solution and its UV spectrum remained unaffected by addition of sodium acetate solution. This suggests that the only methoxyl group present in the compound must be at C-3 [3]. Thus the new xanthone was characterized as 1,5,7-trihydroxy-3-methoxyxanthone (**1**). Finally, the identification of the trimethyl derivative (**2**) as 1,3,5,7-tetramethoxy xanthone [4] by comparison of physical constants and spectral data confirmed the above structure for **1**.

EXPERIMENTAL

Mp: uncorr. The plants were collected from Santiniketan and their identification verified by Mr. H. R. Chowdhury and Mr P. K. Dan of the Botany Dept. Visva-Bharati University. A voucher specimen is preserved in the herberium of the Phytochemical Research Laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan, India.

Extraction of H. fastigiata. Air-dried powdered defatted whole plants (1.5 kg) of *Hoppea fastigiata* were extracted with C_6H_6 for 56 hr. The concd extract was chromatographed over silica gel (60–120 mesh). Using C_6H_6 as eluate frs 95–121 were collected.

Isolation of 1,5,7-*trihydroxy*-3-*methoxyxanthone* (**1**). The C_6H_6 eluate (frs 95–121) yielded 1,5,7-trihydroxy-3-methoxyxanthone. It crystallized from EtOH to give golden yellow plates (yield 4.2 g) mp 245–247°, analysed for $C_{14}H_{10}O_6$, MS *m/z* 274 $[M]^+$, 259, 258, 245 and 239. UV, IR and ^1H NMR (100 MHz, $CDCl_3$) are given in the text.

Methylation of **1** *with* Me_2SO_4. Compound **1** (150 mg) was dissolved in 175 ml Me_2CO and 3.0 g K_2CO_3 added before addition of Me_2SO_4 (8.5 ml). The mixt. was boiled for 40 hr, the suspension filtered and the filtrate evapd to yield a solid which was purified by prep. TLC to give 1,3,5,7-tetramethoxyxanthone (**2**) (92 mg) mp 226°; λ_{max}^{EtOH} nm (log ε): 250 (4.50), 285 (4.10), 345 (3.75). IR ν_{max}^{KBr} cm^{-1}: 1655, 1620, 1605 and 1580. Compound **2** did not respond to the $FeCl_3$ test.

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A XANTHONE FROM *SWERTIA CHIRAYITA**

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Key Word Index—*Swertia chirayita*; Gentianaceae; chiratol, swerchirin, methyl swertianin.

Abstract—The structure of new xanthone from *Swertia chirayita* has been established as 1,5-dihydroxy-3,8-dimethoxy xanthone (chiratol) on the basis of spectral and chemical evidence. Two other xanthones, i.e. swerchirin (1,8-dihydroxy-3,5-dimethoxy xanthone) and 7-*O*-methyl swertianin (1,8-dihydroxy-3,7-dimethoxy xanthone) have been isolated. Swerchirin was identified as the hypoglycaemic principle of the plant.

INTRODUCTION

Swertia chirayita (Roxb. ex. Flem) Karsh grows abundantly in the temperate regions of the Himalayas. It is used in India as a traditional remedy for chronic fever, anaemia, asthma and liver disorders, and as a bitter tonic [1–3]. A recent report [4] on the hypoglycaemic activity of the hexane extract of the plant prompted us to undertake the isolation of active principle(s) responsible for this activity.

In the earlier chemical investigation of *S. chirayita* a number of xanthones [5–7], 1,5,8-trihydroxy-3-methoxy

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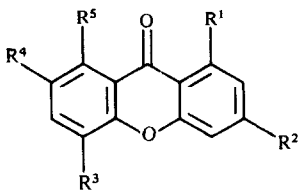

1 $R^1 = R^3 = OH, R^2 = R^5 = OMe, R^4 = H$
2 $R^1 = OH, R^2 = R^3 = R^5 = OMe, R^4 = H$
3 $R^1 = R^5 = OH, R^2 = R^3 = OMe, R^4 = H$
4 $R^1 = R^5 = OH, R^2 = R^4 = OMe, R^3 = H$

xanthone, 1-hydroxy-3,5,8-trimethoxy xanthone, 1-hydroxy-3,7,8-trimethoxy xanthone, 1,8-dihydroxy-3,5-dimethoxy-xanthone, 1,8-dihydroxy-3,7-dimethoxy xanthone, 1,3,6,7-tetrahydroxy xanthone C-2-β-D-glucoside (mengiferin), *i*,3,8-trihydroxy-5-methoxy xanthone, 1,3,5,8-tetrahydroxy xanthone and 1,3,7,8-tetrahydroxy xanthone, a novel dimeric xanthone (chiratanin) [8], a number of triterpenes including swertanone [9, 10] and the alkaloids gentianine, gentiocrucine and enicoflavine [11] were isolated. We report the isolation and characterization of a new xanthone in addition to the two, 1,8-dihydroxy-3,5-dimethoxy xanthone (swerchirin) and 1,8-dihydroxy-3,7-dimethoxy xanthone (7-*O*-methyl swertianin), reported earlier from this plant [10].

RESULTS AND DISCUSSION

The hexane extract of the plant showed significant hypoglycaemic activity when administered to albino rats. The solid mass which separated out when the extract was left to stand for several days contained mainly three compounds (**1**, **3**, **4**). These were separated and purified by repeated column chromatography over silica gel.

Compound **1** gave $[M]^+$ *m/z* 288. Its UV spectrum showed λ_{max} at 233, 253, 277 and 333 nm, which is characteristic of a 1,3,5,8-tetraoxygenated xanthone [12]. The tetraoxygenated pattern was substantiated by its ^{1}H NMR spectrum in which two *meta* coupled proton signals appeared at δ6.20 and 6.37 (J=2.5 Hz) and two *ortho* coupled proton signals at δ6.55 and 7.09 (J=9 Hz) in addition to two singlets at δ3.76 and 3.83 (6H) due to the methoxyl groups. The chelated phenolic hydroxyl proton appeared at δ11.83 as a singlet. One of the hydroxyl groups could thus be located at either C-1 or C-8. On methylation, compound **1** yielded a product (**2**) which was identical with 1-hydroxy-3,5,8-trimethoxy xanthone in all respect [7, 13]. This confirmed the oxygenation pattern of compound **1**, as well as the position of the chelated hydroxyl group at C-1 and a methoxyl group at C-8. As compound **1** was insoluble in 5% Na_2CO_3 solution and did not show any UV bathochromic shift in the presence of sodium acetate, the presence of the second hydroxyl group at C-3 was ruled out [14] and therefore C-3 must be occupied by a methoxyl group. The remaining hydroxy group must be at C-5, the position so far unaccounted for. Compound **1** is designated as chiratol.

The other two yellow crystalline xanthones, compound **3** $[M]^+$ *m/z* 288 and compound **4** $[M]^+$ *m/z* 288, were identified as 1,8-dihydroxy-3,5-dimethoxy xanthone (swerchirin) and 1,8-dihydroxy-3,7-dimethoxy xanthone (7-*O*-methyl swertianin) respectively on the basis of their mp and UV, ^{1}H NMR and mass spectral data [7, 13, 15]. ^{13}C NMR assignments of the three xanthones (**1**, **3** and **4**) have also been made on the basis of correlation studies [16, 17] (Table 1).

Table 1. ^{13}C NMR chemical shifts of compounds **1**, **3** and **4**

C	1	3	4
1	163.22	163.37	163.44
2	98.34	98.34	97.90
3	167.96	168.13	168.13
4	93.41	93.58	93.37
4a	158.15	158.25	158.45
4b	154.18	154.86	151.50
5	140.49	140.66	108.47
6	121.23	122.19	123.35
7	109.66	109.76	143.80
8	145.80	146.25	150.46
8a	108.45	108.61	106.01
8b	103.10	103.30	102.86
C=O	184.86	184.91	185.33
OMe	57.27	57.72	57.80
OMe	56.30	56.09	56.07

The hypoglycaemic activity of the hexane fraction was traced to compound **3**, i.e. swerchirin (Mukerjee, S. K., personal communication).

EXPERIMENTAL

Plant material. Swertia chirayita (whole plant) collected in the month of October from the sub-Himalayan region of West Bengal, India, was identified by Dr B. N. Mehrotra (Botany Division, C.D.R.I.) where a voucher specimen of the plant is lodged in the Herbarium.

Mps: uncorr; IR: KBr; UV: EtOH; ^{1}H NMR: 90 and 80 MHz, $CDCl_3$, TMS as int. standard; ^{13}C NMR: 100 MHz, pyridine-d_5. CC: silica gel; TLC: silica gel coated plates with solvent systems (i) C_6H_6–MeOH (9:1), (ii) C_6H_6–EtOAc (19:1) and (iii) $CHCl_3$–MeOH (9:1). The TLC chromatograms were visualized by exposure to I_2 vapour and by spraying with 1% ceric sulphate in 1 M H_2SO_4.

Isolation. Air-dried powdered material (whole plant, 2 kg) was extracted with hexane. The hexane extract (10 l) was concd to 1 l and then allowed to stand at 5° for several days. The solid mass (2 g) which separated out was filtered and washed with *n*-hexane. It was then subjected to CC over silica gel, eluted with C_6H_6 and C_6H_6–$CHCl_3$ containing increasing proportions of $CHCl_3$. The C_6H_6 and C_6H_6–$CHCl_3$ (9:1) eluate when repeatedly crystallized with C_6H_6–hexane (4:1) yielded chiratol, swerchirin and methyl swertianin.

Compound **1** (*chiratol*). Pale yellow needles, mp 191° (C_6H_6–hexane). TLC solvent 1 and 2. MS: *m/z* 288 $[M]^+$, 273 $[M-15]^+$; UV λ_{max}^{EtOH} nm: 233, 253, 277 and 333; UV $\lambda_{max}^{EtOH+NaOAc}$ nm: 253, 277 and 332; IR: ν_{max}^{KBr} cm^{-1}: 1642, 1622, 1594, 1498, 1280, 1248, 1150, 1110, 1060, 958; ^{1}H NMR: δ3.76 (3H, *s*, OMe), 3.83 (3H, *s*, OMe), 6.20 (1H, *d*, J=2.5 Hz), 6.37 (1H, *d*, J=2.5 Hz), 6.55 (1H, *d*, J=9 Hz), 7.09 (1H, *d*, J=9 Hz), 11.83 (1H, *s*, OH).

Compound **3** (*swerchirin*). Pale yellow needles, mp 186–187° (C_6H_6–hexane). TLC solvent 1 and 2. MS: *m/z* 288 $[M]^+$, 273

$[M-15]^+$, 256 $[M-32]^+$; UV λ_{max}^{EtOH} nm: 229, 252, 276, 333; UV $\lambda_{max}^{EtOH+NaOAc}$ nm: 230, 252, 276, 333; IR ν_{max}^{KBr} cm^{-1}: 1678, 1645, 1615, 1590, 1500, 1250, 1195, 1170, 1110, 1060, 960; ^1H NMR: δ3.80 (3H, *s*, OMe), 3.85 (3H, *s*, OMe), 6.23 (1H, *d*, $J=2.5$ Hz), 6.41 (1H, *d*, $J=2.5$ Hz), 6.51 (1H, *d*, $J=9$ Hz), 7.12 (1H, *d*, $J=9$ Hz), 11.25 (1H, *s*, OH), 11.84 (1H, *s*, OH).

Compound **4** (7-O-*methyl swertianin*). Pale yellow needles, mp 190° (C_6H_6–hexane). TLC solvent 3. MS: *m/z* 288 $[M]^+$, 273 $[M-15]^+$, 270 $[M-18]^+$, 245 $[M-43]^+$; UV λ_{max}^{EtOH} nm: 237, 262, 332, UV $\lambda_{max}^{EtOH+NaOAc}$ nm: 237, 262, 332; IR ν_{max}^{KBr} cm^{-1}: 1650, 1618, 1590, 1490, 1458, 1272, 1240, 1200, 1145, 1085, 1050, 955; ^1H NMR: δ3.79 (3H, *s*, OMe), 3.84 (3H, *s*, OMe), 6.19 (1H, *d*, $J=3$ Hz), 6.21 (1H, *d*, $J=3$ Hz), 6.70 (1H, *d*, $J=9$ Hz), 7.15 (1H, *d*, $J=9$ Hz), 11.82 (1H, *s*, OH), 11.95 (1H, *s*, OH).

Methylation of compound **1**. A mixt. of compound **1** (50 mg), Me_2SO_4 (0.5 ml), dry K_2CO_3 (200 mg) and Me_2CO (20 ml) was refluxed for 4 hr. After usual work-up the product was crystallized from abs. EtOH to afford 1-hydroxy-3,5,8-trimethoxy xanthone as pale yellow needles (30 mg), mp 212°. ^1H NMR: δ3.91 (3H, *s*, OMe), 3.93 (3H, *s*, OMe), 3.98 (3H, *s*, OMe), 6.34 (1H, *d*, $J=2.5$ Hz), 6.59 (1H, *d*, $J=2.5$ Hz), 6.72 (1H, *d*, $J=9$ Hz), 7.18 (1H, *d*, $J=9$ Hz), 12.56 (1H, *s*, OH).

Methylation of compound **3**. Compound **3** (50 mg) was methylated as above and the product crystallized from abs. EtOH to give 1-hydroxy-3,5,8-trimethoxy xanthone as pale yellow needles (28 mg), mp 212°. ^1H NMR: δ3.90 (3H, *s*, OMe), 3.93 (3H, *s*, OMe), 3.98 (3H, *s*, OMe), 6.34 (1H, *d*, $J=2.5$ Hz), 6.60 (1H, *d*, $J=2.5$ Hz), 6.71 (1H, $J=9$ Hz), 7.17 (1H, *d*, $J=9$ Hz), 12.55 (1H, *s*, OH).

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