1-Phenyl-5*H*-benzo[*e*]pyrrolo[1,2-*b*]isoindol-5-one (**5b**): mp 158–160 °C; ^1H NMR ($CDCl_3$) 6.13 (d, J = 3 Hz, 1 H), 7.07 (d, J = 3 Hz, 1 H), 6.9–7.8 (m, 11 H, Ar H); IR (KBr) 1740 (amide), 1388, 1232, 768, 704 cm^{-1}. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.66; H, 4.39; N, 4.50.

1-Phenyl-5*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindol-5-one (**5c**): mp 136–139 °C; ^1H NMR ($CDCl_3$) 6.20 (d, J = 3 Hz, 1 H), 7.06 (d, J = 3 Hz, 1 H), 7.3–8.0 (m, 10 H, Ar H), 8.7–8.9 (m, 1 H, Ar H); IR (KBr) 1720 (amide), 1594, 1253, 820, 733 cm^{-1}. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.76; H, 4.20; N, 4.80.

Irradiation of 1d in Methanol–Acetonitrile. A solution of 400 mg (2.5 mmol) of **1d** in 400 mL of methanol–acetonitrile (1/1 v/v) was irradiated for 7 h. The solvent was removed in vacuo, and the products were separated by column chromatography (eluted with dichloromethane–ether) to give 213 mg (49%) of **7**. Minor products having methoxy group, probably stereoisomers of **7**, were detected but not isolated in pure forms.

13c*α*-Hydroxy-2*α*-methoxy-1*β*-phenyl-1,2,3,13c-tetrahydro-5*H*-dibenzo[*e*,*g*]pyrrolo[2,1-*a*]isoindol-5-one (**7**): mp 197–200 °C (from benzene–ethanol); ^1H NMR ($CDCl_3$) 3.50 (s, 3 H, OMe), 3.6–3.8 (m, 1 H), 3.9–4.1 (m, 1 H), 4.1–4.5 (m, 2 H), 4.4 (br s, 1 H, OH), 6.6–6.9 (m, 5 H, Ph), 7.4–7.8 (m, 4 H, Ar H), 8.3–8.6 (m, 3 H, Ar H), 9.0–9.2 (m, 1 H, Ar H); IR (KBr) 3340 (OH), 1668 (amide), 1378, 1100, 758, 696 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_3$: C, 78.96; H, 5.35; N, 3.54. Found: C, 79.17; H, 5.29; N, 3.49.

Acid Degradation of 7. Acid degradation of 50 mg of **7** was performed analogously as that of **3a** and **4** to give 39 mg (89%) of **5d**.

1-Phenyl-5*H*-dibenzo[*e*,*g*]pyrrolo[2,1-*a*]isoindol-5-one (**5d**): mp 214–217 °C; ^1H NMR ($CDCl_3$) 6.18 (d, J = 3 Hz, 1 H), 7.0–7.3 (m, 2 H), 7.4–7.8 (m, 9 H, Ar H), 8.5–8.7 (m, 2 H, Ar H), 8.9–9.2 (m, 1 H, Ar H); IR (KBr) 1730 (amide), 1380, 756, 738 cm^{-1}. Anal. Calcd for $C_{25}H_{15}NO$: C, 86.93; H, 4.38; N, 4.06. Found: C, 87.08; H, 4.28; N, 3.98.

Isolation of 1e (Irradiation of 1b in Benzene). A solution of 2 g (16 mmol) of **1b** in 400 mL of benzene was irradiated for 18 h under N_2. Solvent was removed in vacuo, and the residue was dissolved in 100 mL of ethanol by heating. When the mixture was cooled **1b** crystallized. After the crystals were filtered off the filtrate was concentrated to 50 mL. The plates of **1e** deposited on standing. The crystals were purified by repeated recrystallization from ethanol. The yield of **1e** was 130 mg (7%).

cis-*N*-(3-Phenylallyl)naphthalene-2,3-dicarboximide (**1e**): mp 175–177 °C; ^1H NMR ($CDCl_3$) 4.60 (dd, J = 2, 7 Hz, 2 H, NCH_2), 5.66 (dt, J = 7, 12 Hz, 1 H, $CH_2CH{=}C$), 6.60 (dd, J = 2, 12 Hz, 1 H, $PhCH{=}C$), 7.0–7.4 (m, 5 H, Ph), 7.5–7.8 (m, 2 H, Ar H), 7.9–8.1 (m, 2 H, Ar H), 8.25 (s, 2 H, Ar H); IR (KBr) 1772 (imide), 1715 (imide), 1400, 1350, 770 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.65; H, 4.99; N, 4.21.

Structure of Dukunolides, Bitter Principles of *Lansium domesticum*

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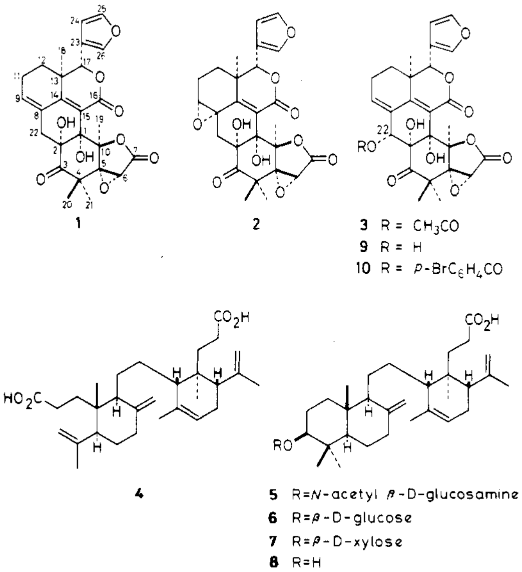
Characteristic bitter principles, named dukunolides A, B, and C, in seeds of *Lansium domesticum* have been proven to be skeletally new tetranortriterpenoids **1**, **2**, and **3**. The structure of **1** is definitely established by X-ray analysis, and that of **2** is confirmed by the chemical correlation with **1** by epoxidation. The absolute configuration of these compounds has been deduced from that of dukunolide C *p*-bromobenzoate, established by X-ray study.

Fruits of *Lansium domesticum* Jack v. duku, a Meliaceous plant, have been called "duku" traditionally and are a very popular dessert in southeast Asia. Kiang et al.[3] have reported the isolation of lansic acid **4** as a major constituent of this fruit skin in 1967. We have also investigated the skin constituents and characterized novel secoonocerane triterpene glycosides, lansiosides A, B, and C (**5**–**7**),[1] and their aglycone **8**.[2] The seeds of duku do not contain the onoceranoids **4**–**8** but gave skeletally new tetranortriterpenoids, named dukunolide A, B, and C (**1**, **2**, and **3**, respectively), as their bitter principles. We herein describe the isolation and structure determination of dukunolides.

Dukunolide A (**1**), mp 279–281 °C, was isolated as colorless needles in 0.03% yield from the powdered seed of *L. domesticum*. The molecular formula $C_{26}H_{26}O_9$ was determined on the basis of the mass spectrum and elemental analysis. The IR spectrum showed the presence of hydroxyls (3500 and 3300 cm^{-1}), carbonyls (1790, 1735, and 1670 cm^{-1}), and double bonds (1625, 1582, 1500, and 960 cm^{-1}). The existence of a $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl moiety was suggested by the UV absorption spectrum (λ_{max} 292 nm ϵ 14600). The ^1H NMR spectrum was rather simple as seen in Figure 3. The presence of 13 quaternary carbon signals in the ^{13}C NMR spectrum (Figure 6) made the structural study very difficult by conventional spectral analysis.

Chart I



1 2

3 R = CH_3CO
9 R = H
10 R = $p\text{-}BrC_6H_4CO$

4

5 R=*N*-acetyl *β*-D-glucosamine
6 R=*β*-D-glucose
7 R=*β*-D-xylose
8 R=H

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[‡] The National Biological Institute.
[§] Shionogi Research Laboratories.

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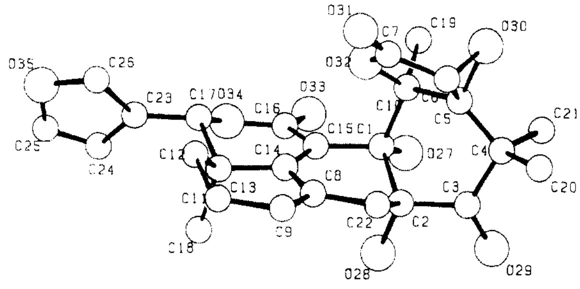

Figure 1. ORTEP drawing of dukunolide A (1).

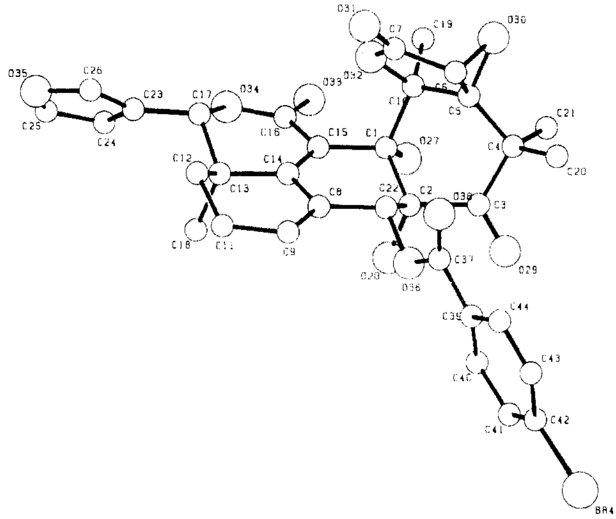

Figure 2. ORTEP drawing of dukunolide C *p*-bromobenzoate (10).

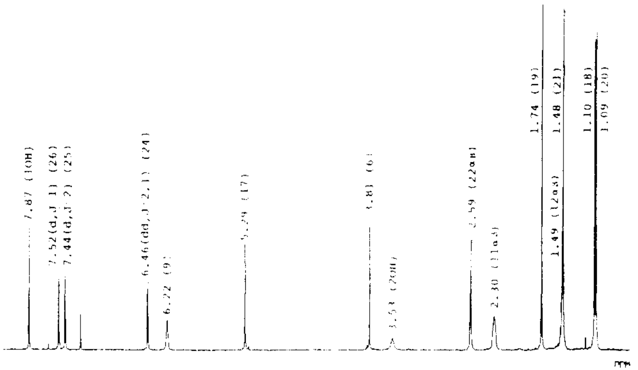

Figure 3. ^{1}H NMR spectrum of dukunolide A (1) in CDCl$_3$ at 400 MHz.

As a result, the correct structure of dukunolide A (1) was established by the single-crystal X-ray diffraction study. The relative configuration of the molecule is shown in Figure 1. The ring junctions at the C-1/C-2 and C-5/C-10 bonds are cis. The γ-lactone ring and the mean plane of C-1/C-2/C-22/C-8/C-14/C-15 face each other with the dihedral angle of 43°, and the distance between C-15 and O-32 is only 2.7 Å and that between C-7 and C-8 is 3.6 Å. A charge-transfer interaction between the C-7 carbonyl group and the $\Delta^{8,9}$ double bond is believed to cause a bathochromic shift of the UV absorption maximum (λ_{max} 292 nm) due to the $\alpha,\beta,\gamma,\delta$-dienolide system. The hydroxyl groups at C-1 and C-2 form intramolecular hydrogen bonds between O-27 and O-33, and O-28 and O-29.[4]

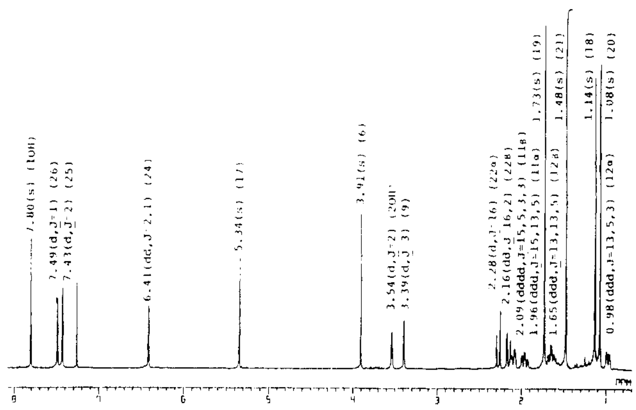

Figure 4. ^{1}H NMR spectrum of dukunolide B (2) in CDCl$_3$ at 400 MHz.

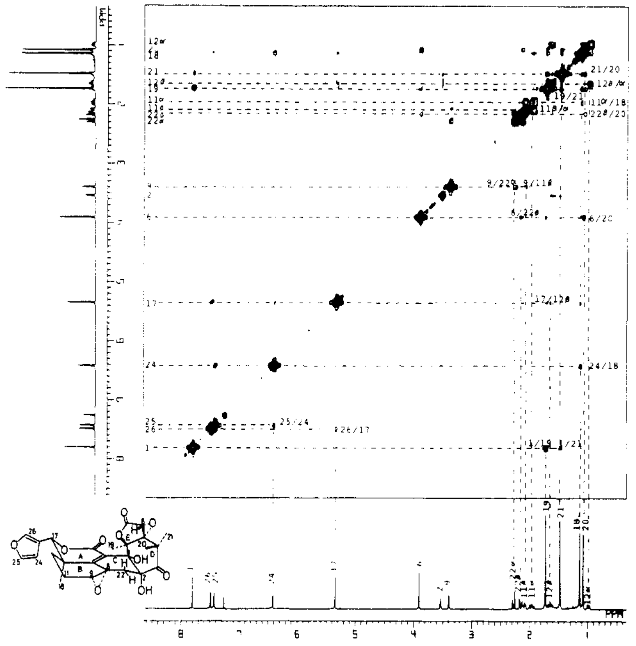

Figure 5. NOESY NMR spectrum of dukunolide B (2) in CDCl$_3$ at 400 MHz.

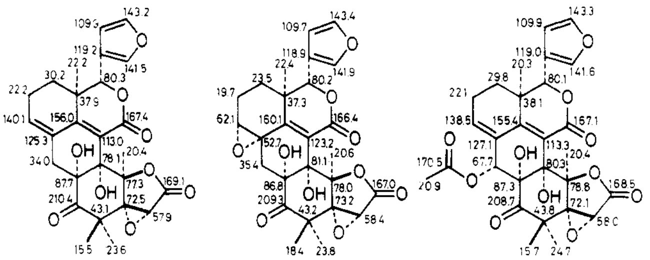

Figure 6. ^{13}C NMR spectrum of dukunolides, δ in CDCl$_3$ at 22.5 MHz.[11]

Dukunolide B (2), $C_{26}H_{26}O_{10}$, mp 248.5–251 °C, was isolated as colorless needles in 0.08% yield. The IR spectrum was similar to that of 1, while the UV spectra of both compounds were entirely different (1, λ_{max} 292 nm, ϵ 14 600; 2, λ_{max} 249 nm, ϵ 5450). This fact indicates that the doubly conjugated δ-lactone group in 1 was saturated at the γ,δ-positions in 2. The NMR spectra supported this assignment. In the ^{1}H NMR spectra of 2 (Figure 4), an oxirane proton signal (δ 3.39 d, J = 3 Hz) was detected instead of the olefinic proton signal in 1 (δ 6.22 br). Therefore, the corresponding C-8/C-9 epoxide structure

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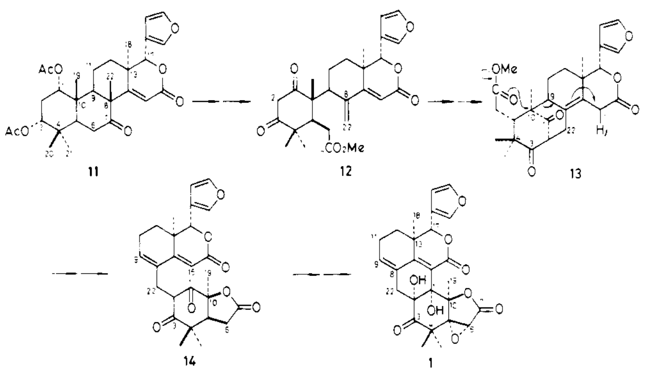
was assumed to occur in **2**. In the ^{13}C NMR spectrum, a pair of olefinic carbon signals in **1** (δ 125.3 s and 140.1 d) is replaced by a pair of oxirane carbon signals (δ 52.7 s and 62.1 d) in **2**. The δ-values of other carbon signals as shown in Figure 4 were consistent with the assumed structures of both compounds. All proton signals of **1** and **2** were fully assigned on the basis of the ^{2}D NMR experiment (COSY, NOESY, and C/H correlated spectroscopy), which also led the reasonable stereochemistry of the compound **2**. The signal at δ 3.91 was assigned to be the H-6 oxirane proton. The NOESY NMR (Figure 5) indicated the presence of NOE interaction between H-6 and H-20 (methyl, δ 1.08 s), and H-6 and H-22β (δ 2.16 dd, *J* = 16 and 2 Hz). The hydroxylic proton at C-1 was observed at very low field (δ 7.80) as a sharp singlet because of the strong hydrogen bonding with the C-16 carbonyl oxygen. This proton interacted (NOE) with H-21 (methyl, δ 1.48 s) and H-19 (methyl, δ 1.73 s). This behavior is closely related to those of **1**, showing that the both compounds assume a very similar conformation around the C/D/E ring system. The stereochemistry of the C-8 and C-9 oxirane ring in **2** was also established by the NOE experiment. The observed NOE between H-18 (methyl, δ 1.14 s) and H-11α (δ 1.96 ddd, *J* = 15, 13, 5 Hz), H-11β (δ 2.09 dddd, *J* = 15, 5, 3, 3 Hz) and H-9 (δ 3.39, d, *J* = 3 Hz), and H-9 and H-22α (δ 2.28, d, *J* = 16 Hz), but not between H-18 and H-9 indicated that the oxirane ring must be located on the α-side. Absence of the vicinal proton coupling between H-11α and H-9 suggested that the conformation of **2** around A/B/C ring system is analogous to **1**.

Finally the structure of dukunolide B (**2**) was confirmed by the direct chemical correlation with dukunolide A. Treatment of **1** with *m*-chloroperbenzoic acid selectively afforded **2**. The β-side of the C-8/C-9 double bond of **1** is entirely shielded by the γ-lactone ring and the C-2 hydroxyl group also assisted the peracid attack from the α-side. Thus, the stereochemistry of the C-8/C-9 epoxy group was established to be α.

Dukunolide C (**3**), $C_{28}H_{28}O_{11}$, was isolated as colorless needles, mp 217–218 °C, in 0.04% yield. UV and IR spectra were quite similar to those of dukunolide A (**1**). The ^{1}H NMR spectrum of **3** was also quite similar to that of **1**, except for the presence of a secondary acetoxyl moiety, which was suggested by a sharp three-proton singlet at δ 2.15 and a broad one-proton signal at δ 5.84. The absence of any signals around δ 2.6 (C-22 methylene signals for **1**) indicated that the acetoxyl group was placed at C-22. The ^{13}C NMR spectrum (δ 20.9 q, 67.7 d, 170.5 s) supported this assignment. Upon irradiation of a proton at δ 4.08, which was assigned to be the C-6 oxirane proton, 5% NOE enhancement was observed at the C-22 proton (δ 5.84), indicating the stereochemistry of the acetoxyl group to be α.

In order to establish the absolute configuration of dukunolides, **3** was converted to the *p*-bromobenzoate **10** as follows. Selective methanolysis of the acetoxyl group with a catalytic amount of LiOH in dry methanol gave alcohol **9**. Upon treatment of **9** with *p*-bromobenzoyl chloride and triethylamine, *p*-bromobenzoate **10** was obtained as colorless crystals. The absolute configuration of **10**, as shown in Figure 2, was determined by the X-ray method, from which that of **1** presented in Figure 1 was deduced. The structural features exhibited in **10** are common to those in **1**.

Chart II



11 12 13 14 1

The skeletally new tetranortriterpenoids,[5,6] dukunolide A, B, and C, obtained from *L. domesticum* seeds are closely related to mexicanolide (**13**)[7] isolated from the heart-wood of *Cedrela odorata* (Meliaceae). Chemical transformation of khivorin (**11**), a metabolite of *Khaya senegalensis*,[8] to **13** via diketone **12** has been reported.[9] Dukunolide could be derived from mexicanolide by the fragmentation of the C-9/C-10 bond along with the simultaneous γ-lactone formation to give **14** and following cyclization at C-1 and C-15, since we recently have detected mexicanolide as a minor constituent in the seed extract of *L. domesticum*.

Experimental Section

General Procedures. Analytical thin layer chromatography (TLC) was done on Merck silica gel 60 F_{254} precoated plates. Fuji-Devison BW-820 MH silica gel was employed for column chromatography. Intensity data for X-ray analysis were collected on a Rigaku AFC-5 diffractometer and computations were carried out on a FACOM M-340R computer.

Isolation of Dukunolides A, B, and C (1, 2, and 3). Seed of *L. domesticum* (1.2 kg), collected at Bogor, Indonesia, was powdered and extracted with dichloromethane (1.5 L) by using Soxhlet apparatus to give 34.2 g of a gummy extract. This extract was chromatographed on a column of silica gel (550 g) using eluents of increasing polarity from dichloromethane to ether affording fractions a (1.59 g), b (0.53 g), c (3.36 g), d (1.82 g), e (2.75 g), f (3.12 g), g (9.00 g), and h (7.6 g). The fraction e was further chromatographed on a column of silica gel (85 g) using eluents of increasing polarity from hexane to ethyl acetate to give dukunolide A (**1**) as crystals (280 mg, 0.03% yield). Recrystallization from dichloromethane and hexane afforded pure colorless needles: mp 279–281 °C; $[\alpha]^{20}_{D}$ +166° (*c* 0.9, $CHCl_3$); IR (ν_{max} in $CHCl_3$) 3550, 3300, 1790, 1735, 1670, 1625, 1582, 1500, 960 cm^{-1}; UV (λ_{max} in C_2H_5OH) 292 nm (ε 14 600); high resolution mass spectrum, 482.1586 (M$^+$), calcd for $C_{26}H_{26}O_9$ 482.1576. Anal. Calcd for $C_{26}H_{26}O_9$: C, 64.72; H, 5.43. Found: C, 64.46; H, 5.45.

Column chromatography on silica gel (100 g) of fractions c and d using eluents of increasing polarity from hexane to ethyl acetate afforded dukunolide B (**2**) (908 mg, 0.08% yield) and dukunolide C (**3**) (460 mg, 0.04% yield). Recrystallization of these materials from hexane and dichloromethane afforded pure crystals of dukunolide B (**2**) [mp 248.5–251.0 °C; $[\alpha]^{20}_{D}$ +82.2° (*c* 0.9, $CHCl_3$); IR (ν_{max} in $CHCl_3$) 3530, 3275, 1785, 1725, 1670, 950 cm^{-1}; UV (λ_{max} in C_2H_5OH) 249 nm (ε 5450); high resolution mass spectrum, 498.1502 (M$^+$), calcd for $C_{26}H_{26}O_{10}$ 498.1525. Anal. Calcd for $C_{26}H_{26}O_{10}$: C, 62.64; H, 5.26. Found: C, 62.66; H, 5.45.] and dukunolide C (**3**) [mp 217–218 °C; $[\alpha]^{20}_{D}$ +206° (*c* 0.89, $CHCl_3$); IR (ν_{max} in $CHCl_3$) 3550, 3300, 1790, 1745, 1670, 1625, 1590, 1510, 950 cm^{-1}; UV (λ_{max} in C_2H_5OH) 289 nm (ε 14 300); ^{1}H NMR (δ in $CDCl_3$) 7.83 (1 H, s, Cl), 7.52 (1 H, d, *J* = 1 Hz, C26), 7.45 (1 H, d, *J* = 2 Hz, C25), 6.46 (1 H, dd, *J* = 2, 1 Hz, C24), 6.26 (br, C9), 5.84 (1 H, br, C22), 5.30 (1 H, s, C17), 4.08 (1 H, s, C6), 3.78

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Table I. Crystallographic Details for Dukunolide A (1) and Dukunolide C *p*-Bromobenzoate (10)

	1	10
	($C_{26}H_{26}O_9$)	($C_{33}H_{29}O_{11}Br$)
F.W.	482.5	681.5
space group	$P2_12_12_1$	$P2_12_12$
a (Å)	12.404 (1)	8.963 (1)
b (Å)	21.483 (2)	38.092 (6)
c (Å)	8.747 (1)	8.817 (1)
Z	4	4
D_c (g/cm^3)	1.37	1.50
data collection		
radiation	CuK_α	Cu K_α (λ = 1.54178 Å)
θ_{max} (deg)	65.0	65.0
no. of unique reflections	2278	2969
no. of unobservedly weak reflections $[\lvert F_o \rvert \leq \sigma_1(F_o)]$	201	115
scan technique	$\omega-2\theta$	$\omega-2\theta$
scan width parameters A (deg) and B in width = $A + B \tan\theta$	1.0, 0.2	1.0, 0.2
ω scan speed (deg/min)	3.0	3.0
structure refinement		
R	0.056	0.035
no. of reflections used	1949	2631

(1 H, s, C2), 2.36 (2 H, m, C11), 2.15 (3 H, s, Ac), 1.77 (3 H, s, C19), 1.52 (3 H, s, C21), 1.50 (2 H, m, C12), 1.13 (3 H, s, C18), 1.03 (3 H, s, C20); high resolution mass spectrum, 540.1629 (M$^+$), calcd for $C_{28}H_{28}O_{11}$, 540.1630. Anal. Calcd for $C_{28}H_{28}O_{11}\cdot CH_3OH$: C, 60.48; H, 6.00. Found: C, 60.65; H, 5.60.].

Mexicanolide (13). A minor constituent of fraction e described above was purified by recrystallization by using hexane and ethyl acetate. The spectral data (IR, optical rotation, ^{1}H NMR, and ^{13}C NMR) of these crystals (ca. 0.002% yield, mp 228–232 °C) were identical with that reported for mexicanolide.[7]

Dukunolide B (2) from Dukunolide A (1). To a stirred solution of dukunolide A (1) (12.9 mg, 0.027 mmol) in dichloromethane (0.5 mL) and saturated sodium bicarbonate solution (0.5 mL) was added *m*-chloroperbenzoic acid (15 mg, 0.068 mmol), and the mixture was stirred for 4 h at room temperature. Dichloromethane extraction and subsequent preparative TLC afforded dukunolide B (2) 6.3 mg (47% yield) along with the recovery of dukunolide A (3.2 mg). The spectral properties of this product were identical with those of the natural material.

Deacetyldukunolide C (9). To a stirred solution of dukunolide C (3) (56.4 mg, 0.104 mmol) in anhydrous methanol (15 mL) was added lithium hydroxide (0.067 M methanol solution, 0.2 mL, 0.013 mmol, 0.12 equiv), and the mixture was stirred for 6 h at room temperature. After evaporation of methanol under reduced pressure, brine was added, and the mixture was extracted with chloroform. Column chromatography on silica gel (5 g) using an eluent of dichloroemthane and ether (10:1) afforded **9** 36 mg (70% yield) along with recovered **3** (3.3 mg). Recrystallization from ethyl acetate and hexane afforded pure crystals: mp 247.5–249.5 °C; $[\alpha]^{17}{}_D$ +140° (c 0.14, $CHCl_3$); IR (ν_{max} in $CHCl_3$) 3530, 3300, 1785, 1720, 1665, 950 cm^{-1}; UV (λ_{max} in C_2H_5OH) 291 nm (ϵ 11 800); ^{1}H NMR (δ in $CDCl_3$) 7.52 (1 H, s, C1), 7.48 (1 H, d, J = 1 Hz, C26), 7.41 (1 H, d, J = 2 Hz, C25), 6.76 (1 H, m, C9), 6.42 (1 H, dd, J = 2, 1 Hz, C24), 5.25 (1 H, s, C17), 4.45 (1 H, d, J = 12 Hz, C22), 3.89 (2 H, s, C2, C6), 2.55 (1 H, d, J = 12 Hz, C22-OH), 2.34 (2 H, m, C11), 1.71 (3 H, s, C19), 1.52 (2 H, m, C12), 1.43 (3 H, s, C21), 1.13 (3 H, s, C18), 1.09 (3 H, s, C20); ^{13}C NMR (δ in $CDCl_3$) 208.6 (3), 168.7 (7), 167.3 (16), 155.4 (14), 143.3 (25), 141.7 (26), 139.9 (9), 131.5 (8), 119.2 (23), 113.0 (15), 110.0 (24), 87.8 (2), 82.1 (17), 80.3 (1), 78.7 (10), 73.0 (5), 67.9 (22), 58.3 (6), 43.1 (4), 38.0 (13), 30.0 (12), 23.6 (21), 22.2 (11), 22.1 (18), 20.4 (19), 15.8 (20). Anal. Calcd for $C_{26}H_{26}O_{10}\cdot CH_2Cl_2$: C, 55.58; H, 4.84. Found: C, 55.56; H, 4.88.

Dukunolide C *p*-Bromobenzoate (10). To a stirred solution of **9** (29.8 mg, 0.061 mmol) and triethylamine (69 mg, 0.68 mmol, 11 equiv) in dichloromethane (1 mL) was added a solution of *p*-bromobenzoyl chloride (85 mg, 0.39 mmol, 6.5 equiv), and the mixture was stirred for 3 h at room temperature. The reaction mixture was directly subjected to column chromatography on silica gel (5 g) using an eluent of dichloromethane and ether (50:1) to give **10** (24.6 mg, 60% yield). Recrystallization from dichloromethane afforded pure crystals: mp 146.5–148.5 °C; $[\alpha]^{14}{}_D$ +137° (c 0.63, $CHCl_3$); IR (ν_{max} in $CHCl_3$) 3530, 3300, 1785, 1725, 1665, 950 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 7.90 (2 H, d, J = 8 Hz), 7.75 (1 H, s, *1*), 7.58 (2 H, d, J = 8 Hz), 7.52 (1 H, d, J = 1 Hz, C26), 7.44 (1 H, d, J = 2 Hz, C25), 6.43 (1 H, dd, J = 2, 1 Hz, C24), 6.20 (1 H, m, C9), 6.05 (1 H, m, C22), 5.28 (1 H, s, C17), 4.13 (1 H, s, C6), 3.26 (1 H, s, C2), 2.30 (2 H, m, C11), 1.75 (3 H, s, C19), 1.55 (2 H, m, C12), 1.48 (3 H, s, C21), 1.15 (3 H, s, C18), 0.96 (3 H, s, C20); ^{13}C NMR (δ in $CDCl_3$) 208.5 (3), 168.5 (7), 167.2 (16), 155.4 (14), 143.3 (25), 141.7 (26), 138.6 (9), 127.0 (8), 119.0 (23), 113.6 (15), 110.0 (24), 87.5 (2), 80.6 (17), 80.2 (10), 79.0 (1), 72.5 (5), 68.6 (22), 58.3 (6), 43.8 (4), 38.3 (13), 30.0 (12), 24.8 (21), 22.3 (11), 21.2 (18), 20.5 (19), 15.9 (20), 169.1, 165.5, 132.2, 131.6, 129.7. Anal. Calcd for $C_{33}H_{29}O_{11}Br\cdot H_2O$: C, 56.66; H, 4.47. Found: C, 56.35; H, 4.27.

X-ray Analysis of Dukunolide A (1) and Dukunolide C *p*-Bromobenzoate (10). Crystallographic details are listed in Table I. The structure of dukunolide A (1) was solved by using the program MULTAN 78,[10] and that of dukunolide C *p*-bromobenzoate (10) was solved by the conventional heavy-atom method. All hydrogen atoms were located in a difference electron density map. The structures were refined by the block-diagonal least-squares technique for the positional parameters of all atoms and anisotropic thermal ones of non-hydrogen atoms. Each hydrogen atom was given the equivalent isotropic temperature factor of the atom to which it was bound. No peaks higher than those of the hydrogen atoms were found in the final difference Fourier map.

The function minimized in the refinement was $\Sigma(w|\Delta F|^2)$. The weighting scheme was $w = 1/\sigma^2 (F_o)$ for observed reflection with $|F_c| \geqslant \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$, and $w = 0$ otherwise stated. $\sigma(F_o)$ was estimated as $\sigma(F_o) = [\sigma_1{}^2 (F_o) + c^2|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the standard deviation due to counting errors. The values of c^2 were 0.00205 and 0.00150 for **1** and **10**, respectively.

The absolute configuration of **10** was determined on the basis of the Bijvoet inequality relation due to the anomalous dispersion of bromine atom by Mo Kα radiation (λ = 0.71069 Å, $\Delta f'_{Br}$ = –0.374, $\Delta f''_{Br}$ = 2.456).

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Supplementary Material Available: Tables of atomic fractional coordinates, anisotropic thermal parameters, bond distances, and bond angles for 1 and 10 (10 pages). Ordering information is given on any current masthead page.

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(10) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data", Universities of York, England, and Louvain, Be lgium.

(11) The assignment was based on the ^{1}H/^{13}C correlated spectra and INEPT experiment.