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TWO FURANOXANTHONES FROM *MAMMEA ACUMINATA*

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Key Word Index—*Mammea acuminata*; Guttiferae; furanoxanthone; acuminol A; acuminol B.

Abstract—From the stems of *Mammea acuminata*, two new furanoxanthones, acuminols A and B, were isolated, in addition to four known xanthones (1,7-dihydroxy-, 2-hydroxy-, 4-hydroxy- and 3-hydroxy-2-methoxyxanthone). The structures were established by spectral analysis.

INTRODUCTION

The genus *Mammea* is the same subfamily (Calophylloideae) as *Calophyllum* and *Mesua* [1]. Plants in this subfamily are known to contain abundant amounts of coumarins [2, 3] and xanthones with alkyl group(s) [1]. Potent anti-HIV activity has recently been reported for such coumarins [4], and other bioactivities (e.g. antileukaemic [5], antimicrobial [6], hypoglycemic [7]) have been reported for the xanthones. In our search for biologically active compounds in Guttiferaeous plants [8–11], we have isolated two new furanoxanthones from the stem of *M. acuminata* Kosterm, in addition to four known xanthones with a simple oxygenation pattern.

RESULTS AND DISCUSSION

The stems of *M. acuminata* collected in Indonesia were dried, ground, and extracted with benzene, acetone and 70% MeOH, successively. The benzene extract was repeatedly chromatographed on silica gel and Sephadex LH-20 to give six xanthones (**1**–**6**).

Compound **1**, acuminol A, gave a positive Gibbs test. The high-resolution EI-mass spectra showed the $[M]^+$ at *m/z* 252.0432 corresponding to $C_{15}H_8O_4$. The ^1H NMR spectrum established the presence of a 1,2-disubstituted benzene ring (δ 7.45 (1H, *t*-like *m*), 7.62 (1H, *br*, *d*, $J = 7.8$ Hz), 7.83 (1H, *t*-like *m*) and 8.29 (1H, *dd*, $J = 8.1$, 1.8 Hz)) and a hydroxyl group (δ 9.51 (1H, *br s*)) in addition to a singlet aromatic proton (δ 8.07). These findings and the UV spectral data suggested that **1** was a xanthone derivative and that one of two aromatic rings in the xanthone nucleus had no substituent. This partial structure was supported by comparison of the ^1H and ^{13}C NMR spectral data with those of two known xanthones: 2-hydroxy- (**4**) and 4-hydroxyxanthone (**5**). The ^1H NMR spectrum further showed the presence of a furan ring (δ 7.08 and 7.97 (1H each, *d*, $J = 2.0$ Hz)), which was confirmed by the chemical shifts of the methine carbons (δ 109.2 and 148.6) in the ^{13}C NMR spectrum (Table 1). The positions of the furan ring fused with the xanthone nucleus and of the hydroxyl group (δ 9.51) were determined as follows. In the ^{13}C NMR spectrum, three aromatic carbons with *O*-functions were observed at δ 132.2, 143.5 and 148.7, which suggested that the second aromatic ring of the xanthone nucleus was a 1,2,3-trioxygenated benzene. The aromatic proton at δ 8.07 was shifted to a low field under the influence of

Table 1. ^{13}C NMR spectral data of compounds **1** and **3**–**5**

C	1	3	4	5*
1	108.2	162.8	110.2	115.1
2	126.8	110.6	154.9	123.8
3	148.7	137.8	125.1	120.1
4	132.2	107.7	120.3	146.4
5	118.7	120.2	119.0	118.0
6	135.7	126.2	135.7	135.1
7	124.6	155.0	124.7	124.0
8	127.3	109.2†	127.1	125.8
9	177.4	183.0	176.9	175.9
4a	143.5	157.4	151.1	145.0
8a	121.8	121.9	122.1	120.8
9a	120.3	109.2†	123.4	122.1
10a	157.1	151.1	157.2	155.2
11	109.2			
12	148.6			

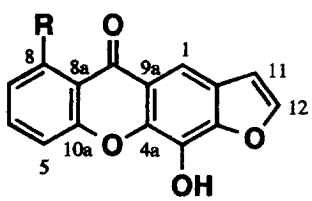
Measured in acetone-d_6. All carbons were assigned by the aid of ^1H–^{13}C COSY, COLOC and/or HMBC spectrum

a carbonyl group, indicating that the hydroxyl group was located at C-4 and that the furan ring was fused with the xanthone at C-2 and C-3. Comparison of the ^1H and ^{13}C NMR spectral data with those of other furanoxanthones with a same partial structure such as subelliptenones C and D [11], showed them to be identical to each other. The structure of acuminol A was then characterized as **1**.

Compound **2**, acuminol B, gave positive Gibbs and $FeCl_3$ tests. The $[M]^+$ at *m/z* 268.0383 in the high-resolution EI-mass spectrum corresponds to a molecular formula of $C_{15}H_8O_5$. The ^1H NMR spectrum established the presence of two aromatic hydroxyl groups (δ 9.75 (1H, *br s*) and 12.86 (1H, *s*, chelated OH)], a 1,2,3-trisubstituted benzene ring (δ 6.79 (1H, *br d*, $J = 8.3$ Hz), 7.05 (1H, *dd*, $J = 8.3$, 0.9 Hz), 7.72 (1H, *t*, $J = 8.3$ Hz)), and a singlet aromatic proton (δ 8.08) as well as furan ring (δ 7.12, 8.03 (1H each, *d*, $J =$ 2.2 Hz)). These data and the UV absorption suggested that **2** was also a xanthone derivative. The chemical shifts based on the furan ring and the aromatic proton (δ 8.08) resembled those of **1**, indicating that **2** had a same partial structure as **1**. The structural difference between **2** and **1** was that **2** had a chelated hydroxyl group at C-8. On comparing the ^1H NMR spectral data with those of 1,7-dihydroxyxanthone (**3**), the chemical shifts of H-5, H-6 and H-7 were found to be in good agreement. The lowfield proton at δ 8.08 was assignable to H-1 for the same reason as mentioned above. Therefore, the furan ring was fused with the xanthone at C-2 and C-3. The structure of acuminol B was thus characterized as **2**.

Compounds **3**–**6** were identified as 1,7-dihydroxy- (**3**) [12], 2-hydroxy- (**4**) [13], 4-hydroxy- (**5**) [13] and 3-hydroxy-2-methoxyxanthone (**6**) [13], respectively, by spectroscopic analysis including two-dimensional NMR. As the ^{13}C NMR spectral data of the above xanthones with these simple oxygenation patterns have not been described in detail, we report the ^{13}C NMR spectral data in Table 1.

To the best of our knowledge, only two furanoxanthones (subelliptenones C and D) [11], both from *Garcinia subelliptica* have been reported as natural products. We can now add two new furanoxanthones from *Mammea*.



EXPERIMENTAL

Plant material. Mammea acuminata Kosterm. was collected in Indonesia, in October, 1994. The voucher specimens are deposited in the herbarium of Gifu Pharmaceutical University.

Extraction and isolation. Dried and ground stems with bark of *M. acuminata* (600 g) were extracted under reflux with benzene (21 × 24 hr × 3 times) (weight of extractive after removed of solvent: 27 g), Me_2CO (21 × 24 hr × 3) (18 g) and 70% MeOH (21 × 24 hr × 3) (50 g), successively. The benzene extract (14 g) was subjected to vacuum LC on silica gel eluted with a benzene–Me_2CO system. The benzene–Me_2CO (20:1) eluent was further chromatographed on Sephadex LH-20 eluted with Me_2CO to give three frs. The third fr. was repeatedly purified by using prep. TLC (*n*-hexane–EtOAc–MeOH (8:2:1), benzene–Me_2CO (20:1) and $CHCl_3$–MeOH (75:1)] to give **1** (3 mg), **2** (1 mg), **3** (3 mg), **4** (5 mg), **5** (3 mg) and **6** (3 mg).

Compound **1** (*acuminol A*). Pale yellow amorphous solid. HREIMS *m/z* 252.0432 for $C_{15}H_8O_4$ (calc. 252.0422); EIMS *m/z* (rel. int.): 252 $[M]^+$ (100), 224 (4), 195 (5), 168 (7), 149 (8), 139 (12); UV λ_{max} (nm, MeOH): 232, 259, 296sh, 368; ^1H NMR (400 MHz, acetone-d_6) δ: 7.08 (1H, *d*, $J = 2.0$ Hz, H-11), 7.45 (1H, *t*-like *m*, H-7), 7.62 (1H, *br d*, $J = 7.8$ Hz, H-5), 7.83 (1H, *t*-like *m*, H-6), 7.97 (1H, *d*, $J = 2.0$ Hz, H-12), 8.07 (1H, *s*, H-1), 8.29 (1H, *dd*, $J = 8.1$, 1.8 Hz, H-8), 9.51 (1H, *br s*, C-4-OH).

Compound **2** (*acuminol B*). Pale yellow amorphous solid. HREIMS *m/z* 268.0383 for $C_{15}H_8O_5$ (calc. 268.0372). EIMS *m/z* (rel. int.): 268 $[M]^+$ (100), 212 (9), 43 (47); UV λ_{max} (nm, MeOH): 232sh, 254sh, 259, 322, 365sh; ^1H NMR (400 MHz, acetone-d_6) δ: 6.79 (1H, *br d*, $J = 8.3$ Hz, H-7), 7.05 (1H, *dd*, $J = 8.3$, 0.9 Hz, H-5), 7.12 (1H, *d*, $J = 2.2$ Hz, H-11), 7.72 (1H, *t*, $J = 8.3$ Hz, H-6), 8.03 (1H, *d*, $J = 2.0$ Hz, H-12), 8.08 (1H, *s*, H-1), 9.75 (1H, *br s*, C-4-OH), 12.86 (1H, *s*, C-8-OH).

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