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XANTHONES OF *SWERTIA BIMACULATA**

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Key Word Index—*Swertia bimaculata*, Gentianaceae; tetra- and penta-oxygenated xanthones, 1,3,5-trimethoxy-8-hydroxyxanthone, 1,4-dihydroxy-2,3,7-trimethoxyxanthone, 1,3-dihydroxy-4,5,8-trimethoxyxanthone, xanthone *O*-glycosides

Abstract—The whole plant of *Swertia bimaculata* Hf. & T. has been shown to contain four tetra- and five penta-oxygenated xanthones, three of which are previously unreported in nature. The xanthones are broadly based on 1,3,5- and 1,3,7-oxygenated systems with added oxygen functions at C_2, C_4 and/or C_8 positions and represent a number of methoxylated patterns. In addition, three xanthones have been found to be present in a bound form, the sugar moiety containing glucose and glucuronic acid. This is the first demonstration of the occurrence of xanthones and xanthone disaccharides in a *Swertia* species which are common to both *Swertia and Frasera* species. The results are thus of considerable phylogenetic significance.

INTRODUCTION

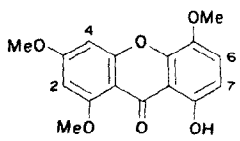
Swertia bimaculata Hf. & T. (Gentianaceae), native to the mountains of the Eastern Himalayas, is a tall flowering species and differs considerably in its form from the smaller members of the genus, e.g. *S. lawii* [1] and *S. purpurascens* [2]. Previously, Inouye *et al* [3] reported 1,3-dihydroxy-4,5-dimethoxyxanthone and its 1- and 3-*O*-glucosides in this species. The present investigation with the whole plant resulted in the isolation and structure elucidation of a number of tetra- and penta-oxygenated xanthones and xanthone-*O*-glycosides previously unreported in this species as well as in this genus.

RESULTS AND DISCUSSION

Preliminary examination of the petrol and EtOH extracts of the roots of *S. bimaculata* by analytical TLC showed the presence of well over a dozen xanthones of varying polarity. The TLC patterns of these constituents and those obtained from the aerial portions did not show any significant qualitative difference. The whole plant was therefore used for the detailed chemical investigation.

From the whole plant, four tetra- and five penta-oxygenated xanthones were isolated in quantities sufficient for their complete characterization. Chemical transformation, spectral (UV, IR, PMR, MS) properties and comparison with reference samples, where available, established their structures as: 1,3-dihydroxy-4,5-dimethoxyxanthone (**1**); 1,8-dihydroxy-3,5-dimethoxyxanthone (**2**); 1,3,5-trimethoxy-8-hydroxyxanthone (**3**); 1-hydroxy-3,7,8-trimethoxyxanthone (**4**); 1-hydroxy-2,3,4,5-tetramethoxyxanthone (**5**); 1-hydroxy-2,3,4,7-tetramethoxyxanthone (**6**); 2-hydroxy-1,3,4,7-tetramethoxyxanthone (**7**); 1,4-dihydroxy-2,3,7-trimethoxyxanthone (**8**); 1,3-dihydroxy-4,5,8-trimethoxyxanthione (**9**). In addition, xanthones (**1**), (**2**) and (**8**) were found to be present in a bound (*O*-disaccharide) form in which the glycosidic linkage was located at C_1 position. Acid hydrolysis of the glycosides yielded the corresponding xanthones, glucose and another sugar

* Part 18 in the series "Chemical Constituents of Gentianaceae" For Part 17 see Chaudhuri, R K, Singh, A K and Ghosal, S (1975) *Chem Ind* (*Lond*) 127



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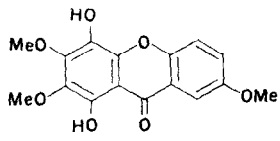

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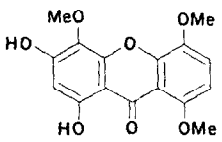

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whose PPC and TLC characteristics were very similar to those of glucuronic acid Xanthones (**8**) and (**9**) were not encountered before in nature or prepared synthetically, while (**3**) was known before only as a synthetic compound. The characterization of only the new naturally occurring xanthones is described here

1,3,5-*Trimethoxy*-8-*hydroxyxanthone* (**3**). This xanthone, mp 215–216°, $C_{16}H_{14}O_6$ (M^+, 302), is a monohydroxytrimethoxyxanthone in which the hydroxyl group is strongly chelated since it remained unaffected with ethereal diazomethane but formed the permethyl ether with dimethyl sulphate and alkali. Its UV spectrum is characteristic of 1,3,5,8-tetraoxygenated xanthones [2] The PMR spectrum of the compound showed signals due to a chelated OH group, located either at C_1 or C_8 [4], three OMe groups, and four aromatic protons appearing as two pairs of doublets with J's of 3 and 9 Hz. These data suggest either 1-hydroxy-3,5,8-trimethoxyxanthone or 1,3,5-trimethoxy-8-hydroxyxanthone as its structure Comparison with the former compound [5] showed that they were different although their permethyl ether was identical. Finally, direct comparison of the xanthone with the aglucone (1,3,5-trimethoxy-8-hydroxyxanthone) of isoswertianolin [6] confirmed their identity

1,4-*Dihydroxy*-2,3,7-*trimethoxyxanthone* (**8**) This xanthone, mp 160–161°, (M^+, 318), is a dihydroxytrimethoxyxanthone in which one of the OH groups may be placed at C_1 since its PMR spectrum showed a chelated OH group and the UV spectrum is characteristic of 1,2,3,4,7-pentaoxygenated xanthones [7]. The chromophoric and $NaOAc-H_3BO_3$ but was destroyed in presence of EtOH–NaOH indicating the presence of a *para* dihydroxyl function. The xanthone responded to the goss-ypetone [8] and Tollens tests The two OH groups are therefore located at C_1 and C_4. In the PMR spectrum, a coupled set of three protons appeared in the aromatic region indicating the presence of a C_7-oxy substituent [7] The chemical shifts of these protons remained unaltered in the corresponding acetyl derivative The C_7 position is therefore methoxylated Selective demethylation of 1-hydroxy-2,3,4,7-tetramethoxyxanthone with DDQ [9] afforded 1,4-dihydroxy-2,3,7-trimethoxyxanthone together with 1,2-dihydroxy-3,4,7-trimethoxyxanthone (as a minor entity) [10] The major product was found to be identical with naturally occurring (**8**)

1,3-*Dihydroxy*-4,5,8-trimethoxyxanthone (**9**). This xanthone, mp 210–212°, $C_{16}H_{14}O_7$ (M^+, 318), is also a dihydroxytrimethoxyxanthone in which one of the OH groups may be placed at C_1 since the PMR spectrum showed a strongly chelated OH group and the UV spectrum is closely similar to that of 4,5-di-*O*-methylcorymbin (= 1,3,8-trihydroxy-4,5-dimethoxyxanthone) [11]. It was soluble in aq. Na_2CO_3 and showed a bathochromic shift in the UV maxima (λ 300 and 350 → 372 nm) in presence of NaOAc The second OH group is therefore located at C_3. The PMR spectrum showed signals due to three OMe groups, an aromatic proton singlet (δ 6.4) and a pair of doublets (J 9 Hz) The high-field position of the singlet suggests C_2-H as its source. The monomethyl ether, prepared with ethereal diazomethane, was found to be identical in all respects with 1-hydroxy-3,4,5,8-tetramethoxyxanthone [2]. These data suggest 1,3-dihydroxy-4,5,8-trimethoxyxanthone as the structure for (**9**)

The oxygenation patterns of the xanthones of some 15 *Swertia* species investigated so far are the very common ones of 1,3,5,8 and 1,3,7,8 tetraoxygenated systems (as the hydroxylated and methoxylated derivatives) [1] In two *Swertia* species, viz *S. lawii* and *S. purpurascens*, in addition to the tetraoxygenated xanthones, a number of 1,3,4,5,8- and 1,3,4,7,8-pentaoxygenated xanthones were encountered [1,2] These observations indicate a close relationship between the genera *Swertia* and *Gentiana*, the latter also liber-

genated xanthones. Also, interestingly, the "standard" 1,3,5- and 1,3,7-trioxygenated xanthones [7,12] are missing from members of both the genera with the sole exception of *Gentiana lutea* which produces 1,3,7-trioxygenated xanthones in lieu of the tetra- and penta-oxygenated ones. The genus *Swertia* was, however, initially often combined with *Frasera* [13] but was later separated from it on the basis of difference in the oxygenation patterns of their contained xanthones [7,14,15]. A number of other taxonomic differences were also cited [7,16] to support this separation. Investigation with about half-a-dozen *Frasera* species [7,14] yielded the "standard" 1,3,5- and 1,3,7-trioxygenated xanthones and xanthones with added oxygen functions at C_2 and/or C_4. The oxygenation patterns of xanthones of the *Frasera* were thus known to be significantly different from those of the *Swertia* until this investigation. The present investigation has demonstrated for the first time the occurrence in *S. bimaculata* of xanthones which bear characteristics of both *Swertia* (1,3,5,8- 1,3,7,8- and 1,3,4,5,8-oxygenated systems) and *Frasera* (1,3,4,5- 1,2,3,4,5- and 1,2,3,4,7-oxygenated systems) species Additionally, the occurrence of xanthone *O*-disaccharides in *S. bimaculata* finds precedent in the genus *Frasera* [14]. In other *Swertia* species, the occurrence of only xanthone-*O*-monosaccharides has been reported [6]. However, one notable difference between the xanthones of *S. bimaculata* and those of the *Frasera* is the large abundance of C_8-oxygenated xanthones in the former species. In this respect, *S. bimaculata* is closer to the parent genus

EXPERIMENTAL

The general descriptions are same as reported in a recent paper [6]

Isolation of xanthones from S bimaculata. Dried and milled whole plants* (2 kg) were continuously extracted in a Soxhlet with light petrol (60–80°) and then with EtOH (24 hr, each) The 2 extracts were separately processed

Treatment of the petrol extract The petrol extract was concentrated (*ca* 500 ml) and the concentrate was kept overnight at room temp when a dull yellow solid (Fraction A, 8 2 g) separated The solid was collected by filtration and the petrol mother liquor was evaporated to give a greenish–brown gum (Fraction B, 154 g)

Separation of xanthones from Fraction 4 A portion of the solid (3 g) was mixed with equal amount of Si gel (BDH, 60–120 mesh) and was placed over a column of Si gel (3 × 24 cm) C_6H_6 and $CHCl_3$ (6 1 each) were used as eluents Fractions (500 ml) were collected Fractions 2–4 gave a complex mixture of triterpenes and sterols and only traces of xanthones and were not processed further at this stage Fractions 8–20, containing appreciable quantity of a mixture of xanthones, were combined, concentrated and rechromatographed. Petrol (500 ml), petrol–C_6H_6 (1 1, 1 1), C_6H_6 (5 1) and $CHCl_3$ (5 1) were used as eluents Fractions (100 ml) were collected The total petrol and early petrol–C_6H_6 eluates showed spots on TLC due to 1 major and 2 minor xanthones

1-*Hydroxy*-2,3,4,7-*tetramethoxyxanthone* (**6**) The major xanthone was purified by repeated crystallization of the mixture from EtOH 1-Hydroxy-2,3,4,7-tetramethoxyxanthone was obtained as bright yellow needles (138 mg), mp 116–117° [Lit [7] mp 116 7–117 7°], R_f 0 73 (C_6H_6–AcOH, 50 1), UV λ_{max} 235 (0 61), 270 (0 74), 303 (0 25), 390 nm (0 14), PMR ($CDCl_3$) δ 12 64 (1H, *s*, C_1-OH), 7 61 (1H, *q*, H-8), 7 44 (2H, *m*, H-5, H-6), 4 15–3 90 (12H, OMe) (Anal Calc for $C_{17}H_{16}O_7$ C, 61 44, H, 4 81 Found C, 61·03; H, 4 66%) The permethyl ether, prepared with dimethyl sulphate and K_2CO_3 in dry acetone, under reflux (40 hr), crystallized from EtOH as yellow needles, mp 120–121° [Lit [7] mp 122–122 7°]

One of the 2 minor xanthones was separated by repeated PLC and was identified as 1,8-dihydroxy-3,5-dimethoxyxanthone by direct comparison with an authentic sample [2] (mmp, co-TLC, UV)

The later petrol–C_6H_6 and early C_6H_6 eluates showed 3 spots on analytical TLC and were separated by PLC using $CHCl_3$ as the developer

1,3,5-*Trimethoxy*-8-*hydroxyxanthone* (**3**) The upper yellow zone (R_f ~ 0 8) from the PLC yielded 1,3,5-trimethoxy-8-hydroxyanthone as yellow needles (16 mg), mp 215–216° The mmp remained undepressed when admixed with an authentic sample [6] The R_f, UV, PMR, and MS data were also indistinguishable from those of the aglucone of isoswertianolin [6] The permethyl ether, prepared in the usual way, crystallized from EtOH as pale yellow needles, mp 208–210° The mp, mmp and R_f's were identical with those of 1,3,5,8-tetramethoxyxanthone [2, 5]

1,3-*Dihydroxy*-4,5,8-*trimethoxyxanthone* (**9**). The lower brown streak in the PLC zone (R_f ~ 0 8) was cut out, eluted with EtOH and the EtOH solution on concn furnished 1,3-dihydroxy-4,5,8-trimethoxyxanthone as orange–yellow microcrystals (8 mg), mp 210–212°, UV. λ_{max} 232 (0 46), 258 (0 67), 278 (0 34), 300 *sh* (0 089), 350 nm (0 28), PMR ($CDCl_3$) δ 12 74 (1H, C_1-OH), 7 15 (1H, *d*, *J* 9 Hz, H-6), 6 78 (1H, *d*, *J* 9 Hz, H-7), 6 40 (1H, *s*, H-2), 4 02–3 95 (9H, OMe), MS *m/e* 318 (M^+, rel intensity, 100%), significant fragment ion peaks at *m/e* 303 (22), 289 (18), 275 (21) The 3-*O*-methyl ether, prepared with ethereal CH_2N_2, crystallized from EtOH as pale yellow needles, mp 187–188° The mp, mmp, and R_f's were found to be identical with those of 1-hydroxy-3,4,5,8-tetramethoxyxanthone [6]

1-*Hydroxy*-2,3,4,5-tetramethoxyxanthone (**5**) The PLC of the middle layer zone (R_f ~ 0 6) afforded a yellow solid (22 mg) which crystallized from EtOH as needles, mp 147–148° [Lit [7], mp 155–156°], R_f 0 68, UV λ_{max} 220 (0 25), 244 (0 39), 260 (0 50), 275 *sh* (0 33), 318 (0 14), 380 nm (0 09), PMR ($CDCl_3$) δ 12 66 (1H, *s*, C_1-OH), 7 88 (1H, *q*, H-8), 7 34 (2H, *m*, H-6, H-7), 4 1-3 92 (12H, OMe), MS *m/e* 332 (M^+, rel. intensity, 100%), significant fragment ion peaks at *m/e* 317

* The plant material was supplied by Messrs Mukherjee & Co, Kalimpong, India A voucher specimen has been preserved at the Pharmaceutical Chemistry Research Laboratory, Department of Pharmaceutics, Banaras Hindu University, Varanasi

(34) 303 (22), 302 (14), 289 (42) 287 (25), 274 (8), 260 (8), 259 (12) (Anal Calc for $C_{17}H_{16}O_7$ C 61 44, H, 4 81 Found C 60 98, H, 4 49%)

2-Hydroxy-1 3,4 7-tetramethoxyxanthone (**7**) The brown upper streak in the middle PLC zone was dissolved in $CHCl_3$ and the solution was filtered through a small column of Si gel The residue from the $CHCl_3$ soln crystallized from CH_2Cl_2 hexane as fine yellow needles (5 mg), mp 145 146 R_f 0 77, MS *m/e* 332 (M^+ rel intensity 100%) significant fragment ion peaks at *m/e* 317 (28) 303 (18), 289 (35) 260 (12), 259 (6) 150 (5) Correspondence of the above data with those reported for 2-hydroxy-1 3 4 7-tetramethoxyxanthone [7] showed that they are identical

1,4-Dihydroxy-2 3 7-trimethoxyxanthone (**8**) The lower R_f zone (~ 0 2) was eluted with $CHCl_3$, the solvent was removed and the residue crystallized from CH_2Cl_2 hexane as orange needles (24 mg) mp 160 161 , R_f 0 32, UV λ_{max} 236 (0 32), 269 (0 38), 305 (0 12), 392 nm (0 06), PMR ($CDCl_3$) δ 12 05 (1H s C_1-OH) 7 64 (1H, *q* H-8), 7 46 (2H *m*, H-6, H-7), 4 12 4 02 (9H, OMe), MS *m/e* 318 (M^+ rel intensity 100%) significant fragment ion peaks at *m/e* 303 (22) 289 (14), 288 (18), 275 (14), 245 (8), 230 (5) (Anal $C_{16}H_{14}O_7$ requires C, 60 37, H, 4 40 Found C 59 88, H, 4 72%) The monomethyl ether, prepared with ethereal CH_2N_2 was found to be identical with xanthone (**6**) in all respects

1 3-Dihydroxy-4 5-dimethoxyxanthone (**1**) The later C_6H_6 and early $CHCl_3$ eluates afforded a yellow solid which crystallized from EtOH as bright yellow needles (388 mg), mp 262 The mp remained undepressed when admixed with an authentic sample of 1 3-dihydroxy-4 5-dimethoxyxanthone [3], co-TLC in 3 different solvent systems also showed that they are identical The permethyl ether prepared in the usual way, crystallized from C_6H_6 as colourless needles mp and mmp [3] 172 174

Separation of xanthones from fraction B A portion (*ca* 10 g) of the greenish brown gum was dissolved in Et_2O (500 ml) and the phenolic and non-phenolic constituents were separated in the usual way A pale yellow solid separated during the processing at the interface of the Et_2O and aq NaOH layers It was collected by filtration The solid was washed with aq HCl and then with H_2O until the washing was neutral The dull yellow solid crystallized from EtOH to give a further crop (252 mg) of xanthone (**6**), while the EtOH mother liquor on further concn gave yellowish orange crystals containing a mixture of xanthones The phenolic constituents obtained as a dull yellow powder was dissolved in $CHCl_3$ (15 ml) and chromatographed over a column of Si gel (2 × 24 cm) Petrol (500 ml) petrol C_6H_6 (1 1, 2 1) C_6H_6 (1 1) C_6H_6, $CHCl_3$ (1 1, 1 1) and $CHCl_3$ (1 1) were used as eluents Fractions (100 ml) were collected The residue obtained from the petrol and early petrol C_6H_6 eluates was boiled in petrol, the petrol-insoluble solid was dissolved in $CHCl_3$ (15 ml), and was subjected to PLC using $CHCl_3$ HOAc (50 1) as the developer Three distinct zones were separated

1,8-Dihydroxy-3 5-dimethoxyxanthone (**2**) The upper PLC zone (R_f ~ 0 75) was eluted with $CHCl_3$ and the residue from the $CHCl_3$ soln crystallized from EtOH as bright yellow needles (91 mg) mp 183 184 Direct comparison (co-TLC mmp, IR) with an authentic sample of 1,8-dihydroxy-3,5-dimethoxy xanthone established that they are identical

The middle PLC zone (R_f ~ 0 5) gave a further crop (7 mg) of xanthone (**3**)

1-Hydroxy-3 7 8-trimethoxyxanthone (**4**) The lower PLC zone (R_f ~ 0 2) gave 1-hydroxy-3 7 8-trimethoxyxanthone as yellow crystals (12 mg), mp 149 150 The mp, mmp, co-TLC, UV and PMR spectra of the compound were identical with those of decussatin [5]

The brown streaks appeared at the solvent front and base line were eluted with $CHCl_3$ The residue from the $CHCl_3$ soln from each layer showed the presence of a new xanthone the identity of which is being investigated

Treatment of the EtOH extract The EtOH extract was concentrated under reduced pressure to a syrupy liquid It was poured into aq HOAc (4%, 400 ml) The mixture was kept at room temp overnight when a brown amorphous solid separated The clarified acidic aq soln was extracted with Et_2O (10 × 250 ml) and the combined Et_2O extracts was evaporated to give a dull yellow residue (Fraction C, 6 8 g) The aq layer was concentrated (*ca* 100 ml) and extracted with EtOAc (5 × 250 ml) Residue from the combined ethyl acetate extracts a dull yellow solid (fraction D 1 3 g) contained only strongly polar xanthones

Separation of xanthones from fraction C A portion (0 5 g) of the solid was boiled with $CHCl_3$ (250 ml) and the solution was filtered It was concentrated and chromatographed over Si gel (1 2 × 22 cm) Elutions were carried out with C_6H_6, $CHCl_3$ and different proportions of mixtures thereof when further crops of xanthone (**1**) (56 mg) xanthone (**9**) (8 mg), and of mixed xanthones (67 mg) were obtained The $CHCl_3$-insoluble solid showed several spots on TLC in which the presence of xanthones (**1, 5, 6, 8**) as major entities, was detected by co-TLC and UV spectra of the individual entities

Separation of xanthones from fraction D A portion (0 1 g) of the solid was hydrolysed with 2 N HCl (10 ml) for 30 min on a steam bath The hydrolysed product was passed through a column of polyamide powder (1 × 5 cm) packed in H_2O The column was washed with H_2O until the eluate was neutral Subsequently the column was washed with MeOH TLC of the MeOH washings showed the presence of xanthones (**1, 2, 8**) and a strongly polar phenolic compound Preliminary examination of the last named compound showed it to be a xanthone-*C*-glycoside [17] The aq washings were combined neutralized and concentrated at ordinary temperature TLC and PPC [6] of the aq concentrate showed the presence of glucose and another sugar whose R_f values in 3 solvents, were closely similar to those of glucuronic acid Sugars were detected with sodium metaperiodate-benzidine reagent

Another portion of fraction D (0 1 g) was crystallized from MeOH dioxane when yellow crystals (18 mg) separated, mp 268 272 , R_f 0 12 ($CHCl_3$ HOAc, 20 1) Hydrolysis of this compound (5 mg) with emulsin (2 mg) in purified H_2O (5 ml) yielded 1 8-dihydroxy-3 5-dimethoxyxanthone (co-TLC UV) In the aq soln, the presence of glucose and a strongly polar sugar component could be detected only after further hydrolysis with 2 N HCl The residue from the MeOH dioxane mother liquor after separation of the xanthone disaccharide mp 268 272 was methylated with MeI and NaH in tetrahydrofuran at room temp according to the method of Stoochnoff and Benoiton [18] The product was dissolved in $CHCl_3$ and chromatographed over Si gel (1 2 × 22 cm) Elution was carried out with $CHCl_3$ and $CHCl_3$ EtOAc (10 1 to 1 1) Fractions (25 ml) were collected and monitored by TLC Three permethyl ethers (R_f 0 72 0 6 and 0 4 $CHCl_3$ HOAc 50 1) were separated Each was separately hydrolysed with 2 N HCl and extracted with $CHCl_3$ The acid hydrolysed product from the permethyl ether, R_f 0 72 afforded 1-hydroxy-3,5,8-trimethoxyxanthone Likewise the other 2 permethyl ethers R_f 0 6 and 0 4 yielded 1-hydroxy-2 3 4 7-tetramethoxyxanthone and 1-hydroxy-3 4 5-trimethoxyxanthone respectively

Selective demethylation of 1-hydroxy-2 3 4 7-tetramethoxyxanthone with DDQ This xanthone (52 mg) and DDQ (40 mg) were mixed and refluxed in C_6H_6 (10 ml) under N_2 for 3 hr The reaction was cooled filtered and the filtrate was eva-

porated The orange–yellow amorphous powder was boiled with MeOH The residue from the MeOH solution was dissolved in $CHCl_3$ and chromatographed over Si gel (1 5 × 22 cm) The elution was carried out with C_6H_6 and C_6H_6–EtOAc (9 1 to 1 1), 2 l each The C_6H_6–EtOAc (9 1) eluates yielded a yellow solid which was subjected to PLC (C_6H_6–HOAc, 100 3) The upper yellow zone (main band) was eluted with $CHCl_3$ and the solvent was removed The residue crystallized from CH_2Cl_2–hexane as yellow needles (7 mg), mp 159–161° The mp, mmp, co-TLC and UV spectrum of the compound were identical with those of xanthone (**8**) From the lower PLC zone, 1,2-dihydroxy-3,4,7-trimethoxyxanthone was obtained as an orange–yellow solid which crystallized from EtOH as microcrystals (3 mg), mp 234–236° Lack of a reference sample [10] precluded a direct comparison, but correspondence of mp and spectroscopic data (UV, MS) of the compound with the published data established its identity

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