by PC. MS of the aglucone showed retro-Diels-Alder fragments at 152(25.6) and 40(8.4). The peak at *m/e* 164(79.9) is obtained by the loss of CO from the M^+ peak. UV spectrum (λ_{max}^{MeOH} (log ε) 255(4.16), 295(3.91); $AlCl_3$, 262, 306, 365; $AlCl_3$–HCl, 262, 306, 362; NaOAc, 260, 315 nm) of the aglucone suggested the two hydroxyls to be at 5 and 7 positions. The aglucone and its monomethyl ether, mp 119–20° (methylation with CH_2N_2) on degradation with conc KOH gave phloroacetophenone and 4-methylphloroacetophenone, respectively. Thus the structure 2-methyl-5,7-dihydroxychromone can be assigned to the aglucone. It was found to be identical with a synthetic sample (co-IR, co-TLC).

A comparison of UV values of the aglucone with those of the glucoside suggested the presence of the glucose moiety at position 7. Permethylation by Hakomori's method [5] followed by hydrolysis of the permethylate yielded 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside suggesting thereby that the 7-hydroxyl of the chromone moiety is attached to the C-1′(OH) of the glucose. The glucoside could also be hydrolysed with emulsin indicating the presence of a β-linkage. Therefore, the new structure must be 2-methyl-5,7-dihydroxychromone 7-*O*-β-D-glucopyranoside.

REFERENCES

1. Gupta, S. R., Malik, V. K. and Seshadri, T. R. (1969) *Indian J. Chem.*, 7, 457.
2. Burnett, A. R. and Thomson, R. H. (1968) *J. Chem. Soc. C* 850.
3. Pandey, V. B. and Das Gupta, B. (1970) *Experientia* **26**, 1187.
4. Joshi, K. C., Prakash, L. and Singh, L. B. (1975) *Phytochemistry* **14**, 441.
5. Hakomori, S. (1964) *J. Biochem.* **55**, 205.

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2,3-DIMETHOXYXANTHONE FROM *HYPERICUM MYSORENSE**

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Key Word Index—*Hypericum mysorense*; Hypericaceae; Guttiferae; 2,3-dimethoxyxanthone; screening; PMR.

Abstract—Different parts of *Hypericum mysorense* have been examined for the presence of 2,3-dimethoxyxanthone which comprised the major constituent of the timber. Presence of simple xanthones in this genus supports the classification of *Hypericum* in the subfamily Hypericoideae in Guttiferae.

INTRODUCTION

Following Engler's system [1], the genus *Hypericum* has been included in the subfamily Hypericoideae of the Guttiferae, a family characterized by the occurrence of xanthones. However, Bentham and Hooker [2] and Hutchinson [3] have maintained Hypericaceae to be a separate, though closely related family. Celebixanthone (1-isoprenyl-3,4,8-trihydroxy-2-methoxyxanthone) from *Crataxylon celebicum* [4] and 1,7-dihydroxyxanthone from *Harungana madagascariensis* [5] are the only xanthones isolated from any member of the subfamily Hypericoideae, apart from mangiferin, the 2-*C*-β-glucoside of 1,3,6,7-tetrahydroxyxanthone, which occurs in a number of *Hypericum* species [6]. It was of chemotaxonomic interest therefore, to know whether any other member of this subfamily contains xanthones. This and the reported medicinal uses [7] of some *Hypericum* species prompted us to investigate the commonly available submontane species, *H. mysorense* Wight and Arn. and we herein report the isolation of 2,3-dimethoxyxanthone. This constitutes the first report of the occurrence of this xanthone in nature. To our knowledge no previous chemical studies have been made on this species.

RESULTS AND DISCUSSION

The neutral fraction of the $CHCl_3$ extract of the defatted timber was essentially a single compound which deposited colourless needles on recrystallization from Me_2CO–petrol. From the spectral evidence this compound was shown to be 2,3-dimethoxyxanthone (see Experimental and Table 1). Comparison with an authentic sample [8] established its identity. PMR spectrum in C_6D_6 was of some interest. It showed the expected solvent induced paramagnetic shifts for H-1 and H-8 protons

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Table 1. PMR spectra of 2,3-dimethoxyxanthone

Solvent	1-H	2-OMe	3-OMe	4-H	5-H, 6-H, 7-H	8-H
$CDCl_3$	7.67*s*	4.00*s*	4.00*s*	6.93*s*	7.87–7.32*m*	8.33*br d*, J = 7.5 Hz
$CDCl_3$*	7.72*s*	4.04*s*	4.04*s*	6.95*s*	7.90–7.35*m*	8.42*br d*, J = 7.5 Hz
C_6D_6	7.77*s*	3.37*s*	3.23*s*	6.43*s*	7.20–6.73*m*	8.50*br d*, J = 7.5 Hz

Chemical shift values are in δ(ppm) using TMS as internal reference. Multiplicities: *s* = singlet; *br d* = broad doublet; *m* = multiplet. * Ref. [8].

and diamagnetic shifts for H-4, H-5, H-6 and H-7 protons [9]. Further, in C_6D_6 the two OMe signals appeared as separate singlets at higher fields (Table 1). Minor amounts of this xanthone were also isolated from the root extracts whereas bark, flower, fruit and leaf extracts were devoid of it. The NaOH soluble fraction of the $CHCl_3$ extracts of timber and roots was found to contain minor quantities of several other xanthones.

Occurrence of simple xanthones, especially large amounts of 2,3-dimethoxyxanthone in *H. mysorense* is significant as no simple xanthones have been reported from this genus. Presence of xanthones in this genus supports inclusion of Hypericoideae within the Guttiferae.

EXPERIMENTAL

General procedures. Mps are uncorr. UV spectra taken in EtOH; IR spectra in KBr disc. PMR spectra were recorded in a Varian T60-A. Petrol refers to the fraction of bp 60–80°. Si gel (Merck) plates (0.25 mm) were used for TLC; for PLC these were 1 mm thick.

Extraction. The plant material of *H. mysorense* collected at Horton Plains, Sri Lanka was separated into various parts. The following amounts of dried material were subjected to successive extractions with hot petrol, hot $CHCl_3$ and hot MeOH; leaves (30 g), bark (50 g), timber (100 g), roots (50 g), flowers (25 g) and fruits (20 g). Only the timber (1.2%, y) and the roots (0.03%) contained the new xanthone.

Isolation of 2,3-dimethoxyxanthone. The timber, after defatting with hot petrol was extracted with hot $CHCl_3$. The $CHCl_3$ extract (2.5 g) with Et_2O was washed ×3 with aq. NaOH (10%) and then with satd brine until neutral. The neutral Et_2O fraction was dried and evapd to yield crude 2,3-dimethoxyxanthone (1.18 g, 1.2%) which separated from Me_2CO–petrol as colourless needles; mp 165–167°, lit 154–155°* [8], mmp 165–167°, TLC R_f 0.6 (C_6H_6–Me_2CO, 9:1), blue fluorescent spot in UV, UV λ_{max}^{EtOH} nm (ε), 242.5 (33000), 272 (7000), 307 (11500), 349 (9600). IR ν_{max} cm^{-1}: 1663, 1657, 1650, 1617, 1573, 1132, 785, 760 and 705. PMR spectral results, see Table 1. MS: *m/e* 256 (100%), 241 (32), 213 (28), 185 (8), 149 (8), 103 (20). (Found: M^+, 256.0740. $C_{15}H_{12}O_4$ requires: M^+, 256.0736). It was found to be identical (IR, mmp and co-TLC) with an authentic sample [8], 2,3-Dimethoxyxanthone was also obtained from the hot petrol extract of the timber, by the following procedure; the extract (0.5 g) in methanolic KOH (10%, 10 ml) was refluxed for 1 hr, after which MeOH was evapd and excess crushed ice added. The ppt. thus obtained was recrystallized from Me_2CO–petrol to obtain colourless needles (103 mg, 0.1%), mp 164–66°, mmp 163–165°. From hot petrol and hot $CHCl_3$ extracts of the roots this xanthone was isolated by PLC with C_6H_6–$CHCl_3$ (1:3) and crystallized from Me_2CO–petrol, mp and mmp 165–167°, identical (IR, co-TLC) with the above obtained sample of 2,3-dimethoxyxanthone.

* In our hands the authentic sample had mp 165–167°.

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REFERENCES

1. (1964) A. Engler's *Syllabus der Pflantzenfamilien*, Vol. II, (revised by Melchior, P.). Bortraeger, Berlin.
2. Appendix to Willis, J. C. (1966) *A Dictionary of the Flowering Plants and Ferns*, 7th edn. Cambridge University Press.
3. Hutchinson, J. (1959) *The Families of Flowering Plants*, 2nd edn. Oxford University Press, London.
4. Stout, G. H., Stout, V. F. and Welsh, M. J. (1963) *Tetrahedron* **19**, 667.
5. Ritchie, E. and Taylor, W. C. (1964) *Tetrahedron Letters* 1431.
6. Lebreton, P. and Bouchez, M. P. (1967) *Plant. Med. Phytother.* **1**, 188; (1968) *Biol. Abstr.* **49**, 47248.
7. Chopra, R. N., Chopra, I. C., Handa, K. L. and Kapur, L. D. (1958) *Chopra's Indigenous Drugs of India*, 2nd edn. U. N. Dhur, Calcutta.
8. Locksley, H. D. and Murray, I. G. (1971) *Phytochemistry* **10**, 3179.
9. Laszlo, P. (1967) in *Progress in NMR Spectroscopy* (Emsley, J. W., Feeney, J. and Sutcliffe, L. H., eds.) Vol. 3, p. 231. Pergamon Press, Oxford.