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TWO XANTHONES WITH A 1,1-DIMETHYLALLYL GROUP IN ROOT BARK OF *GARCINIA SUBELLIPTICA*

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Key Word Index—*Garcinia subelliptica*; Guttiferae; root bark; xanthone; subelliptenone H; subelliptenone I.

Abstract—Two new prenylated xanthones, subelliptenone H and I, were isolated from the root bark of *Garcinia subelliptica*. The structures were determined by NMR spectroscopy including 2D techniques and chemical transformation. They both had a 1,1-dimethylallyl group and an isoprenyl group cyclized with the O-function.

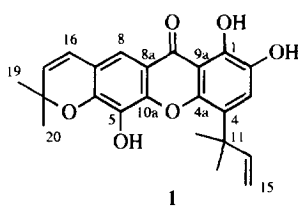
INTRODUCTION

Guttiferous plants are known to be an abundant source of xanthones [1]. In our previous papers, we elucidated the structures of seven new xanthone derivatives (subelliptenones A–G [2–4]), isolated from the root bark of *Garcinia subelliptica* and five new xanthones (caloxanthones A–E [5–7]) from *Calophyllum inophyllum*. In a further search for biologically active compounds in guttiferous plants, two minor xanthones (**1** and **2**) have been isolated from the root bark of *G. subelliptica*.

RESULTS AND DISCUSSION

Root bark of *Garcinia subelliptica* collected in Okinawa, Japan, was dried and ground, and extracted with *n*-hexane, benzene, acetone and 70% MeOH, successively. The acetone extract poured into water was extracted with EtOAc. The EtOAc-soluble extract was repeatedly chromatographed on silica gel and Sephadex LH-20 to give subelliptenones H (**1**) and I (**2**).

Compound **1** (subelliptenone H), obtained as a yellow amorphous material, reacted positively to $FeCl_3$ and Gibb's tests. The HREI-mass spectrum showed a $[M]^+$ at *m/z* 394.1403 which corresponds to $C_{23}H_{22}O_6$. Its IR and UV spectra suggested **1** to be a xanthone derivative. In the ^1H NMR spectrum, the presence of two aromatic protons in a singlet (δ7.32 and 7.46), a 1,1-dimethylallyl group [δ1.65 (6H, *s*), 5.02 (1H, *dd*, *J* = 11, 1 Hz), 5.15 (1H, *dd*, *J* = 18, 1 Hz) and 6.35 (1H, *dd*, *J* = 18, 11 Hz)] and a dimethylchromene ring [δ1.52 (6H, *s*), 5.91 and 6.59 (1H each, *d*, *J* = 10 Hz)] were exhibited, in addition to three hydroxyl groups, including a chelated one [δ7.65 and 8.29 (1H each, *br s*) and 12.94 (1H, *s*, chelated OH)]. All protonated carbons were assigned by means of a ^{13}C–^1H COSY spectrum (Table 1). In the HMBC spectrum (Fig. 1), the chelated hydroxyl group was correlated to three quaternary carbons at δ109.8, 140.1 and 147.0. The latter two carbons were substituted with O-functions. This spectral evidence showed that one hydroxyl group was located at the C-2 position of the xanthone skeleton. In the HMBC spectrum, one of the quaternary carbons (δ147.0), which caused cross-peaks to the chelated hydroxyl group, was also correlated to the aromatic proton (δ7.32). The aromatic proton was further correlated to the quaternary carbon (δ41.0) of the 1,1-dimethylallyl chain. Therefore, the possible partial structure of **1** was a 1,2-dihydroxy-4-(1,1-dimethylallyl)xanthone from the above serial correlations. The substitution of the other ring of the xanthone skeleton was decided as follows. In the HMBC spectrum (Fig. 1), a singlet aromatic proton at δ7.46 caused cross-peaks



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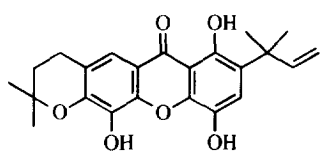

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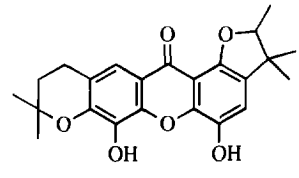


2a

Table 1. ^{13}C NMR spectrum of compounds **1** and **2**

C	1	2
1	147.0	153.7
2	140.1	129.2
3	122.8	123.2
4	126.7	137.0
5	134.5	134.5
6	146.8[a]	149.4
7	119.4	120.5
8	113.2	116.7
9	183.3	183.4
4a	147.9	143.0
8a	114.9	114.5
9a	109.8	109.2
10a	147.4[a]	144.7
11	41.0	41.2
12	27.7	27.2
13	27.7	27.2
14	148.1	148.3
15	111.4	111.0
16	122.1	22.9
17	132.7	33.3
18	79.2	77.4
19	29.3	27.3
20	29.3	27.3

Measured in acetone-d_6. All carbons were assigned with the aid of ^{13}C–^1H COSY and HMBC spectra.

[a] Interchangeable.

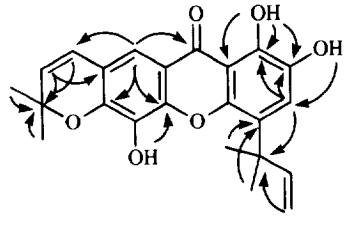
with a carbonyl carbon (δ183.3) and one of the *cis*-olefinic carbons of the dimethylchromene ring (δ122.1). These results suggested that the aromatic proton (δ7.46) was located at a *peri*-position (C-8) to the carbonyl group and that the chromene ring was fused in a linear form. The location of the remaining hydroxyl group (δ8.29) was at C-5 as a natural consequence. The structure of subelliptenone H was thus characterized as **1**, which was confirmed by other correlations in the HMBC spectrum.

Compound **2** (subelliptenone I) was also obtained as a yellow amorphous material and reacted positively to the $FeCl_3$ and Gibb's tests. The $[M]^+$ at m/z 396.1595 in the HREI-mass spectrum corresponds to the empirical formula $C_{23}H_{24}O_6$. In the ^1H NMR spectrum, protons based on two aromatics in a singlet (δ7.29 and 7.53), a 1,1-dimethylallyl group [δ1.53 (6H, *s*), 5.00 (1H, *dd*, J = 11, 1 Hz), 5.04 (1H, *dd*, J = 18, 11 Hz), 6.31 (1H, *dd*, J = 18, 11 Hz)] and a dimethylchromane ring [δ1.42 (6H, *s*), 1.94 and 2.97 (2H, each, *t*, J = 7 Hz)] were observed, in addition to three hydroxyl groups, including a chelated one [δ8.46 (2H, *br s*) and 13.18 (1H, *s*, chelated OH)]. Treatment of **2** with H_2SO_4 in MeOH gave **2a** which gave a negative reaction to the $FeCl_3$ test. In the ^1H NMR spectrum of **2a**, the 1,1-dimethylallyl group was converted to a 2,3,3-trimethyldihydrofuran ring [δ1.12, 1.59 (3H, each, *s*), 1.41 (3H, *d*, J = 7 Hz), 4.47 (1H, *q*, J = 7 Hz)]. In the HMBC spectrum of **2** (Fig. 1), the aromatic proton at δ7.29 was correlated to the quaternary carbon (δ41.2) of the 1.1-dimethylallyl group, as well as to three quaternary carbons with an O-function (δ134.5, 143.0 and 153.7). The last carbon was correlated to the chelated hydroxyl group in the HMBC spectrum. These results suggested that the partial structure of **2** was a 1,4-dihydroxy-2-(1,1-dimethylallyl)xanthone, which was superimposed on that of subelliptenone A [1] when compared with the ^1H and ^{13}C NMR spectral data. In the ^{13}C NMR spectrum of **2**, aromatic carbons with an O-function were observed at δ134.5, 144.7 and 149.4, indicating the presence of a 1,2,3-trioxygenated benzene ring. Therefore, the dimethylchromane ring was fused at C-7 through an oxygen at C-6 and a free hydroxyl group was located at C-5; this was substantiated by the HMBC spectrum (Fig. 1). The structure of subelliptenone I then could be characterized as **2**.

EXPERIMENTAL

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

Extraction and isolation. Dried and ground root bark (2.8 kg) was successively extracted with *n*-hexane (4.5 l × 3), benzene (4 l × 3), Me_2CO, (5 l × 3) and 70% MeOH (5 l × 3) at room temp. After each solvent was removed by evapn, the resulting Me_2CO extract (135 g) was suspended in H_2O and partitioned with EtOAc and *n*-BuOH, successively. The EtOAc-soluble extract (90 g) was chromatographed on silica gel CC eluted with a benzene–Me_2CO system. The benzene–Me_2CO (10:1) eluate was subjected to silica gel vacuum liquid chromatography (VLC) eluted with a *n*-hexane–EtOAc



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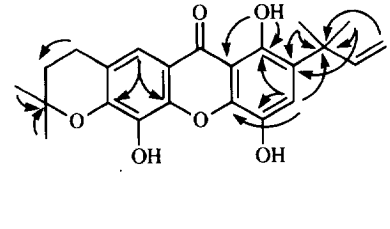

2

Fig. 1. Long-range correlations of **1** and **2** in HMBC spectra (J = 10 Hz).

system to give 9 frs. The third fr. (10:1) was repeatedly chromatographed on Sephadex LH-20 eluting with Me_2CO and MeOH, successively, to give **1** (5 mg). The ninth fr. (3:1, 100% EtOAc) was also subjected to VLC eluting with a *n*-hexane–EtOAc system. The *n*-hexane–EtOAc (5:1) eluate was rechromatographed on Sephadex LH-20 eluting with Me_2CO and MeOH, successively, to give **2** (4 mg).

Compound **1** (*subelliptenone H*). Yellow amorphous. HREI-MS *m/z*: 394.1403 (calc. 394.1416 for $C_{23}H_{22}O_6$). EIMS *m/z* (rel. int.): 394 $[M]^+$ (100), 379 (81), 361 (54), 333 (16), 203 (6), 189 (5), 173 (8), 159 (11), 149 (6), 115 (5). UV λ (MeOH) nm: 217, 229sh, 240, 280, 289, 330, 401; + NaOMe: 258, 316, 375sh; + $AlCl_3$: 222, 257, 265sh, 302, 376, 473. IR ν^{KBr} cm^{-1}: 3480, 3420, 1635. ^1H NMR (400 MHz, acetone-d_6): δ1.52 (6H, *s*, H-19, H-20), 1.65 (6H, *s*, H-12, H-13), 5.02 (1H, *dd*, J = 11, 1 Hz, H-15*E*), 5.15 (1H, *dd*, J = 18, 1 Hz, H-15*Z*), 5.91 (1H, *d*, J = 10 Hz, H-17), 6.35 (1H, *dd*, J = 18, 11 Hz, H-14), 6.59 (1H, *d*, J = 10 Hz, H-16), 7.32 (1H, *s*, H-3), 7.46 (1H, *s*, H-8), 7.65 (1H, *br s*, C-3-OH), 8.29 (1H, *br s*, C-5-OH), 12.94 (1H, *s*, C-1-OH). ^{13}C NMR: Table 1.

Compound **2** (*subelliptenone I*). Yellow amorphous. HREI-MS *m/z* 396.1595 (calc. 396.1573 for $C_{23}H_{24}O_6$). EIMS *m/z* (rel. int.): 396 $[M]^+$ (99), 381 (100), 355 (35) 341 (13), 325 (23), 285 (7), 165 (7). UV λ (MeOH) nm: 231, 259, 287, 300sh, 335, 401; + NaOMe: 273, 290sh, 376; + $AlCl_3$: 231, 259, 286, 300sh, 335, 401. ^1H NMR (400 MHz, acetone-d_6): δ1.42 (6H, *s*, H-19, H-20), 1.53 (6H, *s*, H-12, H-13), 1.94 (2H, *t*, J = 7 Hz, H-17), 2.97 (2H, *t*, J = 7 Hz, H-16), 5.00 (1H, *dd*, J = 11, 1 Hz, H-15*E*), 5.04 (1H, *dd*, J = 18, 11 Hz, H-15*Z*), 6.31 (1H, *dd*, J = 18, 11 Hz, H-14), 7.29 (1H, *s*, H-3), 7.53 (1H, *s*, H-8), 8.46 (2H, *br s*, C-5, C-4-OH), 13.18 (1H, *s*, C-1-OH). ^{13}C NMR: Table 1.

Acid transformation of **2** *into* **2a**. Compound **2** (2 mg) was heated with 10% H_2SO_4 in MeOH (2 ml) for 10 hr on a water bath. The reaction mixt. was poured into H_2O and extracted with EtOAc. Upon concn of organic solvent, the residue was subjected to prep. TLC (*n*-hexane–EtOAc–MeOH, 8:2:1) to give **2a** (1 mg). *Compound* **2a**. Yellow oil. EIMS *m/z* (rel. int.): 396 $[M]^+$ (86), 381 (100), 341 (14), 325 (28), 297 (8). ^1H NMR (400 MHz, acetone-d_6): δ1.12 and 1.59 (3H, each, *s*, H-12, H-13), 1.40 (6H, *s*, H-19, H-20), 1.41 (3H, *d*, J = 7 Hz, H-15), 1.91 (2H, *t*, J = 7 Hz, H-17), 2.93 (2H, *t*, J = 7 Hz, H-16), 4.47 (1H, *q*, J = 7 Hz, H-14), 7.12 (1H, *s*, H-3), 7.45 (1H, *s*, H-8), 8.30 (2H, *br s*, C-5, C-4-OH).

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