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NEW TETRAOXYGENATED XANTHONES OF *CANSCORA DECUSSATA**

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Key Word Index—*Canscora decussata*, Gentianaceae, 1,3,6,7-tetrahydroxyxanthone, 1,3,5,6-tetrahydroxyxanthone-C_2-glucoside, 1,5,6-trihydroxy-3-methoxyxanthone, MS fragmentation

Abstract—From the alcoholic extract of *Canscora decussata* Schult (Gentianaceae), the previously unreported 1,3,6,7-tetrahydroxyxanthone (I), 1,3,5,6-tetrahydroxyxanthone-C_2-glucoside (II), and 1,5,6-trihydroxy-3-methoxyxanthone (III), have been isolated and identified The structures of these xanthones have been established by chemical transformations, synthesis (in case of III), and spectral (UV, IR, PMR, MS) evidence II and III have not been encountered before in nature, while I is reported for the first time in this genus The significance of mass spectral fragmentation in the structural elucidation of oxygenated xanthones is discussed

INTRODUCTION

NEARLY two dozen polyoxygenated (tri-, tetra-, penta-, and hexa-) xanthones have been isolated from the roots of *Canscora decussata* Schult (Gentianaceae) [1-3] Among these, one was shown to be 1,3,6,7-tetrahydroxyxanthone-C_2-β-D-glucoside (mangiferin) and another five were 1,3,5,6-tetraoxygenated xanthones These findings were of considerable systematic value, since, (a) mangiferin is a unique taxonomic character in plants and both in its distribution and biogenesis it is more closely related to flavonoids than to xanthones,[4,5] (b) reports of simple 1,3,5,6-tetrahydroxy/methoxy xanthones in nature are relatively rare; and (c) the co-occurrence of 1,3,6,7- and 1,3,5,6-tetraoxygenated xanthones has been reported only once before in nature (in *Symphonia globulifera* L , Guttiferae) [5] The co-occurrence of these two types of xanthones in *Mammea africana* G Don (Guttiferae) is still unpublished (see Ref 5) From the biogenetic point of view, if the two types of xanthones (1,3,6,7- and 1,3,5,6-) are derived from the common benzophenone precursor,[5] maclurin, then their co-occurrence should be more frequent than recorded so far Recently, mangiferin has been found to co-occur with another group of polyoxygenated xanthones (1,3,5,8- and 1,3,7,8-) in *Swertia chirata* Buch -Ham (Gentianaceae) [6] The purpose of this paper is to record some new xanthones from the more polar fractions of the alcoholic extract of *C decussata*

RESULTS AND DISCUSSION

From the more polar fraction of the alcoholic extract of *C decussata*, collected in flowers from Varanasi, three previously unreported xanthones (I–III) were isolated One was immediately identified as 1,3,6,7-tetrahydroxyxanthone (I), by direct comparison with

* Part VI in the series "Chemical Constituents of the Gentianaceae" For Part V see Ref 6

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material prepared from mangiferin [1] Although I has been found before, this is the first report of its occurrence in *Canscora* The structures of the other two xanthones were determined as follows

Xanthone II, $C_{19}H_{18}O_{11}$ (M^+, 422, 6%), was obtained as a minor constituent along with xanthone III Xanthone II showed UV absorption λ_{max} 240 sh (log ϵ, 4 32), 250 (4 44), 280 inflec (3 88), 335 nm (3 90), characteristic of 1,3,5,6-tetraoxygenated xanthones [1] It, however, differed from 1,3,5,6-tetrahydroxyxanthone in that it had a lower R_f in BAW and a higher R_f in 15% acetic acid compared to the latter This is a property typical of glucosidic xanthones [7] The IR spectrum of the xanthone, ν_{max} 3400 (broad, OH groups of the sugar moiety), 1650, 1612, 1598 (chelated xanthone CO),[8] 1462, 1245, 1210 ~ 1050 (complex bands due to C–O–C of sugar), and 895 cm^{-1} (bending vibration due to C_1–H of sugar),[9] is also characteristic of xanthone *C*-glucosides The mass fragmentation pattern of the xanthone, exhibiting significant peaks at *m/e* 404 (8%), 386 (6%), 368 (30%), 326 (6%), 302 (5%), 300 (18%), 289 (12%), 274 (11%), 273 (100%), 180 (20%) indicates a tetrahydroxyxanthone-C_2-glucosidic structure [1 10 11] The xanthone resisted acid hydrolysis The R_f and optical rotation $[\alpha]_D^{24}$ +48 6° (*c* 0 3, pyridine) are significantly higher than those of isomangiferin[12] but similar to those of mangiferin [1] From these and related data [13 14] xanthone II is provisionally identified as 1,3 5,6-tetrahydroxyxanthone-C_2-glucoside

Xanthone III, $C_{14}H_{10}O_6$ (M^+, 274, 100%) is a monomethoxytrihydroxyxanthone in which one of the hydroxyl groups is strongly chelated since it forms a dimethyl ether with CH_2N_2 and a diacetate but a trimethyl ether with Me_2SO_4 It has a UV spectrum λ_{max} 248 (log ϵ 4 61), 280 inflec (3 94), and 335 nm (3 98), characteristic of 1,3,5,6-tetraoxygenated xanthones [3] The UV spectrum showed pronounced bathochromic shifts of the longer wavelength maxima on addition of H_3BO_3–NaOAc, indicating the presence of OH groups at positions C_5 and C_6 in xanthone III The PMR spectrum of the xanthone in DMSO-d_6 showed a three-proton singlet at 3 95 ppm (aromatic methoxyl), four aromatic protons exhibiting *meta* and *ortho*-split doublets at 6 32 (*d*, *J* 3 Hz H-2), 6 50 (*d*, *J* 3 Hz, H-4), 6 88 (*d*, *J* 10 Hz, H-7), and 7 60 (*d*, *J* 10 Hz, H-8) ppm, and a one-proton broad singlet at 13 1 ppm (chelated 1-OH) In its mass spectrum, apart from the dominant molecular ion peak, there were significant fragment ion peaks at *m/e* 246 (M–CO, 5%), 245 (M–CHO, 12%, *m** 219 0), 244 (M–CH_2O, 18%, *m** 217 5), 231 (M–C_2H_3O, 14%, *m** 195), 217 (M–CO–CHO, 11%), 202 (M–C_2H_3O–CHO, 4%) The MS fragmentation data and the absence of any M–Me peak locate the methoxyl group of xanthone III at C_3 The dimethyl ether of the xanthone was found to be identical with 1-hydroxy-3,5 6-trimethoxyxanthone[3] in all respects Finally, structure III for the compound was established by its synthesis from 1,3,5,6-tetrahydroxyxanthone [1] Synthesis of III was accomplished by preferential methylation of the C_3–OH group of 1,3,5,6-tetrahydroxyxanthone in presence of boric acid with Me_2SO_4 and alkali The product was found to be identical with the natural sample in all respects

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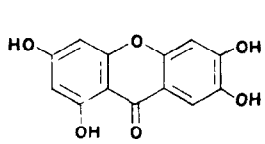
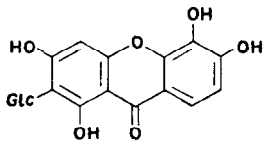


(I)



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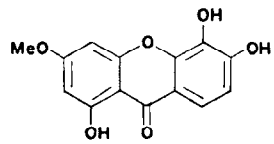

(III)

EXPERIMENTAL

All m ps were determined on a Toshniwal melting point apparatus, in open capillaries, and were uncorrected UV spectra were determined in 95% EtOH IR spectra were taken in KBr pellets or mineral oil Separation, by column chromatography, was carried out on silica gel (B D H , 60–120 mesh), by PPC (Whatman paper No 1), and TLC (silica gel G, E Merck) Three solvent systems, viz $CHCl_3$–HOAc (6 1, solvent 1), *n*-BuOH–HOAc–H_2O (4 1 2, solvent 2), and 15% aq HOAc (solvent 3) were used $FeCl_3$ and I_2 vapour were used for detection

Isolation of tetraoxygenated xanthones and xanthone C-glucoside The defatted (petrol 60–80°) roots (1 2 kg) of *Canscora decussata* were extracted (Soxhlet, 30 hr) with EtOH The ethanolic extract, upon concentration, afforded mangiferin[1] (31 g) The ethanolic mother liquor, after separation of mangiferin, was further concentrated to a syrupy liquid to which aq HOAc (4%, 200 ml) was added The mixture was kept at room temp overnight The aq acidic suspension was extracted with $CHCl_3$ (3 × 50 ml) and the $CHCl_3$-insoluble residue was collected by filtration The dull yellow solid was triturated with hot EtOH to remove mangiferin as EtOH-insoluble solid The solvent was removed from the EtOH-soluble fraction and the residue was extracted with a large volume of EtOAc The EtOAc-freely soluble and sparingly soluble fractions were separately processed

1,3,6,7-*Tetrahydroxyxanthone* (I) The residue from the EtOAc freely soluble fraction (312 mg) showed two spots on TLC, R_f 0 73 and 0 51 (solvent 1) The two components were separated by preparative TLC when 1,3,6,7-tetrahydroxyxanthone was obtained from the lower layer It crystallized from MeOH as straw coloured needles, m p and m m p 370–372° (lit [15] m p 370–371°), co-TLC with an authentic sample from mangiferin,[1] showed a single spot at R_f 0 51 Methylation with ethereal CH_2N_2 gave 1-hydroxy-3,6,7-trimethoxyxanthone, light yellow needles from EtOH m p and m p m 220–222° The tetraacetate crystallized from EtOAc–petrol as needles, m p 195–197° (lit [15] m p 197°)

The xanthone in the upper layer of the preparative TLC plate (R_f 0 73), was identified as 1,3,5-trihydroxy-6-methoxyxanthone [1] The EtOAc-sparingly soluble solid was triturated with a large volume of hot MeOH The MeOH-soluble fraction, on removal of the solvent, afforded a residue (68 mg) which showed two spots on PPC, R_f 0 48 (orange fluorescence in UV light) and 0 72 (solvent 2) In another solvent, the rate of flow of the two components was reversed, R_f 0 40 (orange fluorescence in UV light) and 0 12 (solvent 3) The two components were separated by repeated crystallizations from MeOH–dioxan in which the xanthone-*C*-glucoside was less soluble

1,3,5,6-*Tetrahydroxyxanthone-C*$_2$-*glucoside* (II) The first crop from the MeOH–dioxan crystallization, upon crystallization from the same solvent, afforded the xanthone-*C*-glucoside as (12 mg) yellow needles, m p 265–268°, R_f (PPC) 0 48 (solvent 2) and 0 40 (solvent 3) (Found C, 53 82, H, 4 31 $C_{19}H_{18}O_{11}$ requires C, 54 03, H, 4 26%)

1,5,6-*Trihydroxy*-3-*methoxyxanthone* (III) The MeOH–dioxan mother liquor, on concentration and cooling, gave a solid (42 mg) which crystallized from the same solvent as brown micro-needles, m p 270–272°, R_f 0 72 (solvent 2) and 0 12 (solvent 3) It gave a dark green with ethanolic $FeCl_3$ and a positive Tollens test The IR spectrum showed characteristic bands at ν_{max} (mineral oil) 3410, 1662, 1630, 1610, 1582, 1325, 1292, 1218, 1205, 1098, 1062, 965, 888 cm^{-1} The diacetate, crystallized from MeOH as needles, m p 208–210° It showed characteristic IR bands at ν_{max} (mineral oil) 3350 (broad), 1780, 1665, 1630, 1610, 1295, 1270, 1205, 1050 cm^{-1} (Found C, 59 88, H, 4 14 $C_{18}H_{14}O_8$ requires C, 60 30, H, 3 91%)

Synthesis of III *by partial methylation of* 1,3,5,6-*tetrahydroxyxanthone* To a solution of 1,3,5,6-tetrahydroxyxanthone (80 mg) in $Na_2B_4O_7$ (5%, 15 ml), Me_2SO_4 (0 6 ml) and NaOH (5%, 10 ml) were added under stirring for 3 hr The crude product, obtained as a brown amorphous powder, showed two major spots on TLC It was dissolved in MeOH (10 ml) and passed through a column of silica gel (100 g) Elution with $CHCl_3$–MeOH (1 2) afforded brown micro crystals which showed two spots on TLC corresponding to unchanged 1,3,5,6-tetrahydroxyxanthone (minor component) and the product (major component) The desired product crystallized from MeOH–dioxan as brown needles (22 mg), m p and m m p 270–272°, co-TLC and superimposable IR spectra with the naturally occurring compound

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