Enantioselective Total Syntheses of (−)-7*βH*-Eudesmane-4α,11-diol and (+)-*ent*-7*βH*-Eudesmane-4α,11-diol

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The syntheses of (−)-7*βH*-eudesmane-4α,11-diol (**2**) and (+)-*ent*-7*βH*-eudesmane-4α,11-diol (***ent*-2**) were carried out starting from (−)- and (+)-dihydrocarvones. As a result, the structure, including absolute configuration, of the naturally occurring eudesmane-4,11-diol isolated from *Pluchea arguta* was determined to be (+)-*ent*-7*βH*-eudesmane-4α,11-diol (***ent*-2**).

Recently, a new eudesmane-4,11-diol, the so-called 4,5-*epi*-cryptomeridiol, was isolated from a Pakistani medicinal plant, *Pluchea arguta* Boiss. (Asteraceae) by Ahmad et al.,[1] and the structure was proposed as 5*βH*-eudesmane-4*β*,11-diol (**1**) (Figure 1). Two years later, we attempted the synthesis of **1** to confirm the structure of the natural eudesmane-4,11-diol.[2] Because the ^{1}H- and ^{13}C-NMR spectra, as well as the physical constants, of our synthetic **1** were different from those of the natural eudesmane-4,11-diol, we concluded that the structure of the natural product assigned as **1** must be erroneous. We reexamined the structure of this natural product based on ^{13}C-NMR shielding data as well as the synthesis of model compounds, and revised the structure from **1** to 7*βH*-eudesmane-4α,11-diol (**2**), except for the absolute configuration.[2]

Here we report the results of the syntheses of **2** and ***ent*-2** by stereochemically defined procedures to obtain the unambiguous structure of the natural eudesmane-4,11-diol isolated by Ahmad et al.,[1] including its absolute configuration.

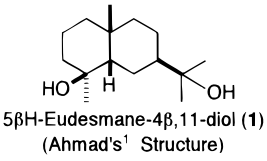

Figure 1.

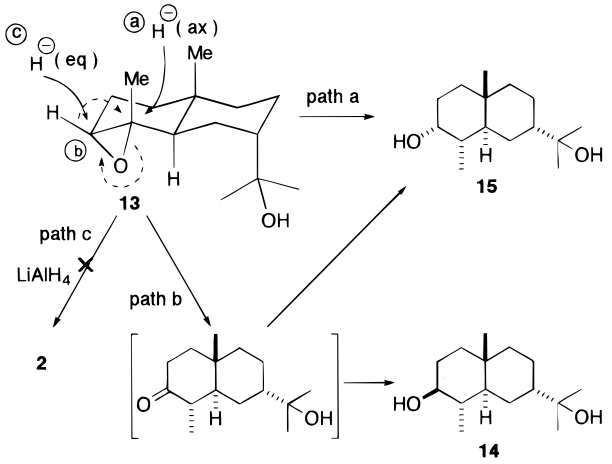

Figure 2.

Results and Discussion

In the first synthetic plan for **2**, the reduction of 7*βH*-eudesmane-3α,4α;11ξ,12-diepoxide (**12**) was envisioned as the final step. The starting material was 7*βH*-eudesma-4,11-dien-3-one (**4**), which was conveniently prepared via condensation of (−)-dihydrocarvone with ethyl vinyl ketone and dehydration of the resulting ketol **3**[3,4] (Scheme 1). Birch reduction of **4**,[4] using EtOH as the proton donor gave 7*βH*-eudesm-11-en-3-one (**5**) in 61% yield.

Reduction of **5** with $NaBH_4$ in a mixture of MeOH and ether gave the α- and *β*-alcohols **6** and **7** in 19% and 78% yields, respectively. Mesylation of **6** with methanesulfonyl chloride and pyridine and successive treatment of the resulting mesylate **8** with a mixture of Li_2CO_3 and LiBr in DMF at 150 °C gave an inseparable 10:1 mixture of 7*βH*-eudesma-3,11-diene (**10**) and 7*βH*-eudesma-2,11-diene (**11**) in 77% overall yield.[5] By analogy, mesylation of **7** and successive treatment of the resulting mesylate **9** under the same reaction conditions mentioned above gave an 8:1 mixture of **10** and **11** in 86% overall yield. It is noteworthy that both the 3α-alcohol **6** and 3*β*-alcohol **7** gave the same 3,11-diene (**10**), as a major product.[6]

Epoxidation of **10** with 2 molar equivalents of *m*-CPBA gave 7*βH*-eudesmane-3α,4α;11ξ,12-diepoxide (**12**) as a 3:2 diastereomeric mixture at C-11 in 80% yield. Reduction of **12** with $LiAlH_4$ in ether at room temperature gave 7*βH*-3α,4α-epoxyeudesman-11-ol (**13**) in quantitative yield (Figure 2). Further treatment of **13** with a large excess of $LiAlH_4$ for 43 h gave the undesired diols **14** and **15** in 6% and 23% yields, respectively. Unfortunately, the target molecule, 7*βH*-eudesmane-4α,11-diol (**2**) could not be detected, probably because **2** is the stereoelectronically unfavorable reaction product (path c). The formation of **15** is explained by the stereoelectronically favorable, but sterically hindered, *β*-axial attack of hydride toward the 3α,4α-epoxide at C-4 (path a). The formation of minor 3*β*-alcohol **14** may

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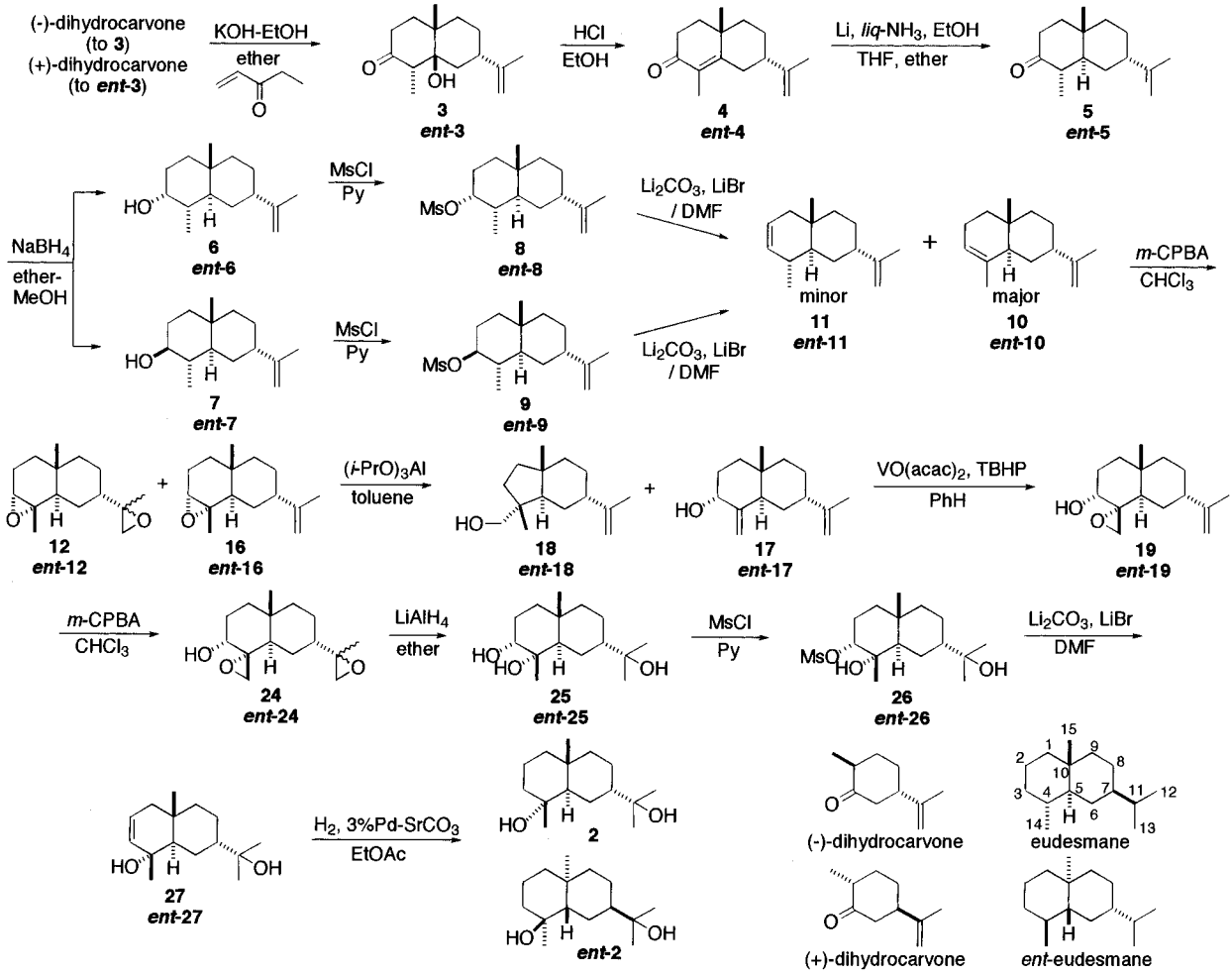
Scheme 1



be explained by rearrangement of epoxide **13** and successive reduction of the resulting ketone (path b).

The second plan for the synthesis of **2** was based on the reduction of 3α-(mesyloxy)-11ξ,12-epoxyeudesman-4α-ol (**22**) in the final step. Epoxidation of **10** with 1 molar equivalent of *m*-CPBA gave the 3α,4α-monoepoxide **16** and 3α,4α;11ξ,12-diepoxide **12** in 78% and 13% yields, respectively. Treatment of **16** with Al(*i*-PrO)$_3$ in boiling toluene gave the desired allylic alcohol **17** in 71% yield, accompanied by the rearranged product **18** in 15% yield. Sharpless oxidation[7] of **17** with *tert*-butyl hydroperoxide (TBHP) in benzene, in the presence of vanadyl acetylacetonate [VO(acac)$_2$], gave 7β*H*-4α,14-epoxyeudesman-3α-ol (**19**) in 78% yield. Reduction of **19** with LiAlH$_4$ in ether gave the 3α,4α-diol **20** in 95% yield (Figure 3). Mesylation of **20** and successive epoxidation of the resulting mesylate **21** with *m*-CPBA gave the desired **22** in 49% yield. The attempted synthesis of 7β*H*-eudesmane-4α,11-diol (**2**) by the reductive elimination of the C-3 mesyloxy group of **22** was unsuccessful. Reduction of **22** with LiAlH$_4$ gave a rearranged product **23** (40% yield). The formation of **23** may be reasonably explained by migration of the methyl group from C-4 to C-3 and successive reduction of the resulting ketone.

Finally, we succeeded in the synthesis of 7β*H*-eudesmane-4α,11-diol (**2**) by the method shown in Scheme 1. Thus, further epoxidation of **19** with *m*-CPBA in CHCl$_3$ gave the diepoxide **24** in 95% yield. Reduction with LiAlH$_4$ in ether gave 7β*H*-eudesmane-3α,4α,11-triol (**25**) in 97% yield. Mesylation of **25** with mesyl chloride in pyridine gave 7β*H*-3α-mesyloxyeudesmane-4α,11-diol (**26**) in 74% yield. Treatment of **26** with Li$_2$CO$_3$ and LiBr in DMF at 140 °C for 3 h gave 7β*H*-eudesm-2-ene-4α,11-diol (**27**) in 59% yield. Catalytic hydrogenation of **27** in the presence of 3% Pd−SrCO$_3$ in EtOAc gave 7β*H*-eudesmane-4α,11-diol (**2**) in quantitative yield. The ^{1}H-NMR and ^{13}C-NMR spectral data of **2** were in good agreement with those of natural eudesmane-4,11-diol.[1] The [α]$_D$ value of **2** was identical with that of the natural product[1] in absolute value at the same concentration, but the sign was opposite.

Attention then focused on the synthesis of ***ent*-2**. The starting material, *ent*-7β*H*-eudesma-4,11-dien-3-one (***ent*-4**),[8,9] was efficiently prepared via condensation of (+)-dihydrocarvone with ethyl vinyl ketone and dehydration of the resulting ketol ***ent*-3**.[8] The target molecule, *ent*-7β*H*-eudesmane-4α,11-diol (***ent*-2**), was synthesized from ***ent*-4** in 12 steps in 15.1% overall yield by the analogous procedure employed in the synthesis of **2** (see Scheme 1). The melting point and [α]$_D$ value of synthetic ***ent*-2** were in good agreement with those of the natural eudesmane-4,11-diol.[1] The ^{1}H- and ^{13}C-NMR spectra of ***ent*-2** were identical with those of **2** at the same concentration.

In conclusion, the structure of the natural eudesmane-4,11-diol isolated from the Pakistani medicinal plant *Pluchea arguta*[1] was established unambiguously to be

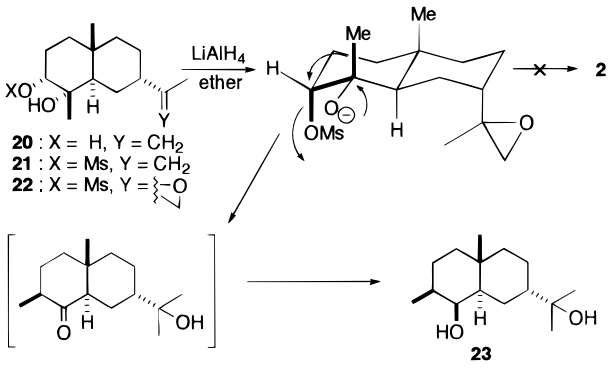


Figure 3.

ent-7*βH*-eudesmane-4α,11-diol (***ent*-2**) by synthesis as mentioned above.

Experimental Section

General Experimental Procedures. All melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 MHz and at 50 MHz, respectively, using $CDCl_3$ as solvent unless otherwise stated. The assignments of ^{1}H-NMR spectra were determined by decoupling and H−H COSY experiments. The assignments of ^{13}C-NMR spectra were determined by DEPT and C−H COSY experiments. EIMS, GCEIMS, and HREIMS were recorded on a JEOL-HX 110 instrument. Optical rotations were determined on a Horiba SEPA-200 polarimeter. All reactions were run under an atmosphere of N_2 or Ar. THF and Et_2O were distilled from sodium benzophenone ketyl. $CHCl_3$ was dried over $CaCl_2$ and distilled. Benzene and toluene were dried over $CaCl_2$, distilled, and stored in a bottle with Na wire equipped with mercury seal. CH_2Cl_2, DMF, and pyridine were distilled from CaH_2. MeOH and EtOH were distilled from $Mg(OMe)_2$ and $Mg(OEt)_2$, respectively. To describe HPLC conditions, the column, solvent, flow rate (mL/min), and retention time (t_R in min) are designated in order. The column codes are as follows: A, 250 × 4 mm i.d. stainless column packed with 10 μm Si gel; B, 250 × 8 mm i.d. stainless column packed with 10 μm Si gel; C, 250 × 4.6 mm i.d. stainless column packed with 10 μm Si gel.

7*βH*-5*β*-Hydroxyeudesm-11-en-3-one (3). Compound **3** was prepared by the modified method reported in the literature[3,4] as colorless crystals: mp 101 °C; $[\alpha]^{20}_D$ −44.0° (*c* 3.74, $CHCl_3$); *anal.* C 75.80%, H 10.15%, calcd for $C_{15}H_{24}O_2$, C 76.22%, H 10.24%.

7*βH*-Eudesma-4,11-dien-3-one (4). Compound **4** was prepared by the method reported in the literature[4] as a colorless oil in 82% yield: $[\alpha]^{20}_D$ +177.1° (*c* 3.20, $CHCl_3$); HREIMS *m/z* 218.1662 (calcd for $C_{15}H_{22}O$ 218.1671).

7*βH*-Eudesm-11-en-3-one (5). Into a stirred solution of liquid NH_3 (154 mL) and Li (216 mg, 31.1 mmol) was added **4** (617 mg, 2.83 mmol) dissolved in a mixture of Et_2O (10 mL) and THF (14 mL) under stirring at −65 °C. After stirring was continued for 20 min at this temperature, EtOH (1.4 mL) was added. The reaction mixture was allowed to stand at room temperature overnight, poured into a saturated aqueous solution of NaCl (25 mL), and extracted with Et_2O (3 × 30 mL). The combined extracts were dried (Na_2SO_4) and concentrated to give an oily crude product that was purified by column chromatography [Si gel 44 g, EtOAc−hexane (2:8)] to give **5** (380 mg, 61%) as colorless plates: mp 37 °C; $[\alpha]^{20}_D$ +12.2° (*c* 3.61, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3096, 1700, 1640, 896 cm^{-1}; ^{1}H NMR δ 1.00 (3H, d, J = 6.5 Hz, H-14), 1.13 (3H, s, H-15), 1.71 (3H, s, H-12), 2.17 (1H, dq, J = 12.1, 6.5 Hz, H-4), 2.31 (1H, ddd, J = 15.0, 5.1, 2.4 Hz, H-2*eq*), 2.36 (1H, m, $W_{h/2}$ = 12.0 Hz, H-7), 2.51 (1H, ddd, J = 15.0, 15.0, 6.6 Hz, H-2*ax*), 4.77 (1H, br m, H-13a), 4.90 (1H, m, H-13b); ^{13}C NMR δ 11.14 (q, C-14), 16.05 (q, C-15), 22.65 (q, C-12), 22.97 (t, C-8), 27.49 (t, C-6), 33.94 (s, C-10), 36.28 (t, C-9), 38.15 (t, C-2), 38.28 (d, C-7), 41.69 (t, C-1), 45.19 (d, C-4), 45.61 (d, C-5), 110.99 (t, C-13), 146.22 (s, C-11), 213.15 (s, C-3); *anal.* C 81.47%, H 11.03%, calcd for $C_{15}H_{24}O$, C 81.76%, H 10.98%.

7*βH*-Eudesm-11-en-3α-ol (6) and 7*βH*-Eudesm-11-en-3*β*-ol (7). To a stirred solution of **5** (56 mg, 0.26 mmol) in a mixture of Et_2O (6 mL) and MeOH (4 mL) at 0 °C was added $NaBH_4$ (29 mg, 0.76 mmol). The solution was stirred for 3 h at room temperature, poured into a saturated aqueous solution of NaCl (30 mL), and extracted with Et_2O (3 × 50 mL). The combined extracts were worked up as usual to give an oily crude product (63 mg) that was separated by HPLC [B, EtOAc−hexane (1:9), 6.2 mL/min]. The first peak (t_R 4.8 min) gave **6** (11 mg, 19%) as a colorless viscous oil: $[\alpha]^{20}_D$ −16.3° (*c* 1.12, $CHCl_3$); IR (neat) ν_{max} 3416, 1642, 890 cm^{-1}; ^{1}H NMR δ 0.89 (3H, s, H-15), 0.93 (3H, d, J = 6.3 Hz, H-14), 1.73 (3H, s, H-12), 2.34 (1H, m, $W_{h/2}$ = 10.0 Hz, H-7), 3.76 (1H, m, $W_{h/2}$ = 6.0 Hz, H-3), 4.83 (1H, m, H-13a), 4.90 (1H, m, H-13b); ^{13}C NMR δ 15.76 (q), 15.85 (q), 22.81 (q, C-12), 23.28 (t), 25.90 (t), 29.01 (t), 34.04 (s, C-10), 35.27 (t), 35.50 (d), 37.23 (t), 37.62 (d), 39.17 (d, C-7), 72.29 (d, C-3), 110.77 (t, C-13), 146.95 (s, C-11); HREIMS *m/z* 222.2019 (calcd for $C_{15}H_{26}O$ 222.1984).

The second peak (t_R 8.0 min) gave **7** (44 mg, 78%) as colorless micro crystals: mp 72 °C; $[\alpha]^{20}_D$ +19.7° (*c* 2.59, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3620, 3472, 3096, 1640, 896 cm^{-1}; ^{1}H NMR δ 0.90 (3H, s, H-15), 0.97 (3H, d, J = 6.2 Hz, H-14), 1.73 (3H, s, H-12), 2.33 (1H, m, $W_{h/2}$ = 10.0 Hz, H-7), 3.10 (1H, ddd, J = 11.0, 9.5, 5.1 Hz, H-3), 4.80 (1H, m, H-13a), 4.90 (1H, m, H-13b); ^{13}C NMR δ 14.83 (q, C-14), 16.63 (q, C-15), 22.77 (q, C-12), 23.04 (t), 26.01 (t), 30.87 (t), 33.71 (s, C-10), 37.06 (t), 38.84 (d, C-7), 39.13 (d), 39.89 (t), 43.17 (d), 76.77 (d, C-3), 110.61 (t, C-13), 147.03 (s, C-11); *anal.* C 79.95%, H 11.65%, calcd for $C_{15}H_{26}O$, C 81.02%, H 11.79%.

7*βH*-Eudesm-11-en-3α-ol Methanesulfonate (8). A mixture of **6** (102 mg, 0.46 mmol) and methanesulfonyl chloride (71 μL, 0.92 mmol) in pyridine (8 mL) was stirred for 30 min at 0 °C and then at 23 °C for 9 h. The reaction mixture was worked up as usual to give **8** (130 mg, 94%) as a viscous oil: IR ($CHCl_3$) ν_{max} 3096, 1642, 1334, 1170 cm^{-1}; ^{1}H NMR δ 0.90 (3H, s, H-15), 0.97 (3H, d, J = 6.5 Hz, H-14), 1.73 (3H, s, H-12), 2.36 (1H, m, $W_{h/2}$ = 11.0 Hz, H-7), 3.01 (3H, s, −OSO_2**Me**), 4.81 (1H, m, $W_{h/2}$ = 5.0 Hz, H-3), 4.81 (1H, m, H-13a), 4.92 (1 H, m, H-13b).

7*βH*-Eudesm-11-en-3*β*-ol Methanesulfonate (9). The methanesulfonate **9** was prepared as a viscous oil (235 mg, 98%) by the analogous method mentioned

above: IR (neat) ν_{max} 3096, 1642, 1354, 1176 cm^{-1}; ^{1}H NMR δ 0.92 (3H, s, H-15), 0.99 (3H, d, J = 6.4, H-14), 1.72 (3H, s, H-12), 2.35 (1H, m, $W_{h/2}$ = 11.0 Hz, H-7), 3.01 (3 H, s, −OSO$_2$**Me**), 4.23 (1 H, ddd, J = 10.8, 10.8, 5.2 Hz, H-3), 4.78 (1H, m, H-13a), 4.91 (1H, m, H-13b).

***7βH*-Eudesma-3,11-diene (10) from 8.** A mixture of **8** (50 mg, 0.17 mmol), LiBr (29 mg, 0.33 mmol), and Li_2CO_3 (37 mg, 0.5 mmol) in DMF (5 mL) was stirred at 150 °C (bath temperature) for 1 h, cooled, and filtered under reduced pressure. The filtrate was poured into a saturated aqueous solution of NaCl (50 mL) and extracted with Et_2O (3 × 30 mL). The combined extracts were worked up as usual to give a pale yellow oil (39 mg) that was purified by column chromatography (column 1.4 cm i.d., Si gel; 2.0 g, solvent hexane) to give a 10:1 mixture of **10** and **11** (28 mg, 82%) as a viscous oil. The ratio of **10** and **11** was determined by the analysis of ^{1}H-NMR spectrum of the mixture: IR ($CHCl_3$) ν_{max} of the mixture 3096, 1642, 892 cm^{-1}; ^{1}H-NMR spectrum of the major component **10** δ 0.85 (3H, s, H-15), 1.62 (3H, s, H-14), 1.76 (3H, s, H-12), 2.41 (1H, m, $W_{h/2}$ = 13.0 Hz, H-7), 4.86 (1H, m, H-13a), 4.92 (1H, m, H-13b), 5.32 (1H, m, $W_{h/2}$ = 13.0 Hz, H-3); ^{13}C-NMR spectrum of the major component **10** δ 15.52 (q, C-15), 21.17 (q, C-14), 22.85 (q, C-12), 22.85 (t), 23.41 (t), 25.29 (t), 32.84 (s, C-10), 36.10 (t), 38.25 (t), 39.45 (d, C-7), 41.20 (d, C-5), 110.76 (t, C-13), 121.16 (d, C-3), 135.16 (s, C-4), 147.08 (s, C-11); GCEIMS of the major component **10** m/z 204 [M]$^+$ (50), 189 (14), 161 (100), 122 (60), 107 (19); HREIMS m/z 204.1882 (calcd for $C_{15}H_{24}$ 204.1878).

***7βH*-Eudesma-3,11-diene (10) from 9.** The methanesulfonate **9** (30 mg, 0.10 mmol) was treated in the same way as described in the preparation of **10** from **8** to give an 8:1 mixture of **10** and **11** (18 mg, 88%) as a viscous oil.

***7βH*-Eudesm-11-en-3α,4α-epoxide (16).** A solution of **10** (50 mg, 0.25 mmol) in $CHCl_3$ (3 mL) and 87% *m*-CPBA (48 mg, 0.25 mmol) was allowed to stand at 0 °C for 30 min. The mixture was poured into a mixture of 0.1 M aqueous solution of KI (15 mL) and a saturated aqueous solution of NaCl (30 mL) and extracted with $CHCl_3$ (3 × 15 mL). The combined extracts were washed successively with 0.1 M aqueous solution of $Na_2S_2O_3$ (2 × 20 mL), a saturated aqueous solution of $NaHCO_3$ (2 × 20 mL), and a saturated aqueous solution of NaCl (2 × 20 mL); dried (Na_2SO_4); and concentrated to give a crude product (60 mg). This was then separated by the combination of column chromatography [Si gel 3.0 g, 1.4 cm i.d. column, EtOAc−hexane (1:9)] and HPLC [A, EtOAc−hexane (1:9), 3.1 mL/min].

The first peak (t_R 1.8 min) gave **16** (42 mg, 78%) as a colorless oil: $[\alpha]^{20}_D$ +20.7° (*c* 1.87, $CHCl_3$); IR (neat) ν_{max} 1642, 1384, 888 cm^{-1}; ^{1}H NMR δ 0.84 (3H, s, H-15), 1.23 (3H, s, H-14), 1.75 (3H, s, H-12), 2.40 (1H, m, $W_{h/2}$ = 11.0 Hz, C$_7$−H), 2.91 (1H, m, $W_{h/2}$ = 5.0 Hz, C$_3$−H), 4.84 (1H, s, H-13a), 4.91 (1H, m, H-13b); ^{13}C NMR δ 16.01 (q, C-15), 21.02 (q, C-14), 21.39 (t), 22.81 (q, C-12), 23.15 (t), 25.79 (t), 31.82 (s, C-10), 34.89 (t), 35.24 (t), 39.22 (d, C-7), 41.97 (d, C-5), 58.73 (s, C-4), 60.88 (d, C-3), 111.15 (t, C-13), 146.04 (s, C-11); EIMS m/z 220 [M]$^+$ (32), 205 (100), 177 (12), 161 (47), 138 (13), 122 (27), 107 (16); HREIMS m/z 220.1822 (calcd for $C_{15}H_{24}O$ 220.1827).

The second peak (t_R 5.8 min) gave **12** as a colorless oil (7.2 mg, 13%): IR ($CHCl_3$) ν_{max} 1385 cm^{-1}; ^{1}H NMR δ 0.82 (3H, s, H-15), 1.23 (3H, s, H-14), 1.37 (3H, s, H-12), 2.52 (0.4H, d, J = 6.3 Hz, H-13a), 2.55 (0.6H, d, J = 6.3 Hz, H-13a), 2.79 (0.4H, d, J = 8.0 Hz, H-13b), 2.82 (0.6H, d, J = 8.0 Hz, H-13b), 2.92 (1H, m, $W_{h/2}$ = 5.0 Hz, H-3); EIMS m/z 236 [M]$^+$ (6), 221 (24), 205 (100), 177 (27), 161 (44), 122 (22), 107 (15); HREIMS m/z 236.1776 (calcd for $C_{15}H_{24}O_2$, 236.1776).

***7βH*-Eudesma-4(14),11-dien-3α-ol (17).** A solution of **16** (94 mg, 0.43 mmol) in toluene (12 mL) was refluxed under stirring with aluminum isopropoxide (890 mg, 4.36 mmol) for 3 h. The solution was concentrated under reduced pressure. The residue was poured into a cold mixture of EtOAc (10 mL), 2 M aqueous solution of HCl (2 mL), and a saturated aqueous solution of NaCl (15 mL), stirred for 30 min, and filtered through Celite. The organic layer was separated, and the aqueous layer was further extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl (2 × 15 mL), dried (Na_2SO_4), and concentrated to give an oily crude product (108 mg) that was purified by HPLC [B, EtOAc−hexane (5:95), 6.2 mL/min].

The first peak (t_R 8.2 min) gave **18** (14 mg, 15%) as colorless needles: mp 43 °C; $[\alpha]^{20}_D$ −0.4° (*c* 1.13, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3640, 3484, 3096, 1642, 892 cm^{-1}; ^{1}H NMR δ 0.92 (3H, s, H-15), 0.95 (3H, s, H-14), 1.22 (1H, dd, J = 12.5, 3.0 Hz, H-5), 1.73 (3H, s, H-12), 2.40 (1H, m, $W_{h/2}$ = 12.0 Hz, H-7), 3.27 (2H, s, −C**H**$_2$OH), 4.83 (1H, m, H-13a), 4.89 (1H, m, H-13b); ^{13}C NMR δ 18.58 (q, C-15), 20.92 (q, C-14), 22.95 (q, C-12), 23.88 (t), 24.36 (t), 34.34 (t), 37.77 (t), 39.38 (d, C-7), 40.34 (t), 42.59 (s), 42.90 (s), 46.97 (d, C-5), 72.95 (t, C-3), 110.50 (t, C-13), 147.59 (s, C-11); *anal.* C 80.37%, H 12.04%, calcd for $C_{15}H_{26}O$, C 81.02%, H 11.79%.

The second peak (t_R 9.6 min) gave **17** (67 mg, 71%) as a colorless oil: $[\alpha]^{20}_D$ +8.4° (*c* 1.26, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3616, 3460, 3092, 1644, 906 cm^{-1}; ^{1}H NMR δ 0.74 (3H, s, H-15), 1.74 (3H, s, H-12), 2.46 (2H, m, H-5, H-7), 4.28 (1H, dd, J = 2.6, 2.6 Hz, H-3), 4.60 (1H, dd, J = 1.8, 1.8 Hz, H-14a), 4.83 (1H, br s, H-13a), 4.93 (1H, m, H-13b), 4.93 (1H, m, H-14b); ^{13}C NMR δ 15.22 (q, C-15), 22.88 (q, C-12), 23.27 (t), 25.57 (t), 29.66 (t), 35.95 (t), 36.21 (t), 36.33 (s, C-10), 38.13 (d), 38.86 (d), 73.74 (d, C-3), 108.72 (t, C-14), 110.88 (t, C-13), 146.68 (s, C-11), 152.37 (s, C-4); EIMS m/z 220 [M]$^+$ (7), 202 (77), 187 (39), 177 (22), 159 (100), 145 (38), 107 (22); HREIMS m/z 220.1822 (calcd for $C_{15}H_{24}O$ 220.1827).

***7βH*-4α,14-Epoxyeudesm-11-en-3α-ol (19).** A solution of **17** (120 mg, 0.55 mmol) in C_6H_6 (5 mL) containing VO(acac)$_2$ (7 mg, 0.03 mmol) was treated at room temperature with *tert*-butyl hydroperoxide (TBHP) (164 μL, 1.20 mmol). After the addition was completed, stirring was continued for additional 18 h at room temperature. The mixture was poured into an aqueous solution of KI (299 mg, in 60 mL of H_2O) and extracted with EtOAc (3 × 20 mL). The combined extracts were washed successively with 0.1 M aqueous solution of $Na_2S_2O_3$ (3 × 30 mL), a saturated aqueous solution of $NaHCO_3$ (3 × 30 mL), and a saturated aqueous solution of NaCl (30 mL); dried (Na_2SO_4); and concentrated to give an oily crude product (127 mg), which was chromatographed over Si gel [6.3 g, 1.8 cm i.d., EtOAc−

hexane (5:95)]. The major fraction gave **19** (101 mg, 78%) as colorless needles: mp 77 °C; $[\alpha]^{20}_D$ −26.0° (*c* 0.84, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3604, 3504, 3096, 1642, 1384, 896 cm^{-1}; ^1H NMR δ 0.91 (3H, s, H-15), 1.71 (3H, s, H-12), 2.29 (1H, dd, J = 13.0, 2.5 Hz, H-5), 2.37 (1H, m, H-7), 2.60 (1H, d, J = 4.3 Hz, H-14a), 2.85 (1H, d, J = 4.3 Hz, H-14b), 3.37 (1H, dd, J = 2.8, 2.8 Hz, C_3−H), 4.83 (1H, m, H-13a), 4.93 (1H, m, H-13b); ^{13}C NMR δ 16.24 (q, C-15), 21.10 (t), 22.70 (q, C-12), 23.36 (t), 27.29 (t, C-2), 34.41 (d, C-5), 35.07 (t), 35.94 (s, C-10), 36.55 (t), 38.48 (d, C-7), 50.33 (t, C-14), 61.95 (s, C-4), 73.31 (d, C-3), 111.18 (t, C-13), 146.00 (s, C-11); *anal.* C 74.69%, H 10.10%, calcd for $C_{15}H_{24}O_2$, C 76.22%, H 10.24%.

7*βH*-4α,14;11*ξ*,12-Diepoxyeudesman-3α-ol (24a and 24b). A solution of **19** (1.69 g, 7.15 mmol) and 84% *m*-CPBA (2.28 g, 11.1 mmol) in $CHCl_3$ (7 mL) was stirred at 0 °C for 3 h. The reaction mixture was worked up as usual manner to give a crude crystalline material (1.92 g), which was chromatographed over Si gel [58 g, 4.3 cm i.d., EtOAc−hexane (2:8)] to give **24** (1.71 g, 95%) as a 1:1 diastereomeric mixture concerning C-11. This mixture was employed in the following reaction. A part of this mixture was separated by HPLC [B, EtOAc−hexane (3:7), 6.2 mL/min].

The first peak (t_R 8.4 min) gave an isomer concerning C-11 (**24a**) as colorless prisms: mp 74 °C; $[\alpha]^{20}_D$ −47.7° (*c*, 0.25, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3604, 3500, 1386 cm^{-1}; ^1H NMR δ 0.88 (3H, s, H-15), 1.35 (3H, s, H-12), 1.85 (2H, m, H-2), 1.98 (1H, m, H-7), 2.36 (1H, br s, $W_{h/2}$ = 4.8 Hz, −O**H**), 2.48 (1H, dd, J = 13.4, 3.1 Hz, H-5), 2.49 (1H, d, J = 4.7 Hz, H-13a), 2.60 (1H, d, J = 4.3 Hz, H-14a), 2.76 (1H, d, J = 4.7 Hz, H-13b), 2.84 (1H, d, J = 4.3 Hz, H-14b), 3.39 (1H, m, $W_{h/2}$ = 4.0 Hz, H-3); ^{13}C NMR δ 15.93 (q, C-15), 19.79 (t), 21.95 (q, C-12), 21.95 (t), 27.31 (t, C-2), 34.94 (t, C-1), 35.11 (d, C-5), 35.29 (s, C-10), 38.86 (d, C-7), 37.53 (t, C-9), 49.92 (t, C-14), 52.55 (t, C-12), 59.09 (s, C-11), 62.12 (s, C-4), 73.20 (d, C-3); *anal.* C 71.18%, H 9.45%, calcd for $C_{15}H_{24}O_3$, C 71.39%, H 9.59%.

The second peak (t_R 9.6 min) gave another isomer concerning at C-11 (**24b**) as colorless prisms: mp 96 °C; $[\alpha]^{20}_D$ −16.2° (*c* 0.23, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3604, 3492, 1386 cm^{-1}; ^1H NMR δ 0.86 (3H, s, H-15), 1.30 (3H, s, H-12), 1.85 (2H, m, H-2), 2.03 (1H, m, $W_{h/2}$ = 12.0 Hz, H-7), 2.30 (1H, dd, J = 13.4, 3.1 Hz, H-5), 2.40 (1H, br s, $W_{h/2}$ = 5.7 Hz, −O**H**), 2.52 (1H, d, J = 4.5 Hz, H-13a), 2.57 (1H, d, J = 4.3 Hz, H-14a), 2.81 (1H, d, J = 4.5 Hz, H-13b), 2.84 (1H, d, J = 4.3 Hz, H-14b), 3.36 (1H, dd, J = 2.8, 2.8 Hz, H-3); ^{13}C NMR δ 15.97 (q, C-15), 20.44 (t), 20.58 (t), 22.28 (q, C-12), 27.28 (t, C-2), 34.84 (d, C-5), 35.03 (t, C-1), 35.24 (d, C-7), 35.64 (s, C-10), 37.79 (t, C-9), 49.94 (t, C-14), 52.90 (t, C-13), 58.65 (s, C-11), 62.01 (s, C-4), 73.13 (d, C-3); *anal.* C 70.70%, H 9.55%, calcd for $C_{15}H_{24}O_3$, C 71.39%, H 9.59%.

7*βH*-Eudesmane-3α,4α,11-triol (25). A solution of **24** (146 mg, 0.58 mmol) in Et_2O (17 mL) was slowly added into $LiAlH_4$ (53 mg, 1.40 mmol) under stirring. Stirring was continued at room temperature for 3 h after completion of addition of **24**, and the reaction mixture was poured into a saturated aqueous solution of NaCl (50 mL), stirred for 30 min, and filtered through Celite. The filtrate was worked up as usual to give a pale yellow crude product (168 mg) as a crystalline material, which was chromatographed over Si gel [10 g, 2.2 cm i.d., EtOAc−hexane (1:1)].

The major fraction gave **25** (144 mg, 97%) as colorless micro crystals: mp 93 °C; $[\alpha]^{20}_D$ −53.0° (*c* 0.91, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3620, 3436 cm^{-1}; ^1H NMR δ 0.93 (3H, s, H-15), 1.11 (3H, s, H-14), 1.29 (6H, s, H-12, H-13), 2.55 (1H, br s, $W_{h/2}$ = 9.2 Hz, −O**H**), 2.65 (1H, br s, $W_{h/2}$ = 11.0 Hz, −O**H**), 3.60 (1H, dd, J = 2.8, 2.8 Hz, H-3); ^{13}C NMR δ 18.19 (q, C-15), 20.33 (t), 20.90 (q, C-14), 21.42 (t), 25.92 (t), 29.45 (q, C-12), 29.96 (q, C-13), 33.86 (s, C-10), 34.10 (t, C-1), 41.35 (t, C-9), 41.79 (d, C-5), 42.07 (d, C-7), 73.72 (s, C-11), 74.73 (d, C-3), 74.89 (s, C-4); *anal.* C 69.91%, H 10.92%, calcd for $C_{15}H_{28}O_3$, C 70.27%, H 11.01%.

7*βH*-3α-(Mesyloxy)eudesmane-4α,11-diol (26). To a stirred solution of **25** (78 mg, 0.30 mmol) in pyridine (2 mL) was added methanesulfonyl chloride (46 μL, 0.60 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min and then at room temperature for 3 h and worked up as usual to give **26** (76 mg, 74%) as a colorless oil: IR ($CHCl_3$) ν_{max} 3600, 3460, 1348, 1174 cm^{-1}; ^1H NMR δ 0.96 (3H, s, H-15), 1.16 (3H, s, H-14), 1.28 (6H, s, H-12), 3.09 (3H, s, −OSO_2**Me**), 4.58 (1H, dd, J = 3.0, 3.0 Hz, H-3).

7*βH*-Eudesm-2-ene-4α,11-diol (27). A mixture of **26** (33 mg, 0.10 mmol), LiBr (17 mg, 0.020 mmol), and Li_2CO_3 (22 mg, 0.30 mmol) in DMF (5 mL) was stirred at 140 °C for 3 h, cooled, and filtered under reduced pressure. The filtrate was worked up as usual to give a pale yellow oil (28 mg) that was chromatographed over Si gel (1.4 g, 1.2 cm i.d.) to give **27** (15 mg, 59%) as colorless micro crystals: mp 115 °C; $[\alpha]^{20}_D$ −8.4° (*c* 0.18, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3608, 3432 cm^{-1}; ^1H NMR δ 0.91 (3H, s, H-15), 1.14 (3H, s, H-14), 1.28 (3H, s, H-12), 1.29 (3H, s, H-13), 5.52 (1H, dd, J = 10.2, 2.3 Hz, H-3), 5.60 (1H, ddd, J = 10.2, 5.0, 1.7 Hz, H-2); ^{13}C NMR δ 19.26 (q, C-15), 21.32 (t), 21.40 (t), 22.67 (q, C-14), 29.38 (q, C-12), 29.73 (q, C-13), 33.49 (s, C-10), 39.13 (t, C-9), 41.59 (t, C-1), 42.40 (d, C-7), 47.01 (d, C-5), 71.63 (s, C-4), 74.63 (s, C-11), 125.76 (d, C-2), 134.90 (d, C-3); *anal.* C 74.90%, H 11.16%, calcd for $C_{15}H_{26}O_2$, C 75.58%, H 11.00%.

(−)-7*βH*-Eudesmane-4α,11-diol (2). A mixture of **27** (49.9 mg, 0.21 mmol) and 3% Pd−$SrCO_3$ (34 mg) in EtOAc was shaken under 1 atm of H_2 for 3 h, filtered, and concentrated to give a crystalline crude product that was recrystallized from pentane to give **2** (49.8 mg, 100%) as colorless needles: mp 105 °C; $[\alpha]^{20}_D$ −2.2° (*c* 0.723, $CHCl_3$), −18.1° (*c* 0.072, $CHCl_3$), −58.8° (*c* 0.017, $CHCl_3$), $[\alpha]^{29}_D$ −66.7° (*c* 0.015, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3616, 3412 cm^{-1}; ^1H NMR (500 MHz) δ 0.92 (3H, s, H-15), 1.11 (3H, s, H-14), 1.28 (3H, s, H-12), 1.29 (3H, s, H-13), 1.65 (1H, dd, J = 13.7, 3.7 Hz, H-5), 2.09 (1H, br d, J = 13.7 Hz, H-6*eq*); ^{13}C NMR (*c* 0.1 mol/L) δ 18.72 (q, C-15), 20.27 (t), 20.78 (t, C-6), 21.29 (t), 22.03 (q, C-14), 29.64 (q, C-12), 29.75 (q, C-13), 34.33 (s, C-10), 41.67 (t), 41.67 (t), 41.95 (d, C-7), 43.70 (t), 49.14 (d, C-5), 72.62 (s, C-4), 74.76 (s, C-11); *anal.* C 74.42%, H 11.17%, calcd for $C_{15}H_{28}O_2$, C 74.95%, H 11.74%.

***ent*-7*βH*-5*β*-Hydroxyeudesm-11-en-3-one (*ent*-3).**[8] Robinson annulation of (+)-dihydrocarvone with ethyl vinyl ketone in the presence of KOH in the mixture of EtOH and Et_2O gave ***ent*-3** as colorless crystals: mp 97 °C; $[\alpha]^{20}_D$ +40.7° (*c* 4.03, $CHCl_3$); *anal.* C 75.94%, H

10.35%, calcd for $C_{15}H_{24}O_2$, C 76.22%, H 10.24%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-3** identical with those of **3**.

***ent*-7βH-4,11-Eudesmadien-3-one (*ent*-4).**[8,9] Treatment of ***ent*-3** with 6 M HCl in EtOH gave ***ent*-4** (81%) as colorless oil: $[\alpha]^{20}_D$ −180.9° (*c* 4.13, $CHCl_3$); HREIMS *m/z* 218.1677 (calcd for $C_{15}H_{22}O$ 218.1671); IR (neat), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-4** identical with those of **4**.

***ent*-7βH-Eudesm-11-en-3-one (*ent*-5).** Birch reduction of ***ent*-4** by the analogous method employed in the preparation of **5** from **4** gave ***ent*-5** (86%) as colorless plates: mp 37 °C; $[\alpha]^{20}_D$ −13.3° (*c* 4.26, $CHCl_3$); HREIMS *m/z* 220.1808 (calcd for $C_{15}H_{24}O$ 220.1827); *anal.* C 81.49%, H 10.91%, calcd for $C_{15}H_{24}O$, C 81.76%, H 10.98%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-5** identical with those of **5**.

***ent*-7βH-Eudesm-11-en-3α-ol (*ent*-6) and *ent*-7βH-Eudesm-11-en-3β-ol (*ent*-7).** Reduction of ***ent*-5** with $NaBH_4$ by the analogous method employed in the preparation of **6** and **7** from **5** gave ***ent*-6** (23%) and ***ent*-7** (74%) after separation by HPLC [C, EtOAc−hexane (1:9), 3 mL/min].

***ent*-6:** colorless oil; $[\alpha]^{20}_D$ +18.5° (*c* 3.06, $CHCl_3$); HREIMS *m/z* 222.1957 (calcd for $C_{15}H_{26}O$ 222.1984); IR (neat), ^{1}H-NMR, and ^{13}C-NMR spectra ***ent*-6** identical with those of **6**.

***ent*-7:** colorless micro crystals; mp 53 °C; $[\alpha]^{20}_D$ −19.9° (*c* 3.87, $CHCl_3$); HREIMS *m/z* 222.1993 (calcd for $C_{15}H_{26}O$ 222.1984); *anal.* C 80.56%, H 12.12%, calcd for $C_{15}H_{26}O$, C 81.02%, H 11.79%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-7** identical with those of **7**.

***ent*-7βH-Eudesm-11-en-3α-ol Methanesulfonate (*ent*-8).** Mesylation of ***ent*-6** with methanesulfonyl chloride in pyridine by the analogous method employed in the preparation of **8** from **6** gave ***ent*-8** (100%) as colorless oil. The IR (neat) and ^{1}H-NMR spectra of ***ent*-8** were identical with those of **8**.

***ent*-7βH-Eudesm-11-en-3β-ol Methanesulfonate (*ent*-9).** Mesylation of ***ent*-7** with methanesulfonyl chloride in pyridine by the analogous method employed in the preparation of **9** from **7** gave ***ent*-9** (97%) as colorless oil. The IR (neat) and ^{1}H-NMR spectra of ***ent*-9** were identical with those of **9**.

***ent*-7βH-Eudesma-3,11-diene (*ent*-10).** The methanesulfonates ***ent*-8** and ***ent*-9** were treated in the same way as described in the preparation of **10** from **8** gave 1:8 and 1:6 mixtures of ***ent*-11** and ***ent*-10** in 74% and 89% yields, respectively. The IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of the major component of this mixture, ***ent*-10** were identical with those of **10**.

***ent*-7βH-Eudesm-11-en-3α,4α-epoxide (*ent*-16).** Epoxidation of ***ent*-10** with 1 molar equivalent *m*-CPBA gave ***ent*-16** (71%) accompanied by diepoxide ***ent*-12** (6%) by the analogous method employed in the preparation of **16** from **10**.

***ent*-16:** colorless oil; $[\alpha]^{20}_D$ −25.6° (*c* 4.11, $CHCl_3$); HREIMS *m/z* 220.1848 (calcd for $C_{15}H_{24}O$ 220.1827); IR (neat), ^{1}H- NMR, and ^{13}C-NMR spectra of ***ent*-16** identical with those of **16**.

***ent*-12:** colorless oil; ^{1}H- and ^{13}C-NMR spectra identical with those of **12**.

***ent*-7βH-Eudesma-4(14),11-dien-3α-ol (*ent*-17).** Treatment of ***ent*-16** with Al(*i*-PrO)$_3$ by the analogous method employed in the preparation of **17** from **16** gave ***ent*-17** (61%) and the rearranged product ***ent*-18** (14%).

***ent*-17:** colorless oil; $[\alpha]^{20}_D$ −9.6° (*c* 4.33, $CHCl_3$); HREIMS *m/z* 220.1797 (calcd for $C_{15}H_{24}O$ 220.1827); IR (neat), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-17** identical with those of **17**.

***ent*-18:** colorless needles; mp 43 °C; $[\alpha]^{20}_D$ +0.6° (*c* 2.31, $CHCl_3$); *anal.* C 80.66%, H 11.50%, calcd for $C_{15}H_{26}O$, C 81.02%, H 11.79%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-18** identical with those of **18**.

***ent*-7βH-4α,14-Epoxyeudesm-11-en-3α-ol (*ent*-19).** Sharpless oxidation of ***ent*-17** with TBHP in the presence of VO(acac)$_2$ by the analogous method employed in the preparation of **19** from **17** gave ***ent*-19** (80%) as colorless needles: mp 79 °C; $[\alpha]^{20}_D$ +28.6° (*c* 3,79, $CHCl_3$); *anal.* C 74.77%, H 10.50%, calcd for $C_{15}H_{24}O_2$, C 76.22%, H 10.24%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra identical with those of **19**.

***ent*-7βH-4α,14;11ξ,12-Diepoxyeudesman-3α-ol (*ent*-24a and *ent*-24b).** Epoxidation of ***ent*-19** with *m*-CPBA by the analogous method employed in the preparation of **24a** and **24b** from **19** gave diastereomeric isomers at C-11, ***ent*-24a** and ***ent*-24b** (100%), which were separated by HPLC.

***ent*-24a:** colorless prisms; mp 74 °C; $[\alpha]^{20}_D$ +57.8° (*c* 2.40, $CHCl_3$); *anal.* C 70.81%, H 9.62%, calcd for $C_{15}H_{24}O_3$, C 71.39%, H 9.59%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-24a** identical with those of **24a**.

***ent*-24b:** colorless prisms; mp 93 °C; $[\alpha]^{20}_D$ +26.3° (*c* 2.69, $CHCl_3$); *anal.* C 70.56%, H 9.51%, calcd for $C_{15}H_{24}O_3$, C 71.39%, H 9.59%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-24b** identical with those of **24b**.

***ent*-7βH-Eudesmane-3α,4α,11-triol (*ent*-25).** Reduction of the mixture of ***ent*-24a** and ***ent*-24b** with $LiAlH_4$ by the analogous method in the preparation of **25** from **24** gave ***ent*-25** (97%) as colorless micro crystals: mp 93 °C; $[\alpha]^{20}_D$ +53.3° (*c* 3.79, $CHCl_3$); *anal.* C 68.16%, H 11.02%, calcd for $C_{15}H_{28}O_3 \cdot {}^1/_2H_2O$, C 67.88%, H 11.02%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-25** identical with those of **25**.

***ent*-7βH-3α-(Mesyloxy)eudesmane-4α,11-diol (*ent*-26).** Treatment of ***ent*-25** with methanesulfonyl chloride by the analogous method employed in the preparation of **26** from **25** gave ***ent*-26** (77%) as a colorless oil. The IR ($CHCl_3$) and ^{1}H-NMR spectra of ***ent*-26** were identical with those of **26**.

***ent*-7βH-Eudesm-2-ene-4α,11-diol (*ent*-27).** A mixture of ***ent*-26** (41 mg, 0.12 mmol), LiBr (21 mg, 0.24 mmol), and Li_2CO_3 (22 mg, 0.37 mmol) in DMF (5 mL) was stirred at 110 °C for 2.5 h and treated as usual manner to give a pale yellow oil that was separated by HPLC [C, EtOAc−hexane (1:1), 3.0 mL/min]. The first peak (t_R 3.6 min) gave ***ent*-27** (14 mg, 44%) as colorless micro crystals: mp 111 °C; $[\alpha]^{20}_D$ +8.8° (*c* 0.07, $CHCl_3$); *anal.* C 74.76%, H 10.72%, calcd for $C_{15}H_{26}O_2$, C 75.58%, H 11.00%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra of ***ent*-27** identical with those of **27**. The second peak (t_R 8.8 min) gave recovered ***ent*-26** (19 mg, 47%).

***ent*-7βH-Eudesmane-4α,11-diol (*ent*-2).** Catalytic hydrogenation of ***ent*-27** (8.0 mg, 0.034 mmol) by the analogous procedure employed in the preparation of **2** from **27** gave ***ent*-2** (8 mg, 100%) as colorless needles: 104 °C; $[\alpha]^{20}_D$ +72.7° (*c* 0.02, $CHCl_3$), $[\alpha]^{29}_D$ +73.3° (*c*

0.015, $CHCl_3$); *anal.* C 74.76%, H 11.52%, calcd for $C_{15}H_{28}O_2$, C 74.95%, H 11.74%; IR ($CHCl_3$), ^{1}H-NMR, and ^{13}C-NMR spectra identical with those of **2**.

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