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A SECOIRIDOID AND OTHER CONSTITUENTS OF *GONOCARYUM CALLERYANUM*

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Key Word Index—*Gonocaryum calleryanum*; Icacinaceae; secoiridoid glycoside; gonocaryoside E; kingiside derivative.

Abstract—Investigation of the leaves, branch, stem and root bark of *Gonocaryum calleryanum* resulted in the isolation of a new secoiridoid glycoside, gonocaryoside E, together with 14 known compounds. Their structures were elucidated by spectral analysis and chemical transformation. Gonocaryoside E was shown to be a derivative of kingiside in which the lactone ring was open, and with the 8-hydroxy group esterified with tiglic acid. Alkaline hydrolysis of these secoiridoids is discussed. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Gonocaryum calleryanum (Baill) Becc is a small evergreen tree which is widely distributed from Indonesia to the Philippines to Taiwan. This plant is the only species of *Gonocaryum* native to the southern part of Taiwan [1]. The leaves of this plant are used for the treatment of stomach disease in Philippine folk medicine [2]. However, it is apparently not used in Taiwan folk medicine. Kaneko *et al.* reported the isolation of secoiridoid glycosides and flavonoid glycosides from the leaves of this plant [3]. We were interested to investigate the constituents of *G. calleryanum* due to the lack of phytochemical work on the plants of this genus. We describe herein the isolation and structure determination of a new secoiridoid glycoside, gonocaryoside-E (**1a**), together with 14 known compounds from leaves, branch, stem and root bark of *G. calleryanum*.

RESULTS AND DISCUSSION

Gonocaryoside-E (**1a**) was isolated as an optically active amorphous powder. It gave rise to a quasimolecular ion peak at *m/z* 505 $[M+H]^+$ on FAB-mass spectrometry. High mass measurement established the molecular formula as $C_{22}H_{32}O_{13}$. The UV spectrum of compound **1a** showed an intense absorption band at 221.8 nm characteristic of a conjugated carbonyl function. Furthermore, its ^1H and ^{13}C NMR spectra displayed a carbomethoxyl signal at δ_H 3.57 (δ_C 166.3 and 50.3) and a trisubstituted double bond at δ_H 7.73 (δ_C 152.3, 109.5) and a ketal signal at δ_H 6.28 (δ_C 95.3). These data together with a positive H_2SO_4-vanillin reaction suggested **1a** to be an iridoid. The ^1H NMR signals at δ 7.06 (*q*, J = 7.0 Hz), 1.88 (3H, *s*), and 1.62 (3H, *d*, J = 7.0 Hz) together with those in the ^{13}C NMR spectrum at δ 166.5 (*s*), 137.0 (*d*), 128.5 (*s*), 13.5 (*q*) and 11.5 (*q*) suggested the presence of a tiglic acid moiety in the molecule. On alkaline hydrolysis, **1a** afforded two (**1c** and **18a**) hydrolysis products of which one (**1c**) was one of the alkaline hydrolysis products (**1b**, **1c**, **1d** and **18b**) of gonocaryoside-A (**2**) which was isolated from the same plant as a major product. **18a** was identified as tiglic acid by comparison of its spectral data. The connection between **1c** and **18a** as well as the full ^{13}C NMR and ^1H NMR chemical shift assignments were made by means of COSY, HMQC, NOESY (Fig. 1)

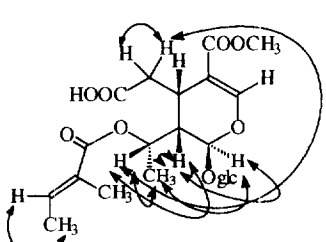

Fig. 1. NOESY spectrum of Gonocaryoside E.

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Table 1. Alkaline hydrolysis of secoiridoids

Compound	Reagent	Temp.	Time	Product
2	10% NaOH	60–70°C	1 hr	**1b**
2	5% KOH	RT	20 hr	**1b**
1b	5% KOH	RT	3 day	no reaction
1b	5% KOH	60–70°C	8 hr	no reaction
1b	10% KOH	60–70°C	7 hr	no reaction
1b	10% NaOH	60–70°C	7 hr	no reaction
1b	5% KOH, HMPA	RT	overnight	**1c**, **1d**, **18b**
1a	5% KOH, HMPA	RT	overnight	**1c**, **18a**

Table 2. ^2J, ^3J-correlation of HMBC of Gonocaryoside E

C	δ, ppm	H
1	95.3	3 (7.73), 5 (3.80), 8 (5.68), G-1 (5.41)
3	152.3	1 (6.28), 5 (3.80)
4	109.5	3 (7.73), 5 (3.80), 6 (3.10), 6 (2.86)
5	28.9	1 (6.28), 3 (7.73), 6 (3.10), 6 (2.86)
6	34.9	5 (3.80)
7	174.2	5 (3.80), 6 (3.10), 6 (2.86)
8	68.8	1 (6.28), 5 (3.80), 10 (1.47)
9	42.7	5 (3.80), 6 (3.10), 10 (1.47)
11	166.3	3 (7.73), OCH_3 (3.57)
1′	166.5	3′ (7.06), 4′ (1.88), 5′ (1.62)
2′	128.5	3′ (7.06), 4′ (1.88), 5′ (1.62)
3′	137.0	4′ (1.88), 5′ (1.62)
4′	13.5	3′ (7.06)
5′	11.5	3′ (7.06), 4′ (1.88)
G-1	99.8	1 (6.28), G-2 (4.03)
G-2	73.9	G-3 (4.24)
G-3	77.6	G-2 (4.03)
G-4	70.6	G-2 (4.03), G-3 (4.24), G-6 (4.50), G-6 (4.34)
G-5	77.9	G-1 (5.41), G-4 (4.20)
G-6	61.9	G-4 (4.20)

and HMBC (Table 2). The ^1H-^{13}C long range correlation between the H-8 (δ 5.68) and a C-1′ carbonyl carbon signal at δ 166.5 indicated that the tiglic acid (**18a**) must be connected with the hydroxyl group at C-8 of **1c**. Based on the above results, the structure of gonocaryoside E was assigned as **1a**.

In our hands, alkaline hydrolysis of **2** was more difficult than reported by Kaneko's group [3]. Using their conditions for 20 hours, we obtained only partial hydrolysis to **1b** (Table 1. Entry 2). This result could not be improved by increasing the alkaline concentration or the temperature. However, when HMPA was added to the solution of **1b**, the products, **1c**, **1d** and **18b** were successfully obtained.

The known compounds, gonocaryoside A (**2**) [3], -B (**3**) [3], β-amyrin acetate (**4**) [4], oleanolic aldehyde-3-acetate (**5**) [5], β-amyrin (**6**) [6], erythrodiol-3-acetate (**7**) [7], oleanolic acid (**8**) [8], 3-acetyl oleanolic acid (**9**) [5, 7], β-sitosteryl-β-D-glucoside (**11a**) [6], stigmasteryl-β-D-glucoside (**11b**) [6], ursolic acid (**10**) [9], 5-hydroxymethyl-2-furaldehyde (**12**) [10] and betunilic acid (**15**) [8] were isolated and characterized from the root and stem bark of *G. calleryanum*. Gonocaryoside A (**2**) [3], β-amyrin (**6**) [6], oleanolic acid (**8**) [8], α-amyrin (**13**) [11] and lupeol (**14**) [6, 12] were isolated and identified from the branch of the same plant. On the other hand, gonocaryoside A (**2**) [3], β-amyrin (**6**) [6], α-amyrin (**13**) [11], lupeol (**14**) [6, 12], ursolic acid (**10**) [9], methylparaben (**16**) [12], *p*-hydroxybenzaldehyde (**17**) [12], 2*S*,3*S*-angliceric acid (**18b**) [3], *cis*-methylcaffeate (**19**) [13] and *trans*-methyl caffeate (**20**) [13] were also isolated from the leaves of the same plant. This is the first report of the separation of α-amyrin (**13**), β-amyrin (**6**) and lupeol (**14**) by HPLC.

EXPERIMENTAL

General

UV: MeOH; IR: $CHCl_3$, except where noted; ^1H (400 or 200 MHz) and ^{13}C (100 or 50 MHz) NMR: TMS as int. standard; CC: silica gel (70–230 mesh, 230–400 mesh, Merck), highly porous polymer resin (Diaion HP-20, Mitsubishi Chem. Ind., Japan) and Sephadex LH-20 (Pharmacia Fine Chem.); HPLC: KR-100-5-C18 (4.6 mm × 25 cm, Kromasil Sweden). The mobile phase was MeOH at a flow-rate of 1.0 ml/min. The UV detector wavelength was set at 210 nm. All solvent systems for chromatography were homogeneous.

Plant material

The bark of stem and root, leaves and branch of *G. calleryanum* (Baill) Becc. were collected from Hengchun Peninsula, Pingtung Hsien, Taiwan in December, 1990. The plant was identified by Prof. Chang-Shen Kuoh of this University. A voucher specimen was deposited in the Herbarium of Cheng Kung University, Tainan, Taiwan, R.O.C.

Extraction and separation

A. The dried stem and root bark (900 g) were extracted with hot MeOH (×3). The combined

MeOH extract was concd *in vacuo* to give a brown syrup which was partitioned between H_2O and $CHCl_3$. The $CHCl_3$ layer (23 g) was fractionated on a silica gel column eluted with a gradient of benzene and Me_2CO to afford 20 frs. Each fr. was rechromatographed on silica gel and prep. TLC or subjected to recrystallization. Pure compounds were obtained as follows. Frs. 3 and 4 gave **4** (158 mg). Frs. 5, 6 and 7 gave **5** (95 mg). Fr. 9–13 gave **6** (17.6 g) and **7** (81 mg). Frs. 15 and 16 gave **7** (5 mg) and **8** (2 mg), respectively. Fr. 20 gave **11a** and **11b** mixture (18 mg), **9** (42 mg), **8** and **10** mixture (52 mg), successively. The H_2O layer was concd *in vacuo* to give a residue (227 g) which was chromatographed on silica gel column eluted with a gradient of $CHCl_3$ and MeOH to afford 17 frs. Frs. 1–4 were combined and rechromatographed on a silica gel column eluted with *n*-hexane-EtOAc (5 : 1) to give **6** (18 mg). Similarly, the combined frs. 5–11 eluting with $CHCl_3$–MeOH (9 : 1) gave **15** (1 mg). **11a** and **11b** mixture (36 mg), **8** and **10** mixture (16 mg). Frs. 12–15 were also combined and rechromatographed over a silica gel column eluted with $CHCl_3$–MeOH–H_2O (100 : 20 : 1) to give **2** (25.1 g) and **1a** (32 mg). Frs. 16 and 17 were chromatographed on Diaion HP-20 eluting with a gradient of H_2O and MeOH to give **12** (8 mg), **3** (0.3 g) and **2** (5.6 g), successively.

B. The dried and powdered branch (190 g) was extracted with hot MeOH (×3). The combined MeOH extracts were concd. under red. press. to give a brown syrup which was directly subjected to silica gel column CC and eluted with a gradient of $CHCl_3$ and MeOH to afford 6 frs. Fr. 2 was separated by HPLC using MeOH as eluent to give **14** (82 mg), **6** (11 mg) and **13** (28 mg), successively. Frs. 3 and 4 gave **8** (284 mg). Frs. 5 and 6 afforded **2** (5.2 g).

C. The powdered leaves (360 g) was extracted with hot MeOH (×3). After concentration of the combined extracts *in vacuo*, the residue was chromatographed on a silica gel column developed with C_6H_6, $CHCl_3$, $CHCl_3$–MeOH (9 : 1), $CHCl_3$–MeOH (5 : 1) and MeOH to give Frs. 1–12, 13–19, 20–24, 25–30 and 31, successively. Frs. 14–17 gave a mixture of triterpenoids which was separated by HPLC on RP-18 (MeOH) to afford **14** (68 mg, 19.08 min), **6** (8 mg, 24.21 min) and **13** (31 mg, 27.83 min), respectively. Frs. 20–22 gave **16** (5 mg). Frs. 24 was rechromatographed on silica gel using n-hexane-Me_2CO (5 : 1) to give unknown c (3 mg). Frs. 25–27 afforded **10** (26 mg). Frs. 28 was purified by silica gel, sephadex LH-20 and prep. TLC to give **17** (4 mg), **2** (0.3 g), **18b** (13 mg), a mixture of **19** and **20** (12 mg), **3** (81 mg), successively. Frs. 31 gave **2** (2.3 g). Gonocaryoside E (**1a**), colorless amorphous powder, $[\alpha]_D$ −49.68° (*c*, 1.263, MeOH). FAB-HRMS: *m/z* 505.1923 ($[M+H]^+$ ($C_{22}H_{33}O_{13}$), requires: *m/z* 505.1921); UV λ_{max} nm: 221.8, 280.6, 320.3; IR ν_{max} cm^{-1}: 3404, 1713, 1640, 1505; FAB-MS (rel. int.) *m/z*: 505 ($[M+H]^+$, 2.8), 460 (4), 391 (14), 307 (25), 289 (12), 154 (100), 137 (72), and 136 (71); ^1H NMR (C_5D_5N): δ 7.73 (1H, *s*, H-3), 7.06 (1H, *q*, *J* = 7.0 Hz, H-3′), 6.28 (1H, *d*, *J* = 6.6 Hz, H-1), 5.68 (1H, *m*, H-8), 5.41 (1H, *d*, *J* = 7.8 Hz, G-1), 4.50 (1H, *dd*, *J* = 11.8, 2.2 Hz, G-6), 4.34 (1H, *dd*, *J* = 11.8, 5.2 Hz, G-6), 4.24 (1H, *t*, *J* = 8.9 Hz, G-3), 4.20 (1H, *t*, *J* = 8.9 Hz, G-4), 4.03 (1H, *t*, *J* = 8.9 Hz, G-2), 3.96 (1H, *m*, G-5), 3.80 (1H, *m*, H-5), 3.57 (3H, *s*, 11-OMe), 3.10 (1H, *dd*, *J* = 16.2, 4.7 Hz, H-6), 2.86 (1H, *dd*, *J* = 16.2, 7.8 Hz, H-6), 2.56 (1H, *m*, H-9), 1.88 (3H, *s*, 5′-Me), 1.62 (3H, *d*, *J* = 7.0 Hz, 4′-Me), 1.47 (3H, *d*, *J* = 6.4 Hz, 10-Me); ^{13}C NMR (C_5D_5N): δ 174.2 (C-7), 166.5 (C-1′), 166.3 (C-11), 152.3 (C-3), 137.0 (C-3′), 128.5 (C-2′), 109.5 (C-4), 99.8 (G-1), 95.3 (C-1), 77.9 (G-5), 77.6 (G-3), 73.9 (G-2), 70.6 (G-4), 68.8 (C-8), 61.9 (G-6), 50.3 (OMe), 42.7 (C-9), 34.9 (C-6), 28.9 (C-5), 18.6 (C-10), 13.5 (C-4′), 11.5 (C-5′).

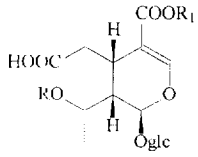
Alkaline hydrolysis of compound **2**

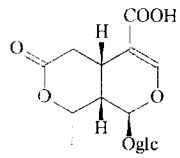
A. A soln of **2** (500 mg) in 5% aq. KOH (12.5 ml) was allowed to stand for 20 hr at room temp. The reaction mixture was neutralized with Ion exchange I (Merck) ion-exchange resin. After removal of the solvent, the residue was purified by C_{18} CC using H_2O as eluent to give **1b** (426 mg). Compound **1b**: colorless amorphous powder, $[\alpha]_D$ −123.9° (*c*, 0.4, MeOH). UV λ_{max} nm: 231.4; IR ν_{max} cm^{-1}: 3404, 1720, 1645, 1595, 1515; FAB-MS (*m/z*): 525 ($[M+H]^+$ 1.3), 413 (27), 195 (20), 173 (20), 157 (33), 131 (50), 115 (100); ^1H NMR (C_5D_5N): δ 7.90 (1H, *s*, H-3), 6.00 (1H, *d*, *J* = 5.6 Hz, H-1), 5.35 (1H, *d*, *J* = 7.8 Hz, G-1), 4.72 (1H, *m*, H-8), 4.50 (1H, *br d*, *J* = 11.6 Hz, G-6), 4.35–4.20 (4H, *m*, H-3′, G-6, G-3, G-4), 4.07 (1H, *t*, *J* = 7.8 Hz, G-2), 3.98 (1H, *m*, G-5), 3.60 (1H, *m*, H-5), 3.28 (1H, *dd*, *J* = 16.4, 7.2 Hz, H-6), 3.12 (1H, *dd*, *J* = 16.4, 4.0 Hz, H-6), 2.51 (1H, *m*, H-9), 1.83 (3H, *s*, 5′-Me), 1.58 (3H, *d*, *J* = 7.0 Hz, 4′-Me), 1.50 (3H, *d*, *J* = 6.0 Hz, 10-Me); ^{13}C NMR (C_5D_5N): δ 17.6 (C-10), 17.9 (C-4′), 22.3 (C-5′), 26.9 (C-5), 33.7 (C-6), 38.8 (C-9), 62.1 (C-6″), 70.9 (C-4″), 72.8 (C-3′), 74.2 (C-2″), 74.6 (C-8), 77.8 (C-3″), 78.1 (C-5″), 80.2 (C-2′), 93.4 (C-1), 100.3 (C-1″), 111.4 (C-4), 152.0 (C-3), 168.5 (C-11), 171.3 (C-7), 180.4 (C-1′).

B. A soln. of **1b** (544 mg) in 5% aq. KOH (25 ml) and 15 drops HMPA was stirred at room temp overnight. The reaction mixture was treated as just described to give **1c** (356 mg), **1d** (16 mg) and **18b** (126 mg) which were identified by comparison of their spectral data with literature values [3].

Alkaline hydrolysis of compound **1a**

A. A soln. of **1a** (20 mg) in 5% aq. KOH (2 ml) and 1 drop HMPA was stirred at room temp overnight. The reaction mixture was treated as above to give **1c** (92 mg) and **18a** (26 mg) which were identified by comparison of their spectral data with literature values [3, 14]. Compound **1c**: colorless amorphous powder, $[\alpha]_D$ 118.17° (*c*, 0.5, MeOH). UV λ_{max} nm: 231.8; IR ν_{max} cm^{-1}: 3395, 1718, 1560, 1546, 1400,





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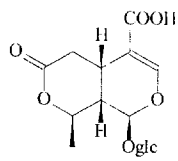
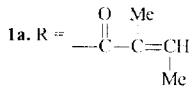
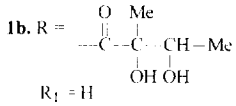


1d



1a. R =



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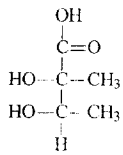
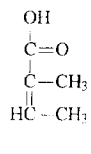
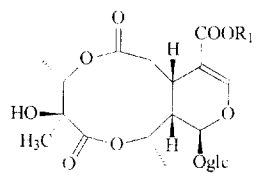


18b



18a



2. R = Me
3. R = H

1259, 1076; FAB-MS (*m/z*): 391 ([M+H]$^+$, 14), 229 (30), 155 (28), 154 (100), 139 (22), 138 (42), 137 (88), 136 (85), 125 (28), 123 (20), 107 (38); ^{1}H NMR (D_2O): δ 7.43 (1H, *s*, H-3), 5.57 (1H, *d*, J = 4.8 Hz, H-1), 4.70 (1H, *m*, H-8), 4.60 (1H, *d*, J = 8.8 Hz, G-1), 3.78 (1H, *dd*, J = 12.2, 1.4 Hz, G-6), 3.58 (1H, *dd*, J = 12.2, 5.6 Hz, G-6), 3.35 (1H, *m*, G-5), 3.32 (1H, *t*, J = 8.8 Hz, G-3), 3.24 (1H, *t*, J = 8.8 Hz, G-4), 3.21 (1H, *m*, H-5), 3.16 (1H, *t*, J = 8.8 Hz, G-2), 2.93 (1H, *dd*, J = 16.6, 6.6 Hz, H-6), 2.64 (1H, *dd*, J = 16.6, 4.8 Hz, H-6), 2.49 (1H, *m*, H-9), 1.36 (3H, *d*, J = 6.8 Hz, 10-Me); ^{13}C NMR (D_2O): δ 17.5 (C-10), 26.6 (C-5), 33.8 (C-6), 39.0 (C-9), 61.5 (C-6′), 70.4 (C-4′), 73.5 (C-2′), 76.5 (C-3′), 76.6 (C-8), 77.2 (C-5′), 94.4 (C-1), 99.2 (C-1′), 111.2 (C-4), 154.8 (C-3), 170.7 (C-11), 177.2 (C-7). Compound **1d**: colorless amorphous powder, $[\alpha]_D$ −14.69° (*c*, 0.8, MeOH). UV λ_{max} nm: 225.6; IR ν_{max} cm^{-1}: 3419, 1731, 1651, 1564, 1384, 1076; FAB-MS *m/z*: 391 ([M+H]$^+$ 12), 176 (56), 167 (21), 154 (52), 149 (100), 138 (28), 137 (50), 136 (59), 123 (20), 113 (42), 109 (21), 107 (38), 105 (29); ^{1}H NMR (D_2O): δ 6.92 (1H, *s*, H-3), 5.64 (1H, *d*, J = 5.4 Hz, H-1), 4.79 (1H, *d*, J = 8.0 Hz, G-1), 4.08 (1H, *m*, H-8), 3.87 (1H, *dd*, J = 12.5, 2.0 Hz, G-6), 3.68 (1H, *dd*, J = 12.5, 5.7 Hz, G-6), 3.46 (2H, *m*, G-5, G-3), 3.37 (1H, *t*, J = 9.3 Hz, G-4), 3.30 (1H, *t*, J = 9.3 Hz, G-2), 3.14 (1H, *m*, H-5), 2.58 (1H, *dd*, J = 15.8, 4.2 Hz, H-6), 2.23 (1H, *dd*, J = 15.8, 10.4 Hz, H-6), 2.01 (1H, *q*, J = 5.5 Hz, H-9), 1.25 (3H, *d*, J = 6.6 Hz, 10-Me); ^{13}C NMR (D_2O): δ 20.9 (C-10), 30.3 (C-5), 38.1 (C-6), 43.8 (C-9), 60.6 (C-6′), 65.9 (C-8), 69.6 (C-4′), 72.7 (C-2′), 75.5 (C-3′), 76.3 (C-5′), 95.5 (C-1), 98.5 (C-1′), 117.4 (C-4), 145.9 (C-3), 175.5 (C-11), 181.3 (C-7). Compound **18b**: colorless amorphous powder, $[\alpha]_D$ −2.25° (*c*, 3.67, MeOH). IR ν_{max} cm^{-1}: 3360, 1732, 1558, 1541; FAB-MS *m/z*: 135 ([M+H]$^+$, 2.7), 115 (100); ^{1}H NMR (D_2O): 3.85 (1H, *q*, J = 6.4 Hz, H-3), 1.29 (3H, *s*, 2-CH_3), 1.05 (3H, *d*, J = 6.4 Hz, 3-CH_3). Compound **18a**: colorless amorphous powder. IR ν_{max} cm^{-1}: 1672, 1560, 1508, 1429, 1294; EI-MS *m/z*: 100 ([M]$^+$, 58), 85 (22), 83 (81), 82 (26), 71 (20), 69 (20), 57 (34), 55 (100), 54 (22); ^{1}H NMR (D_2O): 6.82 (1H, *q*, J = 4.3 Hz, H-3), 1.75 (3H, *d*, J = 4.3 Hz, 3-CH_3), 1.74 (3H, *s*, 2-CH_3).

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