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THREE XANTHONES FROM ROOT BARK OF *GARCINIA SUBELLIPTICA*

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Key Word Index—*Garcinia subelliptica*; Guttiferae; xanthone; subelliptenone E; subelliptenone F; subelliptenone G; 1,5-dihydroxy-3-methoxyxanthone.

Abstract—Two new prenylated xanthones (subelliptenones E and F) and a new simple oxygenated xanthone (subelliptenone G) were isolated from the root bark of *Garcinia subelliptica* in addition to a known xanthone (1,5-dihydroxy-3-methoxyxanthone). The structures were determined by means of spectroscopic analysis.

INTRODUCTION

In our previous papers of the chemical constituents in Guttiferaeous plants, the structures of new xanthones, subelliptenones A and B [1], subelliptenones C and D [2] isolated from the root bark of *Garcinia subelliptica* were described, in addition to new xanthones in *Calophyllum inophyllum* [3, 4]. Further search for components with biological activities in the root bark of *G. subelliptica* resulted in the isolation of four xanthones including three new ones. In the present paper, the isolation and characterization of three new xanthones is described.

RESULTS AND DISCUSSION

The root bark of *G. subelliptica* collected in Naha city, Japan was dried and ground, and successively extracted with *n*-hexane, benzene, acetone and 70% MeOH. The acetone extract suspended in water was partitioned with EtOAc. The EtOAc soluble extract was chromatographed on silica gel and Sephadex LH-20 to give four xanthones (**1–4**).

Compound **1**, subelliptenone E, obtained as a yellow amorphous solid, reacted positively to the $FeCl_3$ test. The $[M]^+$ at *m/z* 482.2289 in the high resolution EIMS corresponds to $C_{28}H_{34}O_7$. The UV and the IR spectra suggest **1** is a xanthone derivative. In the ^1H NMR spectrum, a chelated hydroxyl [δ 13.56 (1H, *s*)] and two aromatic hydroxyl groups [8.03 and 8.15 (1H each, *br s*)], and an aromatic proton [7.26 (1H, *s*)] were observed in addition to the presence of a 1,1-dimethylallyl group [1.53 (6H, *s*, Me × 2), 5.02 (1H, *dd*, $J = 11$, 1 Hz), 5.05 (1H, *dd*, $J = 18$, 1 Hz), 6.31 (1H, *dd*, $J = 18$, 11 Hz)], a dimethylchromane ring [1.40 (6H, *s*, Me × 2), 1.95 and 2.94 (2H each, *t*, $J = 7$ Hz)] and a 3-hydroxy-3-methylbutyl group [1.32 (6H, *s*, Me × 2), 1.72 and 3.40 (2H each, *m*)]. All protonated carbons were assigned by CH COSY experiment (Table 1). In the HMBC spectrum (Fig. 1), the chelated hydroxyl group was correlated to three quaternary carbons (δ 109.8, 128.9 and 154.0), one of which (154.0) was further correlated to the aromatic proton (7.26) which gave a cross peak with an aromatic carbon at δ 122.6 in the CH COSY spectrum. One of the aromatic hydroxyl groups (δ 8.15) was correlated with the protonated aromatic carbon (122.6) in the HMBC spectrum (Fig. 1) and an NOE was observed between the methyl protons (δ 1.53) of the 1,1-dimethylallyl group and the aromatic proton (7.26) in the ^1H NMR spectrum. These spectral data indicated that **1** was in part a 1,4-dihydroxy-2-(1,1-dimethylallyl-3-propenyl)xanthone. In the ^{13}C NMR spectrum, chemical shifts of the other quaternary carbons with *O*-functions observed at δ 132.8, 145.7 and 149.0 suggested the presence of a 1,2,3-trioxygenated benzene ring system in another ring of the xanthone skeleton. The locations of the dimethylchromane ring and the 3-hydroxy-3-methylbutyl group were substituted at C_7–C_6 [O] and at C_8 as a natural consequence. Therefore subelliptenone E was characterized as **1**. When subelliptenone A [1,4,5,6-tetrahydroxy-2-(1,1-dimethylallyl-3-propenyl)-7,8-di-(3-methyl-2-butenyl)xanthone] was treated with MeOH–HCl, **1** was obtained in addition to the other three derivatives as mentioned in a previous paper [1]. The spectral data on EIMS and ^1H NMR were identical.

Compound **2**, subelliptenone F, obtained as a yellow amorphous solid, positively reacted with the $FeCl_3$ and Gibbs tests. The HR EIMS showed a molecular ion at *m/z* 328.0958 corresponding to $C_{18}H_{16}O_6$. Its UV and the IR spectrum indicated **2** was also a xanthone. The ^1H NMR spectrum showed the presence of a chelated hydroxyl [δ 13.09 (1H, *s*)], a 1,1-dimethylallyl group [1.54

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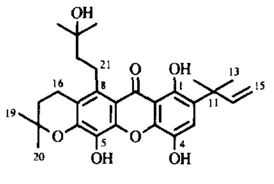

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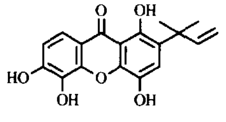

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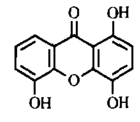

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Table 1. ^{13}C NMR spectra of compounds **1–4**

C.	**1**	**2**	**3**	**4**
1	154.0	153.5	154.9	165.3
2	128.9	129.5	110.5	98.7
3	122.6	122.7	124.5	168.8
4	136.0	136.7	138.1	94.2
5	132.8	133.2	147.1	147.8
6	149.0	152.4	122.1	122.3
7	119.0	114.2	125.4	125.8
8	136.1	117.9	116.6	117.2
9	185.5	183.1	183.2	182.6
4a	142.1	142.3	144.0	159.3
8a	112.4	114.7	122.2	123.1
9a	109.8	108.8	109.5	105.1
10a	145.7	146.5	145.8	147.1
11	41.1	41.0		
12	27.2	27.0		
13	27.2	27.0		
14	148.4	148.1		
15	110.8	110.9		
16	20.3			
17	33.5			
18	76.3			
19	27.1			
20	27.1			
21	25.3			
22	44.5			
23	70.6			
24	29.3			
25	29.3			
OMe				57.3

Measured in acetone-d_6. All carbons were assigned by the aid of CH COSY and HMBC spectrum.

(6H, *s*, Me × 2), 5.00 (1H, *dd*, *J* = 11, 1 Hz), 5.04 (1H, *dd*, *J* = 18, 1 Hz), 6.31 (1H, *dd*, *J* = 18, 11 Hz)], an aromatic proton [δ 7.28 (1H, *s*)], and *ortho*-coupled protons [7.00 and 7.69 (1H each, *d*, *J* = 9 Hz)]. Although the spectrum showed only two unchelated hydroxyl groups [δ 8.80 (2H, *br s*)], another hydroxyl group existed in **2**, supported by the HR EIMS results. In the HMBC spectrum of **2** (Fig. 1), the chelated hydroxyl group (δ 13.09) gave cross peaks to three quaternary carbons (108.8, 129.5 and 153.5), and one of which (153.5) was further correlated to the aromatic proton [7.28 (*s*)] which has cross peaks with a quaternary carbon (41.0) of 1,1-dimethylallyl group and with the other aromatic carbons possessing *O*-function (136.7 and 142.3). These results indicate that **2** has a 1,3,4-trioxygenated benzene ring system of one benzene ring in xanthone and is a 1,4-dihydroxyl-2-(1,1-dimethyl-3-propenyl)xanthone like **1**. The positions of the other two hydroxyl groups were allotted as follows: chemical shifts of aromatic carbons with *O*-function were observed at δ 133.2, 146.5 and 152.4 in the ^{13}C NMR spectrum, indicating the presence of 1,2,3-trioxygenated benzene system of another benzene ring. Therefore, the aromatic hydroxyl groups were located at C_5 and C_6 position. This partial structure was confirmed by the long range correlations of the HMBC spectrum (Fig. 1). Subelliptenone F is thus characterized as **2**. The structure is an oxygenated derivative of 12β-hydroxy-des-D-garcigerin [2, 5].

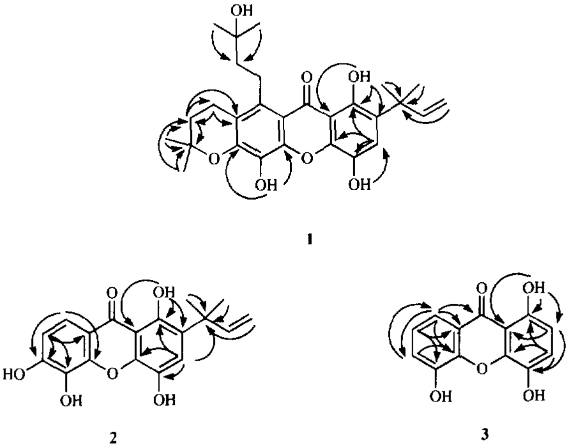

Fig. 1. HMBC spectrum of **1–3**.

Compound **3**, subelliptenone G, was a xanthone reacting positively to FeCl$_3$ and Gibbs tests. The [M]$^+$ at *m*/*z* 244.0384 in the HR EIMS corresponds to $C_{13}H_8O_5$. The ^{1}H NMR spectrum showed the presence of three aromatic hydroxyl groups [δ 8.83 (2H, *br s*)] including a chelated one [11.93 (1H, *s*)] in addition to *ortho*-coupled protons [6.70 and 7.32 (1H each, *d*, *J* = 9 Hz)] and ABC system protons [7.35 (1H, *t*, *J* = 8 Hz), 7.39 and 7.72 (1H each, *dd*, *J* = 8, 2 Hz)]. In the HMBC spectrum of **3** (Fig. 1), the chelated hydroxyl group (δ 11.93) was correlated to three aromatic carbons (109.5, 110.5 and 154.9), one of which (110.5) gave a cross peak to one of the *ortho*-coupled protons (6.70) in the CH COSY spectrum (Table 1). These results show **3** to be a 1,4-dihydroxyxanthone. On the other hand, another hydroxyl group was located at either C_5 or C_8 position because of the protons in an ABC system. Chemical shifts of the aromatic carbons having *O*-function (δ 145.8 and 147.1) suggested the presence of 1,2-dioxygenated benzene system on another benzene of xanthone skeleton, which was confirmed by the HMBC spectrum. Therefore, **3**, subelliptenone G, is 1,4,5-trihydroxyxanthone. Compound **4** was determined by the spectral analysis to be 1,5-dihydroxy-3-methoxyxanthone, which has been isolated from *Kielmeyera rupestris* [6] and *Mesua ferrea* [7].

EXPERIMENTAL

Plant material. Root bark of *G. subelliptica* was collected at Naha city, Okinawa, Japan in April, 1993. The voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation. The dried and ground root bark (2.8 kg) was successively extracted with *n*-hexane (4.51 × 3), benzene (41 × 3), Me_2CO (51 × 3) and 70% MeOH (51 × 3) at room temp. After each solvent was removed, the resulting Me_2CO extract (135 g) was suspended into H_2O and partitioned with EtOAc and *n*-BuOH, successively. The EtOAc soluble extract (90 g) was chromatographed on silica CC eluted with benzene–Me_2CO system. A benzene–Me_2CO (10:1) eluent was further purified by vacuum liquid chromatography on silica with *n*-hexane–EtOAc system. Compounds **3** (2 mg) (5:1) and **4** (2 mg) (7:1) were purified by recrystallization. The eluent with *n*-hexane–EtOAc (3:1) was further chromatographed on Sephadex LH-20 eluted with Me_2CO to give **2** (3 mg), and the *n*-hexane–EtOAc (2:1) eluent was further purified by Sephadex LH-20 CC eluted with MeOH to give **1** (15 mg).

Compound **1** (*subelliptenone E*). A yellow amorphous solid; HR EIMS *m/z* 482.2289 ($C_{28}H_{34}O_7$; calcd 482.2304); EIMS *m/z* (rel. int.): 482 (100), 464 (17), 449 (27), 423 (30), 421 (57), 409 (14), 393 (16), 365 (14), 351 (9), 337 (12), 325 (9), 311 (7), 189 (5), 147 (6), 119 (7), 105 (13), 91 (36); UV λ (MeOH, nm) (log ε): 232 (4.69), 262 (4.85), 286 (4.59), 310 sh, 345 (4.49), 403 (3.97); + NaOMe: 211, 262, 274, 293, 320 sh, 374; IR ν (KBr, cm^{-1}): 3500, 2950, 1640, 1615, 1590; ^1H NMR (400 MHz, Me_2CO-d_6) δ: 1.32 (6H, *s*, Me × 2, H-24, H-25), 1.40 (6H, *s*, Me × 2, H-19, H-20), 1.53 (6H, *s*, Me × 2, H-12, H-13), 1.72 (2H, *m*, H-22), 1.95 (2H, *t*, *J* = 7 Hz, H-17), 2.94 (2H, *t*, *J* = 7 Hz, H-16), 3.40 (2H, *m*, H-21), 5.02 (1H, *dd*, *J* = 11, 1 Hz, H-15 *Z*), 5.05 (1H, *dd*, *J* = 18, 1 Hz, H-15 *E*), 6.31 (1H, *dd*, *J* = 18, 11 Hz, H-14), 7.26 (1H, *s*, H-3), 8.03 (1H, *br s*, C_5-OH), 8.15 (1H, *br s*, C_4-OH), 13.56 (1H, *s*, C_1-OH).

Compound **2** (*subelliptenone F*). A yellow amorphous solid; HR EIMS *m/z* 328.0958 ($C_{18}H_{16}O_6$; calcd 328.0947); EIMS *m/z* (rel. int.): 328 (77), 313 (100), 301 (8), 299 (11), 295 (12), 287 (24), 285 (13), 273 (21), 187 (5), 153 (7), 149 (17), 105 (7), 101 (7), 91 (14), 59 (15), 58 (20); UV λ (MeOH, nm) (log ε): 230 (4.28), 255 (4.49), 280 sh, 307 (3.92), 332 (4.01), 394 (3.60); + NaOMe: 268, 315, 383; IR ν (KBr, cm^{-1}): 3500, 3340, 2960, 1665, 1605, 1595; ^1H NMR (400 MHz, Me_2CO-d_6) δ: 1.54 (6H, *s*, Me × 2, H-12, H-13), 5.00 (1H, *dd*, *J* = 11, 1 Hz, H-15 E), 5.04 (1H, *dd*, *J* = 18, 1 Hz, H-15 *Z*), 6.31 (1H, *dd*, *J* = 18, 11 Hz, H-14), 7.00 (1H, *d*, *J* = 9 Hz, H-7), 7.28 (1H, *s*, H-3), 7.69 (1H, *d*, *J* = 9 Hz, H-8), 8.80 (2H, *br s*, OH × 2), 13.09 (1H, *s*, C_1-OH).

Compound **3** (*1,4,5-trihydroxyxanthone, subelliptenone G*). A yellow amorphous solid; HR EIMS *m/z* 244.0384 ($C_{13}H_8O_5$; calcd 244.0372); EIMS *m/z* (rel. int.): 244 (100), 226 (3), 215 (3), 187 (4), 149 (3), 136 (3), 131 (3), 123 (4), 122 (4), 121 (3), 108 (3), 77 (4); UV λ (MeOH, nm) (log ε): 247 (4.33), 260 sh, 317 (3.75), 397 (3.43); + NaOMe: 254, 321, 350 sh, 400 sh; IR ν (KBr, cm^{-1}): 3300, 1645, 1600; ^1H NMR (400 MHz, Me_2CO-d_6) δ: 6.70 (1H, *d*, *J* = 9 Hz, H-2), 7.32 (1H, *d*, *J* = 9 Hz, H-3), 7.35 (1H, *t*, *J* = 8 Hz, H-7), 7.39 (1H, *dd*, *J* = 8, 2 Hz, H-6), 7.72 (1H, *dd*, *J* = 8, 2 Hz, H-8), 8.83 (2H, *br s*, C_4, C_5-OH), 11.93 (1H, *s*, C_1-OH).

Compound **4** (*1,5-dihydroxy-3-methoxyxanthone*). A yellow amorphous solid; EIMS *m/z* 258 (100), 229 (65), 215 (10), 201 (9), 187 (9), 136 (7), 115 (7), 92 (6), 77 (5); UV λ (MeOH, nm): 215, 247, 269 sh, 310, 353; ^1H NMR (400 MHz, Me_2CO-d_6) δ: 3.96 (3H, *s*, C_3-OMe), 6.36 (1H, *d*, *J* = 2 Hz, H-2), 6.56 (1H, *d*, *J* = 2 Hz, H-4), 7.30 (1H, *t*, *J* = 8 Hz, H-7) 7.37 (1H, *dd*, *J* = 8, 2 Hz, H-6), 7.68 (1H, *dd*, *J* = 8, 2 Hz, H-8) 9.23 (1H, *br s*, C_5-OH), 12.92 (1H, *s*, C_1-OH).

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