(4H, overlapping, H-2, 3, 4, 5), 3.66 (1H, *dd*, $J = 12.3$, 2.6 Hz, H-6a), 3.69 (3H, *s*, OMe), 3.80 (6H, *s*, OMe × 2), 3.92 (1H, *dd*, $J = 12.3$, 5.3 Hz, H-6b), 4.82 (1H, *d*, $J = 7.6$ Hz, H-1), 6.48 (2H, *s*, H-2′, 6′).

Acetylation of **3**. Compound **3** (10 mg) was treated with Ac_2O–pyridine for 24 hr at room temp. to afford a tetraacetate. Amorphous yellow powder, 5.9 mg, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3054, 1760, 1600, 1510, 1220; EIMS *m/z*: 514 $[M]^+$, 331, 184, 169; ^1H NMR ($CDCl_3$): δ 2.03–2.08 (each 3H, *s*, OCOMe × 4), 3.79 (3H, *s*, OMe), 3.83 (6H, *s*, OMe × 2), 3.85 (1H, *m*, H-5), 4.25 (1H, *dd*, $J = 12.3$, 5.3 Hz, H-6a), 4.29 (1H, *dd*, $J = 12.3$, 2.6 Hz, H-6b), 5.04 (1H, *d*, $J = 7.6$ Hz, H-1), 5.15 (1H, *dd*, $J = 9.3$, 7.6 Hz, H-2), (1H, *dd*, $J = 9.3$, 9.3 Hz, H-4), 5.30 (1H, *dd*, $J = 9.3$, 9.3 Hz, H-3), 6.27 (2H, *s*, H-2′, 6′).

Acid hydrolysis of compound **3**. Compound **3** (20 mg) was treated with 3% HCl for 1.5 hr at 80–90° to afford D-glucose and 3,4,5-trimethoxyphenol. D-Glucose was identified by TLC comparison with an authentic sample. 3,4,5-Trimethoxyphenol, amorphous white powder, 5.4 mg, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 3320, 1605, 1515, 1480, 1210, 1138; EIMS *m/z*: 184 $[M]^+$, 169, 141; ^1H NMR ($CDCl_3$): δ 3.78 (3H, *s*, OMe), 3.82 (6H, *s*, OMe × 2), 6.09 (2H, *s*, H-2, 6).

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ANTHAXANTHONE, A 1,3,7,8-TETRAOXYGENATED XANTHONE FROM *HAPLOCLATHRA LEIANTHA*

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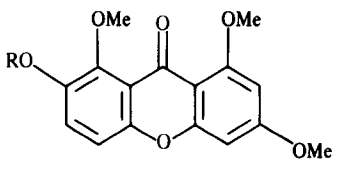
Key Word Index—*Haploclathra leiantha*; Guttiferae; trunk wood; 7-hydroxy-1,3,8-trimethoxyxanthone; anthaxanthone.

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

INTRODUCTION

In connection with our work in trunk wood of *Haploclathra leiantha* (Benth) Benth, we undertook investigation of other fractions from this species. Previously, the isolation of 'Leiaxanthone' was reported from this Laboratory, besides several known xanthones (see Experimental part of ref [1]). Now we are describing the isolation and characterization of a new 1,3,7,8-tetraoxygenated xanthone, for which we give the trivial name 'anthaxanthone'. 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.



	R
1	H
2	Me
3	Ac

RESULTS AND DISCUSSION

Anthaxanthone (**1**) obtained from the polar fraction by CC6 column chromatography was crystallized from ethanol as yellow crystals mp 202–204°. On the basis of elementary analysis and mass spectrometry, the molecular formula was assigned as $C_{16}H_{14}O_6$.

The UV spectrum of **1** showing λ_{max} at 240, 259, 313 and 370 (ε respectively 21 900, 23 700, 10 900 and 5300) is characteristic of a 1,3,7,8-tetraoxygenated xanthone [2]. The presence of the 1,3,7,8-tetraoxygenated system was confirmed by methylation of (**1**) with ether solution of diazomethane. The monomethyl ether (**2**) was found to be identical with 1,3,7,8-tetramethoxyxanthone in all aspects [3]. Hence the xanthone **1** was a hydroxy-trimethoxyxanthone. The hydroxyl group was suggested to be located at C-7 in view of their UV maxima being unaffected in ethanolic sodium acetate and aluminium chloride.

The presence of 1,3,7,8-tetraoxygenated system was newly confirmed by the presence of one pair of each of *ortho*-coupled and *meta*-coupled protons in two different aromatic rings evidenced from the ^{1}H NMR of **1** which showed four aromatic protons exhibiting *meta* split doublets at δ6.42, 6.54 (J = 2.5 Hz) and δ7.09, 7.30 (J = 9.0 Hz), besides the singlets at δ3.84, 3.91 (9 H) due to the methoxyl groups. The phenolic hydroxyl group appeared at δ9.34 in accordance with a hydroxyl group at C-2 or C-7 positions which contain OR substituent at C-1 or C-8 position respectively [4]. Acetylation of **1** caused a 0.16 and 0.25 downfield shift [5, 6] of the H-5 and H-6 signals in the ^{1}H NMR spectrum (related to its position in compound **1**) due to an anisotropic effect of the acetate carbonyl group. However, meta coupled protons remain unaffected. Thus the hydroxyl group is confirmed at the C-7 position.

The mass spectrum showed a dominant molecular ion peak in 302 (100%), as well as significant ion peaks of fragments at m/z 301 (M − 1, 12%), 287 (M − Me, 28%), 285 (M − OH, 19%), 284 (M − H_2O, 56%), 259 (M − C_2H_3O, 45%) which agree with the proposed structure. The loss of water from the molecular ion is due to the operation of an *ortho*-effect caused by the OMe substituent at C-8 [7]. On the basis of these studies and biogenetic considerations [8] we are proposing the structure 7-hydroxy-1,3,8-trimethoxyxanthone for compound **1**.

EXPERIMENTAL

For this experimental part, see ref. [1], which contains other components of this plant. From the 2.4 g of the B_8 fraction was isolated by chromatography in CCG polyamide, 3-hydroxy-1,5,6-trimethoxyxanthone as described before [1]. Reinvestigation of the other group of fractions from the same chromatographic separation yielded xanthone **1** after washing with chloroform and subliming.

7-Hydroxy-1,3,8-trimethoxyxanthone (**1**). Crystallized from EtOH as yellow crystals, mp 202–204°. UV λ_{max}^{EtOH} nm (ε): 240, 259, 313, 370 (ε resp. 21 900, 23 700, 10 900, 5300); $\lambda_{max}^{EtOH+NaOH}$ nm (ε): 249 *sh*, 273, 311 (ε resp. 19 200, 25 000, 14 500) acidification restored the spectrum in EtOH; $\lambda_{max}^{EtOH+NaOAc}$ and $\lambda_{max}^{EtOH+AlCl_3}$ nm (ε): identical to the spectrum in EtOH; IR ν_{max}^{KBr} cm^{-1}: 3275, 1625, 1590, 1500, 1290, 1160, 1110, 1070, 985, 950, 820. ^{1}H NMR (DMSO-d_6, 60 MHz): δ3.84 (3H, *s*, OMe-3); 3.91 (6H, *s*, OMe-1 and 8); 6.42 (1H, *d*, J = 2.5 Hz, C-2); 6.54 (1H, *d*, J = 2.5 Hz, C-4); 7.09 (1H, *d*, J = 9.0 Hz, C-5); 7.30 (1H, *d*, J = 9.0 Hz, C-6); 9.34 (1H, *s*, OH-7). MS m/z (rel. int.): 302 ([M]$^+$, 100), 301 ([M − 1]$^+$, 12), 287 ([M − Me]$^+$, 28), 285 ([M − OH]$^+$, 19), 284 ([M − H_2O]$^+$, 56), 259 ([M − C_2H_3O]$^+$, 45). (Found: C, 63.62; H, 4.70, $C_{16}H_{14}O_6$ requires C, 63.57; H 4.67%.)

1,3,7,8-Tetramethoxyxanthone (**2**). A soln of **1** (30 mg) was methylated with CH_2N_2 in ether soln giving (**2**) as colourless needles, mp 165–167° (lit [3] mp 165°) UV λ_{max}^{EtOH} nm (ε): 242, 252, 303, 351 (ε resp. 33 500, 36 200, 16 100, 4900), 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). (Found: C, 64.19; H, 5.15, $C_{17}H_{16}O_6$ requires C, 64.55; H, 5.10%.)

7-Acetoxy-1,3,8-trimethoxyxanthone (**3**). Treatment of **1** (30 mg) with Ac_2O–pyr at room temp. for 24 hr yielded the monoacetate (**3**) (25 mg) which was crystallized from EtOH as slightly yellow needles, mp 186–188°. UV λ_{max}^{EtOH} nm(ε): 248, 305, 345 (ε resp. 26 000, 13 800, 7700). IR ν_{max}^{KBr} cm^{-1}: 1760, 1655, 1610, 1460, 1210, 1100, 890. ^{1}H NMR (DMSO-d_6): δ2.29 (3H, *s*, OAc), 3.76 (3H, *s*, OMe-6), 3.84 (3H, *s*, OMe-8), 3.86 (3H, *s*, OMe-1), 6.48 (1H, *d*, J = 2.5 Hz, C-2), 6.60 (1H, *d*, J = 2.5 Hz, C-4), 7.25 (1H, *d*, J = 9.0 Hz, C-5), 7.55 (1H, *d*, J = 9.0 Hz, C-6). MS m/z (rel. int.): 344 ([M]$^+$, 10), 302 ([M − C_2H_2O]$^+$, 21), 301 ([M − C_2H_3O]$^+$, 48). (Found C, 62.52; H, 4.68. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.65%.)

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