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GLYCOSIDES OF TWO XANTHONES AND A CHROMONE FROM ROOTS OF *CHROZOPHORA PROSTRATA*

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Key Word Index—*Chrozophora prostrata*, Euphorbiaceae, xanthone, chromone, glycosides.

Abstract—Three new glycosides, two xanthone glycosides, viz. 3,5,6,7,8-pentamethoxyxanthone-1-*O*-rhamnosyl (1 → 6) glucopyranoside, 3,5,8-trimethoxyxanthone-1-*O*-glucopyranoside and a chromone glycoside, viz. 2-acetonyl-5-methyl-7-hydroxy-6-C-glucopyranosyl chromone-2″-*O*-glucopyranoside have been isolated from the roots of *Chrozophora prostrata* The structures were elucidated by means of spectral studies.

INTRODUCTION

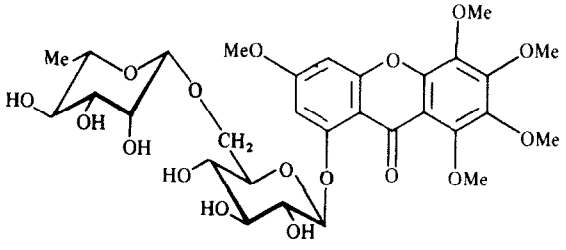
Chrozophora prostrata is known to be rich in leucoanthocyanidin, flavonoid and coumarin derivatives [1] The ashes of roots of *C prostrata* are given to children as a cure for coughs In the present communication, the isolation and characterization of glycosides of two xanthones and a chromone is described. Identification of these compounds may be of considerable help in understanding the therapeutic properties of the roots of *C. prostrata*

RESULTS AND DISCUSSION

The ethanolic extract of the roots yielded two xanthone glycosides (**1**) $C_{30}H_{38}O_{17}$ and (**2**) $C_{22}H_{24}O_{11}$, and a chromone glycoside (**3**) $C_{25}H_{32}O_{14}$

Compound (**1**), $C_{30}H_{38}O_{17}$, mp 270° gave on acid hydrolysis an aglycone, $C_{18}H_{18}O_8$, and two sugars, glucose and rhamnose The aglycone was identified as 1-hydroxy-3,5,6,7,8-pentamethoxy-xanthone on the basis of standard colour reactions, spectral data (UV, IR, NMR and mass) and co-chromatography with an authentic sample [2] Since there was only one hydroxyl group at position C-1, obviously there was only position possible for the attachment of the sugar moiety ^{1}H NMR of the glycoside showed a broad signal at δ0 95 ppm, typical of the rhamnose methyl group. The nature of the intersugar linkage was deduced by comparison of the rhamnose methyl group signal with corresponding signals of neohesperidoside δ1 20 (*d*) and a rutinoside δ0 80–0 95 (*br*) ppm of the rutinoside type [3, 4] The permethylated glycoside, on hydrolysis gave two partially methylated sugars, identified as 2,3,4-tri-*O*-methyl glucose and 2,3,4-tri-*O*-methyl rhamnose This established that the two sugars, were present in the form of a (1→6) bioside [5, 6] and linked at position-1 of the aglycone On the basis of above findings, the structure of the compound could be respresented as 3,5,6,7,8-pentamethoxy xanthone-1-*O*-rhamnosyl (1→6) glucopyranoside (**1**)

Compound (**2**), $C_{22}H_{24}O_{11}$, mp 240° gave on acid hydrolysis an aglycone, $C_{16}H_{14}O_6$, and glucose. The aglycone was identified as 1-hydroxy-3,5,8-trimethoxyxanthone [7, 8] on the basis of UV, IR, ^{1}H NMR and chemical degradation Easy acid hydrolysis of the glycoside clearly indicated a C–O–C type of linkage between



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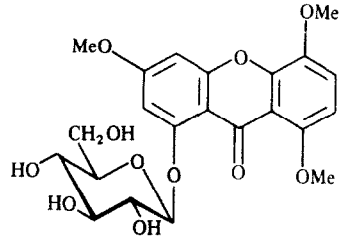

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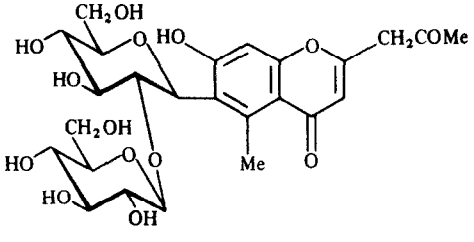

3

the aglycone and sugar. The site of attachment of the sugar was proved to be C-1. Thus, this glycoside has been identified as 3,5,8-trimethoxyxanthone-1-*O*-glucopyranoside

Compound (**3**), $C_{25}H_{32}O_{14}$, mp 290° gave on acid hydrolysis a sugar and an aglycone (**4**) which gave a positive colour test for a glycoside but it could not be hydrolysed by acid showing the presence of C–C linkage. On oxidation with ferric chloride **4** gave an aglycone (**5**) and glucose. **4** was found to be 7-hydroxychromone with the help of colour reactions and UV spectroscopy [9]. The absence of an hydroxyl group, α-to the carbonyl group, was confirmed by its UV spectrum (no shift with $AlCl_3$). Sharp and strong bands at 1717 and 1663 cm^{-1} in the IR spectrum suggested the presence of a saturated carbonyl and an α,β-unsaturated carbonyl group, respectively.

Three aromatic protons at δ6 10 (*s*, 1H), 6.69 (*d*, 1H, J = 2 Hz) and 6 99 (*d*, 1H, J = 2 Hz) in **4** were assigned to the positions C-3, C-6 and C-8 with the help of the ^{1}H NMR spectrum [10] A three proton signal at δ2.66 ppm was found to be a -Me group at position C-5 [11] A second three proton singlet at δ2.20 and a two proton singlet at δ3.79 ppm corresponded to –Ac and $-COCH_2-$, respectively, of an acetonyl group which must be present at C-2. The aglycone was, therefore, 2-acetonyl-5-methyl-7-hydroxy chromone. This was also confirmed by co-chromatography with an authentic sample.

The mass spectrum of the **4** showed three strong peaks due to the sequential loss of three molecules of water. The intensity of the $[M-148]^+$ peak relative to $[M-149]^+$ was 42%, thus indicating that the glucose moiety must be attached to the C-6 position [12] of the chromone nucleus. This was further confirmed by ^{1}H and ^{13}C NMR data

Attachment of the second glucose unit to the C-6 glucose and not directly to the 7-hydroxy was established by UV shifts. This established that the **3** was an α''-*O*-glucoside of 6-*C*-glucosyl-2-acetonyl-5-methyl-7-hydroxychromone. There was no acetyl ^{1}H NMR signal in the range δ1.70–1 85 ppm for the acetyl derivative of **4**. Since a C-2''acetoxyl is expected to give rise to a signal in this region [13–15], it is concluded that the second sugar unit was attached at position-2'' This was also confirmed by the absence of $[M-15]^+$ and $[M-31]^+$ peaks in the mass spectrum of permethylated compounds **3** [16]. Thus, the structure of **3** was assigned as 2-acetonyl-5-methyl-7-hydroxy-6-*C*-glucopyranosyl chromone-2''-*O*-glucopyranoside.

EXPERIMENTAL

Air-dried, crushed and defatted roots of *C prostrata* were extd with boiling EtOH The extract was concd and poured into ice-H_2O separating into H_2O sol and insol. fractions. The H_2O sol. portion was concd and subjected to silica gel CC. Compound **1** was eluted with C_6H_6–EtOAc (1 1), **2** with EtOAc–MeOH (3:2) and **3** with EtOAc–MeOH (3 7)

Compound **1**, 3,5,6,7,8-*pentamethoxyxanthone*-1-*O*-*rhamnosyl* (1→6) *glucopyranoside*. $C_{30}H_{38}O_{17}$, mp 270°. UV λ_{max}^{MeOH} nm 255, 310, 350 (sh), + $AlCl_3$. 260, 315, 355, + NaOAc no shift ^{1}H NMR [$CDCl_3$, 100 MHz] δ 0 95 (*br*, rhamnosyl methyl), 3 40–3.90 (*br*, 11H, sugar protons), 3 86 (*s*, 3H, –OMe), 3 92 (*s*, 3H, –OMe), 4 00 (*s*, 6H, 2 × -OMe), 4 15 (*s*, 3H, –OMe), 5 00 (*s*, 1H, H-1'' rhamnosyl), 5 40 (*s*, 1H, H-1'' glucosyl), 6 40 (*d*, 1H, J = 2 Hz, C-2), 6 70 (*d*, 1H, J = 2 Hz, C-4) ppm

Hydrolysis of **1** with 7% H_2SO_4 afforded an aglycone, $C_{18}H_{18}O_8$, mp 120°. UV λ_{max}^{MeOH} nm. 240 (sh), 258, 315, 355 (sh), + $AlCl_3$. 226, 237, 273, 347, 406, + NaOAc. 240, 274, 304, (sh), 319, 385 IR ν_{max}^{KBr} cm^{-1} 3300, 1659, 1590, 1565 ^{1}H NMR [$CDCl_3$, 100 MHz] δ.3.88 (*s*, 3H, –OMe), 3 93 (*s*, 3H, –OMe), 4 00 (*s*, 6H, 2 × –OMe), 4 12 (*s*, 3H, –OMe), 6 31 (*d*, 1H, J = 2 Hz, C-2), 6 43 (*d*, 1H, J = 2 Hz, C-4), 13 40 (*s*, 1H, OH) ppm. MS, *m/z* 362 (79%), 361 (2), 347 (100), 345 (2), 344 (7), 333 (6), 332 (2), 329 (2), 319 (8), 304 (9), 303 (5). Acetate (with pyridine–Ac_2O at room temp, 48 hr), mp 132° UV λ_{max}^{MeOH} nm 245, 280, 304, 339 (sh) IR ν_{max}^{KBr} cm^{-1} 1760, 1665, 1635, 1598 ^{1}H NMR [$CDCl_3$, 100 MHz] δ 2.84 (*s*, 3H, 1–OAc), 3.92 (*s*, 9H, 3 × –OMe), 3.99 (*s*, 3H, –OMe), 4 11 (*s*, 3H, –OMe), 6 55 (*d*, 1H, J = 2.5 Hz, C-2), 6.82 (*d*, 1H, J = 2 5 Hz, C-4) ppm

Compound **2**, 3,5,8-*trimethoxyxanthone*-1-*O*-*glucopyranoside*. $C_{22}H_{24}O_{11}$, mp 240°. ^{1}H NMR [$CDCl_3$, 100 MHz] δ. 3.50–3.85 (*br*, 6H, sugar protons), 3 86 (*s*, 3H, –OMe), 3 97 (*s*, 6H, 2 × –OMe), 5 42 (*d*, 1H, J = 5 Hz, H-1'' glucosyl), 6.38 (*d*, 1H, J = 3 Hz, C-2), 6 52 (*d*, 1H, J = 3 Hz, C-4), 6 73 (*d*, 1H, J = 10 Hz, C-7), 7 20 (*d*, 1H, J = 10 Hz, C-6) ppm. Hydrolysis with 7% H_2SO_4 gave an aglycone $C_{16}H_{14}O_6$, mp 214°. UV λ_{max}^{MeOH} nm: 220, 240 (sh), 252, 275, 300 (sh), 370 (sh), + $AlCl_3$ 258, 268, 283, 321, 363, + NaOH 244, 264, 274, 331, 380 (sh) IR ν_{max}^{KBr} cm^{-1}. 3300, 1655, 1620, 1580 ^{1}H NMR [$CDCl_3$, 100 MHz] δ 3 86 (*s*, 3H, –OMe), 3.96 (*s*, 3H, –OMe), 3 97 (*s*, 3H, –OMe), 6 32 (*d*, 1H, J = 3 Hz, C-2), 6 50 (*d*, 1H, J = 3 Hz, C-4), 6 72 (*d*, 1H, J = 10 Hz, C-7), 7 20 (*d*, 1H, J = 10 Hz, C-6), 13 22 (*s*, 1H, OH) ppm MS, *m/z* 302 (100%), 301 (4), 287 (40), 284 (40), 273 (31), 269 (9), 259 (9), 258 (22), 256 (7), 255 (7). Acetate (with pyridine–Ac_2O at room temp, 48 hr) ^{1}H NMR [$CDCl_3$, 100 MHz] δ 2 80 (*s*, 3H, –OAc), 3 88 (*s*, 3H, –OMe), 3 98 (*s*, 3H, –OMe), 4 00 (*s*, 3H, –OMe), 6 50 (*d*, 1H, J = 2 Hz, C-2), 6 90 (*d*, 1H, J = 2 Hz, C-4), 6.74 (*d*, 1H, J = 10 Hz, C-7), 7 20 (*d*, 1H, J = 10 Hz, C-6) ppm

Compound **3**, 2-*acetonyl*-5-*methyl*-7-*hydroxy*-6-*C*-*glucopyranosyl chromone* 2''-*O*-*glucopyranoside*. $C_{25}H_{32}O_{14}$, mp 290° UV λ_{max}^{MeOH} nm 216, 248, 254, 297, + $AlCl_3$: no shift, + NaOEt 337, + NaOAc 304. IR ν_{max}^{KBr} cm^{-1}. 3300, 1717, 1663, 1595, 1497, 1321, 1217, 1156, 1081, 911 ^{1}H NMR [DMSO-d_6, 100 MHz] δ 2 20 (*br s*, 3H, –COMe) 2 64 (*s*, 3H, C-Me), 3 40–3 85 (*m*, 11H, sugar protons), 3 79 (*s*, 2H, $-COCH_2-$), 4.24 (*d*, 1H, J = 7 Hz, H = 1'''), 4 72 (*d*, 1H, J = 6 Hz, H = 1''), 6 10 (*s*, 1H, C-3), 6 98 (*s*, 1H, C-8) ppm ^{13}C NMR δ 160 6 (C-2,) 112 4 (C-3), 178 5 (C-4), 114.6 (C-4a), 126 5 (C-6), 160 8 (C-7), 100.6 (C-8), 159.0 (C-1a), 47.8 (C-9), 202 4 (C-10), 29 8 (C-11), 22.5 (C-12), 71 4 (C-1''), 81 7 (C-2''), 78 2 (C-3''), 70 1 (C-4''), 81 1 (C-5''), 60.9 (C-6''), 105 1 (C-1'''), 74.3 (C-2'''), 76 1 (C-3'''), 69.3 (C-4'''), 76 1 (C-5'''), 60 3 (C-6''') Permethylated glycoside, UV λ_{max}^{MeOH} nm 213, 227, 253, 304, 384, 403. IR ν_{max}^{KBr} cm^{-1} 1721, 1647, 1600, 1527, 1314, 1218, 1172 MS, (*m/z*) 668, 449, 433, 417, 385, 289, 275, 273, 259. Hydrolysis: a soln of **3** was hydrolysed with 7% HCl and the aglycone-*C*-glycoside crystallized from EtOAc–petrol, mp 190° UV λ_{max}^{MeOH} nm: 216, 248, 254, 297 IR ν_{max}^{KBr} cm^{-1} 3300, 1720, 1665, 1595, 1497, 1156, 1035, 1010, 730–720 Permethylated aglycone-*C*-glycoside, MS (*m/z*) 464, 449, 433, 417, 385, 289, 275, 273, 259 Acetate (with pyridine–Ac_2O), ^{1}H NMR [DMSO-d_6, 100 MHz] δ· 1 94 (*s*, 3H, –OAc), 2.00 (*s*, 6H, 2 × –OAc), 2.06 (*s*, 3H, –OAc), 2 46 (*s*, 3H, –OAc), 2.20 (*s*, 3H, –COMe), 2 68 (*s*, 3H, –C–Me), 3 80 (*s*, 2H, $-COCH_2-$), 4 56 (*d*, 1H, J = 7 Hz, H = 1''), 6 09 (*s*, 1H, C-3), 7 58 (*s*, 1H, C-8) ppm Aglycone, UV λ_{max}^{MeOH} nm· 217, 245, 250, 295 ^{1}H NMR [DMSO-d_6, 100 MHz] δ 2.20 (*br s*, 3H, –COMe), 2 66 (*s*, 3H, C-Me), 3 79 (*s*, 2H, $-COCH_2-$), 6.10 (*s*, 1H, C-3), 6 69 (*d*, 1H, J = 2 Hz, C-6), 6.99 (*d*, 1H, J = 2 Hz, C-8) ppm.

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TWO XANTHONES FROM *GARCINIA MANGOSTANA*

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Key word Index—*Garcinia mangostana*, Guttiferae, 1,5,8-trihydroxy-3-methoxy-2 [3-methyl-2-butenyl] xanthone, 1,6-dihydroxy-3-methoxy-2 [3-methyl-2-butenyl] xanthone, gartanin; ^{1}H NMR, MS

Abstract—Two new xanthones, 1,5,8-trihydroxy-3-methoxy-2[3-methyl-2-butenyl] xanthone and 1,6-dihydroxy-3-methoxy-2[3-methyl-2-butenyl] xanthone were isolated alongwith the known xanthone gartanin from the leaves of *Garcinia mangostana* and their structures elucidated by ^{1}H NMR, IR and mass spectral studies

INTRODUCTION

Garcinia mangostana L. is known for its medicinal properties. Morellin and neomorellin isolated from *G. morella* have been used as antiprotozoal [1] and anti-bacterial principles [2, 3]. The present paper reports the isolation and characterization of two new xanthones **2** and **3** alongwith the known xanthone gartanin (**1**) from the leaves of *Garcinia mangostana* in addition to several other xanthones reported earlier by other workers [4–6]

RESULTS AND DISCUSSION

Silica gel column chromatography of the benzene extract of dried and powdered leaves of *G. mangostana* yielded two crystalline compounds (**1** and **2**). Compound **1** was found to be identical with gartanin (mp, IR, ^{1}H NMR and MS) reported earlier from fruit hull of *G mangostana* [7]. Recrystallization of **2** yielded a yellow amorphous powder, $C_{19}H_{18}O_6$ (based on $[M]^+$ at m/z 342) which in ethanolic solution gave a red colour with *p*-benzoquinone (gossypetone reaction) indicating the presence of a *p*-quinol moiety [8] It showed UV absorption at λ_{max} 220, 250, 280 and 310 nm in methanol and in the IR spectrum (KBr) ν_{max} 3400 (phenolic OH), 1775 (>C=O), 1650 and 1600 (aromatic system) were noted. The ^{1}H NMR spectrum of **2** showed singlets at δ1 62 and 1.72, each integrating for three protons for geminal methyl groups, a broad signal at δ3 25 for methylene protons, a singlet at δ3.92 for the three methoxy protons and a broad triplet integrating for one proton at δ5 08 for an olefinic proton. A pair of *ortho* coupled doublets (J=8 8 Hz) at δ6 58 and 7 24 were attributable to H-6 and H-7 of the xanthone nucleus [7]. A singlet at δ6 64 integrating for one proton was assigned to H-4 by comparison with other xanthones [9] unsubstituted at position 4. Hydroxy protons showed broad signals at δ10 91, 11 02 and 11 03 The mass spectrum showed a molecular ion at m/z 342 and base peak at m/z 287 [M