Indonesian Medicinal Plants. XIII.[1] Chemical Structures of Caesaldekarins c, d, and e, Three Additional Cassane-Type Furanoditerpenes from the Roots of *Caesalpinia major* (Fabaceae). Several Interesting Reaction Products of Caesaldekarin a Provided by *N*-Bromosuccinimide Treatment

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Following the previous studies on caesaldekarins a (1) and b (2), the chemical structures of three additional cassane-type furanoditerpenes named caesaldekarins c (3), d (4), and e (5), isolated from the roots of *Caesalpinia major* (Fabaceae) collected in Flores Island, Indonesia, have been elucidated on the bases of physicochemical evidence and chemical derivations. Several interesting NBS (*N*-bromosuccinimide) reaction products of 1 have been elucidated.

Key words Indonesian medicinal plant; *Caesalpinia major*; Fabaceae; cassane-type furanoditerpene; caesaldekarin; NBS bromination unusual

In the previous paper,[3] we reported the elucidation of the absolute stereostructures of two new cassane-type furanoditerpenoids named caesaldekarins a (**1**) and b (**2**), together with the isolation of caesaldekarins c, d, and e, all from the roots of *Caesalpinia major* DANDY (Fabaceae). The plant is called "dekar" in the Ruteng area of Flores Island, Nusa Tenggara Timur, Indonesia, and the decoction of the roots has been traditionally used as a tonic and an anthelmintic in the area, as well as for treatment of rheumatism and back-ache.[4] In this paper, we present a full account of the structure elucidation of three new additional cassane-type furanoditerpenoids, designated caesaldekarins c (**3**), d (**4**), and e (**5**).

Caesaldekarin c (3) Caesaldekarin c (**3**), obtained as colorless needles, colored reddish purple with the Ehrlich reagent, indicative of its furanoid structure. In the mass spectrum (MS) and high-resolution MS, **3** gave a molecular ion peak at *m/z* 346 of the composition $C_{21}H_{30}O_4$, together with a fragment ion peak at *m/z* 108 characteristic of a fragment derivable from the furan moiety of **3**.[3] The IR spectrum of **3** showed absorption bands demonstrating the presence of a hydroxyl group (3625 cm^{-1}), an ester moiety (1722 cm^{-1}) and a furan ring (1465, 905 cm^{-1}), while the UV spectrum showed an absorption maximum at 217 nm ($\varepsilon=7000$) attributable to the furan moiety.

The ^1H- and ^{13}C-NMR spectra of caesaldekarin c (**3**) showed the presence of two tertiary methyl groups [δ 0.82, 1.20 (both s); δ_C 15.0, 23.9 (both q)], one secondary methyl group [δ 1.00 (d, $J=7$ Hz); δ_C 17.5 (q)], one methoxycarbonyl group [δ 3.67 (s); δ_C 177.4 (s), 51.6 (q)], and one quaternary carbon linked with an oxygen function [δ_C 76.5 (s)], together with an α,β-disubstituted furan ring [δ 6.18, 7.21 (both br s); δ_C 109.5 (d), 122.3 (s), 140.3 (d), 149.5 (s)].

The ^1H–^1H correlation spectroscopy (COSY) and the ^1H–^{13}C correlation spectroscopy *via* long-range coupling (COLOC) experiments showed that caesaldekarin c (**3**) has a cassane-type diterpenoid framework, in which one of the singlet methyl groups is replaced with a methoxycarbonyl group and the 6-acetoxyl group in caesaldekarin a (**1**) is absent.

In order to elucidate the stereochemical connectivities of the A/B and B/C rings in **3** and to define the location of the methoxycarbonyl group, we next carried out nuclear Overhauser and exchange spectroscopy (NOESY) experiments, which showed the following spatial proximities in caesaldekarin c (**3**): i) between the 10-methyl protons and 4β-methoxy-carbonyl- and 11β-protons, and ii) between the 4α-methyl protons and 6α-proton (Fig. 1). Thus, the location of the methoxycarbonyl group is 4β. Furthermore, the relative configuration of the methoxycarbonyl group in **3** was suggested by a pyridine-induced ^1H-NMR shift study[5] of **3**. Thus, the 4α-methyl proton signal showed a significantly lower shift [$\Delta\delta=\delta C_5D_5N-\delta CDCl_3=0.20$ ppm], which is attributable to the presence of the 5α-hydroxyl moiety (Fig. 1). Thus, the structure of caesaldekarin c (**3**) has been elucidated as shown.

Caesaldekarin d (4) Caesaldekarin d (**4**) was obtained as colorless needles, and colored reddish purple with the Ehrlich reagent. It gave a molecular ion peak at *m/z* 376, which corresponds to the molecular formula $C_{22}H_{32}O_5$, as well as a base peak at *m/z* 108 in the MS. The IR spectrum of **4** showed absorption bands due to a hydroxyl group (3420 cm^{-1}), an acetoxyl group (1730 cm^{-1}), and a furan ring (1510, 890 cm^{-1}), while the UV spectrum showed an absorption maximum at 217 nm ($\varepsilon=7500$) attributable to the furan ring.

The ^1H- and ^{13}C-NMR spectra of caesaldekarin d (**4**) were closely similar to those of caesaldekarin a (**1**) except for additional carbinyl proton [δ 3.65 (br t, $W_{h/2}=ca.$ 8 Hz)] and carbon [δ_c 74.5 (d)] signals in **4**. The COSY (^1H–^1H and ^1H–^{13}C) and the heteronuclear multi-bond connectivity (HMBC) experiments led us to presume that

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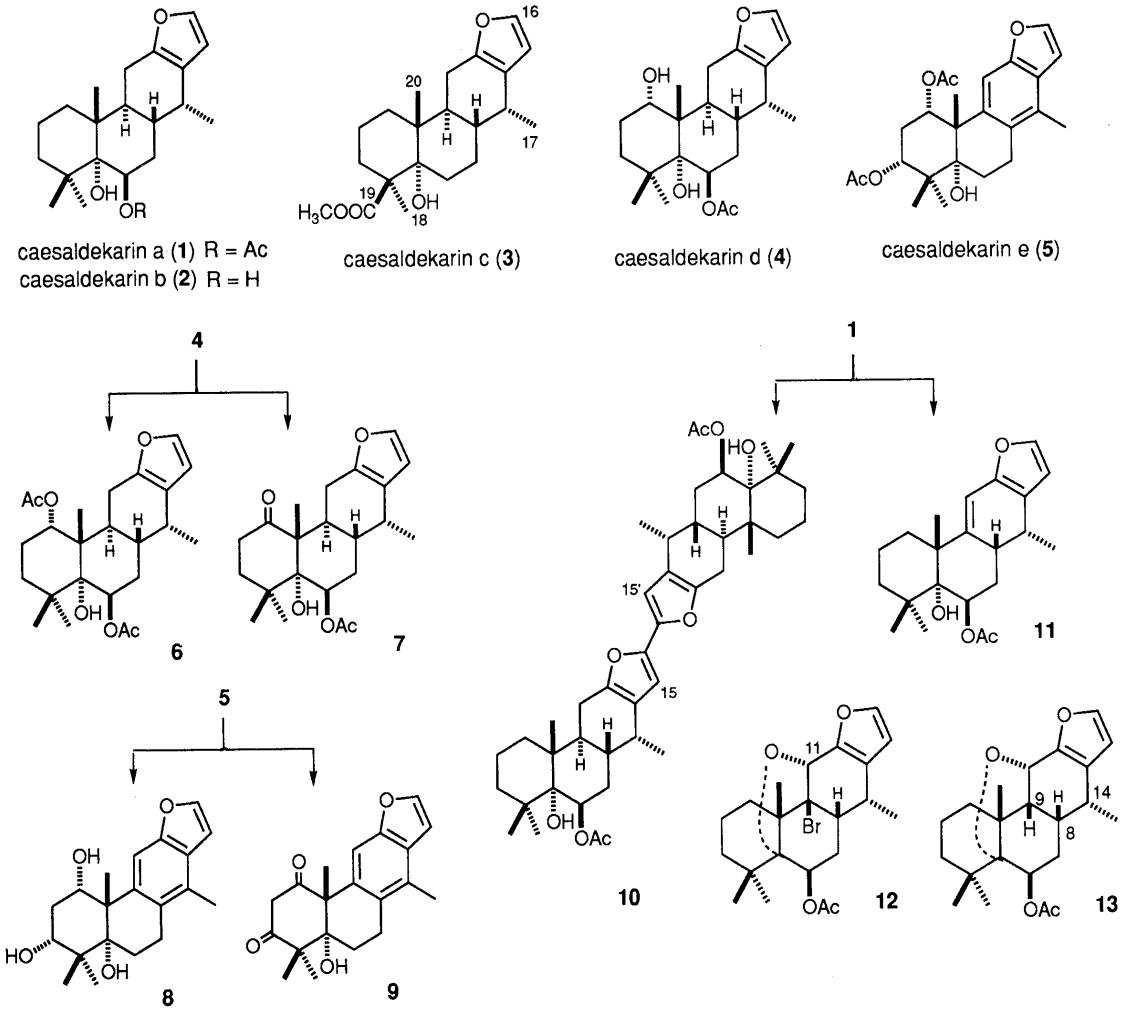

Chart 1

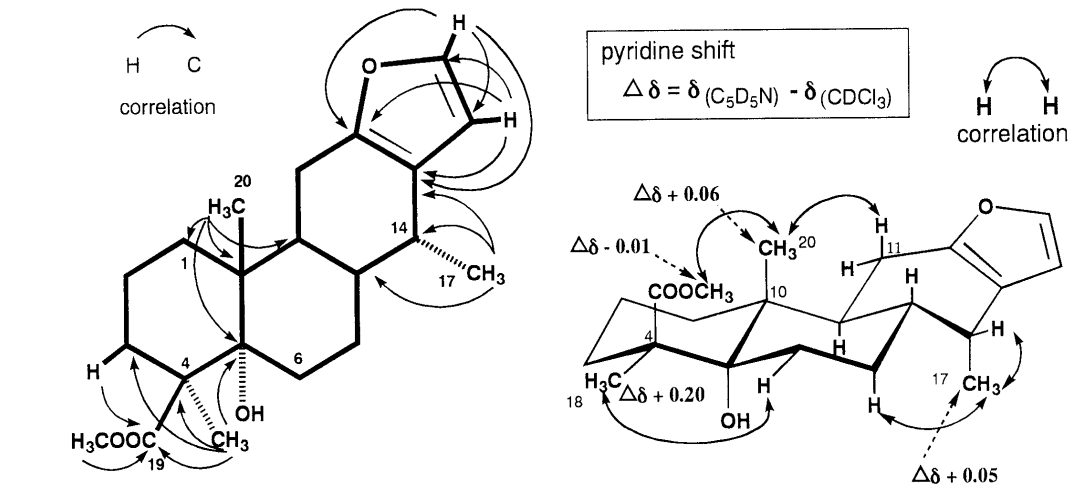

Fig. 1. COLOC and NOESY Observations and Pyridine-Induced Shifts Observed for Caesaldekarin c (**3**)

caesaldekarin d (**4**) is a 1-hydroxylated analog of caesaldekarin a (**1**) (Fig. 2). Furthermore, NOE was observed between the 1β-proton and 10-methyl protons in the ^{1}H-NMR of **4** as shown in Fig. 2. From these findings, it has become clear that the additional hydroxyl group in **4** is located at the 1α position.

In the ^{1}H-NMR spectrum of the diacetate **6**, prepared by ordinary acetylation of caesaldekarin d (**4**), a one-proton doublet of doublets (J=3, 3 Hz) was observed at δ 4.88, which is characteristic of the 1β equatorial proton. In addition, oxidation of **4** with pyridinium chlorochromate (PCC) afforded the 1-oxo derivative **7**.

Consequently, the structure of caesaldekarin d (**4**) has been defined as shown.

Caesaldekarin e (5) Caesaldekarin e (**5**) was also obtained as colorless needles. It colored reddish purple

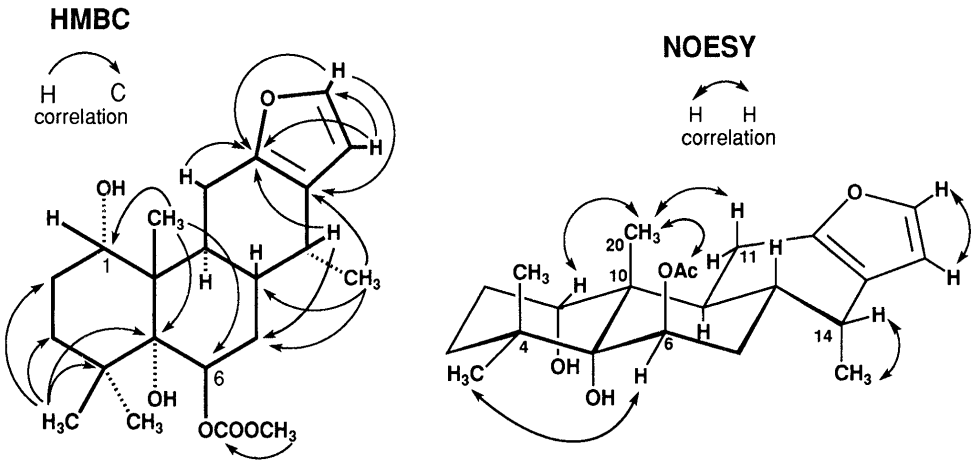

Fig. 2. HMBC and NOESY Observations for Caesaldekarin d (**4**)

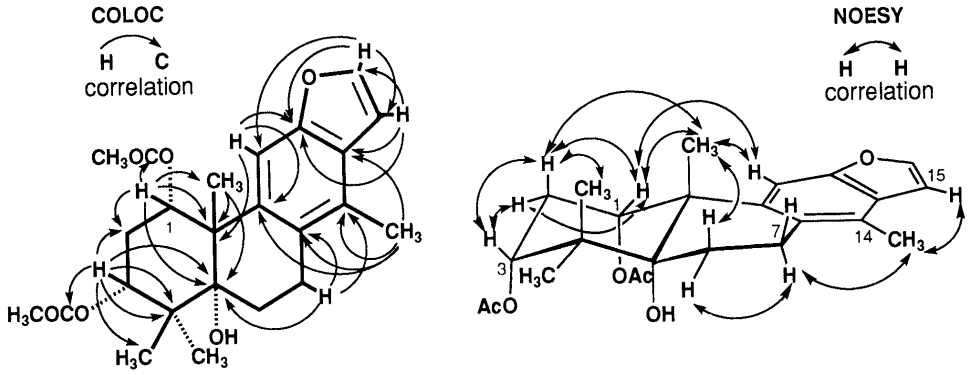

Fig. 3. COLOC and NOESY Observations for Caesaldekarin e (**5**)

with the Ehrlich reagent and gave a molecular ion peak at *m/z* 414, corresponding to $C_{24}H_{30}O_6$ in its MS. The IR spectrum of **5** showed absorption bands due to a hydroxyl group (3600 cm^{-1}) and an acetoxyl group (1731 cm^{-1}), whereas the UV spectrum showed absorption maxima [at 292 nm ($\varepsilon=2300$), 282 nm ($\varepsilon=2300$), 251 nm ($\varepsilon=10500$), 212 nm ($\varepsilon=28700$)] which suggested the presence of a benzofuran moiety in the structure.

The ^{1}H-NMR spectrum of caesaldekarin e (**5**) showed signals ascribable to two methine protons [δ 5.05, 5.75 (both t-like, $J=ca.$ 3 Hz)], each geminal to an acetoxyl function, two acetoxyl protons [δ 1.93, 2.02 (both s)], one aromatic proton [δ 7.00 (s)], and α,β protons [δ 6.72 (d, $J=2.5$ Hz), δ 7.51 (d, $J=2.5$ Hz)] on a furan ring.

On alkaline hydrolysis with 10% potassium hydroxide in methanol, caesaldekarin e (**5**) provided a triol **8**, which was treated with PCC to afford a β-diketone **9** (Chart 1). The ^{1}H-NMR spectrum of **9** showed a pair of one-proton doublets at δ 3.51 and δ 3.86 (1H each, ABq, $J=19.5$ Hz), which were characteristically assignable to methylene protons sandwiched by β-diketones. Furthermore, the ^{1}H–^{1}H and ^{1}H–^{13}C COSY, COLOC, and NOESY data (Fig. 3) substantiated the structure of caesaldekarin e (**5**) as shown.

Finally, in order to confirm the cassane skeleton assigned to previous[3] and present caesaldekarins, we attempted to prepare a heavy atom derivative suitable for X-ray crystallographic analysis. After several trials, we found that treatment of caesaldekarin a (**1**) with *N*-bromosuccinimide (NBS) in chloroform at -40 °C afforded a crystalline compound **10** (15%) without bromine, which was subjected to X-ray analysis to reveal the bisfuranocassane skeleton, as reported previously,[3] and a mixture (40%) of presumably two products. Separation of the mixture by semi-preparative reversed-phase (ODS) HPLC provided compounds **12** and **13**. Compound **12** was readily recrystallized from methanol to afford crystals suitable for X-ray crystallographic analysis. Perspective drawings of the molecule of **12** are shown in Fig. 4. Taking into account the structure **12**, the chemical structure of the other product **13** was figured out mainly from the MS, IR, and NMR spectral data, including the 2D-NMR experiments. Thus, the ^{1}H- and ^{13}C-NMR spectra of **13** suggested the presence of an 11-oxymethine moiety [δ 5.00 (d, $J=3.5$ Hz), δ_C 66.9 (d)]. In a NOESY experiment on **13**, correlations were observed between the 8β-proton and 9β- and 14β-protons, and between the 9β-proton and 11β- and 14β-protons, which supported the *cis*-junction of the B/C rings in **13**. These findings led to the formulation of the structure of **13** as shown.

In order to define the mechanism of formation of **12** and **13** from caesaldekarin a (**1**), we attempted to isolate the reaction intermediate, and obtained it as a fairly unstable 9,11-dehydro derivative **11** [δ 6.20 (s, 11-H), δ_C 109.8 (d, 11-C), 149.0 (s, 9-C)] upon NBS treatment of **1** in chloroform at -60 °C for 30 min. Consequently, **12** and **13** are considered to be produced by initial attack of either a bromonium ion or proton from the β-side of the

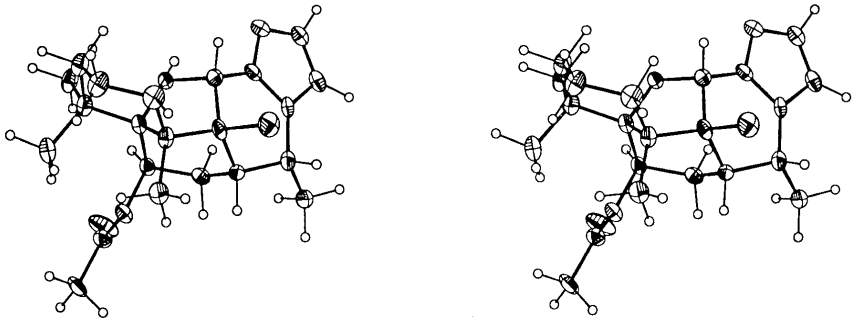

Fig. 4. Perspective Drawings of **12**

9(11)-double bond of the intermediate **11**, followed by nucleophilic attack of the 5α-hydroxyl moiety on the 11α-position.

The absolute stereostructures of caesaldekarins c (**3**), d (**4**), and e (**5**), as well as those of caesaldekarins a (**1**) and b (**2**), are presumed to be as shown.[3] In conclusion, we have characterized five new cassane-type furanoditerpenoids, *i.e.*, caesaldekarins a (**1**), b (**2**), c (**3**), d (**4**), and e (**5**), from the roots of *Caesalpinia major* (Fabaceae), a medicinal plant in Flores Island, Nusa Tenggara Timur, Indonesia.

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper.[6] Plant materials and the isolation procedure for caesaldekarins were described in another paper.[3]

Caesaldekarin c (3) Colorless needles, mp 127—128 °C (*n*-hexane–EtOAc). $[\alpha]_D$ +37° (*c*=2.8, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 3625, 1722, 1465, 905. UV λ_{max}^{MeOH} nm (ε): 217 (7000). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.82 (3H, s, 20-H_3), 1.00 (3H, d, *J*=7 Hz, 17-H_3), 1.20 (3H, s, 18-H_3), 1.42 (1H, m, 1-H_a), 1.46 (3H, m, 2-H_2, 7-H_a), 1.50 (1H, m, 1-H_b), 1.56 (1H, m, 3-H_a), 1.76 (1H, m, 8-H), 1.82 (1H, m, 7-H_b), 1.85 (1H, m, 6-H_a), 2.20 (1H, m, 9-H), 2.28 (1H, m, 6-H_b), 2.34 (1H, dd, *J*=10, 16 Hz, 11β-H), 2.49 (1H, dd, *J*=6.5, 16 Hz, 11α-H), 2.61 (1H, m, 14-H), 3.67 (3H, s, $COOCH_3$), 6.18 (1H, br s, 15-H), 7.21 (1H, br s, 16-H). ^{1}H-NMR (270 MHz, C_5D_5N) δ: 0.88 (3H, s, 20-H_3), 1.05 (3H, d, *J*=7 Hz, 17-H_3), 1.40 (3H, s, 18-H_3), 3.66 (3H, s, $COOCH_3$). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 15.0 (q, 20-C), 17.5 (q, 17-C), 18.7 (t, 7-C), 22.4 (t, 11-C), 23.9 (q, 18-C), 24.7 (t, 2-C), 27.9 (t, 6-C), 31.4 (d, 14-C), 32.0 (t, 3-C), 32.3 (t, 1-C), 34.6 (d, 8-C), 37.6 (d, 9-C), 41.7 (s, 10-C), 49.0 (s, 4-C), 51.6 (q, $COOCH_3$), 76.5 (s, 5-C), 109.5 (d, 15-C), 122.3 (s, 13-C), 140.3 (d, 16-C), 149.5 (s, 12-C), 177.4 (s, $COOCH_3$). MS *m/z* (%): 346 (M^+, 46), 147 (100), 108 (87). High-resolution MS *m/z*: Calcd for $C_{21}H_{30}O_4$: 346.214. Found: 346.214 (M^+). *Anal.* Calcd for $C_{21}H_{30}O_4$: C, 72.80%; H, 8.73%. Found: C, 72.91%; H, 8.64%.

Caesaldekarin d (4) Colorless needles, mp 164—165 °C (*n*-hexane–ether). $[\alpha]_D$ −1.1° (*c*=0.36, in $CHCl_3$ at 20 °C). IR (KBr) ν cm^{-1}: 3420 (br), 1730, 1510, 890. UV λ_{max}^{MeOH} nm (ε): 217 (7500). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.02 (3H, d, *J*=7 Hz, 17-H_3), 1.03 (1H, m, 3-H_a), 1.04 (3H, s, 18-H_3), 1.24 (3H, s, 19-H_3), 1.25 (3H, s, 20-H_3), 1.51 (1H, m, 7α-H), 1.65 (1H, m, 2-H_a), 2.03 (1H, m, 8-H), 2.05 (3H, s, $COOCH_3$), 2.08 (2H, m, 2-, 3-H_b), 2.28 (1H, m, 7β-H), 2.54 (1H, m, 11β-H), 2.59 (1H, m, 11α-H), 2.62 (1H, m, 14-H), 2.91 (1H, m, 9-H), 3.65 (1H, br t, *W* h/2=*ca.* 8 Hz, 1-H), 5.16 (1H, dd, *J*=3, 3.5 Hz, 6-H), 6.20 (1H, d, *J*=1.5 Hz, 15-H), 7.23 (1H, d, *J*=1.5 Hz, 16-H). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ_C: 16.5 (q, 20-C), 17.6 (q, 17-C), 21.4 (t, 11-C), 21.8 (q, $COOCH_3$), 26.1 (q, 19-C), 26.2 (t, 2-C), 27.7 (q, 18-C), 30.2 (d, 8-C), 31.1 (d, 14-C), 31.3 (t, 7-C), 32.0 (t, 3-C), 32.3 (d, 9-C), 39.2 (s, 4-C), 43.7 (s, 10-C), 72.1 (d, 6-C), 74.5 (d, 1-C), 77.2 (s, 5-C), 109.6 (d, 15-C), 122.4 (s, 13-C), 140.4 (d, 16-C), 149.0 (s, 12-C), 169.7 (s, $COOCH_3$). MS *m/z* (%): 376 (M^+, 8), 108 (100). High-resolution MS *m/z*: Calcd. for $C_{22}H_{32}O_5$: 376.222. Found: 376.224 (M^+).

Caesaldekarin e (5) Colorless needles, mp 187—188 °C (*n*-hexane–EtOAc). $[\alpha]_D$ +11° (*c*=0.15, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 3600, 1731, 1643, 876. UV λ_{max}^{MeOH} nm (ε): 292 (2300), 282 (2300), 251 (10500), 212 (28700). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.21 (6H, s, 18-, 19-H_3), 1.41 (3H, s, 20-H_3), 1.93, 2.02 (3H each, both s, $OCOCH_3$ ×2), 2.11 (2H, m, 6-H_2), 2.31, 2.51 (1H each, both ddd, *J*=3, 3, 16 Hz, 2-H_2), 2.40 (3H, s, 17-H_3), 2.85, 2.94 (1H each, m, 7-H_2), 5.05 (1H, t-like, *J*=3 Hz, 3-H), 5.75 (1H, t-like, *J*=3 Hz, 1-H), 6.72 (1H, d, *J*=2.5 Hz, 15-H), 7.51 (1H, d, *J*=2.5 Hz, 16-H), 7.00 (1H, s, 11-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 15.9 (q, 17-C), 21.1, 21.4 (both q, $COOCH_3$ ×2), 23.1 (q, 18-C), 23.4 (t, 7-C), 24.4 (t, 6-C), 25.2 (q, 19-C), 26.9 (t, 2-C), 31.2 (q, 20-C), 41.6 (s, 4-C), 46.7 (s, 10-C), 73.5 (d, 1-C), 75.7 (s, 5-C), 76.7 (d, 3-C), 104.0 (d, 11-C), 104.9 (d, 15-C), 125.5 (s, 13-C), 127.7 (s, 8-C), 128.4 (s, 14-C), 140.3 (s, 9-C), 144.1 (d, 16-C), 153.4 (s, 12-C), 169.5, 169.8 (both s, $COOCH_3$ ×2). MS *m/z* (%): 414 (M^+, 5), 214 (100). High-resolution MS *m/z*: Calcd for $C_{24}H_{30}O_6$: 414.204. Found: 414.204 (M^+). *Anal.* Calcd for $C_{24}H_{30}O_6 \cdot 1/4H_2O$: C, 68.80; H, 7.34. Found: C, 68.94; H, 7.66.

Acetylation of Caesaldekarin d (4) A solution of **4** (10 mg) in pyridine (0.4 ml) was treated with acetic anhydride (0.4 ml). The reaction mixture was stirred at room temperature for 1 h, then poured into ice-water, and the whole was extracted with EtOAc. The EtOAc extract was washed with aqueous 5% HCl, aqueous saturated $NaHCO_3$, and brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product, which was purified by column chromatography (SiO_2 1 g, *n*-hexane : EtOAc = 5 : 1) to afford **6** (4 mg, 37%).

6: IR ($CHCl_3$) ν cm^{-1}: 1735, 1603, 890. UV λ_{max}^{MeOH} nm (ε): 217 (7700). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.01 (3H, d, *J*=7 Hz, 17-H_3), 1.07 (3H, s, 18-H_3), 1.25 (3H, s, 19-H_3), 1.37 (3H, s, 20-H_3), 1.20 (1H, m, 3-H_a), 1.47 (1H, m, 7-H_a), 1.79 (1H, m, 2-H_a), 2.05 (1H, m, 8-H), 2.06, 2.11 (3H each, both s, $COOCH_3$ ×2), 2.09 (2H, m, 2-H_b, 3-H_b), 2.46 (2H, m, 11-H_2), 2.63 (1H, m, 14-H), 2.66 (1H, m, 9-H), 4.88 (1H, dd, *J*=3, 3 Hz, 1-H), 5.24 (1H, t-like, *J*=3 Hz, 6-H), 6.19 (1H, d, *J*=1.5 Hz, 15-H), 7.23 (1H, d, *J*=1.5 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 16.6 (q, 20-C), 17.6 (q, 17-C), 21.3, 21.8 (both q, $COOCH_3$ ×2), 21.4 (t, 11-C), 22.6 (t, 2-C), 26.0 (q, 19-C), 27.7 (q, 18-C), 30.3 (d, 8-C), 31.0 (d, 14-C), 31.1 (t, 7-C), 32.3 (t, 3-C), 32.6 (d, 9-C), 39.1 (s, 4-C), 44.0 (s, 10-C), 71.8 (d, 6-C), 76.7 (d, 1-C), 77.2 (s, 5-C), 109.5 (d, 15-C), 122.5 (s, 13-C), 140.6 (d, 16-C), 148.5 (s, 12-C), 168.8, 169.6 (both s, $COOCH_3$ ×2). MS *m/z* (%): 418 (M^+, 11), 146 (100), 108 (71). High-resolution MS *m/z*: Calcd for $C_{24}H_{32}O_6$: 418.236. Found: 418.236.

Oxidation of 4 with PCC Giving 7 A solution of **4** (14 mg) in CH_2Cl_2 (1 ml) was treated with pyridinium chlorochromate (PCC) (10 mg). The whole mixture was stirred at room temperature for 1 h and then poured into ether (10 ml). The precipitates were removed by filtration (Florisil 5 g, ether) and purification of the product by column chromatography (SiO_2 1 g, *n*-hexane : EtOAc = 4 : 1) afforded **7** (6 mg, 40%).

7: Amorphous powder, $[\alpha]_D$ +23° (*c*=0.06, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 1740, 1715, 1465, 870. UV λ_{max}^{MeOH} nm (ε): 217 (15000). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.03 (3H, d, *J*=7 Hz, 17-H_3), 1.06 (3H, s, 18-H_3), 1.25 (3H, s, 19-H_3), 1.46 (3H, s, 20-H_3), 1.57 (2H, m, 3-H_a, 7-H_a), 2.05 (1H, m, 8-H), 2.09 (3H, s, $COOCH_3$), 2.17 (1H, m, 3-H_b), 2.24 (1H, m, 7-H_b), 2.41 (2H, m, 11-H_2), 2.59 (1H, m, 14-H), 2.71 (1H, m, 9-H), 2.92 (1H, ddd, *J*=6, 13, 13 Hz, 2β-H), 3.07 (1H, ddd, *J*=6, 6, 13 Hz, 2α-H), 5.19 (1H, t-like, *J*=3 Hz, 6-H), 6.17 (1H, d, *J*=2 Hz, 15-H), 7.21 (1H, d, *J*=2 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 16.5 (q, 20-C), 17.2 (q, 17-C), 21.6 (q, $COOCH_3$), 24.0 (t, 11-C), 26.3 (q, 19-C), 26.9 (q, 18-C), 30.3 (d, 8-C), 30.4 (d, 14-C), 31.1 (t, 7-C), 33.0 (d, 9-C), 35.4 (t, 3-C), 38.9 (t, 2-C), 39.3 (s, 4-C), 56.1 (s, 10-C), 72.8 (d, 6-C), 79.8 (s, 5-C), 109.3 (d, 15-C), 121.4 (s, 13-C), 140.4 (d, 16-C), 149.7 (s, 12-C), 169.6 (s, $COOCH_3$), 213.4 (s, 1-C). MS *m/z* (%): 374 (M^+, 28), 155 (100), 108 (30). High-resolution MS *m/z*: Calcd for

$C_{22}H_{30}O_5$: 374.209. Found: 374.209.

Alkaline Treatment of Caesaldekarin e (5) A solution of **5** (18 mg) in MeOH (1 ml) was treated with 20% KOH–MeOH (3 ml) and the mixture was stirred at room temperature for 1 min, then poured into ice-water. The whole was extracted with EtOAc. Work-up of the EtOAc extract in a usual manner gave a product, which was purified by column chromatography (SiO_2 1 g, *n*-hexane : EtOAc = 2 : 1) to afford **8** (5.5 mg, 42%).

8: Colorless needles, mp 200—201 °C (*n*-hexane–EtOAc). $[\alpha]_D$ +44.6° (c = 0.99, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 3682, 3500 (br), 1592, 852. UV λ_{max}^{MeOH} nm (ε): 292 (2300), 282 (2400), 251 (10500), 211 (18600). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.11 (3H, s, 18-H_3), 1.32 (3H, s, 19-H_3), 1.35 (3H, s, 20-H_3), 2.39 (3H, s, 17-H_3), 2.46 (2H, m, 2-H_2), 3.77 (1H, m, 3-H), 4.71 (1H, m, 1-H), 6.74 (1H, d, J = 2 Hz, 15-H), 7.55 (1H, d, J = 2 Hz, 16-H), 7.40 (1H, s, 11-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 15.9 (q, 17-C), 23.3 (t, 7-C), 23.5 (q, 18-C), 24.9 (t, 6-C), 25.2 (q, 19-C), 30.5 (q, 20-C), 31.2 (t, 2-C), 41.8 (s, 4-C), 48.0 (s, 10-C), 73.5 (d, 1-C), 77.2 (s, 5-C), 77.3 (d, 3-C), 105.0 (d, 11-C), 105.3 (d, 15-C), 125.9 (s, 13-C), 128.4 (s, 8-C), 129.0 (s, 14-C), 139.7 (s, 9-C), 144.4 (d, 16-C), 153.6 (s, 12-C). MS m/z (%): 330 (M^+, 13), 214 (100). High-resolution MS m/z: Calcd for $C_{20}H_{26}O_4$: 330.183. Found: 330.183.

Oxidation of 8 with PCC Giving 9 A solution of **8** (5 mg) in CH_2Cl_2 (1 ml) was treated with PCC (9 mg). The reaction mixture was stirred at room temperature for 5 min, then poured into ether (10 ml). The precipitates were removed by filtration (Florisil 5 g, ether) and purification of the product by column chromatography (SiO_2 1 g, *n*-hexane : EtOAc = 2 : 1) afforded **9** (1.5 mg, 30%).

9: Colorless needles, mp 180—181 °C (*n*-hexane–EtOAc). $[\alpha]_D$ +152.2° (c = 0.14, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 1730, 1690, 1590, 860. UV λ_{max}^{MeOH} nm (ε): 290 (1900), 278 (2400), 253 (10200), 211 (21200). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.32 (3H, s, 20-H_3), 1.36 (3H, s, 19-H_3), 1.54 (3H, s, 18-H_3), 2.08 (2H, m, 6-H_2), 2.43 (3H, s, 17-H_3), 2.87, 2.94 (1H each, both m, 7-H_2), 3.51, 3.86 (1H each, ABq, J = 19 Hz, 2-H_2), 6.76 (1H, d, J = 1.5 Hz, 15-H), 7.55 (1H, s, 11-H), 7.60 (1H, d, J = 1.5 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 16.1 (q, 17-C), 22.7 (t, 7-C), 22.8 (q, 18-C), 24.9 (t, 6-C), 26.4 (q, 19-C), 29.7 (t, 2-C), 31.9 (q, 20-C), 52.0 (s, 4-C), 59.2 (s, 10-C), 76.1 (s, 5-C), 104.9 (d, 11-C), 111.7 (d, 15-C), 126.0 (s, 13-C), 127.0 (s, 8-C), 128.4 (s, 14-C), 145.2 (d, 16-C), 145.2 (s, 9-C), 153.1 (s, 12-C), 204.1 (s, 1-C), 210.2 (s, 3-C). MS m/z (%): 326 (M^+, 21), 239 (100). High-resolution MS m/z: Calcd for $C_{20}H_{22}O_4$: 326.152. Found: 326.153 (M^+).

Treatment of Caesaldekarin a (1) with NBS Giving 10, 12, and 13 A solution of **1** (100 mg, 0.28 mmol) in $CHCl_3$ (5.0 ml) was treated with NBS (49 mg) and the mixture was stirred under an argon atmosphere at −40 °C for 2 h, then poured into ice water. The whole was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with aqueous saturated $Na_2S_2O_3$ and brine, then dried over Na_2SO_4. The solvent was removed under reduced pressure to give a product, which was purified by column chromatography (SiO_2 5 g, *n*-hexane : EtOAc = 10 : 1) to afford a mixture of compounds **12** and **13** (49 mg) and a bisfuranoditerpene derivative (**10**, 15 mg).[3] Separation of the mixture by reversed-phase (ODS) HPLC (Cosmosil $^5C_{18}$-AR 10 × 250 mm, eluting with MeOH : H_2O = 95 : 5), afforded **12** (10 mg) and **13** (35 mg).

12: Colorless needles (from MeOH), mp 118—120°C (sublimed), $[\alpha]_D$ −31° (c = 0.1, in $CHCl_3$ at 20 °C). IR (KBr) ν cm^{-1}: 2935, 2872, 1736, 1462, 1373, 1238, 964. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.98 (3H, s, 18-H_3), 1.00 (3H, s, 19-H_3), 1.14 (3H, d, J = 7 Hz, 17-H_3), 1.55 (3H, s, 20-H_3), 2.04 (3H, s, –OCOC<u>H</u>$_3$), 2.51 (1H, m, 8-H), 3.31 (1H, dq, J = 3.5, 7 Hz, 14-H), 5.12 (1H, s, 11-H), 5.17 (1H, d-like, J = *ca.* 7 Hz, 6-H), 6.30 (1H, d, J = 2 Hz, 15-H), 7.42 (1H, d, J = 2 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 15.5 (q, 17-C), 17.4 (q, 20-C), 18.3 (t, 2-C), 21.8 (q, –OCO<u>C</u>H$_3$), 25.3 (q, 19-C), 26.4 (q, 18-C), 29.9 (t, 7-C), 32.0 (d, 14-C), 36.8 (s, 4-C), 37.9 (t, 1-C), 39.3 (t, 3-C), 40.4 (d, 8-C), 47.3 (s, 10-C), 69.8 (d, 6-C), 72.3 (d, 11-C), 80.0 (s, 9-C), 86.4 (s, 5-C), 109.0 (d, 15-C), 122.4 (s, 13-C), 143.7 (d, 16-C), 145.9 (s, 12-C), 169.7 (s, –O<u>C</u>OCH$_3$). MS m/z (%): 436, 438 (M^+, 2), 358 (95), 133 (100). High-resolution MS m/z: Calcd for $C_{22}H_{29}O_4{}^{79}Br$: 436.121, $C_{22}H_{29}O_4{}^{81}Br$: 438.123. Found: 436.120, 438.123.

13: Colorless needles (from MeOH), mp 105—106 °C (sublimed), $[\alpha]_D$ −67° (c = 0.78, in $CHCl_3$ at 20 °C). IR ($CHCl_3$) ν cm^{-1}: 2935, 2872, 1732, 1464, 1373, 1244, 1028, 966. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.96 (3H, s, 18-H_3), 0.98 (3H, s, 19-H_3), 1.12 (3H, d, J = 7 Hz, 17-H_3), 1.53 (3H, s, 20-H_3), 1.81 (1H, t-like, J = *ca.* 3.5 Hz, 9-H), 2.01 (3H, s, –OCOC<u>H</u>$_3$), 2.39 (1H, m, 8-H), 2.70 (1H, dq, J = 3.5, 7 Hz, 14-H), 5.00 (1H, d, J = 3.5 Hz, 11-H), 5.15 (1H, d-like, J = *ca.* 7 Hz, 6-H), 6.25 (1H, d, J = 2 Hz, 15-H), 7.36 (1H, d, J = 2 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 15.9 (q, 17-C), 18.1 (t, C-2), 20.3 (q, C-20), 21.9 (q, –OCO<u>C</u>H$_3$), 25.2 (q, 19-C), 27.0 (q, 18-C), 27.4 (t, 7-C), 32.5 (d, 8-C), 33.1 (d, 14-C), 36.1 (s, 4-C), 36.7 (t, 1-C), 39.7 (t, 3-C), 42.9 (s, 10-C), 54.3 (d, 9-C), 66.9 (d, 11-C), 70.8 (d, 6-C), 85.9 (s, 5-C), 108.9 (d, 15-C), 123.0 (s, 13-C), 142.9 (d, 16-C), 149.1 (s, 12-C), 169.9 (s, –O<u>C</u>OCH$_3$). FAB-MS m/z: 359 ($M+H$)$^+$. High-resolution FAB-MS m/z: Calcd for $C_{22}H_{31}O_4$: 359.223. Found: 359.224.

Treatment of Caesaldekarin a (1) with NBS Giving the 9,11-Dehydro Derivative 11 A solution of **1** (25 mg, 0.07 mmol) in $CHCl_3$ (1.25 ml) was treated with NBS (12.25 mg) and the mixture was stirred under an argon atmosphere at −60 °C for 30 min. The reaction mixture was poured into ice water and the whole was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with aqueous saturated $Na_2S_2O_3$ and brine, then dried over Na_2SO_4. The solvent was removed under reduced pressure to give a product, which was purified by column chromatography (SiO_2 2 g, *n*-hexane : EtOAc = 10 : 1) to afford the 9,11-dehydro derivative **11** (3.5 mg).

11: A colorless glassy solid. IR (KBr) ν cm^{-1}: 3543, 2935, 2872, 1736, 1456, 1377, 1238, 1024. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (3H, s, 18-H_3), 1.18 (3H, s, 19-H_3), 1.19 (3H, d, J = 7 Hz, 17-H_3), 1.70 (3H, s, 20-H_3), 2.13 (3H, s, –OCOC<u>H</u>$_3$), 2.97 (1H, m, 8-H), 3.22 (1H, m, 14-H), 5.22 (1H, t-like, J = *ca.* 3 Hz, 6-H), 6.20 (1H, s, 11-H), 6.26 (1H, d, J = 1.5 Hz, 15-H), 7.24 (1H, d, J = 1.5 Hz, 16-H). ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ_C: 14.6 (q, 17-C), 18.5 (t, 2-C), 21.9 (q, –OCO<u>C</u>H$_3$), 23.1 (q, 20-C), 25.2 (q, 19-C), 27.5 (q, 18-C), 29.3 (d, 14-C), 29.6 (t, 1-C), 31.4 (t, 7-C), 34.9 (d, 8-C), 38.2 (t, 3-C), 38.5 (s, 4-C), 46.1 (s, 10-C), 72.9 (d, 6-C), 77.2 (s, 5-C), 109.1 (d, 15-C), 109.8 (d, 11-C), 118.4 (s, 13-C), 141.1 (d, 16-C), 149.0 (s, 9-C), 149.8 (s, 12-C), 169.6 (s, –O<u>C</u>OCH$_3$). FAB-MS m/z: 358 (M^+). High-resolution FAB-MS m/z: Calcd for $C_{22}H_{30}O_4$: 358.214. Found: 358.215.

Crystallographic Data for 12 Composition: $C_{22}H_{29}O_4Br$, M = 437.36. Orthorhombic, a = 37.661(11) Å, b = 7.990(4) Å, c = 7.356(3) Å, V = 2037.2(8) Å^3. Space group $P2_12_12_1$, z = 4, D_x = 1.426 g cm^{-3}, μ(Cu K_α) = 2.948 cm^{-1}. Crystal size 0.4 × 0.2 × 0.1 mm.

The X-Ray Analysis Intensity data were measured at 293 K with graphite-monochromated Cu K_α radiation on a Rigaku AFC-5R diffractometer. Using the ω-2θ scanning mode, the intensities of 1880 independent reflections with $2\theta < 126°$ were obtained. The structure was solved by direct and difference Fourier methods and refined by the full-matrix least-squares method with anisotropic temperature factors for non-H atoms of **12**. The final R value was 0.0838 for 1933 reflections with $F_o > 3\sigma(F_o)$.

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