1-hydroxy-7-methoxyxanthone* (0.040 g), which afforded yellow crystals, m.p. 128—130° (from acetone) (lit.,[6] m.p. 129—130°), t.l.c. $R_F$ 0.80 (chloroform), $M^+$ 242, identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

1,7-Dihydroxyxanthone (0.005 g) was methylated with an excess of diazomethane in ether. The usual work up gave 1-hydroxy-7-methoxyxanthone (0.005 g), m.p. 129—130° (from light petroleum) (lit.,[8] 129—130°), identical with the foregoing sample (IIb) (mixed m.p., i.r., u.v., and t.l.c. comparison).

*Isolation of* 1-*hydroxy*-5-*methoxyxanthone* (Ib). Elution of

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

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[15] G. G. de Oliveira, A. A. Lins Mesquita, O. R. Gottlieb, and M. Taveira Magalhaes, *Anais Acad. brasil Cienc.*, 1966, **38**, 421.

[16] O. R. Gottlieb, A. A. Lins Mesquita, and T. J. Nagem, *Phytochemistry*, 1971, **10**, 2253.

[17] O. R. Gottlieb, M. Taveira Magalhaes, M. Camey, A. Lins Mesquita, and D. de Barros Correa, *Tetrahedron*, 1966, **22**, 1777.

[18] D. de Barros Correa, O. R. Gottlieb, and M. Taviera Magalhaes, *Anais Acad. brasil. Cienc.*, 1966, **38**, 296.

[19] L. Crombie, D. E. Games, and A. McCormick, *Tetrahedron Letters*, 1966, 145.

[20] J. R. Lewis, *Proc. Chem. Soc.*, 1963, 37.

[21] I. Carpenter, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1969, 2421.

the column with light petroleum–diethyl ether (9:1) gave 1-hydroxy-5-methoxyxanthone* as yellow crystals (from light petroleum) (0.010 g), m.p. 215° (lit.,[5] 213—215°), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

*Isolation of* 2-*methoxyxanthone* (IVa). Elution with light petroleum–diethyl ether (17:3) gave yellow crystals of 2-methoxyxanthone* (0.040 g), m.p. 130° (from light petroleum) (lit.,[6] 131°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

*Isolation of* β-*sitosterol*. Further elution with light petroleum–diethyl ether (4:1) gave β-sitosterol (0.020 g), m.p. 136—137° (lit.,[3] 136—137°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

*Isolation of* 4-*hydroxyxanthone* (V). Elution with light petroleum–diethyl ether (3:1) gave 4-hydroxyxanthone* (0.010 g), pale yellow crystals, m.p. 245—246° (from acetone) (lit.,[7] 245—246°) identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

Further elution with light petroleum–diethyl ether (3:1) gave a mixture of xanthones shown to contain 1,5-dihydroxyxanthone, 1,7-dihydroxyxanthone, and 3-hydroxy-4-methoxyxanthone by t.l.c. comparison.

*Isolation of* 2-*hydroxyxanthone* (IVb). The solid (C) (5.0 g) was separated on a column of silica gel (150 g). Elution with benzene–chloroform (2:3) gave 1,5-dihydroxyxanthone (1.70 g), and with benzene–chloroform (4:1) gave 1,7-dihydroxyxanthone (1.5 g). Elution with chloroform gave 2-hydroxyxanthone* (IVb) (0.150 g) as yellow crystals, m.p. 237° (from acetone) (lit.,[7] 240—242°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

*Isolation of* 1,5,6-*trihydroxyxanthone* (VI). Further elution with chloroform gave 1,5,6-trihydroxyxanthone (VI) (0.020 g) as yellow plates, m.p. 286—287° (from acetone) (lit.,[3] 285—286°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

T.l.c. of the mother liquor (D) showed no spots due to components other than those described so far and this fraction was not investigated further.

The methanol extract (E) (850 g) was re-extracted with hot chloroform and hot ethyl acetate (Soxhlet) for 2 days. T.l.c. showed that both extracts contained the same set of compounds (8.0 g in $CHCl_3$; 18.5 in EtOAc; total 0.48%). The chloroform extract (8.0 g) in diethyl ether was washed with ice cold borax solution (1%). T.l.c. showed that the neutral fraction (F) contained mainly 2-hydroxyxanthone (IVb) and this was not investigated further.

The borax-soluble fraction (G) (2.0 g) was separated on a column of silica gel (60 g). Elution with benzene–chloroform (1:1) gave 2-hydroxyxanthone (0.150 g).

*Isolation of* 1,3,6-*trihydroxy*-7,8-*dimethoxyxanthone* (VIIb). Elution with chloroform gave 1,3,6-*trihydroxy*-7,8-*dimethoxyxanthone* monohydrate (VIIb) (0.100 g) as yellow crystals m.p. 279—280° (from methanol), t.l.c. $R_F$ 0.40 (chloroform–methanol, 40:1), $M^+$ 304 (Found: C, 56.05; H, 4.2. $C_{15}H_{12}O_7$, $H_2O$ requires C, 55.9; H, 4.35%), $\lambda_{max.}$ (EtOH–$AlCl_3$) 228 (log ε 4.30), 264 (4.37), 272 (4.43), 288sh (3.97), 325 (4.15), and 337 nm (4.14); $\lambda_{max.}$ (EtOH–NaOAc) 237 (log ε 4.25), 252 (4.29), 262 (4.27), 270 (4.25), 333 (4.06), and 345 nm (4.09) (no shift with NaOAc–$H_3BO_3$); $\nu_{max.}$ (Nujol) 3 300, 2 427, 2 360, 1 660, 1 616, 1 589, 1 466, 1 382, 1 357, 1 308, 1 290, 1 269, 1 254, 1 213, 1 190, 1 175, 1 140, 1 094, 1 029, 1 009, 922, 829, 805, 780, 764, 733, and 708 $cm^{-1}$; n.m.r. data in Table 1; *m/e* 304 (100%), 303 (20), 290 (8), 289 (30), 288 (10), 275 (13), 274 (12), 261 (20), 260 (10), 259 (14), 246 (14), 245 (10), 244 (20), 243 (23), 233 (8), 231 (8), 218 (8), 215 (21), 203 (5), 191 (7), 190 (5), 188 (11), 161 (4), 153 (10), 138 (16), 134 (10), 130 (6), 123 (5), 108 (7), 105 (5), 95 (7), 79 (8), 69 (30), 45 (25), and 28 (50).

Further elution with chloroform–methanol (19:1) gave 1,5,6-trihydroxyxanthone (0.150 g).

1-*Hydroxy*-3,6,7,8-*tetramethoxyxanthone* (VIIIa). Methylation of 1,3,6-trihydroxy-7,8-dimethoxyxanthone (0.015 g) with diazomethane in ether gave 1-hydroxy-3,6,7,8-tetramethoxyxanthone* (0.015 g) (VIIIa), white crystals (from light petroleum), m.p. 171—172° (lit.,[9] 171—172°), t.l.c. $R_F$ 0.79 (chloroform–methanol, 40:1).

1,3,6,7,8-*Pentamethoxyxanthone* (VIIIc). Methylation of 1,3,6-trihydroxy-7,8-dimethoxyxanthone (0.015 g) with dimethyl sulphate (0.5 ml) in acetone (5 ml) and the usual work-up gave 1,3,6,7,8-pentamethoxyxanthone (0.011 g), m.p. 176° (from acetone) (see below).

1,3,6-*Triacetoxy*-7,8-*dimethoxyxanthone* (VIIIb). Acetylation of 1,3,6-trihydroxy-7,8-dimethoxyxanthone (0.025 g) with pyridine (3 ml) and acetic anhydride (0.5 ml) at room temperature and the usual work-up gave 1,3,6-triacetoxy-7,8-dimethoxyxanthone* (0.020 g), white crystals, m.p. 171—172° (from acetone), t.l.c. $R_F$ 0.78 (chloroform–methanol, 40:1).

*Isolation of* 3,6-*dihydroxy*-1,7,8-*trimethoxyxanthone* (VIIc). Further elution of the column with chloroform–methanol (9:1) gave 3,6-*dihydroxy*-1,7,8-*trimethoxyxanthone dihydrate* (0.055 g), white crystals (from methanol), m.p. 285—287°, t.l.c. $R_F$ 0.31 (methanol–chloroform, 1:40) (Found: C, 53.85; H, 4.73%; $M^+$, 318. $C_{16}H_{14}O_7$, $2H_2O$ requires 54.25; H, 4.55%. $C_{16}H_{14}O_7$ requires *M*, 318); $\lambda_{max.}$ (EtOH) Table 2; $\lambda_{max.}$ (EtOH–NaOAc) 244 (log ε 4.42), 254 (4.51), 283sh (4.06), 311 (4.12), 342 (4.06), and 358 nm (3.85) (no shift with $AlCl_3$ or NaOAc–$H_3BO_3$); $\nu_{max.}$ (Nujol) 3 150, 2 965, 2 860, 1 616, 1 595, 1 578, 1 465, 1 382, 1 335, 1 275, 1 250, 1 209, 1 190, 1 159, 1 139, 1 115, 1 080, 1 021, 982, 920, 832, 794, 786, 727, and 708 $cm^{-1}$; n.m.r. in Table 1; *m/e* 318 (100%), 317 (22), 305 (6), 304 (35), 303 (28), 301 (15), 289 (25), 288 (24), 287 (19), 274 (14), 273 (10), 272 (9), 259 (13.5), 258 (16), 245 (18), 244 (19), 243 (10), 229 (20), 228 (26), 215 (7), 212 (6), 200 (5), 159 (6), 115 (6), 70 (9), 63 (7), and 28 (6).

1,3,6,7,8-*Pentamethoxyxanthone* (VIIIc). Methylation of 3,6-dihydroxy-1,7,8-trimethoxyxanthone (0.020 g) with diazomethane gave 1,3,6,7,8-*pentamethoxyxanthone** (0.020 g), m.p. 176° (from acetone), $R_F$ 0.70 (chloroform–methanol, 40:1), identical with the methylation product of 1,3,6-trihydroxy-7,8-dimethoxyxanthone (mixed m.p., i.r., and t.l.c. comparison).

3,6-*Diacetoxy*-1,7,8-*trimethoxyxanthone* (VIIId). Acetylation of 3,6-dihydroxy-1,7,8-trimethoxyxanthone (0.020 g) with acetic anhydride (0.5 ml) and pyridine (3 ml) gave 3,6-diacetoxy-1,7,8-trimethoxyxanthone* (0.020 g) as white crystals, m.p. 168°, $R_F$ 0.72 (chloroform–methanol, 40:1), $M^+$ 402.

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