TETRAHEDRON

Regio- and Stereoselective Oxyfunctionalization at C-1 and C-5 in Sesquiterpene Guaianolides

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Abstract: The regio- and stereoselective functionalization at C-1 and C-5 positions in a guaiane skeleton by allylic hydroxylation are described. The stereochemistry of the resulting compounds are identical to those of the majority of natural 1- and 5-hydroxy-guaianolides.
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The guaianolides constitute one of the largest groups of sesquiterpene lactones.[1] On account of their wide spectrum of biological activities and their low availability from natural sources their synthesis[2] from easily available compounds has received much attention during the few past years and the synthesis of highly functionalized guianolides still remains a true challenge for synthetic organic chemists.

A number of 1- and 5-hydroxy functionalized guianolides have been isolated from natural sources in recent years.[1] However an efficient methodology for the synthesis of guianolides functionalized at these positions has not been reported yet. In continuation of our research programme on the synthesis[3] of natural sesquiterpene lactones we report in this paper our results on the regio- and stereoselective functionalization on C-1 and C-5 by allylic hydroxylation of suitable alkenes with a guaiane skeleton.

We regarded dienes 1 and 2 as the key synthetic intermediates to carry out the functionalization at C-1 and C-5 respectively. Both dienes have been synthesized previously by Marx et al.[4] using the photochemical rearrangement of the cross-conjugated dienone system[5] present in α-santonin to transform the eudesmane into a guaiane skeleton, and more recently by Ando et al.[6] through a solvolytic rearrangement of an 1-mesyloxy *trans*-decalin derivative prepared from α-santonin. In both cases the overall yield and the regioselectivity in the preparation of dienes 1 and 2 were low and consequently we have searched for more efficient and regioselective synthesis of both compounds.
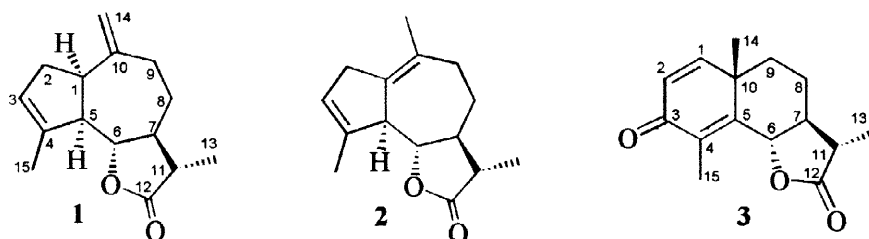
RESULTS AND DISCUSSION

The transformation of the eudesmane skeleton present in santonin (3) into a guaiane skeleton was carried out by a photochemical rearrangement affording O-acetylisophotosantonin (4) as described by Barton.[5] Hydrogenation of 4 over Pd/C in ethyl acetate by standard conditions, followed by acidic treatment with p-toluenesulfonic acid in benzene at reflux gave the saturated ketone 5 as the main product in a 55% yield, which could be noteworthy improved by 1,4-reduction of the enone system with sodium hydrogen telluride[3,7] which took place with high regio- and stereoselectivity to afford 5 as a single stereoisomer (92% yield). The C-3/C-4 double bond was introduced by reduction of the carbonyl group followed by elimination of the resulting alcohols. That was carried out by treatment of 5 with sodium borohydride which afforded a 95:5 mixture of the two epimeric alcohols being the α-OH epimer 6 the major component (94% yield). The elimination of the alcohol mixture was carried out in two steps: treatment with POCl$_3$ in presence of pyridine gave a mixture of two epimeric chlorides which were subjected to elimination by Li$_2$CO$_3$/DMF affording alkene 7 in 52% overall yield from alcohol mixture. Next, we considered the introduction of the second double bond, in exocyclic as well as endocyclic positions. Hydrolysis of the acetate group of 7 by 5% KOH at room temperature gave 8 which upon treatment with SOCl$_2$ and pyridine in THF at -45° (10 min) afforded the dienes 1 (65% overall yield for two steps) and 2 (12% overall yield). On the other hand the regioselectivity of the elimination could be inverted when the hydrolysis of 7 was followed by treatment with triflic anhydride/pyridine in CH$_2$Cl$_2$ at room temperature. In this way we obtained the same dienes 1 and 2, but with a regioselectivity opposite to that of the former method (11% for 1 and 65% for 2 overall yield for the two steps). It is worthy to note that in both cases the regioselectivity in the preparation of both dienes, although moderate, is much higher than that of other procedures described previously.[4,6] Furthermore the synthesis of 1 and 2 from santonin (3) described in this paper were achieved with a 12% overall yield, which is much higher also than that described early.[4,6]
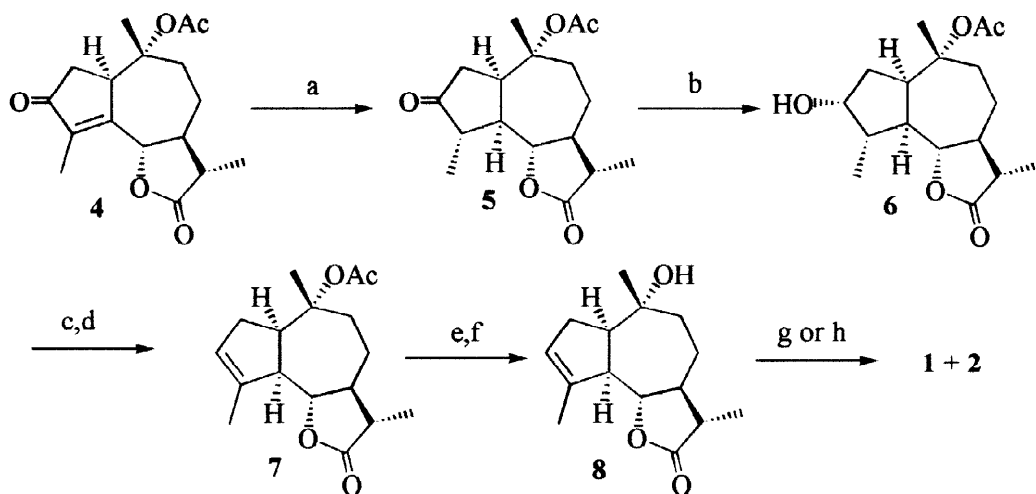

Reagents: a: NaHTe/EtOH; b: NaBH$_4$; c: POCl$_3$/py/Bz, reflux; d: LiBr, Li$_2$CO$_3$/DMF, 120°C; e: 5% KOH;
f: 18% HCl; g: SOCl$_2$/py/THF, -45°C; h: Tf$_2$O/py/CH$_2$Cl$_2$, r.t.

The spectral and physical constants of synthetic **1** and **2** were fully coincident with those described early in the literature for synthetic[4,6] and natural[8] products. Compound **2**, named 11β,13-dihydrokauniolide is a natural product isolated by Bohlmann from *Kaunia* sp.,[8] whilst compound **1** is the isocostus lactone, whose 11β,13-dehydroderivative has been isolated by Kalsi from *Saussurea lappa*.[9]

With both dienes in hand we undertook the oxyfunctionalization at C-1 and C-5. Experiments of allylic hydroxylation with different reagents were carried out with diene **1** in first place. Chromium reagents were fastly cast aside as they gave rise to recovery of unreacted starting material (pyridinium chlorochromate),[10] decomposition (chromium oxide-3,5-dimethylpyrazole)[11] or low yields of the C-2 oxidation products (*tert*-butyl chromate).[12] In contrast, treatment of diene **1** with selenium dioxide/*tert*-butyl hydroperoxyde[13] provided the C-1 oxidation product **9** with excellent regio- and stereoselectivity, and yield (95%). The spectral data of **9** were in complete agreement with its structure, and they were identical to those of naturally occurring 8-deoxy-11β,13-dihydrorupiculin B, isolated from *Artemisia adamsii*.[14] It is interesting to remark that the high stereoselectivity obtained in the synthesis of compound **9** is consequence of both the high stereoselectivity in the C-4/C-5 double bond reduction (**4** to **5**) and the allylic hydroxylation at C-1 (**1** to **9**) reactions and noteworthy it leads to compounds with identical stereochemistry to those of the majority of natural 1-hydroxy-guaianolides [A/B *cis*; 1α-OH; 5α-H].[1]

Next, we considered the allylic hydroxylation of diene **2**, with the aim to functionalize C-5, with selenium dioxide/*tert*-butyl hydroperoxyde. Unfortunately the product resulting of allylic hydroxylation was highly unstable and decomposed to the fulvene guainolide **10**[15] which evolved spontaneously into the C-6 epimeric fulvene guianolide **11**.[16]
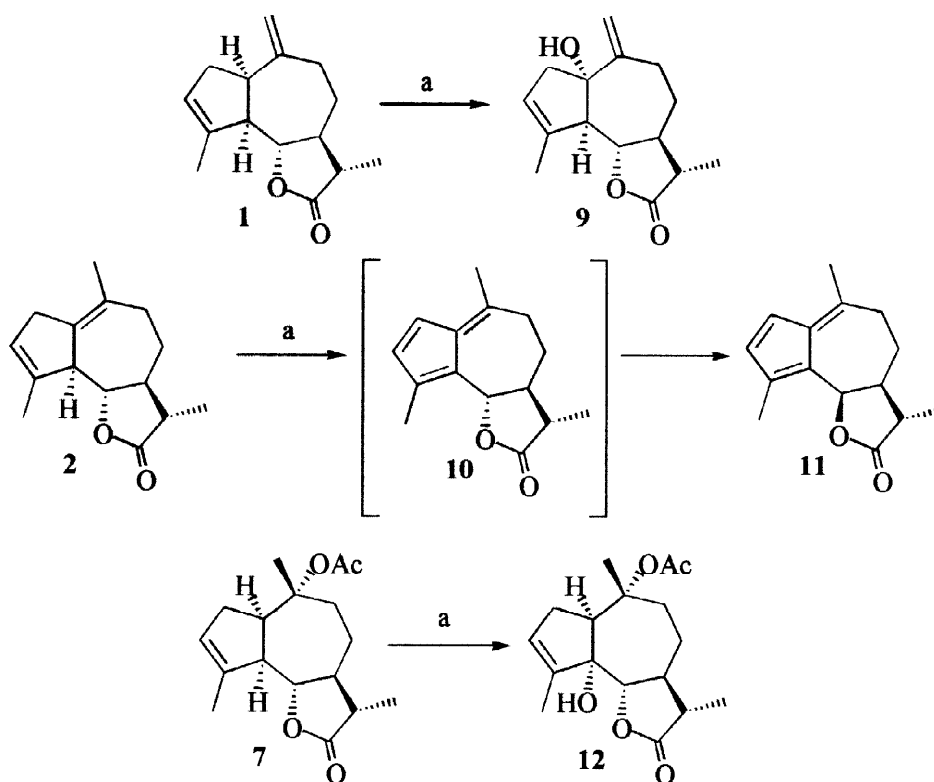
Reagents: a: SeO₂/*tert*-BuOOH

We assumed that the instability of the hydroxylation product of **2** was caused by the presence of the C-1/C-10 double bond which facilitate the dehydration of the resulting allylic alcohol to give the quasi-aromatic fulvene **10**. Therefore we tried out the oxyfunctionalization at C-5 on compound **7** where this double bond is not present. Thus, allylic hydroxylation of alkene **7** in the same conditions used with dienes **1** and **2** allowed us to obtain compound **12** in 62% yield, which could be improved (72% yield) by addition of pyridine to the reaction mixture.[17] The α-orientation of the hydroxyl group in **12** was inferred by the chemical shift of H-7 because a significant deshielding effect was produced upon H-7 signal ($\Delta\delta$ = 0.46 ppm). This deshielding effect is due to an 1,3-interaction between H-7 and the hydroxyl group. Noteworthy, the resulting stereochemistry of the allylic hydroxylation on C-5 is again identical to those of the majority of natural 5-hydroxy-guianolides [A/B *cis*; 1α-H; 5α-OH].[1, 18]

In summary, the method described here is of general application and suitable for the synthesis of guaianolides functionalized at C-1 or C-5 with the most common stereochemistry showed by natural guaianolides. Some of the products synthesized here are natural products, and therefore their stereostructures, initially assigned on the basis of their spectroscopic properties, have been confirmed.

EXPERIMENTAL

Melting points were determined in capillary tubes with a Büchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 281 spectrometer, as liquid films for oils and in KBr disk for solids. NMR spectra were run on a Bruker AC-200 instrument (200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C) in CDCl$_3$ solutions. The carbon type (methyl, methylene, methine or quaternary) was determined by DEPT experiments. Heteronuclear ^{1}H-^{13}C correlation experiments (HMQC) were performed for compound **4**. Mass spectra were recorded at 70 ev. Optical rotations were determined on a Polartronic D polarimeter (Schmidt and Haensch) as solutions in chloroform. Flash chromatography was carried out on SDS Chromagel 60 silica gel.

Compound (**4**).

A solution of 9.5 g (38.6 mmol) of santonin (**3**) in 140 mL of glacial acetic acid was irradiated under argon for 10 h using a 400 W high-pressure mercury arc lamp. The acetic acid was evaporated under reduced pressure and the resulting oil was dissolved in 16 mL of hot methanol and then it was slowly cooled at -20° C. After left overnight it afforded 4.5 g (38%) of *O*-acetylisophotosantonin (**4**) with the following features: m.p. 176-177 °C, $[\alpha]^{D}_{22}$ +49.0° (c, 1); IR (KBr) v_{max} 1775, 1748, 1713, 1656 cm^{-1}; ^{1}H NMR δ 1.06 (3H, s, H$_{14}$), 1.26 (3H, d, J = 6.4 Hz, H$_{13}$), 1.88 (3H, t, J = 1.7 Hz, H$_{15}$), 1.97 (3H, s, CH$_3$CO), 4.13 (1H, br s, H$_1$), 4.77 (1H, dd, J = 10.5 and 1.6 Hz, H$_6$); ^{13}C NMR δ 206.5 (C$_3$), 176.8 (C$_{12}$), 169.9 (CH$_3$*C*O), 160.8 (C$_5$), 142.6 (C$_4$), 85.2 (C$_{10}$), 80.8 (C$_6$), 47.8 (C$_7$), 46.9 (C$_1$), 40.9 (C$_{11}$), 37.6 (C$_9$), 36.5 (C$_2$), 24.9 (C$_8$), 21.9 (*CH$_3$*CO), 19.6 (C$_{14}$), 12.1 (C$_{13}$), 9.1 (C$_{15}$).

Compound (**5**).

A suspension of tellurium powder (2.5 g, 19.6 mmol) and NaBH$_4$ (1.79 g, 47.3 mmol) in 50 mL of deoxygenated ethanol was refluxed under argon for 1 h. After this time, the resulting deep purple solution was cooled at -20° C and a solution of 2.9 mL of glacial acetic acid in 10.5 mL of ethanol was added, followed by

compound **4** (1.5 g, 4.9 mmol) dissolved in a mixture of 7 mL of ethanol and 5.5 mL of benzene. The resulting mixture was stirred at room temperature for 3 days. After this time, the reaction flask was open to air, water was added, and the mixture was stirred for 1 h. The reaction mixture was filtered through Celite and eluted with ethyl acetate. The resulting solution was washed to neutrality with brine, dried, concentrated and chromatographed to afford 1.39 g (92%) of compound **5** with the following features: m.p. 151-152 °C (hexane-ethyl acetate), $[\alpha]^D_{24}$ -24.5 ° (c 1.22); MS m/z 309 (M^++ 1, 5), 249 (100), 231 (40), 220 (31), 175 (50), 61 (38); IR (KBr) v_{max} 1770, 1750, 1735 cm^{-1}; ^{1}H NMR δ 1.20 (3H, d, J = 7.6 Hz, H_{15}), 1.23 (3H, d, J = 6.4 Hz, H_{13}), 1.40 (3H, s, H_{14}), 2.01 (3H, s, CH$_3$CO), 2.47 (1H, dq, J = 6.4 and 6.8 Hz, H_4), 3.28 (1H, q, J = 8.4 Hz, H_1), 4.07 (1H, t, J = 10 Hz, H_6); ^{13}C NMR δ 218.3 (C_3), 177.8 (C_{12}), 170.0 (CH$_3$*CO*), 85.7 (C_{10}), 84.0 (C_6), 50.3, 48.3, 48.2, 43.2, 42.8 (C_1, C_4, C_5, C_7, C_{11}), 39.3, 33.6 (C_9, C_2), 25.8 (C_8), 24.4 (C_{14}), 22.3 (*CH$_3$*CO), 15.8 (C_{15}), 13.0 (C_{13}).

Compound (6).

A solution of compound **5** (1.230 g, 4.01 mmol) in methanol (84 mL) was treated with NaBH$_4$ (0.450 g, 11.8 mmol) at 0° C. After 20 min, the reaction was quenched with aqueous NH$_4$Cl, the methanol was removed and then the aqueous phase was extracted with ethyl acetate. The organic layer was washed with brine and dried over Na$_2$SO$_4$. Removal of the ethyl acetate and purification by column chromatography yielded 1.227 g (99%) of alcohol mixture (95:5). The major compound (**6**) had the following features: m.p. 106-107 °C (CHCl$_3$), $[\alpha]^D_{24}$ -22.6 ° (c, 0.97); MS m/z 311 (M^++1, 20), 293 (3), 251 (67), 234 (62), 233 (100), 159 (82), 61 (70); IR (KBr) v_{max} 3450, 1765, 1730 cm^{-1}; ^{1}H NMR δ 1.09 (3H, d, J = 6.8 Hz, H_{15}), 1.18 (3H, d, J = 6.9 Hz, H_{13}), 1.44 (3H, s, H_{14}), 1.95 (3H, s, *CH$_3$*CO), 2.9 (1H, q, J = 8.6 Hz, H_1), 3.72 (1H, q, J = 7.0 Hz, H_3), 4.22 (1H, t, J = 10.1 Hz, H_6); ^{13}C NMR δ 178.5 (C_{12}), 170.2 (CH$_3$*CO*), 86.6 (C_{10}), 84.4 (C_6), 78.0 (C_3), 51.0, 49.3, 46.9, 45.1, 42.8 (C_1, C_4, C_5, C_7, C_{11}), 35.9, 34.0 (C_9, C_2), 25.7 (C_8), 24.5 (C_{14}), 22.4 (*CH$_3$*CO), 17.9 (C_{15}), 13.0 (C_{13}).

Compound (7).

A solution of the alcohol mixture **6** (381 mg, 1.22 mmol) in benzene (11.4 mL) containing pyridine (1 mL) was treated with POCl$_3$ (0.275 mL, 2.95 mmol) under argon at reflux. After 30 min, the reaction was quenched with aqueous NH$_4$Cl. The mixture was extracted with ethyl acetate, dried and concentrated to give an oil which according to ^{1}H NMR analysis consisted of a mixture of two epimeric chlorides.

A solution of this mixture, LiBr (195 mg, 2.24 mmol) and Li$_2$CO$_3$ (272 mg, 3.66 mmol) in DMF (15 mL) was heated under argon at 120 °C for 10 h. After this time, the reaction mixture was worked up and chromatographed to give 35 mg (9%) of a mixture of chlorides and 186 mg (52%) of compound **7** with the following features: m.p. 64-65 °C (hexane-ethyl acetate), $[\alpha]^D_{22}$ +10.8 ° (c, 1.8); MS m/z 292 (M^+, 0.3), 232 (100), 217 (73), 176 (63), 233 (100), 159 (80), 107 (69); IR (KBr) v_{max} 1769, 1735 cm^{-1}; ^{1}H NMR δ 1.18 (3H, d, J = 6.6 Hz, H_{13}), 1.42 (3H, s, H_{14}), 1.83 (3H, d, J = 1.0 Hz, H_{15}), 1.99 (3H, s, CH$_3$CO), 2.10 (1H, m, H_7), 2.60 (1H, dd, J = 8.2, 10.0 Hz, H_5), 3.00 (1H, q, J = 8.2 Hz, H_1), 4.09 (1H, t, J = 10.0 Hz, H_6), 5.43 (1H, br s, H_3); ^{13}C NMR δ 178.8 (C_{12}), 169.7 (CH$_3$*CO*), 143.1 (C_4), 125.2 (C_3), 86.3 (C_{10}), 84.3 (C_6), 54.3, 51.6, 47.9, 43.1, (C_1, C_5, C_7, C_{11}), 33.2, 31.6 (C_2, C_9), 26.1 (C_8), 25.3 (C_{14}), 22.5 (*CH$_3$*CO), 17.4 (C_{15}), 13.3 (C_{13}).

Compound **(8)**.

A solution of compound **7** (290 mg, 0.99 mmol) in ethanol (4 mL) was treated with 57 mL of 5% aqueous potassium hydroxide with stirring. After 3 h ethyl acetate was added and the reaction mixture was acidified with 18% HCl. After the usual work up, compound **8** (242 mg, 98%) was obtained, with the following features: an oil, $[\alpha]^D_{22}$ +22.9 ° (c, 1.83); HRMS m/z 251.1643 (M^++1, 5, $C_{15}H_{23}O_3$ required 251.1647), 233 (100), 232 (39), 159 (88), 157 (14), 107 (8); IR (NaCl) v_{max} 3423, 1760, 1660, cm^{-1}; ^1H NMR δ 1.11 (3H, s, H_{14}), 1.20 (3H, d, J = 6.6 Hz, H_{13}), 1.80 (3H, d, J = 1.1 Hz, H_{15}), 2.75 (1H, t, J = 8.4 Hz, H_5), 4.09 (1H, t, J = 9.6 Hz, H_6), 5.43 (1H, br s, H_3); ^{13}C NMR δ 178.8 (C_{12}), 141.3 (C_4), 125.6 (C_3), 84.7 (C_6), 73.7 (C_{10}), 53.9, 52.5, 48.2, 42.2 (C_1, C_5, C_7, C_{11}), 38.9, 33.5 (C_2, C_9), 25.9 (C_8), 26.7 (C_{14}), 16.4 (C_{15}), 12.8 (C_{13}).

Compound **(1)**.

The material obtained in the former reaction from **7** (290 mg, 0.99 mmol) was dissolved in 2 mL of THF and cooled at -45 °C under argon. Then, pyridine (0.98 mL, 11.7 mmol) and thionyl chloride (0.98 mL, 13.5 mmol) were added, and the mixture stirred for 10 min. The reaction mixture was quenched with a cold water-ether mixture, extracted with ether, washed with aqueous Na_2CO_3, water and brine, dried and concentrated to furnish an oil, which by flash chromatography on silica gel afforded compound **1** (150 mg, 65%) and compound **2** (28 mg, 12%). Compound (**1**): an oil, $[\alpha]^D_{22}$ +113.5 ° (c, 1.81); MS m/z 232 (M^+, 48), 217 (13), 159 (79), 158 (87), 152 (100), 119 (53), 84 (74); IR (NaCl) v_{max} 1770, 1640, 970 cm^{-1}; ^1H NMR δ 1.20 (3H, d, J = 7.1 Hz, H_{13}), 1.79 (3H, d, J = 1.0 Hz, H_{15}), 2.76 (1H, dd, J = 7.5 and 10.0 Hz, H_5), 3.07 (1H, q, J = 7.5 Hz, H_1), 3.95 (1H, t, J = 10.0 Hz, H_6), 4.80 and 4.84 (2H, two s, H_{14}), 5.50 (1H, br s, H_3); ^{13}C NMR δ 179.7 (C_{12}), 149.6 (C_{10}), 140.0 (C_4), 126.2 (C_3), 112.2 (C_{14}), 84.7 (C_6), 55.5, 50.9, 46.9, 41.7 (C_1, C_5, C_7, C_{11}), 36.7, 36.6, 32.7 (C_2, C_8, C_9), 16.6 (C_{15}), 13.1 (C_{13}).

Compound **(2)**.

The resulting material from the hydrolysis of compound **7** (256 mg, 0.87 mmol) was dissolved in 20 mL of dichloromethane containing pyridine (0.762 mL, 9.4 mmol) and cooled at 0 °C under argon. Then, triflic anhydride (0.470 mL, 2.75 mmol) was added, and the mixture stirred at room temperature for 3 h. The reaction mixture was quenched with aqueous $NaHCO_3$, extracted with dichloromethane, washed with brine and dried over Na_2SO_4. By flash chromatography on silica gel compound **2** (132 mg, 65%) and compound **1** (24 mg, 11%) were obtained. Compound (**2**): m. p. 78-79 °C, $[\alpha]^D_{22}$ +10.3 ° (c, 2.1); MS m/z 232 (M^+, 100), 217 (66), 159 (94), 152 (61), 121 (81), 91 (78); IR (NaCl) v_{max} 1765 cm^{-1}; ^1H NMR δ 1.19 (3H, d, J = 7.0 Hz, H_{13}), 1.69 (3H, s, H_{14}), 1.88 (3H, s, H_{15}), 2.94 (2H, br s, H_2), 3.28 (1H, d, J = 10.0, H_5), 3.63 (1H, t, J = 9.8 Hz, H_6), 5.49 (1H, br s, H_3); ^{13}C NMR δ 178.7 (C_{12}), 135.3, 131.5 (C_{10}, C_1), 140.9 (C_4), 125.9 (C_3), 85.2 (C_6), 56.4, 55.7, (C_5, C_7), 41.4 (C_{11}), 37.7, 34.2, 27.2 (C_2, C_8, C_9), 23.0 (C_{14}), 17.8 (C_{15}), 12.2 (C_{13}).

Compound (9).

To a suspension of selenium dioxide (7.4 mg, 0.066 mmol) in dichloromethane (0.3 mL) at 0 °C under argon, was added dropwise 14 μL (0.143 mmol) of a 80% solution of *tert*-butyl hydroperoxide. A nearly homogeneous solution was obtained after stirring for 30 min. Then, a solution of compound 1 (30 mg, 0.129 mmol) in 0.6 mL of dichloromethane was added dropwise. The mixture was stirred at 4 °C for 18 h. After this time, aqueous NaHCO$_3$ was added and the mixture extracted with dichloromethane, washed with brine and dried over Na$_2$SO$_4$. Flash chromatography of the resulting crude oil gave compound 9 (31 mg, 95%) : an oil, $[\alpha]_D^{22}$ +113.6 ° ; MS *m/z* 248 (M$^+$, 98), 233 (52), 230 (11), 205 (88); IR (NaCl) ν_{max} 3450, 1765, 1640, 890 cm^{-1}; ^{1}H NMR δ 1.21 (3H, d, J = 7.0 Hz, H$_{13}$), 1.87 (3H, br d, J = 1.6 Hz, H$_{15}$), 2.65 (1H, d, J = 10.4 Hz, H$_5$), 3.79 (1H, t, J = 10.0 Hz, H$_6$), 5.02 and 5.10 (2H, two br s, H$_{14}$), 5.50 (1H, br s, H$_3$); ^{13}C NMR δ 178.5 (C$_{12}$), 151.5 (C$_{10}$), 140.1 (C$_4$), 124.1 (C$_3$), 114.7 (C$_{14}$), 84.9 (C$_1$), 83.2 (C$_6$), 63.5, 51.5 (C$_5$, C$_7$), 45.6, 32.7, 31.2 (C$_2$, C$_8$, C$_9$), 41.8 (C$_{11}$), 17.7 (C$_{15}$), 12.9 (C$_{13}$).

Compounds (10) and (11).

To a suspension of selenium dioxide (12 mg, 0.108 mmol) in dichloromethane (0.4 mL) at 0° C under argon, was added dropwise 20 μL (0.204 mmol) of a 80% solution of *tert*-butyl hydroperoxide to give a nearly homogeneous solution after stirring for 30 min. Then a solution of compound 2 (50 mg, 0.214 mmol) in 1 mL of dichloromethane was added dropwise. The mixture was stirred at 0 °C for 3 h. After this time, aqueous NaHCO$_3$ was added and the mixture extracted with ether, washed with brine and dried over Na$_2$SO$_4$. Flash chromatography of the resulting crude oil afford starting material 2 (29 mg, 58%) and a mixture 1:4 of compounds 10 and 11 (21 mg, 42%) with NMR spectral data identical to those described previously for 6-*epi*-tannunolide B[12] and 6-tannunolide B[13] respectively.

Compound (12).

To a suspension of selenium dioxide (12 mg, 0.108 mmol) in dichloromethane (0.4 mL) at 0° C under argon, was added dropwise 80 μL (0.820 mmol) of a 80% solution of *tert*-butyl hydroperoxide to give a nearly homogeneous solution after stirring for 30 min. Then a solution of compound 7 (60 mg, 0.205 mmol) in 1 mL of dichloromethane containing pyridine (66 μL, 0.816 mmol) was added dropwise. The mixture was stirred at 4 °C for 3 days. After this time, aqueous NaHCO$_3$ was added and the mixture extracted with dichloromethane, washed with brine and dried over Na$_2$SO$_4$. Flash chromatography of the resulting crude oil afford compounds 7 (6 mg, 10%), 12 (46 mg, 72%) and 4 (10 mg, 16%). Compound 12: m. p. 121-122 °C (hexane-ethyl acetate), $[\alpha]_D^{22}$ -25.4 ° (c, 1.02); HRMS *m/z* 248.1212 (M$^+$-AcOH, 100, C$_{15}$H$_{20}$O$_3$ required 248.1412), 230 (28), 175 (55), 152 (43); IR (KBr) ν_{max} 3480, 1760, 1720 cm^{-1}; ^{1}H NMR δ 1.22 (3H, d, J = 6.7 Hz, H$_{13}$), 1.48 (3H, s, H$_{14}$), 1.77 (3H, t, J = 1.7 Hz, H$_{15}$) 2.00 (3H, s, CH$_3$CO), 2.56 (1H, m, H$_7$), 3.09 (1H, t, J = 8.7 Hz, H$_1$), 4.18 (1H, d, J = 10.0 Hz, H$_6$), 5.51 (1H, br s, H$_3$); ^{13}C NMR δ 178.4 (C$_{12}$), 170.3 (CH$_3$*CO*), 145.4 (C$_4$), 125.1 (C$_3$), 85.5 (C$_{10}$), 84.9 (C$_6$), 84.1 (C$_5$), 57.7, 43.1, 41.1 (C$_1$, C$_7$, C$_{11}$), 31.5, 31.0, 26.0 (C$_2$, C$_8$, C$_9$), 26.5 (C$_{14}$), 22.5 (*CH$_3$*CO), 13.7, 13.3 (C$_{13}$, C$_{15}$).

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