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Synthesis of (+)-amberketal and its analog from L-abietic acid

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Abstract—(+)-Amberketal (**1**) and its analog (**2**) have been synthesized from commercially available L-abietic acid (**3**) by a selective reduction of an unsaturated aldehyde in the presence of a ketone and simultaneous reduction of an iodide using an aqueous suspension of Raney Ni as the key step.

1. Introduction

Ambergris, the most important animal perfume aside from civet, musk, and castreum, has been particularly used in perfume industry since ancient times for its unique fragrance and fixative properties.[1] The concretion formed in the intestinal tract of the blue sperm whale, after one to three years of aging smells of amber odor, which is used in perfumery in the form of an infusion in alcohol. The high price of ambergris and enforced whale protection has encouraged chemists to search for commercially viable synthetic substitutes.[2] (+)-Amberketal **1** is one of the most important synthetic equivalents to the scarce natural ambergris source, which possess a strong and tenacious ambergris-type odor.[1a] The natural chiral pool of precursors for the synthesis of amberketal include manool,[3] sclareol,[4] communic acid,[5] and anticopalic acid.[6]

Several ambergris-type odorants have been synthesized from commercially available L-abietic acid by different research groups.[7–10] Herein we report the synthesis of (+)-amberketal and its analog by using commercially available L-abietic acid as a starting material(Fig. 1).

The retrosynthetic analysis (Fig. 2) describes the oxidative degradation of the C-ring of either iodo abietane **5** or tosylate **8** of abietol, regioselective construction of a C-8 exocyclic double bond, and subsequent conversion of isopropyl ketone to methyl ketone leading to the exact chiral synthon **15** of (+)-amberketal **1**.

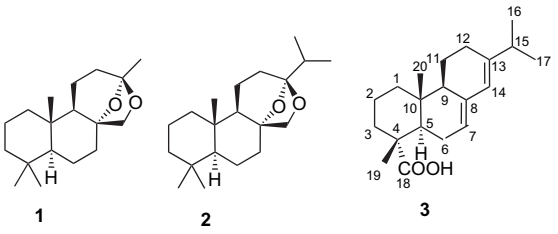

Figure 1.

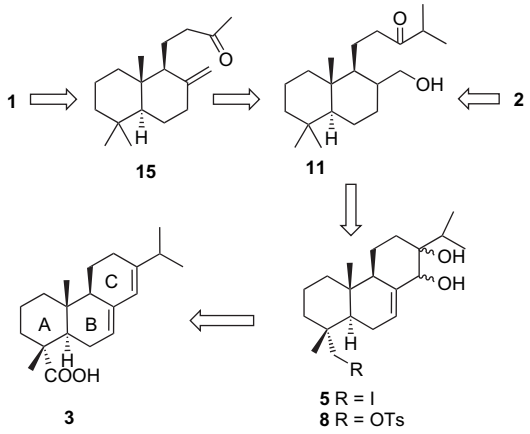

Figure 2. Retrosynthetic analysis.

2. Results and discussion

The synthesis began with the conversion of abietic acid to abietol **4** using $LiAlH_4$ in THF at room temperature in 85% yield. Treatment of **4** with triphenyl phosphine–iodine–imidazole in toluene at room temperature[11] gave iodo abietane **5** in 6% yield. When the reaction was performed at

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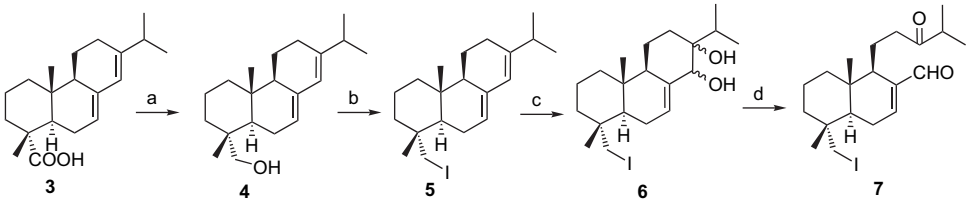
70 °C, the formation of two inseparable side products along with the iodo abietane were observed in TLC. The crude material obtained after filtration through a small pad of silica gel column was directly subjected to regioselective dihydroxylation with a catalytic amount of osmic acid (OsO_4, $Me_3NO\cdot 2H_2O$, *t*-BuOH–py–H_2O, reflux, 48 h).[8] This reaction furnished a diastereomeric mixture of the diol **6** in a ratio of 7:3 (β/α) (determined from their isolated yield) in 25% yield for the two steps. Different solvent systems such as acetone/water (*N*-methyl morpholine *N*-oxide as co-oxidant) and PEG 400[12] ($Me_3NO\cdot 2H_2O$ as co-oxidant) were also studied for the OsO_4 catalyzed regioselective dihydroxylation. However, the starting iodo abietane was recovered without even a trace of the diol **6**. The oxidative cleavage of the mixture of diol **6** was performed using $NaIO_4$ in an ethanol–water mixture (4:1) at room temperature, which resulted in the formation of the key intermediate of our strategy, the conjugate aldehyde **7**, in 70% yield (Scheme 1).[10]

To improve the overall yield of the aldehyde **7** from abietic acid, abietol **4** was tosylated with *p*-TsCl in pyridine at 0 °C to afford the tosylate derivative **8** in 84% yield, which on subjecting to regioselective dihydroxylation afforded diol **9** in 48% yield as a 9:1 (β/α) mixture. The mixture of the diol **9** was then subjected to the oxidative cleavage with $NaIO_4$ in ethanol and water (4:1) to afford the aldehyde **10** as a single product in 85% yield. The displacement of the tosyl group in **10** by iodide was achieved in 50% yield using excess NaI in DMF at 90 °C for 12 h along with 20% yield of an unidentified product (Scheme 2). The aldehyde **7** was obtained in similar overall yield (14.87 and 14.73%) from L-abietic acid in the both Schemes 1 and 2, respectively.

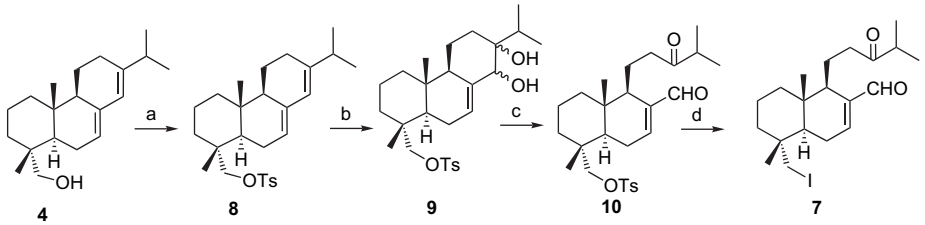
The selective reduction of both the conjugated double bond and the aldehyde group in the presence of ketone group as described by Barrero et al.[13] and simultaneous removal of iodo group was successfully achieved in a single step using aqueous suspension of Raney Ni in THF at room temperature to afford the saturated primary alcohol **11** in 86% yield.

The structure of the alcohol **11** was established by ^1H NMR and ^{13}C NMR. The disappearance of the olefinic proton, aldehydic proton, and CH_2–I protons and the appearance of characteristic peaks at 3.52 ppm (triplet), 3.61 ppm (doublet) for $-CH_2OH$ protons and at 0.81 ppm for the new $-CH_3$ group in ^1H NMR spectrum confirmed the structure of **11**. Our next aim was to construct the *exo*-olefin at C-8 position and transform the isopropyl ketone into a methyl ketone. The alcohol **11** was converted to its tosylate (88%) with *p*-toluenesulfonyl chloride in pyridine at 0 °C for 12 h.[14] The tosylate **12** was treated with *m*-CPBA in CH_2Cl_2 at reflux temperature to afford the isopropyl ester **13** in 68% yield.[15] The ^1H NMR spectra of ester **13** shows the characteristic peak at 4.92 ppm as septet for isopropyl ester proton. The *exo*-olefin **14** was prepared in 80% yield using a reported procedure by the reaction of primary tosylate with 4 equiv of DBU in refluxing toluene for 24 h. The *exo*-olefin **14** was treated with Tebbe's reagent to afford the methyl ketone **15**, the synthon for (+)-amberketal synthesis in 82% yield. The synthon **15** was converted to (+)-amberketal **1** in 60% yield by treatment with a catalytic amount of OsO_4 in refluxing *t*-BuOH–H_2O–pyridine mixture with trimethylamine *N*-oxide as co-oxidant (Scheme 3).[4] (+)-Amberketal **1** was also prepared in two steps, i.e., epoxidation with *m*-CPBA/aq $NaHCO_3$ followed by δ,ε-epoxyketone cyclization with $ZnCl_2$ at 18 °C.[6] All the physical and spectroscopic data of the compound **1** are comparable with the data reported in the literature.[4]

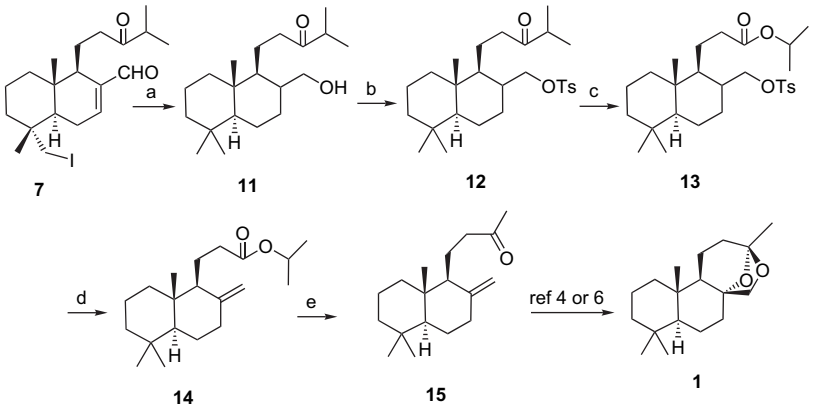
In order to get the amberketal analog **2** the alcohol **11** was treated with Tf_2O in CH_2Cl_2 using pyridine as a base to produce the triflate derivative, which on subsequent treatment with 3 equiv of DBU at room temperature afforded the keto-olefin **16**. The keto-olefin **16** was also obtained from the tosylate **12** by the treatment with 4 equiv of DBU in refluxing toluene. The epoxidation of **16** with *m*-CPBA/aq $NaHCO_3$ gave only α-epoxide **17** (95% yield) diastereoselectively, which under δ,ε-epoxyketone cyclization with $ZnCl_2$ at 18 °C resulted in the amberketal analog **2** (75% yield).[6] The keto-olefin **16** was also converted to the analog



Scheme 1. Reagents and conditions: (a) $LiAlH_4$, THF, 0 °C–rt, 3 h, 85%; (b) I_2, imidazole, Ph_3P, toluene, 70 °C; (c) cat OsO_4, $Me_3NO\cdot 2H_2O$, *t*-BuOH–H_2O–pyridine, reflux, 48 h, 25% in two steps; (d) $NaIO_4$, EtOH–H_2O, rt, 1.5 h, 70%.

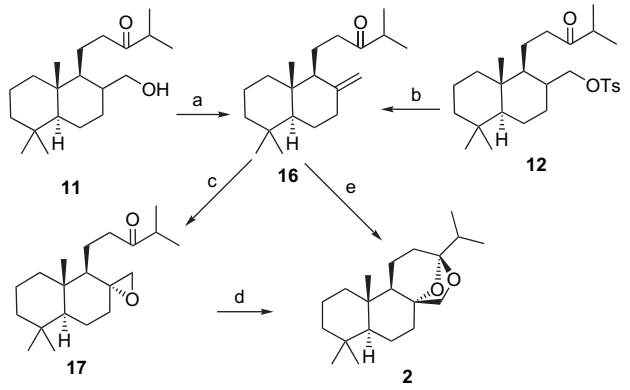


Scheme 2. Reagents and conditions: (a) *p*-TsCl, pyridine, 0 °C, 12 h, 84%; (b) cat OsO_4, $Me_3NO\cdot 2H_2O$, *t*-BuOH–H_2O–pyridine, reflux, 48 h, 48%; (c) $NaIO_4$, EtOH–H_2O, rt, 1.5 h, 85%; (d) excess NaI, DMF, 90 °C, 12 h, 50%.



Scheme 3. Reagents and conditions: (a) Raney Ni, THF, rt, 20 h, 86%; (b) *p*-TsCl, pyridine, 0 °C, 12 h, 88%; (c) *m*-CPBA, CH_2Cl_2, reflux, 24 h, 68%; (d) DBU, toluene, reflux, 24 h, 88%; (e) Tebbe's reagent, −10 °C, 2 h, 82%.

2 by treatment with a catalytic amount of OsO_4 in refluxing *t*-BuOH–H_2O–pyridine mixture with trimethylamine *N*-oxide as co-oxidant (Scheme 4).[4]



Scheme 4. Reagents and conditions: (a) i. Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 2 h, ii. DBU, CH_2Cl_2, rt, 3 h, 84% in two steps; (b) DBU, toluene, reflux, 24 h, 80%; (c) *m*-CPBA, CH_2Cl_2, 3 h, rt, 95%; (d) $ZnCl_2$, CH_2Cl_2, 18 °C, 14 h, 75%; (e) cat OsO_4, $Me_3NO{\cdot}2H_2O$, *t*-BuOH–H_2O–pyridine, reflux, 48 h, 73%.

3. Conclusion

In conclusion, we have used L-abietic acid for the first time to synthesize (+)-amberketal **1** in 10 steps (overall yield 3.31%) and its analog **2** with less ambergris tincture in 8 steps (overall yield 7.95%).

4. Experimental

4.1. General

All commercial chemicals were used without further purification. All solvents were purified by standard techniques. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 683 spectrophotometer using KBr optics. Optical rotations were obtained on Jasco Dip 360 digital polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded on Gemini 200, Bruker Avance 300 MHz, and Unity 400 MHz spectrometers in $CDCl_3$ using TMS as internal standard, with chemical shifts being given in parts per million with respect to internal TMS and *J* values quoted in hertz. Mass spectra were recorded on micromass Quatro LC triple quadrapole mass spectrometer for ESI analysis. All reaction mixtures were stirred magnetically and were monitored by TLC using 0.25 mm E-Merck silica gel 60 F_{254} pre-coated glass plates, which were visualized with UV light and then developed by using iodine mixed with silica gel 60–120 mesh. (N.B. Carbon numbers are not according to IUPAC rule and they are maintained unchanged through out all compounds.)

4.1.1. Abiet-7,13-dien-18-ol (4). To a stirred solution of L-abietic acid (6 g, 19.83 mmol) in dry THF (200 mL) was added $LiAlH_4$ (1.5 g, 2 equiv, 39.67 mmol) portion wise at 0 °C for 30 min. Then the reaction mixture was stirred at room temperature under nitrogen for 2.5 h. After completion of the reaction as monitored by TLC, the reaction mass was slowly poured into a beaker containing 20 g wet Na_2SO_4 with continuous stirring until the formation of a white precipitate. Then the solution was filtered and the filtrate was concentrated under reduced pressure and purified by a silica gel column (20:80 EtOAc–hexane as eluant) to give pure abietol **4** (4.85 g) in 85% yield as a white solid. R_f=0.61 (SiO_2, 30% EtOAc in hexane); mp 79–81 °C, $[\alpha]_D^{25}$ −131.8 (*c* 1.1, $CHCl_3$); IR (KBr): ν 3340, 2925, 1463, 1380, 1030, 884 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.82 (3 H, s, 10-*Me*), 0.86 (3H, s, 4-*Me*), 0.99 and 1.02 (6H, 2d, *J* 3.0 Hz, 15-*Me*$_2$), 1.19–1.45 (4H, m), 1.49–1.62 (3H, m), 1.75–1.88 (3H, m), 1.95–2.05 (4H, m), 2.20 (1H, septet, *J* 6.8 Hz, 15-*H*), 3.07 and 3.32 (2H, 2d, *J* 10.5, 18-*H*), 5.32 (1H, m, 7-*H*), 5.70 (1H, s, 14-*H*); Mass (ESI): *m*/*z* 289 $[M+H]^+$, 305 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{33}O$ 289.2531 $[M+H]^+$ and found 289.2522

4.1.2. 18-Iodo abiet-7,13-diene (5). To a stirred solution of abieta-7,13-dien-18-ol **4** (1 g) in dry toluene (20 mL) triphenyl phosphine (2.7 g, 3 equiv, 10.4 mmol) and iodine (2.8 g, 3.2 equiv, 11.1 mmol) were added successively at room temperature and stirred for 10 min followed by the addition of imidazole (1.4 g, 6 equiv, 20.8 mmol). The reaction mixture was allowed to stir for 1 h at room temperature and the solid obtained after the reaction was filtered off and the filtrate was evaporated and purified by column chromatography eluting with hexane to afford pure iodide **5** (85 mg, 6% yield) as a liquid. To increase the yield, the

reaction mixture with same ratio of reactants was stirred at 70 °C for 20 min and the same purification method was applied to get the iodo derivative **5** (800 mg) that was directly charged for the next reaction. R_f=0.9 (SiO_2, hexane); $[\alpha]_D^{25}$ −37.4 (*c* 0.8, $CHCl_3$); IR (KBr): *ν* 2923, 2854, 1647, 1459, 1378, 1021, 761 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.80 (3H, s, 10-*Me*), 0.99 and 1.01 (6H, 2d, *J* 2.2 Hz, 15-Me_2), 1.08 (3H, s, 4-*Me*), 1.21–1.39 (4H, m), 1.49–1.62 (3H, m), 1.74–2.07 (7H, m), 2.20 (1H, septet, *J* 6.8 Hz, 15-*H*), 3.17 (2H, s, 18-*H*), 5.32 (1H, m, 7-*H*), 5.71 (1H, s, 14-*H*); δ_C (75 MHz, $CDCl_3$) 13.5, 18.6, 18.9, 20.8, 21.4, 22.7, 23.5, 27.9, 28.5, 34.89, 34.98, 35.3, 38.7, 39.7, 47.0, 50.7, 120.4 122.4, 135.5, 145.3.

4.1.3. 13,14-Dihydroxy 18-iodo abietane (6β and 6α). To a stirred solution of the crude iodo derivative **5** (800 mg, 2.0 mmol) in a *t*-BuOH (8 mL) and water (2 mL) mixture was added OsO_4 (2.5 mL of 0.2 wt % in *t*-BuOH, 0.01 equiv), $Me_3NO\cdot 2H_2O$, (670 mg, 3 equiv, 6.0 mmol) and pyridine (0.3 mL). The reaction mixture was then heated at reflux for 48 h. After completion of the reaction (as monitored by TLC), it was cooled to room temperature and treated with a 20% aq solution of $NaHSO_3$ (30 mL) and concentrated under vacuum to remove *t*-BuOH, saturated with NaCl (3 g) and extracted with diethyl ether (4×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography (20:80 EtOAc–hexane) to afford the mixture of 13,14-dihydroxy 18-iodo-abietanes **6β** and **6α** in 7:3 ratio (377 mg, 25% yield in two steps starting from **4**) as a yellow semisolid. The two diols **6β** and **6α** were separated by column chromatography eluting with 15% EtOAc–hexane and their individual spectral data were given.

4.1.3.1. 13β,14β-Dihydroxy 18-iodo abietane (6β). R_f=0.36 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ −25.2 (*c* 0.6, $CHCl_3$); IR (KBr): *ν* 3445, 2928, 2868, 1712, 1659, 1443, 1382, 1021, 762 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.86 (3H, s, 10-*Me*), 0.89 and 0.92 (6H, 2d, *J* 7.1 Hz, 15-Me_2), 0.98 (1H, m), 1.09 (3H, s, 4-*Me*), 1.21–1.56 (7H, m), 1.64–1.92 (5H, m), 2.02–2.21 (2H, m), 3.19 (2H, s, 18-*H*), 3.94 (1H, m, 14-*H*), 5.87 (1H, m, 7-*H*); δ_C (75 MHz, $CDCl_3$) 15.2, 16.5, 18.0, 18.7, 19.6 (2C), 22.9, 26.5, 28.9, 33.2, 35.3, 35.8, 39.69, 39.75, 46.7, 51.1, 73.4, 76.5, 120.0, 138.0. Mass (ESI): *m*/*z* 455 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{33}I\ NaO_2$ $[M+Na]^+$ 455.1423 and found 455.1424.

4.1.3.2. 13α,14α-Dihydroxy 18-iodo abietane (6α). R_f=0.25 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ −15.4 (*c* 0.7, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 0.82 (3H, s, 10-*Me*), 0.87 and 0.90 (6H, 2d, *J* 2.7 Hz, 15-Me_2), 0.96 (1H, m), 1.05 (3H, s, 4-*Me*), 1.10–1.32 (3H, m), 1.40–1.60 (5H, m), 1.62–1.81 (4H, m), 1.84–1.98 (2H, m), 2.10–2.20 (2H, m), 3.15 and 3.23 (2H, 2d, *J* 6.8 Hz, 18-*H*), 4.02 (1H, s, 14-*H*), 5.71 (1H, m, 7-*H*); δ_C (75 MHz, $CDCl_3$) 14.6, 15.8, 16.0, 18.4, 19.3, 20.2, 23.1, 28.5 (2C), 28.6, 29.6, 35.1, 39.1, 39.7, 46.4, 46.8, 75.0, 76.5, 127.1, 137.9.

4.1.4. 18-Iodo abiet-7-en-13-one-8-carbaldehyde (7). A solution of $NaIO_4$ (257 mg, 1.5 equiv, 1.21 mmol) in water (1 mL) was added to a solution of diol **6** (350 mg, 0.81 mmol) in EtOH (6 mL). The reaction mixture was stirred for 1.5 h at room temperature. After removing the solvent under vacuum, the crude product was dissolved in EtOAc (15 mL), washed with water (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by a silica gel column (20:80 EtOAc–hexane) to afford the pure aldehyde **7** (246 mg, 70%) as colorless oil. R_f=0.39 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ +32.2 (*c* 0.75, $CHCl_3$); IR (KBr): *ν* 2965, 2927, 1712, 1687, 1632, 1461, 1382, 1186, 1010, 702 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.82 (3H, s, 10-*Me*), 1.09 (3H, s, 4-*Me*), 1.10 (6H, d, *J* 3.0 Hz, 15-Me_2), 1.37 (2H, s), 1.28–1.41 (2H, m), 1.42–1.58 (3H, m) 1.79–2.10 (3H, m), 2.16–2.24 (2H, m), 2.28–2.44 (1H, m), 2.60 (1H, septet, *J* 6.8 Hz, 15-*H*), 3.09 (3H, m), 6.72 (1H, m, 7-*H*), 9.35 (1H, s, –C*H*O); δ_C (75 MHz, $CDCl_3$) *δ* 13.6, 18.0, 18.1, 18.2, 18.8, 21.0, 24.5, 26.8, 35.2, 36.7, 38.0, 39.1, 40.6, 42.4, 46.0, 50.1, 144.3, 151.6, 194.6, 215.1; Mass (ESI): *m*/*z* 431 $[M+H]^+$, 453 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{31}I\ NaO_2$ $[M+Na]^+$ 453.1266 and found 453.1269.

4.1.5. Abiet-7,13-dien-18-yl *p*-toluenesulfonate (8). To a solution of the alcohol **4** (3 g, 10.41 mmol) in freshly distilled pyridine (30 mL) was added freshly recrystalized *p*-TsCl (2.57 g, 13.54 mmol, 1.3 equiv) at 0 °C and the reaction was stirred for 12 h at 0 °C under a nitrogen atmosphere. After removing the pyridine under vacuum, the crude material was diluted with water (10 mL) and Et_2O (50 mL), and washed with 4% HCl (aq) solution (2×20 mL). The ether layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by a silica gel column (5:95 EtOAc–hexane as eluant) to give pure tosylate **8** (3.9 g) in 84% yield as a gummy liquid. R_f=0.6 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ −47.6 (*c* 1.1, $CHCl_3$); IR (KBr): *ν* 2940, 2923, 2852, 1603, 1484, 1479, 1180, 1101, 975, 821 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.80 (3H, s, 10-*Me*), 0.91 (3H, s, 4-*Me*), 1.02 and 1.05 (6H, 2d, *J* 1.2 Hz, 15-Me_2), 1.19–1.29 (3H, m), 1.37–1.55 (5H, m), 1.74–1.88 (4H, m), 2.05 (2H, d, *J* 5.9 Hz), 2.23 (1H, septet, *J* 6.8 Hz, 15-*H*), 2.49 (3H, s, –OSO_2Ph-*p*-*Me*), 3.48 and 3.60 (2H, 2d, *J* 9.3 Hz, 18-*H*), 5.23 (1H, m, 7-*H*), 5.71 (1H, s, 14-*H*), 7.32 (2H, d, *J* 7.6 Hz, Ar-*H*), 7.74 (2H, d, *J* 8.0 Hz, Ar-*H*); δ_C (100 MHz, $CDCl_3$) 13.9, 17.2, 17.7, 20.7, 21.2, 21.5, 22.4, 23.5, 27.2, 34.5, 34.7, 35.5, 36.6, 38.2, 43.4, 50.4, 77.9, 120.0, 122.2, 127.7 (2C), 129.6 (2C), 132.7, 135.2, 144.4, 145.0; Mass (ESI): *m*/*z* 443 $[M+H]^+$, 465 $[M+Na]^+$; HRMS (ESI): calcd for $C_{27}H_{38}NaO_3S$ $[M+Na]^+$ 465.2439 and 465.2435.

4.1.6. 13,14-Dihydroxy abiet-7-en-18-yl *p*-toluenesulfonate (9β and 9α). To a stirred solution of the tosylate **8** (3 g, 6.787 mmol) in *t*-BuOH (20 mL) and water (8 mL) was added OsO_4 (8.5 mL of 0.2 wt % in *t*-BuOH, 0.01 equiv), $Me_3NO\cdot 2H_2O$ (2.26 g, 20.360 mmol, 3 equiv), and pyridine (1 mL). The reaction mixture was stirred at reflux for 48 h. After completion of the reaction (as monitored by TLC), it was cooled to room temperature and treated with a 20% aq solution of $NaHSO_3$ (25 mL) and concentrated under vacuum to remove *t*-BuOH, saturated with NaCl (6 g) and extracted with diethyl ether (4×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography (20:80 EtOAc–hexane as eluant) to afford the mixture of 13,14-dihydroxy abieta-7-en-18-yl *p*-toluenesulfonates **9β** and

9α in a total yield of 48% (1.55 g, 9β:1α ratio) as a white solid. The two diols **9β** and **9α** were separated by column chromatography eluting first with 200 mL of 15% EtOAc–hexane and then continuing 20% EtOAc–hexane (600 mL) and their individual spectral data were given.

4.1.6.1. 13β,14β-Dihydroxy abieta-7-en-18-yl *p*-toluenesulfonate (9β). R_f=0.2 (SiO_2, 30% EtOAc in hexane); mp 103–105 °C; $[\alpha]_D^{25}$ −7.8 (*c* 2.05, $CHCl_3$); IR (KBr): *ν* 3445, 2925, 2854, 1628, 1459, 1359, 1176, 1097, 1017, 964, 845, 816, 665 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.79 (3H, s, 10-*Me*), 0.88 (3H, s, 4-*Me*), 0.90 and 0.91 (6H, 2d, *J* 1.2 Hz, 15-Me_2), 1.27–1.39 (9H, m), 1.43–1.56 (2H, m), 1.61–1.74 (2H, m), 1.86 (1H, m), 2.14 (1H, septet, *J* 6.8 Hz, 15-*H*), 2.47 (3H, s, –OSO_2Ph-*p*-*Me*), 3.47 and 3.62 (2H, 2d, *J* 9.4 Hz, 18-*H*), 3.80 (1H, m, 14-*H*), 5.72 (1H, m, 7-*H*), 7.30 (2H, d, *J* 7.9 Hz, Ar-*H*), 7.71 (2H, d, *J* 7.9 Hz, Ar-*H*); δ_C (75 MHz, $CDCl_3$) 15.6, 16.2, 17.6, 17.7, 17.8, 19.2, 21.5, 22.8, 26.3, 32.9, 35.2, 35.6, 36.5, 39.0, 42.8, 50.8, 73.0, 76.1, 78.0, 119.5, 127.8 (2C), 129.7 (2C), 132.7, 137.7, 144.6. Mass (ESI): *m*/*z* 476 $[M]^+$; HRMS (ESI): calcd for $C_{27}H_{40}NaO_5S$ $[M+Na]^+$ 499.2494 and found 499.2505.

4.1.6.2. 13α,14α-Dihydroxy abieta-7-en-18-yl *p*-toluenesulfonate (9α). R_f=0.12 (SiO_2, 30% EtOAc in hexane); $[\alpha]_D^{25}$ +1.1 (*c* 0.75, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 0.78 (3H, s, 10-*Me*), 0.87 (3H, s, 4-*Me*), 0.89 (6H, s, 15-Me_2), 1.20–1.87 (14H, m), 2.10 (1H, m), 2.46 (3H, s, –OSO_2Ph-*p*-*Me*), 3.47 and 3.62 (2H, 2d, *J* 9.4 Hz, 18-*H*), 3.94 (1H, s, 14-*H*), 5.58 (1H, m, 7-*H*), 7.32 (2H, d, *J* 7.9 Hz, Ar-*H*), 7.75 (2H, d, *J* 7.9 Hz, Ar-*H*).

4.1.7. 18-(*p*-Toluenesulfonato) abiet-7-en-13-one-8-carbaldehyde (10). A solution of $NaIO_4$ (0.968 g, 4.56 mmol, 1.5 equiv) in water (4 mL) was added to a solution of the mixture diol **9β** and **9α** (1.45 g, 3.04 mmol) in EtOH (16 mL). The reaction mixture was stirred for 1.5 h at room temperature. After removing the solvent under vacuum, the crude product was dissolved in EtOAc (20 mL), washed with water (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by column chromatography (15:85 EtOAc–hexane as eluant) to afford the pure aldehyde **10** (1.23 g, 85%) as colorless oil. R_f=0.31 (SiO_2, 30% EtOAc in hexane); $[\alpha]_D^{25}$ +30.34 (*c* 0.5, $CHCl_3$); IR (KBr): *ν* 2927, 1687, 1461, 1358, 1176, 1096, 1017, 964, 843, 816, 667 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.79 (3H, s, 10-*Me*), 0.89 (3H, s, 4-*Me*), 1.08 (6H, d, *J* 7.0 Hz, 15-Me_2), 1.25–1.61 (9H, m), 1.81–1.98 (2H, m), 2.08–2.18 (1H, m), 2.24–2.43 (1H, m), 2.46 (3H, s, –OSO_2Ph-*p*-*Me*), 2.60 (1H, septet, *J* 6.6 Hz, 15-*H*), 3.02–3.20 (1H, m), 3.42 and 3.68 (2H, 2d, *J* 10.1 Hz, 18-*H*), 6.63 (1H, m, 7-*H*), 7.29 (2H, d, *J* 8.2 Hz, Ar-*H*), 7.71 (2H, d, *J* 8.2 Hz, Ar-*H*), 9.32 (1H, s, –C*H*O); δ_C (75 MHz, $CDCl_3$) *δ* 14.2, 17.3, 17.4, 18.2, 18.3, 20.8, 21.6, 24.8, 35.3, 36.5, 36.7, 37.8, 40.6, 42.4, 42.6, 49.5, 77.3, 127.8 (2C), 129.8 (2C), 132.8, 144.2, 144.8, 151.7, 194.6, 215.2; Mass (ESI): *m*/*z* 475 $[M+H]^+$; HRMS (ESI): calcd for $C_{27}H_{38}NaO_5S$ $[M+Na]^+$ 497.2337 and found 497.2333.

4.1.8. 18-Iodo abiet-7-en-13-one-8-carbaldehyde (7). To a solution of the aldehyde **10** (1.0 g, 2.10 mmol) in dry DMF (20 mL) was added excess NaI (1.89 g, 12.65 mmol, 6 equiv). The reaction mixture was stirred for 12 h at 90 °C, then cooled to room temperature, diluted with water (50 mL), extracted with Et_2O (4×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by column chromatography (10:90 EtOAc–hexane as eluant) to afford the pure aldehyde **7** (460 mg, 50%) as colorless oil (spectral data are same with product obtained in the oxidative cleavage of the diol mixture **6**).

4.1.9. Abiet-13-one-14-ol (11). An aqueous suspension of Raney Ni (4.25 g) was added to a stirred solution of aldehyde **7** (225 mg, 0.523 mmol) in THF (4 mL) and the mixture was stirred at room temperature for 20 h. After completion of the reaction as monitored by TLC, the reaction mixture was diluted with Et_2O (15 mL), filtered through silica gel, and the residue was washed with Et_2O (3×15 mL). The filtrate was evaporated under vacuum and the residue was purified by column chromatography (10:90→40:60 EtOAc–hexane as eluant) to afford saturated alcohol **11** (120 mg, 86%) as colorless oil. R_f=0.35 (SiO_2, 30% EtOAc in hexane); $[\alpha]_D^{25}$ +36.91 (*c* 0.5, $CHCl_3$); IR (KBr): *ν* 3443, 2929, 1707, 1630, 1463, 1384, 1273, 1023, 757 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.71 (3H, s, 10-*Me*), 0.81 and 0.85 (6H, 2s, 4-Me_2), 1.07 (6H, d, *J*=7.1 Hz, 15-Me_2), 1.14–1.52 (11H, m) 1.57–1.78 (3H, m), 1.98 (1H, m), 2.29–2.41 (1H, m), 2.44–2.63 (2H, m), 3.52 (1H, t, *J* 9.8 Hz, 14-*H*), 3.61 (1H, d, *J* 9.8 Hz, 14-*H*); δ_C (75 MHz, $CDCl_3$) 15.6, 17.6, 18.2, 18.3, 18.5, 19.6, 21.5, 29.3, 33.2, 33.4, 38.1, 39.1 (2C) 39.7, 40.8, 41.9, 52.8, 56.5, 61.4, 215.3; Mass (ESI): *m*/*z* 309 $[M+H]^+$, 331 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{36}Na\ O_2$ $[M+Na]^+$ 331.2613 and found 331.2625.

4.1.10. Abiet-13-one-14-yl *p*-toluenesulfonate (12). *p*-TsCl (80 mg, 0.421 mmol, 1.3 equiv) was added, at 0 °C under nitrogen, to a solution of alcohol **11** (100 mg, 0.324 mmol) in freshly distilled pyridine (4 mL), the reaction mixture was stirred for 12 h at 0 °C under nitrogen. After removing pyridine under vacuum, the crude material was diluted with water (10 mL) and Et_2O (15 mL), and washed with 4% HCl (aq) solution (20 mL). The ether layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The concentrate was purified by a silica gel column (10:90 EtOAc–hexane as eluant) to give pure tosylate **12** (132 mg) in 88% yield as a gummy liquid. R_f=0.76 (SiO_2, 30% EtOAc in hexane); $[\alpha]_D^{25}$ +38.45 (*c* 0.5, $CHCl_3$); IR (KBr): *ν* 2927, 2856, 1709, 1599, 1461, 1368, 1262, 1175, 1104, 813 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.65 (3H, s, 10-*Me*), 0.76 and 0.82 (6H, 2s, 4-Me_2), 1.05 and 1.08 (6H, 2d, *J* 1.1 Hz, 15-Me_2), 1.20–1.55 (11H, m), 1.67–1.82 (3H, m), 1.88–1.93 (1H, m), 2.01–2.05 (1H, m), 2.18–2.28 (1H, m), 2.45–2.57 (2H, m), 2.46 (3H, s, –OSO_2Ph-*p*-*Me*), 3.92–4.04 (2H, m, 14-*H*), 7.31 (2H, d, *J* 7.9 Hz, Ar-*H*), 7.74 (2H, d, *J* 8.3 Hz, Ar-*H*); δ_C (75 MHz, $CDCl_3$) 15.6, 17.2, 18.1, 18.2, 18.4, 19.2, 21.3, 21.5, 28.8, 33.1, 33.3, 35.6, 37.8, 38.2, 38.8, 40.8, 41.7, 52.0, 56.1, 69.9, 127.7 (2C), 129.7 (2C), 133.2, 144.6, 214.4; Mass (ESI): *m*/*z* 463 $[M+1]^+$, 485 $[M+Na]^+$; HRMS (ESI): calcd for $C_{27}H_{42}NaO_4S$ $[M+Na]^+$ 485.2701 and found 485.2700.

4.1.11. Abiet-13-oate-14-yl *p*-toluenesulfonate (13). A solution of 77% *m*-CPBA (137 mg, 0.779 mmol, 3 equiv) in CH_2Cl_2 (3 mL) was added to a solution of tosylate **12** (120 mg, 0.259 mmol) in CH_2Cl_2 (7 mL) and the mixture

was stirred at reflux under nitrogen for 24 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL). A saturated solution of $NaHSO_3$ (10 mL) was added to the same and it was washed with saturated $NaHCO_3$ (aq) solution (5×20 mL) and brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The concentrate was purified by a silica gel column (10:90 EtOAc–hexane as eluant) to give pure isopropyl ester **13** (85 mg) in 68% yield as colorless oil. R_f=0.55 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ +34.47 (*c* 0.5, $CHCl_3$); IR (KBr): ν 2927, 2858, 1728, 1599, 1459, 1364, 1261, 1178, 1106, 945, 814, 665 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.59 (3H, s, 10-*Me*), 0.69 and 0.76 (6H, 2s, 4-Me_2), 0.99–1.06 (3H, m), 1.15 (6H, d, *J* 6.2 Hz, 15-Me_2), 1.18–1.49 (9H, m), 1.49–2.27 (5H, m), 2.40 (3H, s, –OSO_2Ph-*p*-*Me*), 3.87–4.00 (2H, m, 14-*H*), 4.92 (1H, septet, *J* 6.2 Hz, 15-*H*), 7.25 (2H, d, *J* 8.2 Hz, Ar-*H*), 7.69 (2H, d, *J* 8.2 Hz, Ar-*H*); δ_C (75 MHz, $CDCl_3$) 15.7, 17.1, 18.4, 20.7, 21.3, 21.5, 21.8 (2C), 28.7, 32.7, 33.1, 33.2, 35.4, 37.8, 38.8, 41.7, 51.9, 56.1, 67.5, 69.7, 127.8 (2C), 129.7 (2C), 133.2, 144.6, 172.9; Mass (ESI): *m*/*z* 479 $[M+1]^+$, 501 $[M+Na]^+$; HRMS (ESI): calcd for $C_{27}H_{42}NaO_5S$ $[M+Na]^+$ 501.2650 and found 501.2654.

4.1.12. Abiet-8(14)-en-13-oate (14). A mixture of isopropyl ester **13** (80 mg, 0.167 mmol) and DBU (50 mg, 0.328 mmol, 2 equiv) in dry toluene (5 mL) was refluxed for 12 h and then another 2 equiv DBU was added to the reaction mixture and stirred again at reflux temperature for 12 more hours. The solvent was removed under vacuum; the crude was diluted with EtOAc (15 mL), and washed with water (2×10 mL) and brine solution (10 mL). The EtOAc layer was dried over anhydrous Na_2SO_4, filtered, and concentrated; and the residue was purified by column chromatography (5:95 EtOAc–hexane as eluant) to afford the pure *exo*-olefin **14** (45 mg, 88% yield) as colorless liquid. R_f=0.81 (SiO_2, 20% EtOAc in hexane); $[\alpha]_D^{25}$ +27.49 (*c* 0.5, $CHCl_3$); IR (KBr): ν 2926, 2851, 1732, 1643, 1460, 1374, 1255, 1174, 1109, 890 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.68 (3H, s, 10-*Me*), 0.80 and 0.87 (6H, s, 4-Me_2), 1.02–1.18 (3H, m), 1.21 (6H, d, *J* 6.0 Hz, 15-Me_2), 1.25 (1H, s), 1.29–1.44 (4H, m), 1.45–1.63 (3H, m), 1.64–2.15 (5H, m), 4.48 (1H, s, 14-*H*), 4.81 (1H, s, 14-*H*), 4.95 (1H, septet, *J* 6.4 Hz, 15-*H*); δ_C (75 MHz, $CDCl_3$) 14.3, 19.1, 19.3, 21.7, 21.84, 21.89, 24.4, 33.55, 33.58, 33.61, 38.2, 38.9, 39.6, 42.1, 55.5, 56.2, 67.2, 106.4, 148.0, 173.7; Mass (ESI): *m*/*z* 307 $[M+1]^+$, 329 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{34}NaO_2$ $[M+Na]^+$ 329.2456 and found 329.2454.

4.1.13. 14,15-Dinorlabd-8(17)-en-13-one (15). To a stirred solution of *exo*-olefin **14** (40 mg, 0.130 mmol) in dry THF (3 mL) was added Tebbe's reagent (0.4 mL of 0.5 M solution in toluene, 0.196 mmol, 1.5 equiv) at −10 °C and the mixture was allowed to warm up to 0 °C in 2 h. After 2 h water (3 mL) was added slowly to the reaction mixture and the solid precipitated was filtered off and washed with Et_2O (3×10 mL). The filtrate was concentrated under vacuum and the residue was purified by column chromatography (10:90 EtOAc–hexane as eluant) to afford the keto-olefin **15** (28 mg, 82% yield) as colorless oil. R_f=0.52 (SiO_2, 10% EtOAc in hexane); $[\alpha]_D^{25}$ +36.6 (*c* 0.4, $CHCl_3$); IR (KBr): ν 2926, 2849, 1716, 1639, 1459, 1360, 1160, 1109, 889, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.69 (3H, s, 10-*Me*), 0.80 and 0.87 (6H, 2s, 4-Me_2), 0.99–1.61 (10H, m), 1.66–2.01 (3H, m), 2.08 (3H, s, –CO*Me*), 2.14–2.41 (2H, m), 2.47–2.62 (1H, m), 4.41 (1H, s, 14-*H*), 4.79 (1H, s, 14-*H*); δ_C (75 MHz, $CDCl_3$) 14.2, 17.4, 19.3, 21.6, 24.4, 29.6, 30.0, 33.6, 38.2, 38.9, 39.7, 42.0, 42.8, 55.4, 56.1, 106.2, 148.3, 209.5; Mass (ESI): *m*/*z* 285 $[M+Na]^+$; HRMS (ESI): calcd for $C_{18}H_{30}NaO$ $[M+Na]^+$ 285.2194 and found 285.2195.

4.1.14. Abiet-8(14)-en-13-one (16). *Method A*: A mixture of tosylate **12** (30 mg, 0.064 mmol) and DBU (19 mg, 0.129 mmol, 2 equiv) in dry toluene (5 mL) was refluxed for 12 h and then another 2 equiv of DBU was added to the reaction mixture and stirred at reflux for another 12 h. The solvent was removed under vacuum; the crude was diluted with EtOAc (15 mL), and washed with water (2× 10 mL) and brine solution (5 mL). The EtOAc layer was dried over anhydrous Na_2SO_4, filtered and concentrated; and the residue was purified by column chromatography (5:95 EtOAc–hexane as eluant) to afford the pure keto-olefin **16** (15 mg, 80% yield) as a colorless liquid. *Method B*: To a stirred solution of the alcohol **11** (20 mg, 0.064 mmol) and pyridine (10 mg, 0.129 mmol, 2 equiv) in dry CH_2Cl_2 (4 mL) was added trifluoromethanesulfonic anhydride (23 mg, 0.084 mmol, 1.3 equiv) at 0 °C and the mixture stirred at room temperature for 2 h under nitrogen. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL) and brine solution (5 mL). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, filtered and concentrated; and the residue was dried under vacuum. To a solution of the dry residue in dry CH_2Cl_2 (4 mL) was added DBU (29 mg, 0.194 mmol, 3 equiv) and the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL) and brine solution (5 mL). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, filtered and concentrated; and the residue was purified by column chromatography (5:95 EtOAc–hexane as eluant) to afford the pure keto-olefin **16** (16 mg, 84%) as a colorless liquid. R_f=0.58 (SiO_2, 10% EtOAc in hexane); $[\alpha]_D^{25}$ +38.11 (*c* 0.75, $CHCl_3$); IR (KBr): ν 2929, 2846, 1710, 1641, 1462, 1383, 1215, 1078, 1013, 888, 761 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.68 (3H, s, 10-*Me*), 0.80 and 0.86 (6H, 2s, 4-Me_2), 1.04 and 1.07 (6H, 2d, *J* 1.8 Hz, 15-Me_2), 1.08–1.09 (3 H, m), 1.15–1.41 (3H, m), 1.44–1.59 (3H, m), 1.61–1.99 (4H, m), 2.22–2.38 (2H, m), 2.42–2.58 (2H, m), 4.42 (1H, s, 14-*H*), 4.79 (1H, s, 14-*H*); δ_C (75 MHz, $CDCl_3$) 14.3, 17.5, 18.20, 18.24, 19.3, 21.6, 24.4, 33.56, 33.60, 38.3, 38.9, 39.3, 39.7, 40.9, 42.1, 55.5, 56.3, 106.2, 148.4, 215.3; Mass (ESI): *m*/*z* 313 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{34}NaO$ $[M+Na]^+$ 313.2507 and found 313.2519.

4.1.15. Abiet-8,14-epoxy-13-one (17). A solution of 77% *m*-CPBA (23 mg, 0.134 mmol, 3 equiv) in CH_2Cl_2 (4 mL) and 2 mL of 5% $NaHCO_3$ (aq) was added to a solution of keto-olefin **16** (13 mg, 0.044 mmol) in CH_2CL_2 (4 mL) and the mixture was stirred at room temperature for 3 h. After dilution with CH_2Cl_2 (10 mL), a saturated solution of $NaHSO_3$ (6 mL) was added to the reaction mixture and it was washed with saturated $NaHCO_3$ (aq) solution (3× 20 mL) and brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by a silica gel column (15:85 EtOAc–hexane as eluant) to give α-epoxide **17** (13 mg) in 95% yield as a colorless liquid. R_f=0.47 (SiO_2, 20% EtOAc

in hexane); $[\alpha]_D^{25}$ +7.32 (*c* 0.6, $CHCl_3$); IR (KBr): *ν* 2959, 2929, 2870, 1725, 1447, 1381, 1283, 1125, 1071, 742, 658 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.84 (6H, d, *J* 2.6 Hz, 4-*Me*$_2$), 0.89 (3H, s, 10-*Me*), 0.97–1.04 (2H, m), 1.05 and 1.08 (6H, 2d, *J* 1.5 Hz, 15-*Me*$_2$), 1.14–1.64 (9H, m), 1.77–1.88 (3H, m), 2.31 (1H, m), 2.42 (1H, d, *J* 4.5 Hz, 14-*H*), 2.42–2.68 (2H, m), 2.78 (1H, dd, *J* 1.5, 4.1 Hz, 14-*H*); δ_C (75 MHz, $CDCl_3$) 13.1, 14.7, 16.7, 16.8, 17.2, 20.1, 20.4, 32.00, 32.08, 35.3, 37.5, 38.9, 39.3, 40.2, 40.5, 49.4, 51.8, 53.6, 58.0, 213.8. Mass (ESI): *m*/*z* 307 $[M+1]^+$, 329 $[M+Na]^+$; HRMS (ESI): calcd for $C_{20}H_{34}NaO_2$ $[M+Na]^+$ 329.2456 and found 329.2462.

4.1.16. (8*R*,13*S*)-8α,13:13,14-Diepoxyabietane (2). *Method A*: To a stirred solution of α-epoxide **17** (12 mg, 0.039 mmol) in dry CH_2Cl_2 (5 mL) was added $ZnCl_2$ (3 mg, 0.022 mmol, 0.6 equiv) and the reaction mixture was stirred at 18 °C for 14 h. After completion of the reaction (as monitored by TLC), the mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (5 mL) and brine solution (5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The concentrate was purified by a silica gel column (5:95 EtOAc–hexane as eluant) to give amberketal analog **2** (9 mg) in 75% yield as a semisolid. *Method B*: A stirred mixture of keto-olefin **16** (13 mg, 0.044 mmol), $Me_3NO\cdot 2H_2O$ (14 mg, 0.134 mmol, 3 equiv), *t*-BuOH (4 mL), water (0.6 mL), pyridine (0.1 mL), and OsO_4 (0.1 mL of 0.2% wt/v in *t*-BuOH, 0.02 equiv) was stirred at reflux temperature for 48 h. The reaction mixture was cooled to room temperature, treated with 20% $NaHSO_3$ (aq) solution (3 mL), concentrated under vacuum to remove *t*-BuOH, saturated with NaCl (400 mg), and extracted with Et_2O (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated; the residue was purified by column chromatography (5:95 EtOAc–hexane) to afford pure amberketal analog **2** (10 mg, 73% yield) as a semisolid. R_f=0.58 (SiO_2, 10% EtOAc in hexane) $[\alpha]_D^{25}$ +11.3 (*c* 0.5, $CHCl_3$); IR (KBr): *ν* 2928, 2869, 1460, 1382, 1257, 1175, 1061, 1025, 906, 759 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.79 (3H, s, 10-*Me*), 0.88 (6H, d, *J* 1.5 Hz, 15-*Me*$_2$), 0.90 and 0.93 (6H, 2s, 4-*Me*$_2$), 1.06–1.24 (3H, m), 1.37–1.45 (4H, m), 1.53–1.81 (10H, m), 3.20 (1H, dd, *J* 1.1, 6.7 Hz, 14-*H*), 4.24 (1H, d, *J* 6.7 Hz, 14-*H*); δ_C (75 MHz, $CDCl_3$) 15.5, 16.8, 17.24, 17.27, 18.24, 20.0, 21.6, 30.6, 33.0, 33.5, 34.7, 35.8, 37.2, 38.6, 41.7, 53.7, 55.6, 73.5, 83.3, 109.5; Mass (ESI): *m*/*z* 307 $[M+H]^+$; HRMS (ESI): calcd for $C_{20}H_{35}O_2$ $[M+H]^+$ 307.2637 and found 307.2640.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.063.

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