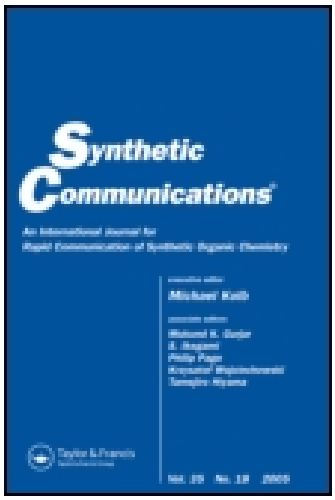

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A Convenient, Large Scale Synthesis of trans-(+)-Sobrerol

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A Convenient, Large Scale Synthesis of *trans*-(+)-Sobrerol

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ABSTRACT

A convenient and highly efficient synthesis of optically pure *trans*-(+)-sobrerol (**1**), starting from methyl 3,5-dihydroxy-4-methyl benzoate **2** in 8 steps with overall yield 26%, is reported. The key intermediate **4** is prepared in remarkably high yield by selectively esterification of **3** using lipase as catalyst. A critical step to stereoselectively inverse the configuration of **7** is realized under Mistunobu conditions.

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INTRODUCTION

The *trans*-(+)-sobrerol (**1**, *trans*-*p*-menth-6-ene-2,8-diol) is a well-known mucolytic drug.[1] Many other important biological activities of this compound have recently been found and attracted increasing attention.[2–3] For example, sobrerol was found to have chemopreventive activity to induce tumor cell apoptosis, and/or to inhibit the post-translational isoprenylation of cell growth-regulating proteins,[2] and to inhibit farnesyltransferase regulating the development of pulmonary hypertension.[3] More interestingly, *trans*-sobrerol (**1**) is also a versatile chiral tool in the asymmetric synthesis of a number of natural products.[4]

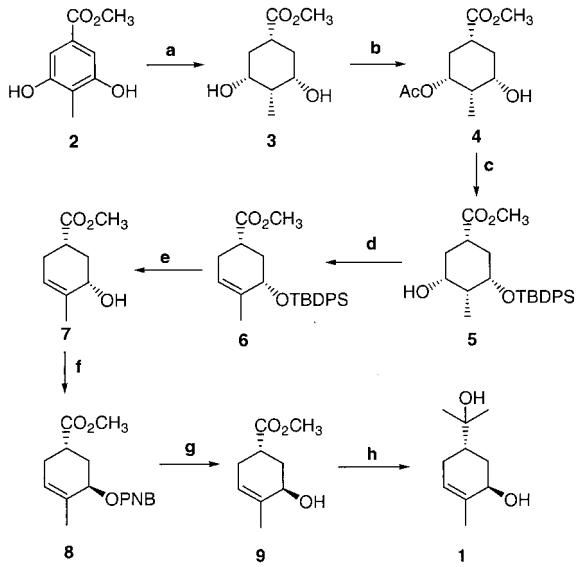
trans-(±)-Sobrerol is commercially available from Aldrich-Sigma. However, reports on the preparation of its optical active isomer, *trans*-(+)-sobrerol, are scarce. Literature methods on the synthesis of compound **1**, including acid-catalyzed cleavage[4] or $RuCl_3$ mediated ring-open[5] of (+)-2,3-epoxy-*cis*-pinane in aqueous systems, and kinetic resolution of (±)-*trans*-sobrerol by lipase-catalyzed acetylation,[1] suffer from either low yield or poor optical purity, and are not suitable for large scale preparation. Herein, we wish to report a convenient and highly efficient stereogenic synthesis of optically pure **1** using readily available starting materials (Sch. 1).

RESULTS AND DISCUSSION

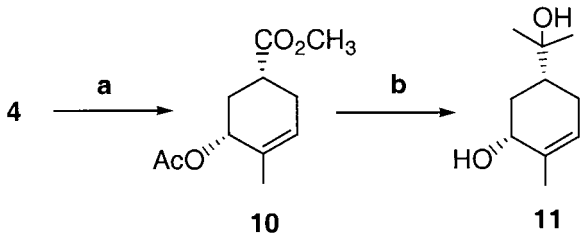
Methyl 3.5-dihydroxy-4-methyl benzoate (**2**) is converted in 65% yield to *all-cis*-3.5-dihydroxy-4-methyl-1-(methoxycarbonyl)cyclohexane (**3**) by Rh/Al_2O_3 catalyzed hydrogenation as described previously,[6,7] which is then esterified using vinyl acetate to generate 93% enantiomerically pure monoacetate (**4**) under enzyme catalyzed condition using lipase (Ps. Fluorescens, Fluka).

The enantiomeric excess is determined by subcritical fluid chromatography (SFC).[8] The absolute configurations of **3** and **4** could be deduced by the structure of *cis*-(−)-sobrerol **11**, which is prepared in two steps from **4** as outlined in Sch. 2. Compound **4** is dehydrated under Mitsunobu conditions,[9] and converted to the corresponding cyclohexene **10**, and further to cis-(-)-sobrerol, **11**, upon reaction with MeMgBr.[10]

Treating **4** *tert*-butyldiphenylsilyl chloride (TBDPS-chloride) and subsequently with K_2CO_3 in dry methanol, the expected TBDPS ether **5** is obtained in 84% yield, which is dehydrated under Mitsunobu conditions to give the corresponding TBDPS-cyclohexenol **6** in 92% yield. Removal of the TBDPS group of **6** using tetrabutylammonium fluoride (TBAF) in



Scheme 1. Reagents and conditions: a) H_2, 5%Rh/Al_2O_3, ethanol, 105□ for 24 h, 65%. b) lipase (Ps. fluorescens), r.t. for 72 h, 93%. c) (1) *t*-$BuPh_2SiCl$, imidazole, DMAP, DMF, r.t. for 20 h. (2) K_2CO_3, MeOH, r.t. for 7 h, 84%. d) Ph_3P, DEAD, THF, r.t. for 15 h, 92%. e) TBAF, THF, r.t. for 20 h, 90%. f) *p*-Nitrobenzoic acid, Ph_3P, DEAD, toluene, r.t. for 9 h, 78%. g) K_2CO_3, MeOH, r.t. for 8h, 93%. h) MeMgBr, THF, −78□ for 6 h, 85%.



Scheme 2. Reagents and conditions: a) Ph_3P, DEAD, THF, r.t. for 15 h, 92%. b) MeMgBr, THF, −78□ for 6 h, 86%.

THF at room temperature gives **7** in 90%. The key conversion to **8** is achieved in 78% yield using triphenylphosphine and *p*-nitrobenzoic acid in the presence of diethylazodicarboxylate at room temperature for 9 h. Deprotection of the *p*-nitrobenzoate ester **8** with anhydrous K_2CO_3 and

dry MeOH give **9** in 93% yield, which is further to converted the target compound, *trans*-(+)-sobrerol **1** in 85% yield with ee > 99% upon treatment with MeMgBr in THF at −78□. The structure of **1** is confirmed by NMR, MS, combustion analysis, which are identical with the literature report.[1,2]

In summary, we here have reported a very convenient, highly efficient method for the synthesis of *trans*-(+)-sobrerol (**1**), which is suitable for larger scale synthesis.

EXPERIMENTAL SECTION

Column chromatography was performed on silica gel. HPLC separations were performed on a Knauer 64 or a Kontron 420 delivery system with RI detection. Optical rotations were measured with a Perkin-Elmer 421 polarimeter. IR spectra were recorded on a Perkin-Elmer FTIR-1600 spectrometer, mass spectra on a HP-5988 Spectrometer. The ^{1}H NMR spectra were recorded at 500 MHz (Brucker AN-500), the ^{13}C NMR Spectra at 50 MHz (Varian Gemini-200). The chemical shifts (δ) are reported in parts per million with reference at 0 ppm (Me_4Si) or 7.26 ppm ($CHC1_3$) for the proton and at 77.0 ppm (centered on the signal of $CDCl_3$) for the carbon. Elemental analyses were carried out on a Perkin-Elmer 240B microanalyzer. Enantiomeric excess (ee) values are determined by SFC (Column chiralpak AD, Diacel, Japan, eluent CO_2 modified with 5% MeOH). All solvents and reagents are purchased from Aldrich, Sigma, or Fluka. Ester **3** is prepared according to the previous reports.[6,7]

(1R,3S,4S,5R)-5-Acetoxy-3-hydroxy-4-methyl-1-(methoxycarbonyl)cyclohexane (4)

A mixture of diol **3** (1.0 g, 5.5 mmol) and lipase (Ps. fluorescens) (650 mg, 42.5 U/mg) in vinyl acetate (30 mL) was stirred in the dark at room temperature. The reaction was monitored by TLC ($H_3PO_4/12MoO_3$ solution as indictor). After 72 h, the reaction mixture was filtered through a pad of celite. The filtrate was concentrated, and purified on a short (2.5 cm × 10 cm) silica gel column (*i*-octane/EtOAc, v/v, 5/5) to give a colorless oil (11.8 g, 93%). R_f 0.36 (*i*-octane/EtOAc, v/v, 5/5). $[\alpha]_D^{25} = -21.9$(c 0.81, $CHCl_3$), ee ≥ 99%. IR (film): $\nu = 3437$, 2953, 1730, 1472, 1439, 1365, 1242, 1197, 1178, 1078, 1026, 981,

875 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, $\delta = 4.8$ (m, 1H), 3.8 (m, 1H), 3.69 (s, 3H), 2.4 (m, 1H), 2.30 (d, $J = 6.4$ Hz, 1H), 2.05 (s, 3H), 1.9 (m, 2H), 1.8 (m, 3H), 0.96 (d, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, $\delta = 174.6$, 170.3, 72.1, 69.6, 52.0, 38.0, 37.6, 30.5, 27.3, 21.2, 6.21 ppm. MS: $m/z = (\%)$: 231 (M^++1,1), 213 (2), 199 (4), 186 (5), 170 (15), 152 (21), 127 (60), 111 (70), 93 (75), 87 (25), 82 (20), 43 (100). Anal. Calcd. for $C_{11}H_{18}O_5$, required: C, 57.38; H, 7.88%. Found: C, 57.21; H, 7.95%.

(1S,R,4R,5S)-5-*t*-Butyldiphenylsilyloxy-3-hydroxy-4-methyl-1-(methoxy-carbonyl)cyclochexane (5)

To a stirred solution of **4** (8.1 g, 35.2 mmol), imidazole (7.2 g, 105.7 mmol) and DMAP (2.2 g) in dry DMF (120 mL) was added dropwise *tert*-butyldiphenyl silyl chloride (TBDPSCl, 18 mL, 70.4 mmol). The mixture was stirred for 20h at room temperature before pouring into water-EtOAc (600 mL, v/v, 1/1). The organic layer was separated and then the aqueous layer was extracted with EtOAc (200 mL × 3). The combined extracts were washed with brine (150 × 3 mL), dried over anhydrous $MgSO_4$ and concentrated to give the crude product, which was then dissolved in 150 mL dry MeOH, and treated with K_2CO_3 (600 mg). The mixture was stirred at room temperature for 10 min. before the second portion K_2CO_3 (380 mg) was added. The mixture was allowed to stir for 6h at room temperature, then partitioned with EtOAc (300 mL) and water (200 mL). The organic phase was separated and aqueous phase was extracted with EtOAc (300 mL × 3). The organic phase and extracts were combined, dried over anhydrous magnesium sulfate, and concentrated under vacuum to give the crude product, which was further purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 9/1) to offer 5 (6.9 g, 98%) as a colorless oil. R_f 0.16 (*i*-octane/EtOAc, v/v, 8/2), $[\alpha]_D^{25} = +33.0$ (c 0.62, $CHCl_3$). IR (film): $\nu = 3448$, 2954, 2858, 1737, 1654, 1472, 1362, 1279, 1240, 1173, 1008, 852, 822, 795, 741, 702, 611 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, $\delta = 7.6$ (m, 4H), 7.4 (m, 2H), 7.4 (m, 4H), 3.70 (m, 1H), 3.64 (s, 3H), 3.5 (m, 1H), 2.2 (m, 1H), 2.1 (m, 1H), 1.8 (m, 1H), 1.69 (*t*, $J = 8.9$ Hz, 2H), 1.56 (q, $J = 12.4$ Hz, 1H), 1.37 (d, $J = 5.3$ Hz, 1H), 1.06 (s, 9H), 1.02 (d, $J = 7.0$ Hz, 3H). MS: m/z (%): 409 (1), 369 (7), 337 (7), 309 (5), 291 (35), 199 (100), 156 (85), 181 (17), 153 (34), 121 (23), 93 (68), 57 (47). Anal. Calcd. for $C_{25}H_{34}O_4$ Si, required: C, 70.38; H, 8.03%. Found: C, 70.55; H, 7.91%.

(4S,6S)-6-*t*-Butyldiphenylsilyloxy-1-methyl-4-(methoxycarbonyl)cyclohexene (6)

To a stirred solution of **5** (19.0 g, 45.0 mmol) and Ph_3P (57.7 g, 220 mmol) in THF (300 mL) at r.t., was added dropwise diethylazodicarboxylate (DEAD, 41 mL, 220 mmol). After stirring overnight at room temperature, the solution was concentrated. The residue was purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 95/5) to afford the expected compound **6** (16.7 g, 92%) as colorless oil. R_f 0.31 (*i*-octane/ EtOAc, 95:5), $[\alpha]_D^{25} = +81.8$ (c l.52, $CHCl_3$). IR (film): $\nu = 2952$, 2857, 1738, 1589, 1472, 1429, 1362, 1308, 1247, 1169, 1111, 1062, 1000, 934, 821, 740, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, $\delta = 7.7$ (m, 10H), 5.4 (m, 1H), 4.24 (s, 1H), 3.59 (s, 1H), 2.4 (m, 1H), 2.3 (m, 3H), 1.7 (m, 1H), 1.66 (s, 3H), 1.07 (s, 9H) ppm ^{13}C NMR (50 MHz, $CDCl_3$), $\delta = 175.2$, 137.5, 136.1, 134.4, 133.7, 129.6, 127.6, 121.9, 71.4, 51.6, 38.9, 35.2, 27.9, 27.1, 20.2, 19.5 ppm MS: *m*/*z* (%): 408 (M^+, 1), 354 (8), 351 (M^+-57, 20), 299 (5), 273 (6), 213 (100), 183 (75), 137 (70). Anal. Calcd. for $C_{25}H_{32}O_3$ Si, required: C, 73.49; H, 7.89%. Found: C, 73.25; H, 7.74%.

(4S,6S)-6-Hydroxyl-1-methyl-4-(methoxycarbonyl)cyclohexene (7)

To a stirred solution of **6** (13.7 g, 34 mmol) in THF (200 mL) was added TBAF (180 mL, **1**M in THF). The mixture was stirred for 20 h at room temperature. THF was evaporated, the residue was purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 8/2) to give the desired compound **7** (5.2 g, 90%) as a colorless oil. R_f 0.18 (*i*-octane/EtOAc, v/v, 8/2). To a stirred solution of **6** (13.7 g, 34 mmol) in THF (200 mL) was added TBAF (180 mL, 1 M in THF). The mixture was stirred for 20 h at room temperature. THF was evaporated, the residue was purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 8/2) to give the desired compound **7** (5.2 g, 90%) as a colorless oil. R_f 0.18 (*i*-octane/EtOAc, v/v, 8/2). $[\alpha]_D^{25} = +16.8$ (c 0.66, $CHCl_3$). IR (film): $\nu = 3432$, 2951, 2850, 1735, 1455, 1435, 1382, 1247, 1185, 1170, 1035, 925 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, $\delta = 5.45$ (t, $J = 1.5$ Hz, 1H), 4.08 (*t*, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 2.7 (m, 1H), 2.3 (m, 3H), 2.15 (brs, 1H), 1.9 (m, 1H), 1.78 (s, 3H). MS *m*/*z* (%): 170 (M^+, 3), 152 (20), 137 (15), 111 (30), 93 (100), 77 (30), 43(50). Anal. Calcd. for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29%. Found: C, 63.31; H, 8.40%.

(4S,6R)-1-Methyl-6-(4′-nitrobenzoyloxy)-4-(methoxycarbonyl)cyclohexene (8)

To a stirred solution of **7** (3.5 g, 16.5 mmol), 4-nitrobenzoic acid (3.04 g, 18.2 mmol) and Ph_3P (4.76 g, 18.2 mmol) in THF (200 mL) was added dropwise DIAD (34 mL, 18.2 mmol) over a period of 30 min at 0–10□, then the reaction mixture was stirred at room temperature for 9 h before filtering through a pad of celite and washing with ethyl acetate. The yellow filtrate was evaporated. The residue was further purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 9/1) to afford 4-nitrobenzoate ester **8** (5.12 g, 78%) as a colorless oil. R_f 0.3 (*i*-octane/EtOAc, v/v, 9/1). $[\alpha]_D^{25} = +281.5$ (c 1.38, $CHCl_3$), IR (film): $\nu = 2950$, 1719, 1607, 1527, 1436, 1343, 1267, 1196, 1167, 1101, 1013, 946, 921, 873, 848, 720 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$ $\delta = 8.29$ (d, $J = 7.9$ Hz, 2H), 8.22 (d, $J = 7.9$ Hz, 2H), 5.79 (brs, 1H), 5.54 (s, 1H), 3.69 (s, 3H), 2.8 (m, 1H), 2.45 (d, $J = 17.8$ Hz, 1H), 2.32 (d, $J = 11.6$ Hz, 1H), 2.25 (*t*, $J = 13.2$ Hz, 1H), 2.0 (m, 1H), 1.75(s, 3H) pp. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 175.5$, 164.5, 150.8, 135.9, 127.1, 123.7, 77.8, 77.2, 76.5, 71.2, 52.0, 35.1, 28.0, 20.9 ppm. MS *m*/*z* (%): 319 (M^+, 1), 259 (8), 152 (20), 150 (75), 121 (20), 93 (100). 77 (40), 50 (30). Anal. Calcd. for $C_{16}H_{17}NO_6$, required: C, 60.18; H, 5.37; N, 4.39%. Found: C, 59.87; H, 5.11; N, 4.01%.

(4S,6R)-6-Hydroxyl-1-methyl-4-(methoxycarbonyl)cyclohexene (9)

To the solution of 4-nitrobenzoate ester **8** (5.0 g, 15.7 mmol) in MeOH (200 mL) was added K_2CO_3 (108 g, 7.85 mmol). The mixture was stirred at room temperature for 8 h before partitioning with EtOAc (300 mL) and water (200 mL). The organic layer was separated, the aqueous layer was extracted with EtOAc (3×100 mL). The combined organic layer and extracts were washed with brine (3×60 mL), dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography over silica gel (*i*-octane/EtOAc, v/v, 8/2) to yield the expected product **9** (2.48 g, 93%) as a colorless oil. R_f 0.22 (*i*-octane/EtOAc, v/v, 8/2). $[\alpha]_D^{25} = +156.3$ (c 0.6, $CHCl_3$). IR (film): $\nu = 3406$, 2952, 1734, 1437, 1250, 1197, 1053, 966, 809 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.56$ (q, $J = 1.4$Hz, 1H), 4.05 (brs, 1H), 3.69 (s, 3H), 2.7 (m, 1H), 2.2 (m, 2H), 1.79 (m, 4H), 1.61 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 176.0$, 134.4, 123.8, 67.3, 51.8, 34.3, 34.2, 27.9, 20.8 ppm, MS *m*/*z* (%): 170 (M^+,15), 139 (15), 120 (10), 110 (70), 95 (100), 77 (70), 67 (50), 55 (80), 43 (70). Anal. Calcd.

for $C_9H_{14}O_3$ (170.21): required: C, 63.51; H, 8.29%. Found: C, 63.42; H, 8.37%.

(4S,6R)-6-Hydroxyl-4-(1-hydroxyisopropyl)-1-methylcyclohexene (1) (*trans*-(+)-Sobrerol) (1)

To a stirred solution of **9** (2.5 g, 11.8 mmol) in THF (60 mL) at −78□ was added dropwise MeMgBr (66 mL, 3.0 M in Et_2O). The mixture was stirred for 6 h at −78□ before slowly warming up room temperature. The mixture is further stirred overnight at room temperature. The reaction was quenched with aqueous saturated NH_4Cl (50 mL) and extracted with EtOAc (3 × 200 mL). The combined organic layers were washed with brine (3 × 100 mL), dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography (*i*-octane/EtOAc, v/v, 6/4) and crystallized from CH_2Cl_2 to give the desired compound **1** (1.68 g, 85%) as colorless needle. m.p. 130–132□, R_f 0.22 (*i*-octane/EtOAc, v/v, 1/1)□ $[\alpha]_D^{25} = +133.4$ (c 0.31, $CHCl_3$), ee ≥ 99%. IR (film)□ $\nu = 3274$□2973□1629□1468□1425□1376□1294 □1251□1156□1052□984□920□824□761□662□611 □468 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.58$ (q, $J = 1.4$ Hz, 1H), 4.05 (s, 1H), 2.1 (m, 1H), 2.01 (dd, $J = 13.4$, 1.4 Hz, 1H), 1.80(s, 3H), 1.8 (m, 1H), 1.54 (br s, 2H),1.4 (m, 2H), 1.22 (s, 2H), 1.19 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 133.5$, 125.5, 72.4, 68.8, 39.0, 32.9, 27.7, 27.2, 21.0 ppm. MS: *m*/*z* (%): 152(M^+-18,6), 149 (7), 137 (10), 119 (5), 109 (55), 97 (8), 95 (15), 79 (50), 69 (25), 59 (90), 55 (35), 43 (100). Anal. Calcd for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66%. Found: C, 70.61; H, 10.85%.

(4R,6R)-6-Acetoxy-1-methyl-4-(methoxycarbonyl)cyclohexene (10)

To a stirred solution of monoacetate **4** (420 mg 1.67 mmol) and Ph_3P (1.32 g, 5.02 mmol) in THF (30 mL) at room temperature was added dropwise DIAD (0.93 mL, 5.02 mmol). After stirring overnight at room temperature, the solution was concentrated under vacuum. The residue was purified by column chromatography over silica gel (*i*-octane/EtOAc, v/v, 95/5) to afford **10** (356 mg, 92%) as a colorless oil. To a stirred solution of monoacetate **4** (420 mg, 1.67 mmol) and Ph_3P (1.32 g, 5.02 mmol) in THF (30 mL) at room temperature was added dropwise DIAD (0.93 mL, 5.02 mmol). After stirring overnight at room temperature, the solution was concentrated under vacuum. The residue was purified by column chromatography over silica gel (*i*-octane/EtOAc,

v/v, 95/5) to afford **10** (356 mg, 92%) as a colorless oil. R_f 0.35 (i-octane/EtOAc, v/v, 9/1). $[\alpha]_D^{25} = -50.5$ (c 0.72, $CHC1_3$). IR (film): $\nu = 3070$, 2951, 2850, 1736, 1456, 1436, 1370, 1343, 1239, 1170, 1074, 1028, 987, 932 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.48$ (d, $J = 1.5$ Hz, 1H), 5.35 (br s, 1H), 3.67 (s, 3H), 2.7 (m, 1H), 2.4 (m, 3H), 2.05 (s, 3H), 1.8 (m, 1H), 1.63 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 174.7$, 170.8, 132.6, 124.7, 71.1, 51.7, 37.6, 31.0, 27.3, 21.0, 19.1 ppm. MS m/z (%): 212 (M^+□5) □199 (8), 184 (8), 170 (95), 152 (85), 139 (62), 121 (45), 111 (75), 93 (100), 77 (80). Anal. Calcd. for $C_{11}H_{15}O_4$, required: C, 62.55; H, 7.16%. Found: C, 62.18; H, 7.23%.

(4R,6R)-6-Hydroxy-4-(1-hydroxyisopropyl)-1-methylcyclohexene (*cis*-(−)-Sobrerol (11)

This compound was prepared as the same method as described for compound **1**. Yield: 86%. M.p. 109–110□. R_f 0.18 (*i*-octane/EtOAc, v/v, 5/5). $[\alpha]_D^{25} = -20.1$ (c 0.72, $CHCl_3$) {lit.[7] $[\alpha]_D^{25} = -16$}. IR (film): $\nu = 3283$, 2969, 2944, 2886, 2849, 1454, 1383, 1320, 1256, 1167, 1148, 1109, 1037, 974, 922 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 5.47$ (t, $J = 1.45$ Hz, 1H), 4.16 (brs, 1H), 2.2 (m, 1H), 2.05 (m, 1H), 1.89 (m, 1H), 1.74 (s, 3H), 1.6 (m, 1H), 1.54 (brs, 2H), 1.32 (m, 1H), 1.19 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.3$, 123.6□ 72.2, 70.8, 43.8, 34.2, 27.3, 26.9, 26.4, 18.7 ppm. MS m/z (%): 169 (M^+-1,4), 152 (13), 149 (4), 137 (16), 119 (11), 109 (59), 94 (57), 79 (60), 69 (34), 59 (100). Anal. Calcd. for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66%. Found: C, 70.38; H, 10.72%.

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