

## NEW BRIARANE DITERPENES FROM A GORGONACEAN *BRIAREUM* SP.

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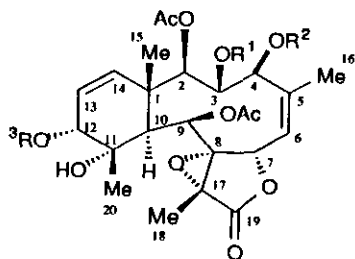
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**Abstract-** Two new diterpenes possessing a 2,3,4-oxidized briarane skeleton have been isolated from a gorgonacean *Briareum* sp.

The genus *Briareum* (subclass Alcyonaria, order Gorgonaceae, family Briareidae) has produced a number of briarane type diterpenes, containing a  $\gamma$ -lactone in a bicyclo [8.4.0] system.<sup>1</sup> The majority of these diterpenes showed interesting biological activity such as cytotoxic, anti-inflammatory, and antiviral activity.<sup>2</sup> We examined bioactive constituents of a *Briareum* sp., formerly classified as *Pachyclavularia violacea* of the soft coral. The methanol extract of the *Briareum* sp., collected in the area of Bonotsu, Kagoshima prefecture, was partitioned between dichloromethane and water. Bioassay guided fractionation of the dichloromethane extract, which showed ichthyotoxicity against Japanese killifish, *Orzia latipes*, by a combination of silica gel column chromatography and HPLC gave two new briarane derivatives (1) and (2).

Compound (1), C<sub>32</sub>H<sub>46</sub>O<sub>12</sub>, showed IR absorption bands of a hydroxy group (3443 cm<sup>-1</sup>), a  $\gamma$ -lactone (1784 cm<sup>-1</sup>), and an ester carbonyl (1741 cm<sup>-1</sup>). The molecular formula indicated ten degrees of unsaturation. Four olefinic resonances [ $\delta_C$  124.2 (d), 125.1 (d), 137.9 (d), and 141.0 (s)] and four ester carbon resonances [ $\delta_C$  168.4, 169.6, 170.5, and 173.5 (each, s)] in the <sup>13</sup>C NMR spectrum accounted for six double bond equivalents, suggesting that 1 is a tetracyclic compound. The <sup>1</sup>H and <sup>13</sup>C spectra and <sup>13</sup>C-<sup>1</sup>H COSY indicated the presence of seven methyl groups: one tertiary methyl [ $\delta_H$  1.32 (3H, s),  $\delta_C$  15.5 (s)], two tertiary methyls on a carbon carrying an oxygen function [ $\delta_H$  1.16 (3H, s),  $\delta_C$  21.4 (s) and 1.70 (3H, s),  $\delta_H$  9.7 (s)], a vinyl methyl [ $\delta_H$  2.08 (3H, d,  $J=1.1$  Hz),  $\delta_C$  25.5 (s)], two acetyl methyls [ $\delta_H$  2.22 (3H, s), 20.9 (s)] and  $\delta_H$  2.27 [(3H, s),  $\delta_C$  21.4 (s)], and a primary methyl due to a *n*-octanoate moiety [ $\delta_H$  0.86 (3H, t,  $J=7.0$  Hz, H-28),  $\delta_C$  14.1 (q);  $\delta_H$  ca. 1.29 (8H, m, CH<sub>2</sub> x 4, H-24, H-25, H-26, and H-27),  $\delta_C$  22.6, 28.9, 29.0, 31.6 (each t);  $\delta_H$  1.63 (2H, m, H-23),  $\delta_C$  24.9 (t), and  $\delta_H$  ca. 2.38 (2H, m, H-22),  $\delta_C$  34.3 (t), and  $\delta_C$  173.5 (s, C-21)].<sup>3</sup> Subtraction of the 12 carbon atoms associated with the three ester moieties from 32 carbon atoms in 1 left 20 carbon atoms, implying that 1 would be a diterpene.



- 1  $R^1=H, R^2=CO(CH_2)_6Me, R^3=H$   
 2  $R^1=Ac, R^2=Ac, R^3=H$   
 3  $R^1=Ac, R^2=CO(CH_2)_6Me, R^3=Ac$

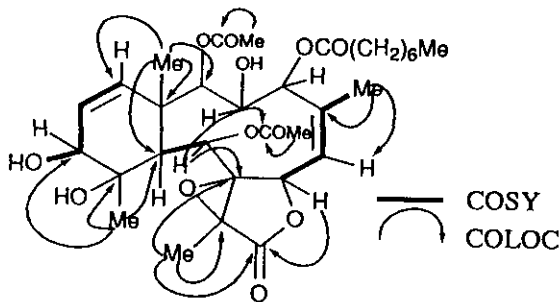


Figure 1.  $^1H$ - $^1H$  COSY and COLOC correlations of 1

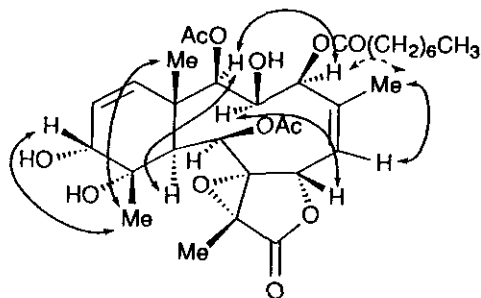


Figure 2. NOE correlations of 1.

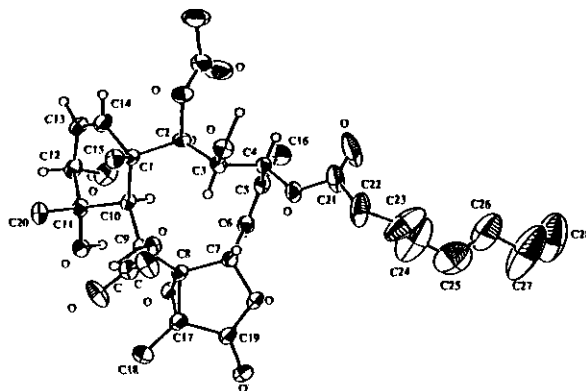


Figure 3. ORTEP representation of 1.

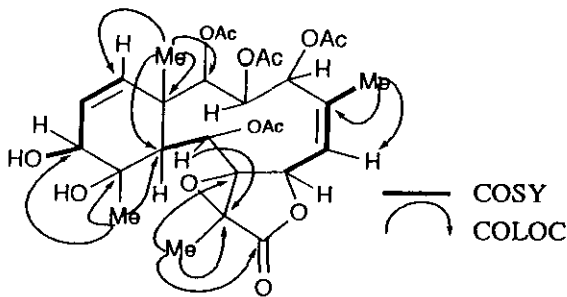


Figure 4.  $^1H$ - $^1H$  COSY and COLOC correlations of 2.

The  $^1H$ - $^1H$  COSY correlations resolved three isolated proton spin systems (Figure 1). H-6 [ $\delta$  5.50 (1H, br d,  $J=9.5$  Hz)] was coupled to H-7 [ $\delta$  5.72 (1H, d,  $J=9.5$  Hz)] and weakly to H-16 ( $\delta_H$  2.08). H-9 [ $\delta$  5.92 (1H, d, 3.8 Hz)] was coupled to H-10 [ $\delta$  2.58 (3H, d,  $J=3.8$  Hz)]. H-12 [ $\delta$  3.69 (1H, t,  $J=6.2$  Hz)] was coupled to a hydroxy proton [ $\delta_H$  ca. 2.38 (1H, overlapped)] and H-13 [ $\delta$  5.82 (1H, dd,  $J=6.2$  and 10.4 Hz)], the latter of which in turn was coupled to H-14 [( $\delta$  5.35, 1H, d,  $J=10.4$  Hz)]. Three resonances at  $\delta$  4.70 (1H, br s), 4.86 (1H, overlapped), and 4.87 (1H, overlapped) were not correlated to each other. The large part of the gross structure was completed by COLOC experiments as shown in Figure 1. The connectivity of C-1 to C-10 and C-14 resulted from cross peaks from H-15 ( $\delta_H$  1.32, 3H, s) to C-1 ( $\delta_C$  47.1, s), C-10 ( $\delta_C$  43.8, d), and C-14 ( $\delta_C$  137.9, d). The linkage from C-10 to C-12 was

suggested by cross peaks from H-20 ( $\delta_{\text{H}}$  1.16) to C-10, C-11 ( $\delta_{\text{C}}$  73.7, s), and C-12 ( $\delta_{\text{C}}$  70.2, d). Therefore the above results indicated the presence of a six-membered ring. Correlations were observed from H-9 to C-8, and C-9 acetoxy carbonyl ( $\delta_{\text{C}}$  168.4) which also showed a cross peak with the acetoxy methyl protons ( $\delta_{\text{H}}$  2.27s). The chemical shift of the remaining acetoxy carbonyl was determined to be  $\delta_{\text{C}}$  169.6 from the correlation of acetoxy methyl protons ( $\delta_{\text{H}}$  2.22, 3H, s) with the carbonyl. Therefore the chemical shift of the  $\gamma$ -lactone carbonyl carbon was concluded to be  $\delta_{\text{C}}$  170.5. H-18 ( $\delta_{\text{H}}$  1.70, s) showed correlations to C-8, C-17 ( $\delta_{\text{C}}$  65.5, s), and the  $\gamma$ -lactone carbonyl carbon at C-19, suggesting an  $\alpha$ -methyl  $\gamma$ -lactone. A Correlation was also observed between H-7 and the  $\gamma$ -lactone carbonyl carbon. Acetylation of **1** with acetic anhydride in pyridine yielded a tetraacetate (**3**),  $\text{C}_{36}\text{H}_{50}\text{O}_{14}$ , the IR spectra of which showed absorption band due to a tertiary hydroxy group ( $3549\text{ cm}^{-1}$ ). Thus, 11 of 12 oxygen atoms in **1** was accounted for. These oxygen atoms were due to three acyl moieties, three hydroxy groups, and a  $\gamma$ -lactone. Based on the results, compound (**1**) was assumed to possess the same briarane skeleton as briarane A which had been isolated from the gorgonacean *Briareum asbestinum*.<sup>4</sup> The presence of an epoxide as the twelfth oxygen atom and the fourth ring between C-8 and C-17 was therefore deduced from the chemical shifts of C-8 ( $\delta_{\text{C}}$  71.3) and C-17 ( $\delta_{\text{C}}$  64.5), which also meant that the tertiary hydroxy group was located at C-11. The remaining problem was to determine the positions of two hydroxy group, an acetoxy group, and a *n*-octanoate group at C-2, C-3, C-4, or C-12. The two hydroxy groups were concluded to be placed at C-3 and C-12, since the H-3 and the H-12 in **1** were shifted to downfield ( $\Delta$  1.22 ppm and  $\Delta$  0.98 ppm, respectively) after acetylation. In the COLOC experiments of **1** in  $\text{C}_5\text{D}_5\text{N}$ , H-16 ( $\delta_{\text{H}}$  2.29, 3H, br s) showed a cross peak with C-4 ( $\delta_{\text{C}}$  78.4, d) as well as the cross peak between H-15 ( $\delta_{\text{H}}$  1.73) and C-2 ( $\delta_{\text{C}}$  78.4, d). Thus, the acetoxy group and the *n*-octanoate group could be placed at C-2 or C-4, and the remaining hydroxy group at C-3.

The relative stereochemistry of all chiral centers was elucidated from NOE experiments of **1** (Figure. 2) and the proton-proton coupling constants of **3**. NOEs between H-20 and H-15 and H-12 showed that these protons occur on the same face of the ring system ( $\beta$ ) and the ring junction is *trans*. An NOE between H-2 and H-10 suggested that they were on the opposite face ( $\alpha$ ) to H-15. In the  $^1\text{H}$  NMR spectrum of the acetate (**3**), signals due to H-2 appeared as a broad singlet at  $\delta_{\text{H}}$  5.02, while signals due to H-3 and H-4 were found as a double doublet ( $J=1.6$  and  $10.3$  Hz) at  $\delta_{\text{H}}$  6.61 and a broad doublet ( $J=10.3$  Hz) at  $\delta_{\text{H}}$  5.69, respectively. This suggested that H-2 and H-3 are orthogonal to each other and H-3 and H-4 are antiparallel. NOEs from H-4 to H-2 and H-16, from H-6 to H-16, and from H-3 to H-7 were observed. On the above results, it was concluded that H-3 and H-4 were  $\alpha$ -oriented and H-7 was  $\beta$ -oriented, and H-6 and H-15 were folded downward as for other briarane derivatives.<sup>5</sup> The *Z* nature of the double bond at C-5 was confirmed on the basis of the NOE between H-6 and H-16 and the C-16 chemical shift ( $\delta_{\text{C}}$  25.5). Configuration of H-9 was deduced to be  $\alpha$  from the observation of a NOE between H-9 and H-18. To determine the positions of the acetoxy group and *n*-octanoate moiety at C-2 or C-4, the stereochemistry of the epoxide, and the conformation of **1** was performed an X-ray diffraction experiment (Figure 3). Thus, it was concluded that the acetoxy and *n*-octanoate groups are located at C-2 and C-4, respectively, and the epoxide is  $\alpha$ -oriented.

The  $^1\text{H}$  NMR spectrum of  $2,6\text{-C}_{28}\text{H}_{36}\text{O}_{14}$ , was similar to that of **1**, except for the presence of two additional acetyl groups and the absence of an octanoate group. The chemical shift corresponding to H-3 ( $\delta$  6.19, br d,  $J=10.5$  Hz) was shifted downfield by 1.21 ppm when compared to that of H-3 in **1**, suggesting that compound (**2**) was concluded to be a 3,4-diacetoxy-4-(deoctanoxy) derivative of **1**. This was confirmed by extensive NMR spectrum, including  $^1\text{H}$ - $^1\text{H}$  COSY,  $^{13}\text{C}$ - $^1\text{H}$ , and HMBC experiments (Figure 4). The relative stereochemistry of **2** was determined to be the same as in **1** by the proton-proton coupling constants and NOE experiments. The  $\beta$ -configurations of H-7, H-12, H-15, M-18, H-20, and H-12 followed from the NOEs from H-3 to H-7 and H-15, from H-7 to H-18, from H-9 to H-18 and H-20, and from H-12 to H-20. The  $\alpha$ -orientations of H-2 and H-10 were deduced from the NOEs from H-2 to H-10 and H-16. Configurations of three acetyl groups at C-2, C-3, and C-4 were determined to be  $\beta$  from the coupling constants between H-2 and H-3 ( $J=0$ ) and between H-3 and H-4 ( $J=10.3$  Hz).

This is the first isolation of briarane diterpenes, in which the successive positions from C-2 to C-4 were oxidized, although there are a few briarane diterpenes possessing an acyl group at C-2 and an epoxide between C-3 and C-4.<sup>7</sup>

## EXPERIMENTAL

**General Experimental Procedures.** Melting points were uncollected. UV and IR spectra were recorded on a UV-210 and a MASCO FT/IR 5300. NMR spectra were recorded with a 400 MHz JEOL NMR instruments using TMS as internal standard and  $\text{CDCl}_3$  as solvents. MS were obtained with a JEOL XD-303. A Rigaku RAXIS-IV diffractometer was used in the X-Ray work.

**Animal Material.** Specimens of *Briareum* were collected at Bonotsu, Kagoshima prefecture. The reference sample (collection no. 222) was deposited at Department of Chemistry and Bioscience and identified by Mr. K. Takemura (Sankei Kagaku, Co., Ltd.).

**Extraction and Isolation.** The organisms (wet weight: 7.6 kg) was chopped into small pieces and extracted with MeOH (30 L) immediately after collection. The MeOH extract (22 g) was suspended in  $\text{H}_2\text{O}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness (9.6 g). Portion (5 g) of the  $\text{CH}_2\text{Cl}_2$  extract was absorbed on silica gel and subjected to chromatography on silica gel packed in hexane, fractions (100 mL) being collected as follows: 1-2 ( $\text{CH}_2\text{Cl}_2$ -hexane, 4:1), 3-34 ( $\text{CH}_2\text{Cl}_2$ ), 5-6 (MeOH- $\text{CH}_2\text{Cl}_2$ , 1:49), 7-8 (MeOH- $\text{CH}_2\text{Cl}_2$ , 1:19), 9-10 (MeOH- $\text{CH}_2\text{Cl}_2$ , 1:9), 11-12 (MeOH- $\text{CH}_2\text{Cl}_2$ , 1:4), and 13-14 (MeOH). Fractions 6-7 (1.9 g), which showed Ichthyotoxic activity, were chromatographed on silica gel using MeOH and  $\text{CH}_2\text{Cl}_2$ , increasing the proportion of MeOH to elute the fractions from the column. The fractions eluted with MeOH- $\text{CH}_2\text{Cl}_2$  (1:49) gave a residue (1.08 g) and crystalline prisms **1** (20 mg). The residue was again subjected to chromatography on silica gel with MeOH- $\text{CH}_2\text{Cl}_2$  (1.5:98.5) and then with MeOH- $\text{CH}_2\text{Cl}_2$  (1.6:98.4) afforded **2** (2.3 mg).

**Compound (1).** Prisms from EtOH, mp 183.8-184.1°C,  $[\alpha]_D^{25} +33.0^\circ$  (c 0.1, MeOH); UV (MeOH)  $\lambda_{\text{max}}$  206 ( $\epsilon$  5200); IR (KBr)  $\nu_{\text{max}}$  3443, 1784, and 1741  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.86 (3H, t,  $J=7.0$  Hz, H-28), 1.16 (3H, s, H-20), ca. 1.29 (8H, overlapped, H-24, H-25, H-26, and H-27),

1.32 (3H, s, H-15), 1.63 (2H, m, H-23), 1.70 (3H, s, H-18), 2.08 (3H, d,  $J=1.1$  Hz, H-16), 2.22 (3H, s, OAc), 2.27 (3H, s, OAc), 2.38 (3H, m, H-22 and OH), 2.58 (1H, d,  $J=3.8$  Hz, H-10), 2.76 (1H, br s, OH), 3.69 (1H, t,  $J=6.2$ , H-12), 4.70 (1H, br s, H-2), 4.86 (1H, overlapped, H-4), 4.87 (1H, overlapped, H-3), 5.35 (1H, d,  $J=10.6$  Hz, H-14), 5.50 (1H, br d,  $J=9.5$  Hz, H-6), 5.72 (1H, d,  $J=9.5$  Hz, H-7), 5.82 (1H, dd,  $J=6.2$  and 10.4 Hz, H-13), and 5.92 (1H, d,  $J=3.8$  Hz, H-9); ( $C_5D_5N$ )  $\delta$  0.79 (3H, t,  $J=7.0$  Hz, H-28), 1.13 (8H, overlapped, H-24, H-25, H-26, and H-27), 1.48 (3H, s, H-20), 1.59 (2H, m, H-23), 1.73 (3H, s, H-15), 2.00 (3H, s, H-18), 2.05 (3H, s, OAc), 2.16 (3H, s, OAc), 2.29 (3H, br s, H-16), 2.33 (1H, m, H-22), 3.32 (1H, d,  $J=3.8$  Hz, H-10 Hz), 3.68 (1H, br s, OH), 4.02 (1H, br d,  $J=6.3$  Hz, H-12), 5.11 (1H, br s, H-2), *ca.* 5.57 (2H, overlapped, H-3 and H-4), 5.80 (1H, br d,  $J=10.3$  Hz, H-6), 5.83 (1H, d,  $J=10.3$  Hz, H-14), 6.05 (1H, dd,  $J=6.3$  and 10.3 Hz, H-13), 6.49 (1H, d,  $J=10.3$  Hz, H-7), and 6.59 (1H, d,  $J=3.8$  Hz, H-9);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  9.7 (q, C-18), 14.1 (q, C-28), 15.5 (q, C-15), 20.9 (q, MeCOO), 21.4 x 2 (q each, MeCOO and H-20), 22.6 (t, C-27), 24.9 (t, C-23), 25.5 (q, H-16), 28.9, (t, C-24 or C-25), 29.0 (t, C-25 or C-24), 31.6 (t, C-26), 34.3 (t, C-22), 43.8 (d, C-10), 47.1 (s, C-1), 64.5 (s, C-17), 65.4 (d, C-9), 70.2 (d, C-12), 71.3 (s, C-8), 71.5 (d, C-3), 73.6 (d, C-7), 73.7 (s, C-11), 76.6 (d, C-4), 76.7 (C-2), 124.2 (d, C-6), 125.1 (d, C-13), 137.9 (d, C-14), 141.0 (s, C-5), 168.4 (s, MeCOO), 169.6 (s, MeCOO), 170.5 (s, C-19), and 173.5 (C-21); FABMS  $m/z$  645.2904 [ $M + Na$ ] $^+$  (calcd for  $C_{32}H_{46}O_{12}Na$  645.2987).

**Compound (2).** Amorphous,  $[\alpha]_D +50.7^\circ$  (c 0.07, MeOH); UV (MeOH)  $\lambda_{max}$  206 ( $\epsilon$  5800); IR (film)  $\nu_{max}$  3505, 1786, and 1747  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  1.14 (3H, t,  $J=7.0$  Hz, H-15), 1.15 (3H, s, H-20), 1.68 (3H, s, H-18), 2.01 (3H, s, MeCOO), 2.08 (3H, s, MeCOO), 2.15 (3H, br s, H-16), 2.17 and 2.30 (3H each, s, MeCOO), 2.69 (1H, br d,  $J=3.7$  Hz, H-10), 2.74 (1H, br s, OH), 3.70 (1H, m, H-12), 4.70 (1H, br s, H-2), 5.12 (1H, br d,  $J=10.3$  Hz, H-4), 5.48 (1H, d,  $J=10.3$  Hz, H-14), 5.58 (1H, br d,  $J=9.9$  Hz, H-6), 5.85 (1H, dd,  $J=6.6$  and 10.3 Hz, H-13), 5.92 (1H, d,  $J=9.9$  Hz, H-7), 5.96 (1H, br d,  $J=3.7$  Hz, H-9), and 6.19 (1H, br d,  $J=10.3$  Hz, H-10);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  10.0 (q, C-18), 15.5 (q, C-15), 20.6, 20.8, 20.9, and 21.2 (q, MeCOO x 4), 21.3 (q, C-20), 25.4 (q, C-16), 43.1 (d, C-10), 46.9 (s, C-1), 64.5 (s, C-9), 65.5 (s, C-17), 70.1 (d, C-12), 71.1 (d, C-3), 71.5 (s, C-8), 73.4 (d, C-7), 74.0 (s, C-11), 76.1 (s, C-4), 125.4 x 2 (d each, C-6 and C-12), 138.5 (d, C-14), 140.3 (s, C-5), 169.0, 170.0 x 2, and 170.1 (s each, MeCOO x 4), 170.7 (s, C-19); FABMS  $m/z$  603.2048 [ $M + Na$ ] $^+$  (calcd for  $C_{28}H_{36}O_{13}Na$  603.2054).

**Acetylation of 3.** Treatment of **1** (4 mg) was acetylated with  $Ac_2O$  (0.5 mL) in pyridine (0.5 mL) to afford a tetraacetate **3** (4 mg); IR (film)  $\nu_{max}$  3549, 1788, and 1748  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  0.88 (3H, t,  $J=7.3$  Hz, H-15), 1.16 (3H, s, H-20), 1.23 (3H, br s, H-20), 1.27 (8H, m, H-24, H-25, H-26 and H-27), 1.56 (2H, overlapped, H-23), 1.67 (3H, s, H-18), 2.07 x 2 (3H each, s, MeCOO), 2.15 (3H each, s, MeCOO), 2.20 (3H, d,  $J=1.5$  Hz, H-16), 2.26 (2H, m, H-22), 2.31 (3H each, s, MeCOO), 2.41 (1H, br s, OH), 2.77 (1H, d, H-10), 4.58 (1H, d,  $J=1.5$  Hz, H-2), 4.69 (1H, d,  $J=6.3$  Hz, H-12), 5.14 (1H, dd,  $J=0.7$  and 10.3 Hz, H-4), 5.57 (1H, d,  $J=10.3$  Hz, H-14), 5.59 (1H, br d,  $J=10.1$  Hz, H-6), 5.92-5.97 (3H, overlapped, H-7, H-9, and H-13), [ $\delta$  5.94 (1H, d,  $J=9.8$  Hz, H-7),  $\delta$  5.94 (1H, dd, 6.3 and 10.6 Hz), H-13 ( $\delta$  5.96, 1H, d,  $J=4.2$  Hz, H-9) at 40°C], and 6.09 (1H, dd,  $J=1.5$  and 10.3 Hz, H-3);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  9.8 (q, C-18), 14.1 (q, C-28), 15.5 (q, C-15), 20.5 and 20.9 x 2

(q each, s, MeCOO), 21.2 (q, s, C-19), 21.3 (q, s, MeCOO), 22.6 (t, C-27), 24.7 (t, C-23), 25.4 (q, C-15), 28.9 (t, C-25 or C-26), 29.0 (t, C-26 or C-25), 31.6 (t, C-26), 34.2 (t, C-22), 43.6 (d, C-10), 47.0 (s, C-1), 64.7 (s, C-17), 65.1 (d, C-9), 70.7 (d, C-3), 71.5 (s, C-8), 72.7 (s, C-11), 73.1 (d, C-12), 73.3 (d, C-7), 76.0 (d, C-4), 76.8 (d, C-2), 123.2 (d, C-13), 125.3 (d, C-6), 140.2 (d, C-14), 140.7 (s, C-5), 168.7, 169.7 x 2, 169.9 (each, s, MeCOO x 4), 170.5 (s, C-19), and 172.8 (s, C-21). (+) FABMS  $m/z$  707 [M + H]<sup>+</sup> and (-) FABMS  $m/z$  859 [M + NBA]<sup>-</sup>.

**X-Ray analysis of 1.** Crystal data: C<sub>32</sub>H<sub>46</sub>O<sub>12</sub>·C<sub>2</sub>H<sub>5</sub>OH, colorless prisms, monoclinic space group C2(#5), a=21.240(4), b=19.15(1), c=9.073(2), β=95.01(1)°, V=3676 Å<sup>3</sup>, Z=4, D<sub>x</sub>1.208 g/cm<sup>3</sup>, F(000)=1440, μ(MoKα)=0.92 cm<sup>-1</sup>, Intensity data were collected on a Rigaku RAXIS-IV diffractometer using graphite monochromated MoKα (λ=0.71070 Å) up to 2θ=55°. Of the total 3498 unique reflections, 2694 were observed [I>3σ(I)]. The structure was solved by direct methods (SIR92)<sup>8</sup> and expanded using Fourier techniques.<sup>9</sup> The non-hydrogen atoms were refined anisotropically. One mole of EtOH is contained in an asymmetric unit. Hydrogen atoms were included but not refined. It was refined by full-matrix least-squares and converged with R=0.056 and Rw=0.077. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Rigaku Corporation.

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