Phytochemistry, 1978, Vol. 17, pp. 2119 2123 © Pergamon Press Ltd. Printed in England. 0031-9422/78/1201-2119 $02.00/0

# NEW GLYCOXANTHONES AND FLAVANONE GLYCOSIDES OF *HOPPEA DICHOTOMA**

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(*Received* 16 *January* 1978)

**Key Word Index**—*Hoppea dichotoma*; Gentianaceae; $C_2$-glucosyl-1-hydroxy-3,5,6-trimethoxyxanthone; $C_2$-glucosyl-1-hydroxy-3,5,6,7-tetramethoxyxanthone; 7-glucosyloxy-1,5,6-trihydroxy-3-methoxyxanthone; 5-glucosyloxy-7-hydroxy-3′,4′-dimethoxyflavanone; 5-glucosyloxy-7-hydroxy-4′-methoxyflavanone; flavone *C*-glucosides; triterpenes.

**Abstract**—The whole plant of *Hoppea dichotoma* has been shown to contain eleven xanthones, two flavanones and two flavones, as major chemical entities, five of which are new naturally occurring compounds. Additionally, four known triterpenes, gluanone, gluanol, friedelin and friedelin-3β-ol, have been isolated as minor entities. The taxonomic significance of the chemical characters of *H. dichotoma*, which are closely similar to those of *Canscora decussata*, is appraised.

## INTRODUCTION

As a part of the study of the xanthones of genera of the Gentianaceae, we have examined a species of a previously unexplored genus *Hoppea*, viz. *H. dichotoma* Willd. The plant is used [2] in the Ayurvedic system of medicine in the treatment of haemorrhoids, in cardiac dropsy and in certain mental disorders. The plant was collected in flower from Banaras Hindu Univeristy Campus and was properly identified.

## RESULTS AND DISCUSSION

The whole plant was extracted successively with petroleum ether and ethanol. From these extracts, eight known and three new xanthones, two new flavanones and two known flavones were isolated in quantities sufficient for complete characterization. The known xanthones **1**–**7** and **11** and the known flavones, vitexin and isovitexin were identified on the basis of correspondence of physical and spectral properties of the compounds, their acetate and methyl ether derivatives with those reported in the literature [3–12] and by direct comparison where possible. Xanthones **1**–**7** were previously reported [3–7] in *Canscora decussata* Schult (Gentianaceae). While glycosylflavones and mangiferin **13** were reported before in a number of *Gentiana* [13, 14] and *Swertia* [14–16] species, homomangiferin was encountered only once before in *Mangifera indica* (Anacardiaceae) [8]. Additionally, four known triterpenes, gluanone, gluanol, friedelin and friedelin-3β-ol, were isolated as minor entities and their identification was confirmed by direct comparison with reference samples [17]. The structural elucidation of the three new xanthones **8**–**10** and two new flavanones **12** and **14** is now described.

Compound **8**, $C_{20}H_{20}O_{12}$, showed UV and IR spectra characteristic of a 1,3,5,6,7-pentaoxygenated xanthone [6, 7]. The changes in the UV maxima in presence of the usual shift reagents [6, 7] indicated the presence of 1-hydroxy and an *ortho*-dihydroxy functions. The compound formed a heptaacetate which did not exhibit any molecular ion peak in its mass spectrum but showed fragment ion peaks due to a monohydroxy-monomethoxy-triacetoxyxanthone moiety (*m/e* 416) and ions arising from acetylated glucose moiety [18]. As expected for an *O*-glycoside, the mass spectrum showed only the ion of the aglucone (*m/e* 290); hydrolysis with emulsin gave glucose and the aglucone. The aglucone formed a tetraacetate and, on methylation with ethereal diazomethane afforded 1-hydroxy-3,5,6,7-tetramethoxyxanthone [6]. The above data would limit the structural possibilities of the glucosyloxyxanthone to four. Permethylation followed by acid hydrolysis gave a monohydroxy-tetramethoxyxanthone (*m/e* 332), the UV spectrum of which remained unaltered in presence of NaOAc hence locating the only methoxy group at $C_3$, narrowing down its structural possibilities to two. The methyl ether of the aglucone was then found to be identical with a synthetic sample of 1,3,5,6-tetramethoxy-7-hydroxyxanthone [19] and thus the glucoside must be 7-glucosyloxy-1,5,6-trihydroxy-3-methoxyxanthone **8**. The $^1$H NMR spectrum of the heptaacetate and further transformations of the xanthone (see Experimental) confirmed this structural assignment.

Compound **9**, $C_{22}H_{24}O_{11}$ ($M^+$, 464), is a monohydroxy-trimethoxyxanthone-*C*-glucoside. The *C*-glucosyl nature of the compound was revealed from its resistance to acid hydrolysis. The UV spectrum was typical of a 1,3,5,6-tetraoxygenated xanthone [3, 4], having a chelated ($C_1$) hydroxy group. The MS showed, aside from the molecular ion peak, significant fragment ion peaks characteristic of a $C_2$-glucosyl-1,3,5,6-tetraoxygenated xanthone [5, 11]. In the mass spectrum of the 1-*O*-methyl

* Part XXV in the series "Chemical Constituents of Gentianaceae". For Part XXIV see ref. [1].

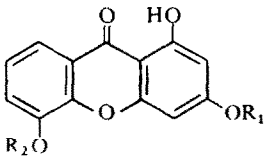
ether tetraacetate, the molecular ion peak showed only 9% abundance while the M − 59 peak appeared as the base peak; this suggested that the glucosyl linkage is at $C_2$ [10]. Further, the permethyl ether exhibited molecular ion and fragment ion peaks whose relative abundance were also consistent with a $C_2$-glucosyl structure; analogous observations have been made in the flavonoid series [20]. Finally, the compound was compared with the 3,5,6-tri-*O*-methyl ether of 'Xanthone-II' which established that they were identical. 'Xanthone-II' was previously reported in *C. decussata* [5]. The compound is thus $C_2$-*β*-D-glucosyl-1-hydroxy-3,5,6-trimethoxyxanthone, **9**.

Compound **10**, $C_{23}H_{26}O_{12}$ ($M^+$, 494), is a monohydroxy-tetramethoxyxanthone glucoside. This compound also resisted acid hydrolysis. The UV spectrum indicated a 1,3,5,6,7-pentaoxygenated xanthone pattern [6, 7]. The MS of the compound, its 1-*O*-methyl ether tetraacetate and of the permethyl ether suggested that that it is $C_2$-*β*-D-glucosyl-1-hydroxy-3,5,6,7-tetramethoxyxanthone.

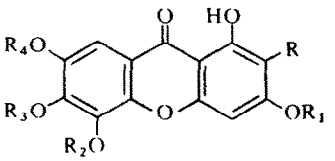
Compound **12**, $C_{23}H_{26}O_{11}$, showed UV, IR and MS characteristic of a flavanone-*O*-glucoside [12, 21]. As expected for an *O*-glucoside, its MS exhibited the aglucone ion ($M^+$, 316) of a dihydroxy-dimethoxyflavanone. The further fragment ion peaks from the aglucone suggested a 5,7-dihydroxy-3',4'-dimethoxy substitution. The glucosyloxyflavanone formed a pentaacetate which, in its mass spectrum, showed fragment ion peaks due to a monohydroxy-monoacetoxy-dimethoxyflavanone and glucose tetraacetate fragments. The $^1$H NMR spectrum of the compound showed five aromatic proton signals ascribable to 2',5',6,6',8-H [12]. A one-proton singlet, exchangeable with $D_2O$, was discernible at $\delta$ 9.22 ppm (in DMSO-$d_6$) and was assigned to $C_5$-OH. The UV max, however, remained unaltered on addition of NaOAc or $AlCl_3$; similar observations have been made with 5,3'-diglucosyloxyeriodictyol [22]. Hydrolysis of the compound with emulsin gave glucose and a flavanone aglucone. The aglucone exhibited the expected $AlCl_3$-induced bathochromic shift of the $\lambda$ 278 nm locating the newly formed OH group at $C_5$. Dehydrogenation of the compound [23], yielded 5,7-dihydroxy-3',4'-dimethoxyflavone [12, 24]. Likewise, the monomethyl ether of the glucoside on dehydrogenation gave luteolin-7-3',4'-tri-*O*-methyl ether [25]. Thus the compound is 5-glucosyloxy-7-hydroxy-3',4'-dimethoxyflavanone **12**.

Compound **14**, $C_{22}H_{24}O_{10}$, exhibited a close similarity with **12** in its UV and IR spectra. It gave a pentaacetate which did not produce any molecular ion peak in its mass spectrum but exhibited significant peaks due to a monohydroxy-monoacetoxy-monomethoxyflavanone and glucose tetraacetate fragments. On hydrolysis with emulsin, the glucoside produced glucose and a dihydroxy-monomethoxyflavanone. The $^1$H NMR spectrum of the glucoside was different from that of **12** in respect only of the B-ring protons which appeared as an $A_2B_2$ quartet ascribable to 2',3',5',6'-H. Methylation of the glucoside followed by acid hydrolysis gave a monohydroxy-dimethoxyflavanone which showed $AlCl_3$-induced bathochromic shift in its longer wavelength UV maximum. This locates the sugar at $C_5$. Dehydrogenation of the glucoside afforded acacetin. The compound is thus 5-glucosyloxy-4'-methoxy-7-hydroxyflavanone **14**.

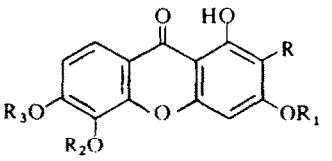
Notwithstanding the close similarity in the chemical constituents between *H. dichotoma* and *C. decussata*, the following points can be cited to suggest their distinctiveness. Mangiferin **13** is absent from *H. dichotoma* while it occurs as a major entity (*ca* 3% yield) in *C.*



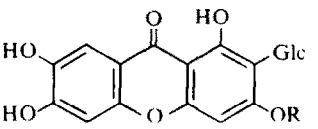
**1** $R_1$ = Me, $R_2$ = H
**2** $R_1$ = $R_2$ = Me



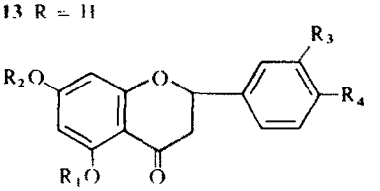
**7** R = $R_3$ = $R_4$ = H, $R_1$ = $R_2$ = Me
**8** R = $R_2$ = $R_3$ = H, $R_1$ = Me, $R_4$ = Glc
**10** R = Glc, $R_1$ = $R_2$ = $R_3$ = $R_4$ = Me



**3** R = $R_1$ = H, $R_1$ = $R_2$ = Me
**4** R = H, $R_1$ = $R_2$ = $R_3$ = Me
**5** R = $R_1$ = $R_2$ = H, $R_3$ = Me
**6** R = $R_1$ = $R_3$ = H, $R_2$ = Me
**9** R = Glc, $R_1$ = $R_2$ = $R_3$ = Me



**11** R = Me
**13** R = H



**12** $R_1$ = Glc, $R_2$ = H, $R_3$ = $R_4$ = OMe
**14** $R_1$ = Glc, $R_2$ = $R_3$ = H, $R_4$ = OMe

*decussata*. *H. dichotoma*, however, produces homomangiferin **11** (although in poor yield). The elaboration of flavanones by *H. dichotoma* in very high yields and the complete absence of these constituents in *C. decussata* is another notable difference between the two species. These observations may be of considerable chemotaxonomic significance since mangiferin, both in its distribution and biogenesis seems to be closely related to flavonoids rather than to xanthones [26]. It is also of note that mangiferin has been recently linked [27] with hispidin in its biogenesis and has been considered to be formed by the condensation of a $C_9$-unit (prephenate or equivalent) with only two, rather than three, acetate units. In view of this hypothesis, it is possible that in *H. dichotoma* mangiferin is vicariously represented by the glucosyloxyflavanones **12** and **14**.

## EXPERIMENTAL

Column chromatography was done on Si gel (B.D.H., 60–120 mesh) or on polyamide powder D (Riedel), and TLC on Si gel G (E. Merck). Spot detection was done by UV fluorescence in the short-wave and treatment with $I_2$ vapour. 4 solvent systems, viz. *n*-BuOH–HOAc–$H_2O$ (4:1:2, solvent 1), $C_6H_6$–HOAc (100:4, solvent 2), $CHCl_3$–HOAc (100:4, solvent 3), and $CHCl_3$–HOAc–MeOH (90:5:5, solvent 4) were used. Physical and spectral data relating to some of the xanthones were reported previously [3–7].

*Extraction procedure*. Dried and powdered whole plants of *H. dichotoma* (580 g) were continuously extracted (Soxhlet) with light petrol (bp 60–80°) for 30 hr. The defatted plant materials were then extracted (30 hr) with EtOH. The 2 extracts were processed separately.

*Petroleum extract*. The extract was processed for carboxylic, phenolic and neutral fractions in the usual way. The neutral fraction was column chromatographed according to a previously described procedure [17] to give gluanone (5 mg), friedelin (7 mg), gluanol (3 mg) and friedelin-3$\beta$-ol (11 mg). The identity of the triterpenes was confirmed by direct comparison (mp, mmp, co-TLC and superimposable IR spectra) with authentic samples [17]. The phenolic fraction was obtained as a brown gum (0.48 g, fraction A) which showed a number of spots on TLC (solvent 2).

*Isolation of xanthones from fraction A*. It was dissolved in $C_6H_6$ (20 ml) and chromatographed on a column (25 × 1.8 cm) of Si gel. Elution was carried out with petroleum (1 l.), $C_6H_6$ (10 l.), $C_6H_6$–$CHCl_3$ (1:1, 2 l.) and $CHCl_3$ (2 l.). Fractions (250 ml) were collected and monitored by TLC.

*Xanthone* **2**. The middle petroleum eluates were combined and the solvent was evapd. The residue crystallized from alcohol as light yellow needles (7 mg), mp 173°. The identity of the compound with 1-hydroxy-3,5-dimethoxyxanthone **2** was established by direct comparison (mp, mmp, co-TLC, IR) with an authentic sample [3].

*Xanthone* **1**. The middle $C_6H_6$ fractions (7–22) were combined and the solvent was evapd. The residue crystallized from alcohol as bright yellow needles (22 mg), mp 271–272°. The identity of the compound with 1,5-dihydroxy-3-methoxyxanthone **1** was established by direct comparison (mp, mmp, co-TLC, UV) with an authentic sample [3]. The later $C_6H_6$ and early $C_6H_6$–$CHCl_3$ fractions (43–52) afforded a light brown solid which showed 2 spots on TLC (solvent 2) and were separated by preparative layer chromatography (PLC) using the same solvent.

*Xanthone* **4**. The upper PLC zone, $R_f \sim 0.5$, was eluted with $CHCl_3$ and the residue from $CHCl_3$ crystallized from alcohol as cream coloured needles (5 mg), mp 179–180°. The identity of this compound with 1-hydroxy-3,5,6-trimethoxyxanthone **4** was established by direct comparison (mp, mmp, co-TLC, UV) with an authentic sample [4].

*Xanthone* **3**. The lower light brown streak, $R_f \sim 0.4$, was eluted with $CHCl_3$–MeOH (95:5) and the solution was filtered through a small column of Si gel (8 × 1.5 cm). Washing out the column with $C_6H_6$–EtOAc (100:10, 500 ml) and evapn of the solvent from the eluates gave a straw coloured solid (8 mg) which crystallized from alcohol as colourless needles, mp 190–192°. The identity of the compound with 1,6-dihydroxy-3,5-dimethoxyxanthone **3** was established by direct comparison (mp, mmp, co-TLC, UV) with an authentic sample [4].

*Xanthone* **7**. The $CHCl_3$ eluates were combined and the solvent was evapd. The residue crystallized from alcohol as buff coloured crystals (15 mg), mp 288–290°, $R_f$ 0.6 (solvent 4). The identity of the compound with 1,6,7-trihydroxy-3,5-dimethoxyxanthone **7** was established by direct comparison (mp, mmp, co-TLC, IR) with an authentic sample [7].

*Alcoholic extract*. The alcoholic extract was concd to a thick syrup and poured into $H_2O$ (200 ml). The mixture was kept at room temp. overnight and then filtered. The water-insoluble residue (22 g) was marked fraction B. The aq. filtrate was extracted with $Et_2O$ (1 l., fraction C) and then with EtOAc (1 l., fraction D).

*Isolation of phenolic constituents from fraction B*. The residue was successively triturated with hot petroleum, $C_6H_6$ and $CHCl_3$ (5 × 100 ml, each). The petroleum and $C_6H_6$ solutions, on evapn, afforded only a small amount of residues and were kept aside.

*7-Glucosyloxy-1,5,6-trihydroxy-3-methoxyxanthone* **8**. The $CHCl_3$ solution showed 2 spots on TLC. $R_f$ 0.28 and 0.52 (solvent 4). The solution was concd (*ca* 40 ml) when a pale yellow solid (48 mg) was separated which was identified as the glucosyloxyxanthone **8** on the basis of the following properties: mp 238–240°; $\lambda_{max}^{MeOH}$ nm: (log $\varepsilon$) 260 (4.53), 295–300 sh (4.07), 308 (4.11), 330 (4.21), 370–375 sh (3.07); $\lambda_{max}^{MeOH-NaOAc}$ nm: (log $\varepsilon$) 265 (4.36), 355 (4.26); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm: (log $\varepsilon$) 262 (4.58), 280 (4.23), 345 (4.10), 360 (4.28), $\lambda_{max}^{MeOH\ AlCl_3}$ nm: 255 sh, 260, 308, 398; *m/e* 290 (100%), 261 (63), 260 (11), 247 (80), 219 (5). (Found: C, 52.7; H, 4.1. $C_{20}H_{20}O_{12}$ requires: C, 53.1; H, 4.4%). Hydrolysis of the glucosyloxyxanthone (18 mg) with emulsin (10 mg) at pH 5, in the usual way, gave glucose (PPC) and 1,5,6,7-tetrahydroxy-3-methoxyxanthone, mp 260–262°. The aglucone showed *m/e* 290 ($M^+$, 100%), 262 (5), 261 (22), 247 (18), 219 (5) and on methylation with ethereal diazomethane gave 1-hydroxy-3,5,6,7-tetramethoxyxanthone, mp and mmp 171–173° [6]. The heptaacetate of the glucosyloxyxanthone crystallized from alcohol as micro-crystals, mp 195–198°; $\delta$ ($CDCl_3$) 7.68 (1H, *s*), 6.83 (1H, *d*, $J$ = 2 Hz), 6.65 (1H, *d*, $J$ = 2 Hz), 4.05 (3H, *s*), 2.45 (6H, *s*), 2.36 (3H, *s*), 2.0–2.1 (12H); *m/e* 416 (relative intensity, 100%), 374 (30), 332 (40), 331 (95), 290 (88), 271 (18), 260 (22), 247 (12), 243 (8), 211 (7), 169 (8).

*1,3,5,6-Tetramethoxy-7-hydroxyxanthone*. The permethyl ether of **8**, prepared with MeI and NaH in THF, was obtained as a brown gum. It was hydrolysed with HCl (4%) on a steam bath (4 hr). The aq. hydrolysate was extracted with $CHCl_3$. The residue from the $CHCl_3$ extract crystallized from alcohol as light brown micro-crystals, mp 197–198°; $R_f$ 0.4 (solvent 2); $\lambda_{max}^{MeOH}$ nm: (log $\varepsilon$) 245 (4.42), 275 (3.95), 305–310 sh (3.64), 320 (3.56), 335 (3.55), 370–375 (3.80) (no shift with NaOAc or $AlCl_3$); $\nu_{max}^{KBr}$ $cm^{-1}$: 3435, 1650, 1592, 1028; *m/e* 332 ($M^+$, 100%), 317 (22), 304 (8), 303 (24), 302 (6), 289 (44), 261 (17). (Found: C, 61.0; H, 4.5. $C_{17}H_{16}O_7$ requires: C, 61.4; H, 4.8%).

*1-Hydroxy-3,7-dimethoxy-5,6-methylenedioxyxanthone*. The glucosyloxyxanthone **8** (32 mg) was treated with $CH_2I_2$ (0.3 ml) and $K_2CO_3$ (0.25 g), in dry AcMe (25 ml), (12 h). The product, an amorphous solid, was hydrolysed with HCl and the aglucone was methylated with ethereal $CH_2N_2$ to give 1-hydroxy-3,7-dimethoxy-5,6-methylenedioxyxanthone (14 mg), mp and mmp with 'xanthone 6' [7] 240–241°.

*5-Glucosyloxy-7-hydroxy-3',4'-dimethoxyflavanone* **12**. The $CHCl_3$-insoluble residue (14.17 g), after separation of **8**, was triturated with hot alcohol. The alcoholic solution on concn gave a cream coloured solid, mp 162–165°; $R_f$ 0.68 (solvent 1); $[\alpha]_D^{28}$ −40° (*c* 0.5, MeOH); $\lambda_{max}^{MeOH}$ nm: (log $\varepsilon$) 275 (4.25), 315–320 (3.40); $\lambda_{max}^{MeOH-NaOMe}$ nm: 282, 335–340 (no shift with NaOAc or $AlCl_3$); $\nu_{max}^{KBr}$ $cm^{-1}$: 3400 (br), 1620, 1600, 1588, 1515, 1025, 892, 848, 815; $\delta$ (DMSO-$d_6$) 9.22 (1H, *s*) (exchangeable with

$D_2O$, $C_7$-OH), 7.02 (3H, *m*, H-2', 5', 6'), 6.18 (1H, *d*, $J$ = 2.5 Hz, H-8), 5.96 (1H, *d*, $J$ = 2.5 Hz, H-6), 5.5 (1H, *br*, H-2), 5.0 (1H, glucosyl anomeric H), 4.8–4.5 (3H, *m*, glucosyl H), 3.80 (6H, *s*, OMe), 3.9–3.5 (3H, *m*, glucosyl H), 2.75 (2H, *m*, H-3 *cis* and *trans*): *m/e* 316 (relative intensity, 52%), 286 (32), 165 (10), 164 (100), 152 (12), 151 (40), 149 (31), 134 (51). (Found: C, 57.2; H, 5.1. $C_{23}H_{26}O_{11}$ requires: C, 57.7; H, 5.4%). The pentaacetate crystallized from alcohol as needles, mp 148–150°; $R_f$ 0.66 (solvent 3): $[\alpha]_D^{28}$ −25.4° (*c* 0.47, $CHCl_3$); $\lambda_{max}^{MeOH}$ nm: (log ε) 275 (4.08), 305–310 (3.68); $\nu_{max}^{KBr}$ $cm^{-1}$: 1795, 1780, 1730, 1678, 1608, 1560, 1265, 1170, 1090, 955; δ ($CDCl_3$) 6.85 (3H, *m*, H-2', 5',6'), 6.40 (1H, *d*, $J$ = 2.5 Hz, H-8), 6.28 (1H, *d*, $J$ = 2.5 Hz, H-6), 3.82 (6H, *s*, OMe), 2.2 (3H, *s*, OAc-7), 2.0–1.95 (12H, glucosyl acetoxy H); *m/e* 358 (relative intensity, 30%), 331 (60), 316 (20), 271 (80), 243 (15), 229 (48), 211 (14), 169 (100), 164 (98), 151 (60), 134 (40). Hydrolysis of **12** (60 mg) with emulsin [28], gave glucose (PPC) and the aglucone, 5,7-dihydroxy-3',4'-dimethoxyflavanone, mp, 133–137°; $R_f$ 0.65 (solvent 3): $\lambda_{max}^{MeOH}$ nm: (log ε) 278 (4.18), 305–310 (3.24); $\lambda_{max}^{MeOH\ AlCl_3}$ nm: (log ε) 305 (4.25); *m/e* 316 ($M^+$, 90%), 286 (62), 164 (100), 151 (58), 149 (40). The pentaacetate of **12** (84 mg) was dehydrogenated according to a published method [23] to give the glucosyloxyflavone pentaacetate (22 mg), $R_f$ 0.32 (solvent 3): $\lambda_{max}^{MeOH}$ nm: 245, 275, 315, 335. It was hydrolysed (HOAc–HCl) and the flavone crystallized from MeOH as light yellow crystals, mp 171–173°. The UV, $^1H$ NMR, and MS data obtained for this compound were consistent with those reported for 3',4'-di-*O*-methyl ether of luteolin in the literature [12, 24, 25]. The alcohol-insoluble solid, obtained after the separation of **12**, was refluxed in absolute MeOH. The MeOH concentrate was passed through a column of polyamide (40 g). The column was washed with $H_2O$ and then percolated with aq. MeOH (1:1) and MeOH.

$C_2$ - β - D - *Glucosyl* - 1 - *hydroxy* - 3,5,6,7 - *tetramethoxyxanthone* **10**. The aq. MeOH percolate was concd and then kept at ordinary temp. for several days when a light brown solid was precipitated (12 mg), mp 245–248° (dec.): $[\alpha]_D^{28}$ +48° (*c* 0.2, Py); $\lambda_{max}^{MeOH}$ nm: (log ε) 242 (4.08), 258 (4.50), 310 (3.92), 355 (3.77); $\lambda_{max}^{MeOH-AlCl_3}$ nm: 236–238, 265, 334 sh, 388; *m/e* 494 ($M^+$, 8%), 479 (7), 466 (2), 465 (5), 451 (12), 361 (22), 346 (14), 330 (100), 195 (17), 194 (12), 179 (22). (Found: C, 53.4; H, 5.2 $C_{23}H_{26}O_{12}.H_2O$ requires: C, 53.9; H, 5.4%). The 1-*O*-methyl ether tetraacetate of **10**, prepared by repeated treatment of the glucoxanthone with ethereal $CH_2N_2$ followed by acetylation, was obtained as a pale yellow gummy material, $R_f$ 0.4 (solvent 3); *m/e* 676 ($M^+$, 4%), 662 (1), 617 (100), 557 (18), 556 (8), 496 (15).

$C_2$ - β - D - *Glucosyl* - 1 - *hydroxy* - 3,5,6 - *trimethoxyxanthone* **9**. The MeOH percolate was concd and kept at ordinary temp. for several days when an amorphous solid (7 mg) was separated. It showed 2 spots on PPC (solvent 1), $R_f$ 0.52 (major) and 0.64 (minor). The solid was refluxed with MeOH (20 ml) and the MeOH-insoluble solid was collected by filtration. It was homogeneous, $R_f$ 0.5 (PPC); mp 290–294°; $\lambda_{max}^{MeOH}$ nm: (log ε) 245 (4.43), 280 infl. (3.98), 312 (4.16), 335 (3.55); $\lambda_{max}^{MeOH-AlCl_3}$ nm: 238–240, 250 sh, 350; *m/e* 464 ($M^+$, 5%), 331 (98), 316 (100), 288 (22), 196 (12), 195 (10), 180 (14), 179 (18) (Found: C, 54.4; H, 5.4. $C_{22}H_{24}O_{11}.H_2O$ requires: C, 54.7; H, 5.3%). Direct comparison with the tri-*O*-methyl ether of the glucosylxanthone-II [5] (co-TLC, UV, MS) established that they were identical. The 1-*O*-methyl ether tetraacetate was obtained as a pale yellow gummy material, $R_f$ 0.38 (solvent 3); *m/e* 646 ($M^+$, 9%), 587 (100). The residue from the MeOH-soluble portion, after separation of **9**, was permethylated (MeI and NaH in THF) to give a mixture of compounds which were separated by PLC using solvent 3.

*Permethyl ether of* **10**. The upper blue fluorescent zone, $R_f$ 0.4, was eluted with $CHCl_3$. The residue from the $CHCl_3$ solution, a pale yellow gummy material, showed $\lambda_{max}^{MeOH}$ nm: 255, 282 infl., 325, 355–360; *m/e* 564 ($M^+$, 18%), 549 (11), 547 (2), 535 (14), 534 (10), 521 (22), 493 (8), 492 (6), 389 (100), 359 (8), 193 (2), 178 (2), 163 (3).

*Permethyl ether of* **9**. The lower sea-green fluorescent zone, $R_f$ 0.3, was worked up to give a pale yellow gummy material which showed $\lambda_{max}^{MeOH}$ nm: 245, 280, 308–310, 355–360; *m/e* 534 ($M^+$, 20%), 519 (8), 517 (3), 505 (12), 504 (7), 491 (18), 463 (5), 462 (4), 359 (100), 329 (7), 193 (2), 178 (2), 163 (5).

*Isolation of phenolic constituents from fraction C*. The solvent was evapd from this fraction when a brown solid (4.2 g) was obtained. It showed a number of spots on TLC (solvents 2 and 4). A portion of the solid (*ca* 1 g) was dissolved in $C_6H_6$ (containing traces of $CHCl_3$) and was subjected to CC (30 × 2.5 cm). Light petroleum (2 l.), $C_6H_6$ (2 l.), $CHCl_3$ (25 l.) and $CHCl_3$–MeOH (95:5, 2 l.) were used as eluents. Fractions (11) were collected and monitored by TLC. Fractions 8–10 on evapn and usual work up afforded a further crop of **2** (22 mg). Fractions 14–17, on evapn, yielded a dull yellow solid (32 mg) which showed 2 major spots on TLC (solvent 3). These were separated by PLC.

*Xanthone* **5**. The upper light brown zone, $R_f$ 0.6, was eluted with $CHCl_3$–MeOH. The solvent was removed and the residue crystallized from alcohol as light brown micro-crystals (8 mg), mp 284–285°; triacetate, mp 193–195°. The identity of the xanthone with 1,3,5-trihydroxy-6-methoxyxanthone was established by direct comparison (mp, mmp, co-TLC, mp and mmp of the triacetate) with an authentic sample [3, 5]. The lower yellow streak, $R_f$ 0.45, on re-PLC afforded a light yellow solid (4 mg), mp 288–289°; *m/e* 274 ($M^+$, 100%). The identity of the compound with 1,3,6-trihydroxy-5-methoxyxanthone **6** was established by direct comparison (mp, mmp, co-TLC) with an authentic sample [3, 5]. Fractions 23–28 were evapd and the residue crystallized from alcohol to give a further crop of **7** (6 mg).

*Isolation of phenolic constituents from fraction D*. The EtOAc extract was concd and kept at ordinary temp. overnight when a tan solid (0.133 g) was separated. It showed 4 spots on TLC, $R_f$ 0.1, 0.18, 0.33, 0.48 (solvent 4). The solid was repeatedly washed with hot alcohol. The alcohol sparingly-soluble solid crystallized from MeOH–dioxane as light brown crystals (82 mg), mp 251–253°. The UV, IR, $[\alpha]_D$ and MS data of this compound were identical with those reported for vitexin [9, 12]. The alcohol washings of vitexin were combined and concd to give isovitexin as a yellow solid (34 mg), mp 240–242°. The UV IR, $^1H$ NMR and MS data of this compound were identical with those reported for isovitexin [9, 12]. The alcoholic mother liquor, after separation of isovitexin, was subjected to CC on polyamide (22 g). The aq. MeOH percolate on concn and keeping for *ca* 1 week at ordinary temp. gave homomangiferin **11** (9 mg), mp 255–257 (mp, mmp, co-TLC, IR).

*5-Glucosyloxy-7-hydroxy-4'-methoxyflavanone* **14**. The MeOH percolate on concn and keeping afforded a straw coloured solid which crystallized from absolute alcohol as needles (55 mg), mp 118–120°; $\lambda_{max}^{MeOH}$ nm: (log ε) 272 (4.14) (no shift with NaOAc or $AlCl_3$); $\nu_{max}^{KBr}$ $cm^{-1}$: 3350, 1625, 1598, 1020; δ (DMSO-$d_6$) 9.28 (1H, *s*, exchangeable with $D_2O$, 7-OH), 7.11 (4H, *q*, H-2',3',5',6'), 6.32 (1H, *d*, $J$ = 2.5 Hz, H-8), 6.05 (1H, *d*, $J$ = 2.5 Hz, H-6), 5.3 (1H, *br*, H-2), 5.0 (1H, glucosyl H-1), 4.85–4.56 (4H, glucosyl H, plus $H_2O$), 3.85 (3H, *s*, OMe), 2.72 (2H, H-3 *cis* and *trans*); *m/e* 286 ($M^+$ of the aglucone, 90%), 152 (10), 151 (40), 134 (100). (Found: C, 58.4; H, 5.38. $C_{22}H_{24}O_{10}$ requires: C, 58.9; H, 5.3%). The pentaacetate crystallized from alcohol as micro-crystals, mp 114–116°; *m/e* 328 (98%), 331 (95), 286 (62), 271 (12), 243 (7), 151 (90), 134 (100). Hydrolysis of **14** with emulsin gave glucose (PPC), and the aglucone as an amorphous solid, $R_f$ 0.7 (solvent 4). $\lambda_{max}^{MeOH}$ nm: (log ε) 272 (4.15), $\lambda_{max}^{MeOH-NaOAc}$ nm: (log ε) 305 (4.22); $\lambda_{max}^{MeOH-AlCl_3}$ nm: 312. The 7-*O*-methyl ether of **14**, prepared with ethereal $CH_2N_2$, on hydrolysis with aq. $H_2SO_4$ (3%) afforded 5-hydroxy-7,4'-dimethoxyflavanone, mp 143–145°; $\lambda_{max}^{MeOH}$ nm 275; $\lambda_{max}^{MeOH\ AlCl_3}$ nm: 315–320, *m/e* 300 ($M^+$, 68%), 134 (100). The glucosyloxyflavanone **14** was dehydrogenated, as described before and the product was hydrolysed with a mixture of HOAc–HCl (3:1) to give acacetin, mp 254–256° (mp, mmp, co-TLC, IR).

*Acknowledgements*—We thank Dr C. S. P. Rao, Department of Botany, for kindly identifying the plant materials. We are indebted to Dr. M. Aritomi, Kumamoto University, Japan, for the reference sample of homomangiferin, to Dr. S. C. Pakrashi,

Indian Institute of Experimental Medicine, Calcutta, India, Dr. D. N. Roy, University of Toronto, Canada, Dr. B. C. Das, CNRS, France and Dr. R. K. Chaudhuri, Pharmazeutisches Institut, Bonn, Germany, for the NMR, mass spectra, and optical rotation data. Financial assistance from the University Grants Commission, New Delhi, India, is gratefully acknowledged.

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