SUPPORTING INFORMATION

(Experimental Data)

Isolation of 6β-acetoxy-1β,4β-dihydroxyeudesmane (3). 6β-acetoxy-1β,4β-dihydroxyeudesmane was isolated from *Sideritis varoi* subsp. *cuatrecasasii*, a synonym of *Sideritis leucantha* Cav. subsp. *meridionalis* (Font Quer) O. Socorro.

Isolation of 6β-acetoxy-1β,4α-dihydroxyeudesmane (4). 6β-acetoxy-1β,4α-dihydroxyeudesmane was isolated from *Sideritis varoi* subsp. *oriensis*.

Oxidation of 3. Jones' reagent was added dropwise to a stirred solution of 6β-acetoxy-1β,4β-dihydroxyeudesmane (**3**, 600 mg) in acetone at 0 °C until an orange-brown color persisted (30 min), following the oxidation by TLC. MeOH was then added and the reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. Chromatography on a silica-gel column yielded 537 mg (90%) of 6β-acetoxy-4β-hydroxyeudesman-1-one (**1**) as a colorless solid: mp 115-117 °C; $[\alpha]_D$ +73° (*c* 1, $CHCl_3$); IR (KBr) ν_{max} 3400, 1730, 1680, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (1H, br s, H-6), 3.08 (1H, ddd, *J* = 15.0, 15.0, 7.0 Hz, H-2β), 2.06 (3H, s, C*H*$_3$CO), 1.50 (3H, s, H-14 or H-15), 1.45 (3H, s, H-14 or H-15), 0.90 (3H, d, *J* = 6.5 Hz, H-12 or H-13), 0.85 (3H, d, *J* = 6.5 Hz, H-12 or H-13); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 215.8 (s, C-1), 171.6 (s, CH_3CO), 71.6 (s, C-4), 71.2 (d, C-6), 53.9 (d, C-5), 49.3 (d, C-7), 48.1 (s, C-10), 42.2 (t, C-3), 34.4 (t, C-2 and C-9), 29.2 (d, C-11), 28.9 (q, C-15), 21.7 (q, CH_3CO), 21.1 (t, C-8), 21.1 (q, C-12 and C-13), 20.6 (q, C-14); HRLSIMS *m/z* 297.2072 $[M+1]^+$, (calcd for $C_{17}H_{29}O_4$, 297.2066).

Oxidation of 4. 6β-acetoxy-1β,4α-dihydroxyeudesmane (**4**, 600 mg) was dissolved in acetone (10 mL) and oxidized with Jones' reagent for 30 min at 0 °C as above. After chromatography, 531 mg (89%) of 6β-acetoxy-4α-hydroxyeudesman-1-one were isolated as a colorless syrup: $[\alpha]_D$ +21° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3464, 1736, 1709, 1243 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.74 (1H, br s, H-6), 2.60 (1H, ddd, *J* = 15.6, 13.0, 5.8 Hz, H-2α), 2.35 (1H, ddd, *J* = 15.6, 4.6, 4.6 Hz, H-2β), 2.08 (3H, s, CH_3CO), 1.72 (1H, d, *J* = 2.0 Hz, H-5), 1.38 (3H, s, H-14 or H-15), 1.29 (3H, s, H-14 or H-15), 0.88 (3H, d, *J* = 6.4 Hz, H-12 or H-13), 0.86 (3H, d, *J* = 6.4 Hz, H-12 or H-13); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.6 (s, C-1), 172.1 (s, CH_3CO), 70.5 (s, C-4), 70.3 (d, C-6), 55.0 (d, C-5), 49.2 (d, C-7), 46.9 (s, C-10), 41.1 (t, C-3), 36.1 (t, C-9), 35.4 (t, C-2), 28.7 (s, C-11), 24.5 (q, C-15), 21.8 (q, CH_3CO), 21.3 and 20.9 (q, C-12 and C-13), 20.6 (t, C-8), 20.6 (q, C-14); HRLSIMS *m/z* 297.2061 $[M+1]^+$, (calcd for $C_{17}H_{29}O_4$, 297.2066).

4β,6β,11-trihydroxyeudesman-1-one (**6**): Colorless solid: mp 110-112 °C; $[\alpha]_D$ +34 (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3384, 1705 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.81 (1H, dd, *J* = 2.0, 2.0 Hz, H-6), 3.16 (1H, ddd, *J* = 14.0, 14.0, 6.1 Hz, H-2β), 1.63 (3H, s, H-14), 1.41 (3H, s, H-15), 1.38 (3H, s, H-12 or H-13), 1.27 (3H, s, H-12 or H-13); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 216.3 (s, C-1), 74.1 (s, C-11), 72.7 (s, C-4), 69.3 (d, C-6), 52.8 (d, C-5), 49.1 (d, C-7), 47.5 (s, C-10), 41.0 (t, C-3), 34.6 (t, C-9), 34.3 (t, C-2), 29.5 (q, C-15), 29.3 and 28.9 (q, C-12 and C-13), 21.9 (q, C-14), 16.8 (t, C-8); HRLSIMS *m/z* 293.1727 $[M+23]^+$, (calcd for $C_{15}H_{26}O_4Na$, 293.1729).

6β-acetoxy-4β,11-dihydroxyeudesman-1-one (7): Colorless solid: mp 126-128 °C; $[\alpha]_D$ +47 (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3464, 1734, 1707, 1258 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.86 (1H, br s, H-6), 3.08 (1H, ddd, *J* = 14.1, 14.1, 6.1 Hz, H-2β), 2.06 (3H, s, C*H*$_3$CO), 1.53 (3H, s, H-14), 1.40 (3H, s, H-15), 1.33 (1H, d, *J* = 1.1 Hz, H-5), 1.18 (3H, s, H-12 or H-13), 1.12 (3H, s, H-12 or H-13); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 215.5 (s, C-1), 172.2 (s, CH_3CO), 72.0 (s, C-11), 71.7 (s, C-4), 70.6 (d, C-6), 53.9 (d, C-5), 52.5 (d, C-7), 48.3 (s, C-10), 42.3 (t, C-3), 34.5 (C-9), 34.3 (t, C-2), 29.3 (q, C-15), 29.1 and 27.1 (q, C-12 and C-13), 22.1 (q, CH_3CO), 21.3 (q, C-14), 19.0 (t, C-8); HRLSIMS *m/z* 313.2018 $[M+1]^+$, (calcd for $C_{17}H_{29}O_5$, 313.2015).