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TWO NEW XANTHONE GLYCOSIDES FROM *TRIPTEROSPERMUM LANCEOLATUM**

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Key Word Index—*Tripterospermum lanceolatum*; Gentianaceae; xanthone glycoside; lanceoside: 1,8-dihydroxy-3,7-dimethoxyxanthone-4-*O*-β-D-glucoside; lancerin: C-4-β-D-glucosyl-1,3,7-trihydroxyxanthone.

Abstract—Oleanolic acid, mangiferin, and two new xanthone glucosides, named lanceoside (1,8-dihydroxy-3,7-dimethoxyxanthone-4-*O*-β-D-glucoside) and lancerin (C-4-β-D-glucosyl-1,3,7-trihydroxyxanthone), respectively, were isolated from the aerial parts of *Tripterospermum lanceolatum*.

INTRODUCTION

As part of a search for constituents in various genera of Formosan Gentianaceae, the fresh aerial parts of *Tripterospermum lanceolatum* was extracted with hot MeOH. Oleanolic acid (**1**), mangiferin (**2**), identified by comparison with authentic samples, and two new xanthone glucosides, named lanceoside (**3**) and lancerin (**7**), respectively, were obtained. In this paper we report the isolation and structural determination of these two new xanthone glucosides.

RESULTS AND DISCUSSION

Lanceoside (**3**), $C_{21}H_{22}O_{12}$, showed UV and IR spectra characteristic of a 1,3,4,7,8-pentaoxygenated xanthone [1]. A bathochromic shift with $AlCl_3$ suggested the presence of a 1- or 8-OH function. The ^1H NMR spectrum (d_6-DMSO) (Table 1) showed six glucosyl protons at 3.50 δ and two 3 H singlets at 3.80 and 3.95 δ assignable to the proton of two OMe groups. The glucose anomeric proton of the 1 H doublet (J = 6 Hz), centered at 4.93 δ, showed a diaxial coupling with the $C_{2'}$-H, suggesting a β-D-glucosidic linkage [2] in the xanthone-*O*-glucoside. A 1 H singlet at 6.58 δ was attributed to the proton located at the 2-position and a pair of 1 H doublets (J = 9 Hz) centered at 7.01 and 7.62 δ was assignable to the proton located at 5- and 6-positions, respectively. Two 1 H singlets at 11.72 and 11.77 δ assignable to the proton of C-1 OH and C-8 OH [3] indicated that **3** is a 1,8-dihydroxyxanthone. Hydrolysis with HCl gave D-glucose and the aglycone (**5**). The UV spectra of **5** showed a bathochromic shift with $AlCl_3$, but was unchanged on addition of NaOAc and NaOAc + H_3BO_3. The mass spectral fragmentation pattern of the triacetate of **5** (**6**) substantiated the proposed structure [4–5]. Based on the above data, **3** is 1,4,8-trihydroxy-3,7-dimethoxyxanthoneglucoside. The UV bathochromic shifts of both **3** and **5** with $AlCl_3$, the absence of shifts of either compound with NaOAc and NaOAc + H_3BO_3, and the positive reaction with Gibb's reagent of **3**, clearly indicated the glycosyl linkage to be at the 4-position.

Lancerin (**7**), $C_{19}H_{18}O_{10}$, was resistant to hydrolysis with HCl, but $FeCl_3$ oxidation yielded arabinose and glucose [6]. Its UV spectrum showed maxima at 237, 261, 313, 375 nm. The above data, IR spectra, and a bathochromic shift with $AlCl_3$ and NaOAc, clearly indicated that **7** possesses a free C-3 OH or C-6 OH with glucose attached to the C-1 or C-8 hydroxyl group. The ^1H NMR spectrum (d_6-DMSO) (Table 1) of **7** showed a 1 H singlet, centered at 6.23 δ assignable to the proton located at the 2-position, a 3 H multiplet centered at 7.37 δ attributed to the aromatic proton, and a strongly deshielded proton at 13.13 δ belonging to the C-1 hydroxyl proton [7].

The ^1H NMR spectrum ($CDCl_3$) of the acetate of **7** showed a 3 H singlet at 1.70 δ, assigned to the acetoxyl at C-2′ or C-β-D-glucopyranosyl compounds [8], a 9 H singlet at 2.06 δ indicating three aliphatic acetyl groups, and 3 H and 6 H singlets at 2.30 and 2.45 δ attributed to three aromatic acetyl groups. The two 1 H singlets at 6.83 and 7.90 δ were assigned to the proton located at C-2 and C-8 respectively, and the 2 H singlet at 7.53 δ was attributed to the proton located at C-5 and C-6. **7** in phenol was decomposed with HI to afford the aglycone (**9**), $C_{13}H_8O_5 . 2H_2O$. The UV spectrum of **9** showed maxima at 233, 257, 307, and 370 nm, and a bathochromic shift with $AlCl_3$ and NaOAc. The IR spectrum of **9** exhibited absorption bands at 1650, 1620 (conjugated CO) and 1600, 1570 (aromatic C=C). The ^1H NMR spectrum (d_6-DMSO) showed a pair of 1 H doublets (J = 2 Hz), centered at 6.15 and 6.33 δ, assignable to the proton located at C-2 and C-4, respectively. The 3 H multiplet, centered at 7.33 δ was attributed to the aromatic proton and a strongly deshielded proton at 12.93 δ belonged to the proton of C-1 OH [7]. Based on the above evidence **9** was identified as 1,3,7-trihydroxyxanthone (gentisein) and the identity was

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Table 1. ^{1}H NMR spectra of xanthones of *Triptospermum lanceolatum*

Compound	Hydroxyl protons	Acetyl protons	Methoxyl protons	Anomeric proton	Aromatic protons
3[b]	11.72 (C-1 OH) 11.77 (C-8 OH)		3.80 (3 H) 3.95 (3 H)	4.93 (J = 6 Hz)	6.85 (C-2 H), 7.01 (C-5 H), 7.62 (C-6 H) (J = 9 Hz)
4[a]		2.04 (6 H), 2.10 (6 H) aliphatic 2.43 (6 H) aromatic	3.99 (6 H)		6.62 (C-2 H), 7.43 (C-5,6 H)
6[a]		2.33 (3 H), 2.44 (6 H) aromatic	4.00 (6 H)		6.63 (C-2 H), 7.50 (C-5,6 H)
7[b]	13.13 (C-1 OH)				6.23 (C-2 H), 7.37 (3 H)
8[b]		1.70 (3 H) glycosyl C_2 2.06 (9 H) aliphatic 2.30 (3 H), 2.45 (6 H) aromatic			6.83 (C-2 H), 7.53 (C5,6 H) 7.90 (C-8 H)
9[b]	12.93 (C-1 OH)				6.15 (C-2 H), 6.33 (C-4 H) (J = 2 Hz) 7.33 (3 H)
10[a]		2.33 (6 H), 2.46 (3 H) aromatic			6.80 (C-2 H), 7.21 (C-4 H) (J = 2 Hz) 7.40 (C-5,6 H), 7.86 (C-8 H)

NMR spectra were measured at 60 MHz, Chemical shifts are expressed in δ values from TMS. Deuterium oxide was added to identify hydroxyl groups.

[a] In deuterochloroform.

[b] In deuterodimethylsulfoxide.

proved by IR comparison (KBr) with an authentic sample. The ^{1}H NMR spectrum of **9** acetate confirmed the identity of the aglycone as gentisein.

Therefore, according to the UV bathochromic shifts of **7** and **9** in $AlCl_3$ and NaOAc, the absence of a signal for a proton located at C-4 in **7**, the presence of a signal for a proton at C-4 in **9** and the identification of **9** as 1,3,7-trihydroxyxanthone indicates that, the glycosidic linkage of **7** should be located at C-4. Consequently, the structure of **7** was determined as C-4-β-D-glucosyl-1,3,7-trihydroxyxanthone.

EXPERIMENTAL

Extraction and separation. Fresh material of *T. lanceolatum* (0.65 kg) collected at Alishan, Taiwan, in Aug. 1977, chipped and extrd several times with hot MeOH. After removal of oleanolic acid (**1**), the MeOH extract was evapd under red. pres. and then treated as described in ref. [9]. Concn of the EtOAc and *n*-BuOH fractions afforded mangiferin (**2**), and the filtrate of the latter was chromatographed on a Si gel column. The column was eluted with $CHCl_3$, $CHCl_3$–MeOH, and MeOH to afford lanceoside (**3**) eluted with $CHCl_3$–MeOH (9:1), lancerin (**7**) eluted with $CHCl_3$ MeOH (6:1) and mangiferin (**2**) eluted with $CHCl_3$–MeOH (2:1).

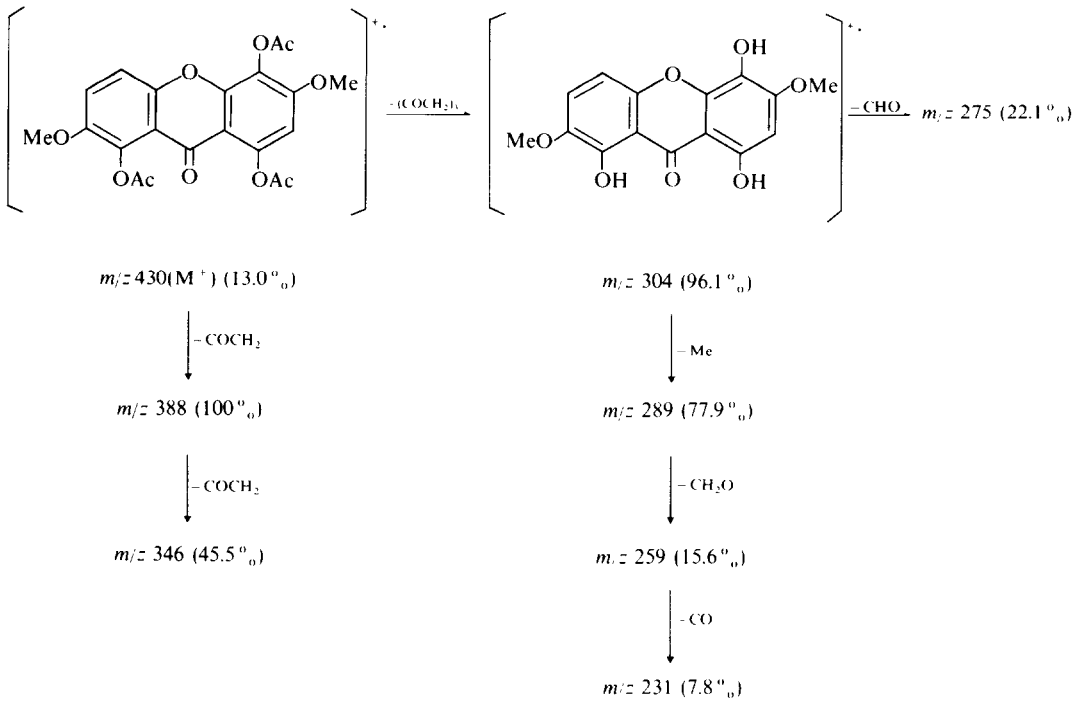
Oleanolic acid (**1**). Recrystallized from MeOH gave colorless needles, mp >300°, purplish red color with the Lieberman–Burchard reaction, identified by IR (KBr) comparison with authentic sample.

Mangiferin (**2**). Recrystallized from MeOH to give yellow needles, mp 268–270° (decomp.), orange-red color with Mg–HCl, greenish brown color with $FeCl_3$, and orange fluorescence under UV. PPC R_f: 0.45 (15% HOAc). The mmp and IR (KBr) spectra were identical with authentic mangiferin.

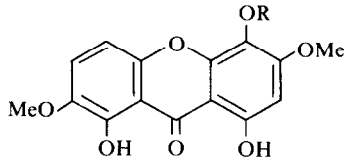
Lanceoside (**3**). Yellow needles (MeOH), mp 238–242°, violet color with Mg–HCl, bluish under UV and positive reactions with Fehling's soln and Gibb's reagent. PPC R_f: 0.51 (15% HOAc), 0.71 (30% HOAc). (Found: C, 54.20; H, 4.64. $C_{21}H_{22}O_{12}$ requires: C, 54.08; H, 4.72.) UV λ_{max}^{MeOH} nm (log ε): 235 (4.24), 266 (4.44), 308 (*sh*) (3.96), 341 (4.05), 400 (*sh*) (3.49). +$AlCl_3$: 236 (*sh*), 278, 324 (*sh*), 387. IR ν_{max}^{KBr} cm^{-1}: 1640, 1620, 1600, 1580. ^{1}H NMR (60 MHz, d_6-DMSO): δ 3.50 (6 H, glucosyl proton), 3.80 (3 H, *s*, OMe), 3.95 (3 H, *s*, OMe), 4.93 (1 H, *d*, J = 6 Hz, C-1 H of β-glucoside), 6.58 (1 H, *s*, C-2 H), 7.01 (1 H, *d*, J = 9 Hz, C-5 H), 7.62 (1 H, *d*, J = 9 Hz, C-6 H), 11.72 (1 H, *s*, C-1 or C-8 OH), 11.77 (1 H, *s*, C-1 or C-8 OH).

Lanceoside acetate (**4**). To a soln of **3** in pyridine was added Ac_2O. After heating at 100° for 3 hr, the reaction mixture was worked up. Recrystallization from MeOH gave colorless needles, mp 211–212°, which gave no color reaction with $FeCl_3$. (Found: C, 55.12; H, 4.78. $C_{33}H_{34}O_{18}$ requires: C, 55.13; H, 4.77%.) ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.04 (6 H, *s*, aliphatic OAc × 2), 2.10 (6 H, *s*, aliphatic OAc × 2), 2.43 (6 H, *s*, aromatic OAc × 2), 3.99 (6 H, *s*, OMe × 2), 6.62 (1 H, *s*, C-2 H), 7.43 (2 H, *d*, C-5,6 H).

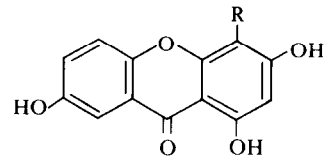
Hydrolysis of **3**. A soln of **3** in conc. HCl was heated at 100° for 2 hr. The reaction mixture was washed with H_2O and the H_2O-insol. part recrystallized from MeOH to give yellow needles of **5**, mp 232–233°, violet color with Mg–HCl, negative reaction with Fehling's soln and orange color under UV. PPC R_f: 0.19 (15% HOAc), 0.38 (30% HOAc). (Found: C, 59.27; H, 3.89. $C_{15}H_{12}O_7$ requires: C, 59.21; H, 3.98%). UV λ_{max}^{MeOH} nm (log ε): 237 (4.26), 269 (4.51), 309 (3.81), 343 (4.04), 400 (3.48). +$AlCl_3$: 245, 280, 327, 383.



Scheme 1. Diagnostic fragmentations in the mass spectrum of the acetate of xanthone **5**.



3 R = glucose
5 R = H



7 R = glucose
9 R = H

IR ν_{max}^{KBr} cm^{-1}: 1640, 1620, 1600, 1580. The H_2O-sol. part was evapd to dryness for examination of sugar PPC R_f · 0.20 (brown) (*n*-BuOH–HOAc–H_2O, 4:1:2) 0.20 glucose (brown). TLC Si gel containing 0.1 N H_3BO_3) R_f: 0.65 (brown) (C_6H_6–HOAc–MeOH, 1:1:3), 0.65 glucose (brown). Sugars were detected with 0.1 N aniline phthalate and heating.

1,4,8-*Trihydroxy*-3,7-*dimethoxyxanthone acetate* (**6**). To a soln of **5** in pyridine was added Ac_2O. After heating at 100° for 3 hr the reaction mixture was worked up. Crystallization from MeOH gave colorless needles, mp 196–197°, which gave no color reaction with $FeCl_3$. (Found: C, 58.64, H, 4.12. $C_{21}H_{18}O_{10}$ requires: C, 58.60, H, 4.19 %.) MS *m/z*: 430 (M^+), 388, 346, 304, 289, 275, 259, 231 (Scheme 1). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.33 (3 H, *s*, aromatic OAc), 2.44 (6 H, *s*, aromatic OAc × 2), 4.0 (6 H, *s*, OMe × 2), 6.63 (1 H, *s*, C-2 H), 7.50 (2 H, *d*, C-5,6 H).

Lancerin (**7**). Yellow needles (MeOH), mp 225–227°, violet colour with Mg–HCl, greenish brown color with $FeCl_3$, dark violet under UV, and resistant to hydrolysis with HCl, PPC R_f: 0.42 (15 % HOAc), 0.53 (30 % HOAc). (Found: C, 56.21; H, 4.29. $C_{19}H_{18}O_{10}$ requires: C, 56.28; H, 4.23 %.) UV λ_{max}^{MeOH} nm (log ε): 237 (4.39), 261 (4.47), 313 (4.10), 375 (3.85); +$AlCl_3$: 230, 273, 325, 421; +NaOAc: 227, 264, 340, 400 (*sh*). IR ν_{max}^{KBr} cm^{-1}: 1650, 1620, 1600, 1570. ^{1}H NMR (60 MHz, d_6-DMSO): δ 6.23 (1 H, *s*, C-2 H), 7.37 (3 H, *m*, aromatic H), 13.13 (1 H, *s*, C-10 H).

Lancerin acetate (**8**). To a soln of **7** in pyridine was added Ac_2O as described for **6**. Recrystallization from MeOH gave colorless needles, mp 176–177°, which gave no color reaction with $FeCl_3$. (Found: C, 56.64; H, 4.42. $C_{33}H_{32}O_{17}$ requires: C, 56.63; H, 4.47.) ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.70 (3 H, *s*, glucosyl C-2OAc), 2.06 (9 H, *s*, aliphatic OAc × 3), 2.30 (3 H, *s*, aromatic OAc), 2.45 (6 H, *s*, aromatic OAc × 2), 6.83 (1 H, *s*, C-2 H), 7.53 (2 H, *s*, C-5, 6 H), 7.90 (1 H, *s*, C-8 H).

Hydrolysis of **7**. To a soln of **7** in PhOH was added HI. After refluxing at 135–137° for 7 hr, the reaction mixture was worked up. Recrystallization from MeOH gave yellow needles of **9**, mp > 300°. (Found: C, 55.83; H, 4.16. $C_{13}H_8O_5 \cdot 2\,H_2O$ requires: C, 55.71; H, 4.28 %.) UV λ_{max}^{MeOH} nm: 233, 257, 307, 370; +ACl_3: 228, 270, 325, 418; +NaOAc: 266, 337, 398 (*sh*). IR ν_{max}^{KBr} cm^{-1}: 1650, 1620, 1600, 1570. ^{1}H NMR (60 MHz, d_6-DMSO), δ 6.15 (1 H, *d*, J = 2 Hz, C-2 H), 6.33 (1 H, *d*, J = 2 Hz, C-4 H), 7.33 (3 H, *m*, aromatic-H), 12.93 (1 H, *s*, C-1 OH). It was identified as gentisein (1,3,7-trihydroxyxanthone) by IR comparison (KBr) with an authentic sample.

Gentisein acetate (**10**). To a soln of **9** in pyridine was added Ac_2O as described for **6**. Recrystallization from MeOH gave colorless needles, mp 217–218°. (Found: C, 61.69; H, 3.74. $C_{19}H_{14}O_8$ requires: C, 61.60; H, 3.81 %.) ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.33 (6 H, *d*, aromatic OAc × 2), 2.46 (3 H, *s*, aromatic OAc), 6.80 (1 H,

d, J = 2 Hz, C-2 H), 7.21 (1 H, *d*, J = 2 Hz, C-4 H), 7.40 (2 H, *d*, C-5,6 H), 7.86 (1 H, *s*, C-8 H).

Oxidation of **7**. **7** (100 mg) was refluxed with an aq. soln of $FeCl_3$ (0.5 g in 2 ml H_2O) for 6 hr. After cooling the reaction mixture was filtered, the filtrate passed through the columns of Amberlite IRC-120 (H^+ form) and IRA-400 (OH^- form) and evapd *in vacuo* to a syrup, which was examined by PPC for sugars. R_f: 0.18 (brown), 0.21 (reddish brown) (*n*-BuOH–HOAc–H_2O, 4:1:2); glucose 0.18 (brown), arabinose 0.21 (reddish brown).

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