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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]

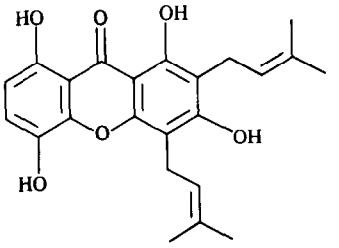
RESULTS AND DISCUSSION

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

−55] Other diagnostic fragment ions were observed at *m/z* 327 [M−15], 299 [M−43] and 271 [M−isoprene −2H or M−isopropyl−CO]

Compound **2**, on acetylation and repeated crystallization from chloroform–ethanol, afforded the acetate **3**, which gave a positive ferric chloride reaction indicating the presence of a phenolic group resistant to acetylation. It showed UV absorption maxima at 310 and 360 nm in chloroform. The ^{1}H NMR spectrum of **3** showed singlets at δ1.69 and 1.75 for geminal methyl groups, singlets at δ2.41 and 2 45 for acetoxy groups, a broad signal at δ3 30 for methylene protons, a singlet at δ3.93 for methoxy protons, a broad triplet integrating for one proton at δ5.10 for olefinic proton and a singlet at δ6.33 for H-4. The doublets (J = 8.8 Hz) at δ6.97 and 7.43 were assigned to H-6 and H-7, respectively. The downfield shift of signals for H-6 and H-7 in **3** compared with that in the parent xanthone (**2**) shows the presence of acetoxy groups at position 5 and 8 of the xanthone nucleus. The MS spectrum of **3** showed a molecular ion at *m/z* 426 and diagnostic fragment ions at *m/z* 384 (M−42), 341 (M−42 −43), 326 (M−42−43−15), 298 (326−CO or 341−43) and 286 (341−55) These data support the structure of **2** as 1,5,8-trihydroxy-3-methoxy-2[3-methyl-2-butenyl] xanthone [10].

When the mother liquor of **2** was acetylated and examined on TLC, it showed the presence of two compounds at R_f 0.26, and 0.40, respectively on silica gel, benzene–chloroform (1:1) which were separated by prep. TLC. The first was found to be identical with **2** while the second was characterized as **4** by UV, ^{1}H NMR and MS data.



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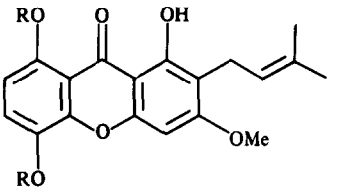
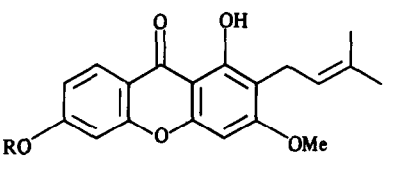


2 R = H
3 R = COMe



5 R = H
6 R = COMe

Compound **4** showed UV absorption maxima at 310 and 360 nm in chloroform. It's ^{1}H NMR spectrum showed singlets at δ1.70 and 1.80 for geminal methyl groups, a singlet at δ2.48 for acetoxy protons, a doublet (J = 6 Hz) at δ3 39 for methylene protons, a singlet at δ3.98 for methoxy protons and a broad triplet at δ5 20 for an olefinic proton. The singlet appearing at δ6 43 integrating for one proton was assigned to H-4 [9] The aromatic region showed a ABX pattern markedly distinct from xanthones with oxygenation at the 7-position [11] and supports the oxygenation at the 6-position. The doublet (J = 9 Hz) at δ7.40 for H-8, doublet (J = 3 Hz) at δ7 48 for H-5 and a double doublet (J = 9, 3 Hz) at δ8 38 for H-7 supports the structure of **4** as 1-hydroxy-6-acetoxy-3-methoxy-2[3-methyl-2-butenyl] xanthone. The double doublet at δ8.38 cannot be assigned to H-8, because *p*-coupling is negligible and H-8 should appear as a doublet. The mass spectrum of **4** showed a molecular ion at *m/z* 368 (88 7) and a base peak at *m/z* 313 [M−55]. The diagnostic fragment ions at *m/z* 353 [34%, M−Me], 325 [80%, M−Ac], 283 [50%, M−15−69−H] and 271 [51%, M−43−55+H] further support the assignment of structure **4** to this compound.

The deacetylation of **4** with ethanol–hydrochloric acid yielded the parent compound **5**. The mass spectrum of **5** showed a molecular ion at *m/z* 326(52 5%) and a base peak at *m/z* 271 [M−55] alongwith the fragment ions at *m/z* 311 [14%, M−Me] and 241 [10%, M−15−69 −H]. The quantity of deacetylated product was not sufficient for ^{1}H NMR. However, on the basis of spectral data for **4** and MS data for **5** the parent xanthone **5** may be characterized as 1,6-dihydroxy-3-methoxy-2[3-methyl-2-butenyl] xanthone.

EXPERIMENTAL

Mps uncorr ^{1}H NMR spectra were recorded at 60 MHz or 80 MHz using TMS as int ref and $CDCl_3$ or DMSO-d_6 as solvent

Plant material The leaves of *G mangostana* were collected from the lower slopes of the Nilgiri hills in India and identified by Professor W. Husain (Department of Botany, A.M U, Aligarh). A Voucher specimen was submitted to the A M U Herbarium, Aligarh (Voucher No Husain-37603)

Isolation Dried leaves (5 kg) were powdered and extracted with EtOH The EtOH extract was concd and treated with petrol and C_6H_6. The C_6H_6 extract (2 5 gm) was chromatographed over a silica gel column The fraction eluted with C_6H_6 gave one major band on TLC (brown in UV light and yellow invisible). On cryst. from C_6H_6–petrol it gave yellow crystals of gartanin[**1**] (1 gm) mp 163–165°, R_f 0 38 (silica gel, C_6H_6–$CHCl_3$ 1·1). UV $\lambda_{max}^{CHCl_3}$ nm 260, 310, 350, ^{1}H NMR (80 MHz, DMSO-d_6): δ1 81, 1 75 (*s*, *s*, 3H each = CMe_2), 5 23 (*br*, 2H, 2 × =CH), 3 50 (*br*, 4H, 2 × CH_2), 6.60 (*d*, 1H, J = 8.8 Hz, H-6), 7.24 (*d*, 1H, J = 8 8 Hz, H-7), 12.20 (*br*, 1H, OH), 11.19 (*br*, 1H, OH), 9 51 (*br*, 2H, OH) IR ν_{max}^{KBr} cm^{-1} 3200, 1630, 1590, 1490, 1265, 1225, 1180, 1005, 810, 730 MS *m/z* (rel. int). 396 (M^+, 48 5), 381 (M^+−15, 9 2), 353 (11.9), 341 (47.8), 325 (52.6), 297 (25 8), 285 (100), 284 (35 8), 273 (7 8)

Further elution of the column with C_6H_6–EtOAc (9:1) gave an oily mass which on repeated cryst, gave crystals of **2** (100 mg), mp 193–195° R_f 0.25 (silica gel, C_6H_6–$CHCl_3$ 1 1), R_f 0 44 (silica gel,

C_6H_6–EtOAc 9 1) It gave green colour with $FeCl_3$, appeared yellow in visible light and was characterized as **2** by UV, ^{1}H NMR, IR and MS UV λ_{max}^{MeOH} nm 220, 250, 280, 310 ^{1}H NMR (DMSO-d_6, 80 MHz), δ1 62, 1 72 (*s*, *s*, 3H each, $=CMe_2$), 3 2 (*br*, 2H, CH_2), 3 92 (*s*, 3H, OMe), 5 08 (*br*, 1H, =CH), 6 58 (*d*, J = 8 8 Hz, 1H, H-6), 6 64 (*s*, 1H, H-4), 7.24 (*d*, J = 8 8 Hz, 1H, H-7), 10 91 (*br*, 1H, 5-OH), 11 02 (*br*, 1H, 1-OH), 11 03 (*br*, 1H, 8-OH) MS *m/z* (rel int) 343 (17 7), 342 (83 3), 327 (61 1), 326 (31 7), 299 (90 4), 287 (100), 286 (16 2), 285 (13 9), 274 (17 3), 271 (50 9)

Compound **2**, on acetylation with Ac_2O–pyridine and repeated cryst from $CHCl_3$–EtOH afforded the acetate **3** (30 mg), mp 172–175° UV $\lambda_{max}^{CHCl_3}$ nm 310, 360 ^{1}H NMR ($CDCl_3$, 60 MHz) δ1 69, 1 75 (*s*, *s*, 3H each, $=CMe_2$), 2 41 (*s*, 3H, OAc), 2 45 (*s*, 3H, OAc), 3 30 (*br*, 2H, CH_2), 3 93 (*s*, 3H, OMe), 5 10 (*br t*, =CH), 6 33 (*s*, 1H, H-4), 6 97 (*d*, 1H, J = 8 8 Hz, H-6) and 7 43 (*d*, 1H, J = 8 8 Hz, H-7); MS *m/z* (rel int) 426 (9), 384 (30 6), 341 (41 4), 326 (23 4), 298 (32 4), 286 (30 6), 56 (100)

The mother liquor of **2** on acetylation with Ac_2O–pyridine yielded **3** and **4** which were separated on PTLC silica-gel, C_6H_6–$CHCl_3$ 1 1) Compound **3** was identical with the acetate of **2** while **4** (25 mg), mp 162°, R_f 0 40 (silica gel, C_6H_6–$CHCl_3$ 1 1) showed UV $\lambda_{max}^{CHCl_3}$ nm 310, 360, ^{1}H NMR ($CDCl_3$, 60 MHz) δ1 70, 1 80 (*s*, *s*, 3H each, $=CMe_2$), 2.48 (*s*, 3H, OAc), 3 39 (*d*, J = 6 Hz, CH_2), 3 98 (*s*, 3H, OMe), 5 20 (*br t*, =CH), 6 43 (*s*, 1H, H-4), 7 40 (*d*, 1H, J = 9 Hz, H-8), 7 48 (*d*, 1H, J = 3 Hz, H-5), 8.38 (*d*, 1H, J = 9, 3 Hz, H-7) MS *m/z* (rel int) 368 (M^+, 88 7), 353 (34), 325 (80), 313 (100), 283 (50) and 271 (51) The deacetylation of a small quantity (15 mg) of **4** with EtOH–HCl yielded the parent compound **5** (10 mg), mp above 240°, MS *m/z* (rel int) 326 (M^+, 52 5), 311 (14), 271 (100) and 241 (10)

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TWO XANTHONE GLYCOSIDES FROM *GENTIANA LUTEA*

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Key Word Index—*Gentiana lutea*, Gentianaceae; gentian, xanthone glycoside, 7-hydroxy-3-methoxy-1-*O*-primeverosylxanthone, 1-hydroxy-3-methoxy-7-*O*-primeverosylxanthone

Abstract—Two new xanthone glycosides have been isolated from the root of *Gentiana lutea* The structures were determined as 7-hydroxy-3-methoxy-1-*O*-primeverosylxanthone and 1-hydroxy-3-methoxy-7-*O*-primeverosylxanthone on the basis of spectroscopic evidence

INTRODUCTION

The dried root of *Gentiana lutea* (gentian) is one of the most important crude drugs used as bitter stomachic and sedative It is known to contain bitter glycosides, such as gentiopicroside [1–3] and amarogentin [4], and xanthone glycosides, gentioside [5, 6] and mangiferin [6] The gentian, used in Japan, is mainly imported from Europe. In past decades, it has been also cultivated in Hokkaido (Japan). The gentian imported from Europe has a yellowish brown internal colour, but that produced in Hokkaido has a white internal colour It is considered