SHORT PAPER

J. Chem. Research (S), 2003, 362–363

A new naturally occurring xanthone bearing rare oxygenation pattern from *Hoppea fastigiata*†

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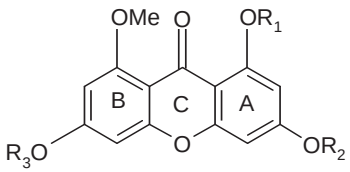
A new xanthone 1,3,6-trihydroxy-8-methoxyxanthone, was isolated from chloroform extract of the whole plant of *Hoppea fastigiata* and the structure was elucidated on the basis of spectroscopic and chemical studies. The xanthone molecule has an unusual oxygenation pattern (1,3,6, 8) and is of chemotaxonomic interest.

Keywords:*Hoppea fastigiata*; Gentianaceae; 1,3,6-trihydroxy-8-methoxyxanthone; structure elucidation

Previous phytochemical investigations of *Hoppea fastigiata* clarke (Gentianaceae), a useful medicinal plant[1], have already led to the isolation of several novel xanthones[2a,b,c]. We now report the isolation and characterisation of one more new xanthone from the same plant. This xanthone bears a rare oxygenation pattern (1,3,6, 8) and is of chemotaxonomic interest.

Results and discussion

Compound **1**, $C_{14}H_{10}O_6$ ($[M]^+$ at *m/z* 274), exhibited UV absorption bands at λ_{max} (MeOH) nm(logε) 216 (4.28), 246 (4.61), 306 (3.85) and 340(2.95),which are characteristic of tetra- oxygenated xanthones.[3a,b,c] The UV spectrum showed a remarkable bathochromic shift of the longer wave length maximum by 22 nm (340–362nm) upon addition of $AlCl_3$. This remained unchanged on addition of hydrochloric acid suggesting the presence of a OH group *peri* to carbonyl group, *i.e.* an OH group at C-1 or C-8 position.[4] Furthermore, the compound **1** was found to be soluble in 5% Na_2CO_3 solution and the UV band at higher wave length maximum also showed a bathochromic shift by 17 nm (340–357nm) in ethanolic NaOAc indicating the presence of free hydroxyl group(s) at C-3 and /or C-6 positions.[4,5a,b] As expected for a xanthone skeleton, the IR spectrum (**1**)· Showed significant absorption peaks at ν_{max} (KBr)/cm^{-1} 3340 (broad chelated hydroxyl), 1645, 1595, 1565, 1495 (chelated α,β-unsaturated carbonyl conjugated with aromatic nucleus), 2840 and 956 (methoxyl) and 785 and 715(*meta*–disubstituted benzene rings). The tetra-oxygenated pattern was substantiated by its ^{1}H NMR spectrum which contained four *meta* coupled doublets were appeared for four aromatic protons at δ 6.30, 6.55, 7.55 and 7.65 (*J*=1.5 Hz for each doublet). Besides a singlet for three protons at δ 3.95 due to a methoxyl function and also a singlet at δ 11.83 due to the phenolic hydroxyl (at C-1 or C-8) no other proton appeared in the ^{1}H NMR spectrum of compound **1**. The EIMS fragmentation pattern was in conformity with the presence of trihydroxy–monomethoxy xanthone skeleton[6] in the molecule. The appearance of four aromatic protons as four different *meta* split doublets in the ^{1}H NMR spectrum of xanthone **1** is indicative of four oxygen functions (three hydroxyls and one methoxyl) distributed in both rings in a 1,3-relationship. On methylation with diazomethane compound **1** yielded a dimethyl derivative **2**, which was found to be identical with 1-hydroxy-3,6,8-trimethoxyxanthone in all respect.[5a] Formation of the dimethyl derivative **2** confirmed the oxygenation pattern of compound **1**, as well as the position of the chelated hydroxy group at C-1 and the methoxy group at C-8. Consequently, the remaining two hydroxyl functions present in the molecule of xanthone **1** must be located at the C-3 and C-6 positions. Thus, the new xanthone **1** was characterised as 1,3,6-trihydroxy-8-methoxy xanthone. This formulation received further support from its conversion to its permethyl derivative **3** identified as 1,3,6,8-tetramethoxyxanthone by comparison of physical and spectral data with that in the literature.[4,5a]



1. R_1 = R_2 = R_3 = H

2. R_1 = H, R_2 = R_3= Me

3. R_1 = R_2 = R_3 = Me

Experimental

Plant materials: Whole plants of *Hoppea fastigiata* were collected from Santiniketan and taxonomically authenticated by a taxonomist of the Botany Department of this University. A herbarium specimen is deposited in the Natural Product Laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan (W.B.). All m.p.s are uncorrected; UV: MeOH; IR: KBr; ^{1}H NMR: 90 MHz, CD_3COCD_3, TMS as int.standard; CC: silica gel (60–120 mesh): mass spectra under electron impact at 70 eV.

Isolation: Air-dried powdered whole plants (1.5 kg) of *Hoppea fastigiata* were extracted with chloroform in a Soxhlet apparatus for 54 hours. The extract was concentrated under reduced pressure and the solid mass obtained was subjected to CC over Si-gel (60–120 mesh); the benzene eluent afforded xanthone **1**.

Compound **1** *(1,3,6-trihydroxy-8-methoxy xanthone)*:Golden yellow plates (yield,0.472g) crystallised from EtOH ; responded positively towords Gibb's test and $FeCl_3$ test; m.p. 240–242°C (Anal. Calcd for $C_{14}H_{10}O_6$: C,61.31; H,3.64. Found: C,61.28; H,3.61%); UV (MeOH) and IR(KBr) data are described in the text;^{1}H NMR (90 MHz, CD_3COCD_3) : δ3.95 (s,3H,C_8-OCH_3), 6.30(d,1H,*J*=1.5Hz,H-4), 6.55 (d,1H,*J*=1.5Hz,H-2), 7.55 (d, 1H, *J*=1.5Hz,H-5), 7.65 (d,1H, *J*=1.5Hz,H-7), 11.83 (s,1H, C_1-O*H*); EIMS *m/z* (intensity %): 274 $[M]^+$ (10.5), 259 $[M–Me]^+$ (13.6), 258 $[M–Me–H]^+$ (100), 257 $[M–OH]^+$ (13.8), 256 [M–OH–H]$^+$ (15.9), 245 [M–CO–H]$^+$ (11.2), 244 [245-H] $^+$ (16.9), 230 $[M–Me–CO–H]^+$ (9.7), 229 [M–Me–CO–2H]$^+$ (71.4), 202 [230 – CO]$^+$(5.8), 201 [202 – H]$^+$(12.6).

Methylation of compound ***1*** *with diazomethane :* Xanthone **1** (100mg) was dissolved in methanol and an ether solution of diazomethane (200 ml) was slowly added keeping the temperature at 5°C. The reaction mixture was left for 24 hours at 5°C. A solid was obtained on removal of the solvent, and crystallised from ethanol to

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

give 1-hydroxy-3,6,8-trimethoxyxanthone **2** (yield,77 mg), $C_{16}H_{14}O_6$, $[M]^+$ at *m/z* 302; m.p. 169–172° C; green colour with $FeCl_3$; UV: λ_{max} (MeOH) nm 236, 260, 300, 315, 365; IR: ν_{max} (KBr)/cm^{-1} 3400, 2969, 1650, 1600, 1585, 1560, 1480, 1030, 1000, 970, 910, 780, 710; ^1H NMR (90 MHz, CD_3COCD_3) : δ3.85(s,3H), 3.91(s,3H), 3.95 (s,3H), 6.41(s,1H), 7.52 (s,2H), 7.7 (s,1H), 12.2 (s,1H) [data comparable with those as reported[5a]].

Methylation of compound **1** *with* Me_2SO_4 : Compound **1** (150 mg) was dissolved in Me_2CO (175 ml) and K_2CO_3 (3.0 g) was added before the addition of Me_2SO_4 (8.5ml). The mixture was boiled on a water bath for 40 hours, the suspension filtered and the filtrate evaporated to yield a solid which was purified by preparative TLC to give 1,3,6,8-tetramethoxyxanthone **3** (yield,121mg), $C_{17}H_{16}O_6$,$[M]^+$ at *m/z* 316; m.p.133–135°C; no colour with $FeCl_3$; UV: ν_{max} (MeOH) nm 240, 256, 280, 312, 348; IR: ν_{max} (KBr)/cm^{-1} 2940, 1648, 1600, 1575, 1565, 1480, 970, 910, 780, 715; ^1H NMR (90 MHz, CD_3COCD_3) : δ 3.91(s,6H), 3.98 (s,6H), 6.71 (s,1H),7.21(s,2H), 7.72 (s,1H) [data comparable to those reported[5a]].

The authors are grateful to RSIC, IIT, Chennai and RSIC,CDRI, Lucknow for spectral measurements and to Dr H. R. Chowdhury, Department of Botany, Visva-Bharati for identification of the plant. Financial support from the Visva-Bharati University is also deeply acknowledged.

Received 15 November 2002; accepted 8 January 2003
Paper 02/1679

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