^{1}H NMR (60 MHz, $CDCl_3$) δ2.40 (*s*, 3H-9, 3H-9'), 3.90, 3.92, 4.02 (3*s*, 6 OMe), 6.85 (*s*, H-2', H-6'), 7.45 (*s*, H-6), 7.80 (*s*, H-7). ^{13}C NMR (20 MHz, $CDCl_3$) δ19.8, 19.9 (C-9, C-9'), 55.6 (3 OMe), 60.9, 61.1 (3 OMe), 101.5 (C-2', C-6'), 121.0 (C-2, C-7), 126.1 (C-1, C-7'), 129.5 (C-8'), 133.0 (C-8, C-1'), 135.1 (C-4'), 140.1 (C-4, C-6), 147.2 (C-3, C-5), 152.2 (C-3', C-5').

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HAPLOXANTHONE FROM *HAPLOCLATHRA* SPECIES

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Key Word Index—*Haploclathra leiantha*; *H. paniculata*; Guttiferae; 1,3,7-trihydroxy-8-methoxyxanthone; haploxanthone.

Abstract—A new xanthone was isolated from the trunk wood of *Haploclathra leiantha* and *H. paniculata* and its structure determined by UV, IR, NMR and mass spectrometry as 1,3,7-trihydroxy-8-methoxyxanthone.

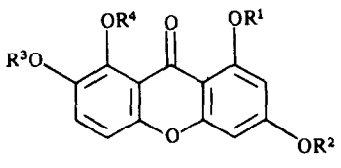
INTRODUCTION

Previously, we reported the isolation of 'Leiaxanthone' [1] and anthaxanthone [2] from *Haploclathra leiantha*., and 3,7-dihydroxy-1,8-dimethoxyxanthone from *H. paniculata* besides several known xanthones (see Experimental of refs [1, 3]). Now we describe the isolation and characterization of a new 1,3,7,8-tetraoxygenated xanthone from both species for which we give the trivial name 'haploxanthone'. In this communication we report its structure as **1** which to our knowledge is the first report of the occurrence of a tetraoxygenated xanthone from this source.

RESULTS AND DISCUSSION

Haploxanthone (**1**), obtained from chloroform–methanol fractions by chromatography of extracts of the trunk wood of *H. leiantha* and H. *paniculata*, was crystallized from ethanol as yellow crystals, mp 250–252°. On the basis of elementary analysis and mass spectrometry the molecular formula was assigned as $C_{14}H_{10}O_6$. The xanthone (**1**) formed a dimethyl ether (**2**) with diazomethane, a trimethyl ether (**3**) with dimethyl sulphate–potassium carbonate and a triacetyl derivative (**4**) with acetic anhydride. Hence, the compound was a trihydroxymethoxyxanthone in which one of the hydroxyl groups is chelated.

The UV spectrum of **1** showing λ_{max}^{EtOH} (nm) 242, 264, 322 and 383 (ε resp. 31 400, 35 800, 21 000 and 13 700) is characteristic of a 1,3,7,8-tetraoxygenated xanthone [4]. The presence of a 1,3,7,8-tetraoxygenated system was



1 $R^1 = R^2 = R^3 = H$, $R^4 = Me$
2 $R^1 = H$, $R^2 = R^3 = R^4 = Me$
3 $R^1 = R^2 = R^3 = R^4 = Me$
4 $R^1 = R^2 = R^3 = Ac$, $R^4 = Me$

confirmed by partial methylation of **1** with diazomethane giving decussatin (**2**) [5] and total methylation with dimethylsulphate–potassium carbonate, leading to the trimethylether derivative (**3**) which was found to be identical with 1,3,7,8-tetramethoxyxanthone in all aspects [6]. This system was newly confirmed by the presence of one pair of each of the *ortho* and *meta*-coupled protons in two different aromatic rings, as evidenced from the ^{1}H NMR spectrum of **1** which showed aromatic protons exhibiting *meta* split doublets centred at δ6.28 (J = 2.1 Hz) and *ortho* split doublets at δ7.14, 7.40 (J = 8.5 Hz), besides the singlets at δ3.95 (3H) and δ11.63 (1H) due to the methoxy and chelated hydroxyl groups. The methoxy group at C-1 or C-8 is strongly indicated by the loss of water from the $[M]^+$ as base peak, due to the operation of an *ortho*-effect caused by a methoxyl substituent at the *peri* position relative to the carbonyl [7]. The absence of a shift of the UV maxima with sodium acetate–boric acid and its high stability in alkali eliminated the possibility of two *ortho* hydroxyl substitutions [8]. Thus, the methoxyl group must be located at the C-8 position, leaving the C-1, C-3 and C-7 positions for the additional hydroxyl groups.

The mass spectrum showed an $[M]^+$ at m/z 274 (69%) as well as significant peaks at m/z 245 ($[M-CHO]^+$, 21%), 244 ($[M-CH_2O]^+$, 16%), 231 ($[M-C_2H_3O]^+$, 55%) and 123 ($[M-CO]^{2+}$, 22%) which are in accordance with the proposed structure. On the basis of these studies and biogenetic considerations [9] we are proposing the structure 1,3,7-trihydroxy-8-methoxyxanthone for compound **1**.

EXPERIMENTAL

For general methods see refs [1, 3], which contain details of other components of the two plant species. Xanthone **1** was isolated from *H. leiantha* (Benth.) Benth. [1] by silica gel chromatography of the B-5 and B-6 fractions (2, 1 g) and from *H. paniculata* (Mart.) Benth. by silica gel chromatography of the remaining groups of fractions (A-17) (1.4 g), which were not studied before [3]. In both cases recrystallization in EtOH was necessary.

1,3,7-*Trihydroxy*-8-*methoxyxanthone* (**1**). Yellow crystals, mp 250–252° (EtOH). UV λ_{max}^{EtOH} nm: 242, 264, 322, 383 (ε resp. 31 400, 35 800, 21 000, 13 700); $\lambda_{max}^{EtOH+NaOH}$ nm: 251, 280, 356 (ε resp. 35 100, 34 900, 28 800)—acidification restored the spectrum in EtOH; $\lambda_{max}^{EtOH+NaOAc}$ nm: 239, 265, 361 (ε resp. 35 400, 27 700, 21 900); $\lambda_{max}^{EtOH+NaOAc+H_3BO_3}$ nm: identical to the spectrum in EtOH; $\lambda_{max}^{EtOH+AlCl_3}$ nm: 238, 265, 276 sh, 333 (ε resp. 32 900, 32 300, 27 000, 22 500); $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm: identical to the spectrum in EtOH + $AlCl_3$. IR ν_{max}^{KBr} cm^{-1}: 3425–3325, 1640, 1595, 1500, 1300, 1170, 1150, 1060, 945, 835, 815. ^{1}H NMR [$(CD_3)_2CO$]: δ11.63 (1H, *s*, OH-1), 3.95 (3H, *s*, OMe-8), 6.27 (1H, *d*, J = 2.1 Hz, H-2), 6.29 (1H, *d*, J = 2.1 Hz, H-4), 7.14 (1H, *d*, J = 8.5 Hz, H-5), 7.40 (1H, *d*, J = 8.5 Hz, H-6). MS m/z (rel. int.): 274 $[M]^+$ (69), 256 $[M-H_2O]^+$ (100), 245 $[M-CHO]^+$ (21), 244 $[M-CH_2O]^+$ (16), 231 $[M-CO-Me]^+$ (55), 123 $[M-CO]^{2+}$ (22). (Found: C, 61.12; H, 3.61. $C_{14}H_{10}O_6$ requires: C, 61.32; H, 3.67%).

1-*Hydroxy*-3,7,8-*trimethoxyxanthone* (**2**). A soln of **1** (50 mg) was methylated with CH_2N_2 in Et_2O soln giving **2** as yellow needles, mp 149–151° (HOAc) (lit. [10] 149–150°). UV λ_{max}^{EtOH} nm: 242, 262, 313, 379 (ε resp. 19 500, 26 300, 14 450, 5700); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 238, 268, 275, 325 (ε resp. 20 300, 19 000, 18 500, 15 200); IR ν_{max}^{KBr} cm^{-1}: 3480–3330, 1650, 1600, 1555, 1475, 1375, 1305, 1270, 1215, 1200, 1100, 1055, 965, 950, 825, 805; ^{1}H NMR ($CDCl_3$): δ13.30 (1H, *s*, OH-1); 3.89, 3.94, 4.01 (all *s*, 9H, OMe-3, 7 and 8), 6.33 (2H, *d*, J = 2.5 Hz, H-2 and H-4); 7.14 (1H, *d*, J = 8.5 Hz, H-5), 7.35 (1H, *d*, J = 8.5 Hz, H-6). MS m/z (rel. int.): 302 $[M]^+$ (100), 287 $[M-Me]^+$ (15), 273 $[M-CHO]^+$ (22), 272 $[M-CH_2O]^+$ (10), 259 $[M-CO-Me]$ (35).

1,3,7,8-*Tetramethoxyxanthone* (**3**). A soln of **1** (50 mg) was methylated with Me_2SO_4–K_2CO_3, yielding **3** as colourless needles, mp 165–167° (MeOH) (lit. [6] mp 165°). UV λ_{max}^{EtOH} nm: 242, 252, 303, 351 (ε resp. 33 500, 36 200, 16 100, 4900). IR ν_{max}^{KBr} cm^{-1}: 2940, 1655, 1600, 1570, 1210, 1155, 1095, 965. ^{1}H NMR ($CDCl_3$): δ3.90, 3.97, 4.03 (all *s*, 12H, 4 × OMe), 6.32 (1H, *d*, J = 2.5 Hz, C-2), 6.41 (1H, J = 2.5 Hz, C-4); 7.11 (1H, J = 9.0 Hz, C-5), 7.27 (1H, J = 9.0 Hz, C-6).

1,3,7-*Triacetoxy*-8-*methoxyxanthone* (**4**). Treatment of **1** (50 mg) with Ac_2O–pyridine at room temp for 12 hr yielded the triacetate (**4**) (40 mg) as colourless needles, mp 168–170°. UV λ_{max}^{EtOH} nm (ε) 232, 268, 335 (ε resp. 38 000, 13 600, 6000) unmodified by use of $AlCl_3$ or NaOAc as additives. IR ν_{max}^{KBr} cm^{-1}: 1780, 1760, 1665, 1610, 1590, 1480, 1425, 1360, 1200, 1180, 1120, 1050, 900, 890. ^{1}H NMR ($CDCl_3$): δ2.34 (6H, *s*, 2 × OAc), 2.49 (3H, *s*, OAc), 3.93 (3H, *s*, OMe), 6.80 (1H, *d*, J = 2.5 Hz, C-2), 7.20 (1H, *d*, J = 2.5 Hz, C-4), 7.22 (1H, *d*, J = 9.0 Hz, C-5), 7.24 (1H, *d*, J = 9.0 Hz, C-6). MS m/z (rel. int.): 400 ($[M]^+$, 1), 358 ($[M-C_2H_2O]^+$, 10), 316 ($[M-2\times C_2H_2O]^+$, 12). (Found C, 60.51, H, 4.06, $C_{20}H_{16}O_9$ requires C, 60.0, H = 4.03%).

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