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Preparation of (2*R*,3*S*)-(−)- and (2*S*,3*R*)-(+)-2,3-Epoxy-2-methylbutanoic Acids and Some of Their Esters

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Abstract: Enantiomerically pure (2*R*,3*S*)-(−)- and (2*S*,3*R*)-(+)-2,3-epoxy-2-methylbutanoic acids **7** and **8** were prepared from 2-methyl-2-butenoic acid **1** (*tiglic acid*). They were characterized by spectroscopic and optical activity data and their absolute configuration was determined by chemical correlation with (*R*)-(+)- and (*S*)-(−)-2-methyl-1,2-butanediols. The corresponding methyl (**16** and **17**), menthyl (**3** and **4**), and 9α-angeloyloxy-1-oxolongipin-2-en-7β-yl (**14** and **15**) esters were also prepared.

INTRODUCTION

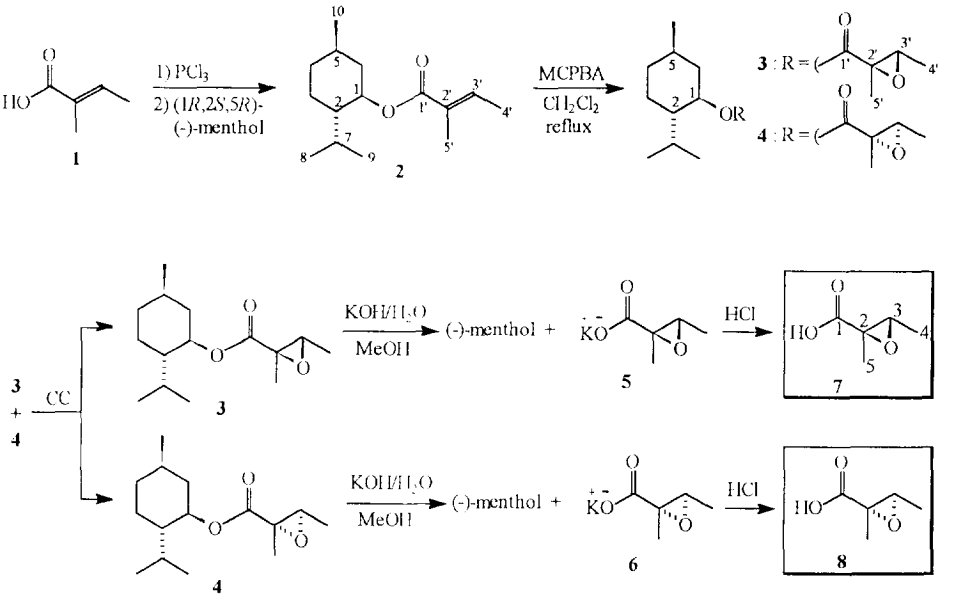
2,3-Epoxy-2-methylbutanoate residues have been found as part of the structures of some natural products[1-4]. In most cases the absolute stereochemistry is unknown[5-9] and in some cases there are uncertainties about its relative stereochemistry.[3,4] A literature search revealed that besides methyl (2*R*,3*R*)-(+)-2,3-epoxy-2-methylbutanoate,[10] the optical activity data for the remaining 2,3-epoxy-2-methylbutanoic acids and methyl esters have not been measured, and thus their absolute configuration has not been determined. In this paper we describe the preparation and absolute configuration of the two enantiomers **7** and **8**, as well as the incorporation of these moieties into some natural products. The data presented herein can be useful to prepare other substances which contain such ester residues and to assign their stereochemistry.

RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of (2*R*,3*S*)-(−)- and (2*S*,3*R*)-(+)-2,3-epoxy-2-methylbutanoic acids (**7** and **8**) which were prepared from tiglic acid **1** in a six-step protocol: (1) transformation to tigloyl chloride; (2) esterification with (1*R*,2*S*,5*R*)-(−)-menthol to give **2**; (3) epoxidation of **2** with MCPBA to give a mixture of **3** and **4**; (4) chromatographic separation of diastereoisomers **3** and **4**; (5) hydrolysis with KOH in MeOH/H_2O to give enantiomerically pure **5** and **6** and (6) neutralization with HCl to generate epoxyacids **7** and **8**.

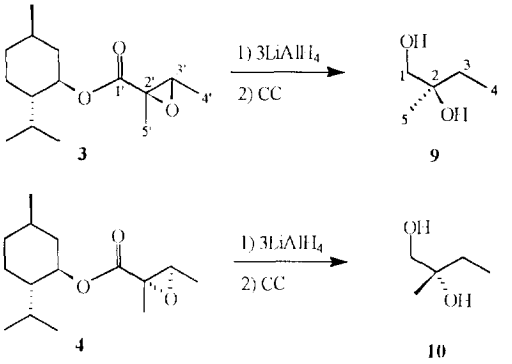
Esterification of tiglic acid **1** with (−)-menthol gave **2** in good yields (*ca.* 95 %). Epoxidation of **2** yielded a 46:54 mixture of **3** and **4** (90 %), as measured by the ^{1}H-NMR spectrum of the crude product, in which the H-3' signal of **3** (*q*, J = 5.4 Hz) appeared at 3.26 ppm, while that for **4** appeared at 3.25 ppm (*q*, J = 5.5 Hz). The mixture of diastereoisomers was separated on a silica gel column using hexane-EtOAc (97:3) as the eluent and the purity of the diasteroisomers (**3** and **4**) was carefully monitored by ^{1}H-NMR at 300 MHz.

Scheme 1



Both esters (**3** and **4**) had negative optical activity $[\alpha]_D^{20} = -69$ (c = 3.3, $CHCl_3$) and $[\alpha]_D^{20} = -76.1$ (c = 3.3, $CHCl_3$), respectively. Each ester was hydrolyzed with aqueous KOH in MeOH at room temperature to give potassium salts **5** and **6** (90 %). The chiral auxiliary, (–)-menthol, was recovered in high yields. Potassium salt **5** showed a positive optical rotation $[\alpha]_D^{20} = +10.0$ (c = 1.50, H_2O), while **6** showed the corresponding negative optical rotation $[\alpha]_D^{20} = -10.0$ (c = 1.50, H_2O). Finally, neutralization of **5** and **6** with aqueous HCl (20%), gave enatiomerically pure **7** $[\alpha]_D^{20} = -5.5$ (c = 12.0, $CHCl_3$), and **8** $[\alpha]_D^{20} = +5.5$ (c = 12.0, $CHCl_3$), respectively.

Scheme 2



9: $[\alpha]_D^{20} = +7.6$ (c = 1.32, $CHCl_3$) (this work).

9: $[\alpha]_D^{20} = +8.7$ (c = 1.35, $CHCl_3$), ee = 94 % (ref. 11).

The absolute configuration of **3-8**, depicted in Scheme 1, was determined by chemical correlation of ester **3** with known[11] (*R*)-(+)-2-methyl-1,2-butanediol (**9**). Treatment of **3** with $LiAlH_4$ in THF gave (*R*)-(+)-2-methyl-1,2-butanediol (**9**). Under the same conditions **4** gave (*S*)-(−)-2-methyl-1,2-butanediol (**10**), as shown in Scheme 2.

Potassium salts **5** and **6** reacted with oxalyl chloride[12] $(COCl)_2$ to give acyl chlorides **11** and **12**, respectively. In order to further evaluate the enantiomeric purity of **5-8**, we allowed to react acyl chlorides **11** and **12** with the sesquiterpene **13**,[13] which has six chiral centers, this yielding esters **14** (37 %) and **15** (40 %), respectively, as shown in Scheme 3. The low yields are probably due to the fact that epoxides can act as HCl scavengers.[14] Therefore, an alternative preparation of diastereoisomers **14** and **15** was carried out by treatment

Scheme 3

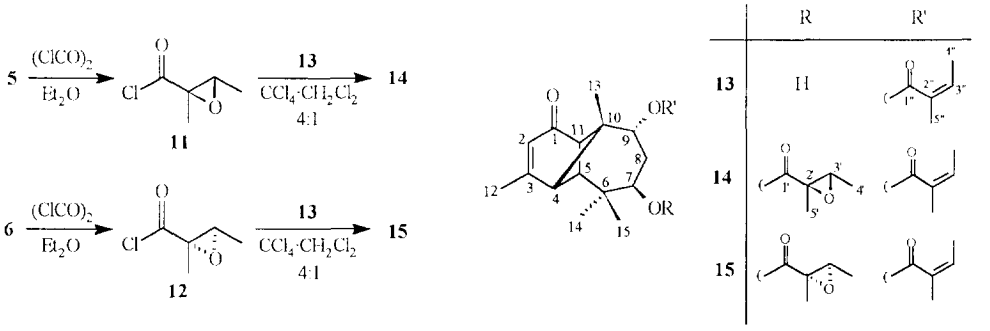


Table 1: ^1H (300 MHz) and ^{13}C (75.4 MHz)-NMR data of compounds **5-10**, **16** and **17**, δ in ppm, (multiplicities) internal standard TMS, solvent $CDCl_3$, unless otherwise stated.

Proton	Compound				Carbon	Compound			
	5/6[a]	**7/8**[b]	**9/10**[c]	**16/17**		**5/6**[d]	**7/8**	**9/10**	**16/17**
H-1	-	-	3.48(d)	-	C-1	178.72	175.81	69.32	171.95
H-1'	-	-	3.41(d)	-	C-2	61.34	57.58	73.35	57.42
H-3	3.01(q)	3.34(q)	1.53(q)	3.31(q)	C-3	58.73	58.57	31.08	58.02
Me-4	1.16(d)	1.38(d)	0.93(t)	1.35(d)	C-4	12.26	13.39	8.05	13.44
Me-5	1.29(s)	1.54(s)	1.16(s)	1.51(s)	C-5	13.50	12.71	22.50	13.29
MeO	-	-	-	3.74(s)	MeO	-	-	-	52.47

[a]Solvent D_2O, HDO signal centered at 4.63 ppm.

[b]COOH: 7.00 ppm (br s).

[c]OH: 2.76 and 2.43 ppm (br s).

[d]Solvent D_2O, 1,4-dioxane as internal standard centered at 66.40 ppm.

J (in Hz) **5**: J_{3-4}=5.6; **7**: J_{3-4}=5.5; **9**: $J_{1-1'}$= 10.8, J_{3-4}=7.6; **16**: J_{3-4}=5.4.

of **13** with epoxyacids 7 or **8** in the presence of dicyclohexylcarbodiimide and 4-*N,N*-dimethylaminopyridine, giving better yields of either **14** (80 %) or **15** (70 %), respectively. These compounds were characterized by spectroscopic data and by comparison of data from closely related longipinene derivatives.[13] Very detailed inspection of the ^{1}H-NMR spectra confirmed the purity of each diastereoisomer. Finally, for comparative purposes with methyl (2*R*,3*R*)-(+)-2,3-epoxy-2-methylbutanoate,[10] methyl (2*R*,3*S*)-(−)-2,3-epoxy-2-methylbutanoate **16** and methyl (2*S*,3*R*)-(+)-2,3-epoxy-2-methylbutanoate **17** were prepared from **7** and **8**, respectively, by treatment with diazomethane.

EXPERIMENTAL SECTION

^{1}H, ^{13}C, COSY, and HETCOR NMR spectra: Varian XL-300 GS. ^{1}H measured at 300 MHz, ^{13}C at 75 MHz. TMS as internal standard, solvent $CDCl_3$, unless otherwise stated. IR spectra: Perkin Elemer 16F PC FT-IR spectrophotometer, recorded in $CHCl_3$, unless otherwise stated. UV-spectra: Unicam SP-800. Mass-spectra: 70 eV. Specific Rotations: Perkin-Elmer 241-Polarimeter. Column Chromatography (CC): Merck silica gel, particle size 0.040-0.063 mm (230-400 mesh ASTM).

Menthyl (2'R,3'S)- and (2'S,3'R)-2',3'-epoxy-2'-methylbutanoate (**3**) *and* (**4**). A solution of menthyl tiglate (**2**)[15] (10 g) in CH_2Cl_2 (40 ml) was treated with MCPBA (80-90 %) (10 g). The mixture was stirred for 12 h at 35 °C, cooled and filtered. The solution was stirred with a saturated solution of $NaHCO_3$ for 1 h at 0 °C and extracted with CH_2Cl_2. The organic layer was washed with water, dried with Na_2SO_4 and evaporated under vacuum to give a mixture of **3** and **4** (9.8 g, 92 %). A portion of this mixture (1 g) was chromatographed over silica gel (60 g) with hexane-EtOAc (97:3) as the eluent to yield pure **3** (50 mg, 5 %), a mixture of **3** and **4** (890 mg, 89 %), and **4** (60 mg, 6 %). The mixture of **3** and **4** (890 mg) could be fully separated by successive rechromatographies under the same conditions. **3**: ^{1}H-NMR: δ = 4.73 (*d/t*, *J* = 4.4/10.8 Hz, H-1), 1.07 (*m*, H-2), 1.72 (*m*, H-3eq), 1.47 (*m*, H-4), 1.16 (*m*, H-5), 1.97 (*m*, H-6eq), 1.00 (*m*, H-6ax), 1.85 (*d sep*, *J* = 2.7/6.9 Hz, H-7), 0.89 (*d*, *J* = 6.9 Hz, Me-8,9), 0.76 (*d*, *J* = 6.9 Hz, Me-8,9), 0.91 (*d*, *J* = 7.0 Hz, Me-10), 3.26 (*q*, *J* = 5.5 Hz, H-3'), 1.34 (*d*, *J* = 5.5 Hz, Me-4'), 1.49 (*s*, Me-5') ppm. ^{13}C-NMR: δ = 75.52 (C-1), 46.94 (C-2), 23.60 (C-3), 31.41 (C-4), 34.22 (C-5), 40.71 (C-6), 26.36 (C-7), 20.68 (C-8,9), 16.44 (C-8,9), 21.98 (C-10), 171.10 (C-1'), 57.65 (C-2'), 57.70 (C-3'), 13.49 (C-4'), 13.38 (C-5') ppm. IR ($CHCl_3$): ν_{max} =1720, 1456, 1292, 1184, 1128 cm^{-1}. **4**: ^{1}H-NMR: δ = 4.72 (*d t*, *J* = 4.4/10.9 Hz, H-1), 1.10 (*m*, H-2), 1.71 (*m*, H-3eq), 1.48 (*m*, H-4), 1.15 (*m*, H-5), 2.00 (*m*, H-6eq), 1.03 (*m*, H-6ax), 1.83 (*d sep*, *J* = 2.8/7.0 Hz, H-7), 0.90 (d, J = 7.0 Hz, Me-8,9), 0.75 (*d*, *J* = 7.0 Hz, Me-8,9), 0.90 (*d*, *J* = 6.7 Hz, Me-10), 3.25 (*q*, J = 5.5 Hz, H-3'), 1.35 (*d*, *J* = 5.5 Hz, Me-4'), 1.50(*s*, Me-5') ppm. ^{13}C-NMR: δ. 75.54 (C-1), 46.81 (C-2), 23.15 (C-3), 31.34 (C-4), 34.11 (C-5), 40.59 (C-6), 26.15 (C-7), 20.79 (C-8,9), 16.03 (C-8,9), 21.92 (C-10), 171.01 (C-1'), 57.59 (C-2'), 57.82 (C-3'), 13.49 (C-4'), 13.37 (C-5') ppm. IR ($CHCl_3$): ν_{max} = 1724, 1456, 1292, 1182, 1128 cm^{-1}.

Potassium salts of (2R,3S)-(+)- and (2S,3R)-(+)-2,3-epoxy-2-methylbutanoic acids (**5**) *and* (**6**). A solution of **3** (0.50 g) or a solution of **4** (0.50 g) in MeOH (10 ml) was stirred with aqueous KOH (0.11 g) for 2 h at room temperature. The solvent was removed with a nitrogen stream and acetone (10 ml) was added to precipitate each potassium salt. The suspension was filtered and washed with acetone (10 ml) to give potassium salt **5** (270 mg, 90%) or salt **6** (275 mg, 91 %). The chiral auxiliar, (−)-menthol, was recovered after evaporation of acetone. ^{1}H- and ^{13}C-NMR (see Table 1). IR (KBr): ν_{max} = 1620, 1406, 866, 764, 724 cm^{-1}.

(2R,3S)-(+)- and (2S,3R)-(+)-2,3-Epoxy-2-methylbutanoic acids (**7**) *and* (**8**). A solution of potassium salt **5** or potassium salt **6** (380 mg, each) in water (5 ml), was neutralized with 20 % HCl and extracted with Et_2O. The organic layer was dried with Na_2SO_4 and the solvent was evaporated to provide **7** (208 mg, 73 %) or **8**

(200 mg, 70 %) respectively. ^{1}H- and ^{13}C-NMR (see Table 1). IR ($CHCl_3$): ν_{max} = 3668, 3498, 1732, 1454, 1240, 1182, 1100 cm^{-1}. MS: m/z (%) = 116 (M^+, 12), 100 (7), 88 (8), 73 (30), 72 (14), 43 (100), 41 (5), 39 (3), 36 (2).

(2R)-(+)-2-Methyl-1,2-butanediol (**9**). A solution of ester **3** (320 mg.) in THF (10 ml) was treated with $LiAlH_4$ (190 mg) at 0 °C. The mixture was stirred under reflux for 4 h, cooled to 0 °C, treated with EtOAc, (10 ml) MeOH (10 ml) and H_2O (10 ml), filtered and extracted with more EtOAc (25 ml). The organic layer was washed with H_2O, dried with Na_2SO_4 and evaporated under vacuum. The crude product was chromatographed on silica gel eluting with CH_2Cl_2 followed by CH_2Cl_2-EtOAc 1:1 (v/v). The CH_2Cl_2 fractions gave (–)-menthol and the CH_2Cl_2-EtOAc fractions gave **9** (100 mg, 76 %) as colorless oil identical with that reported in ref. 5. ^{1}H- and ^{13}C-NMR (see Table 1). $[\alpha]_D^{20}$ = + 7.6 (*c* = 1.32, $CHCl_3$).

(2S)-(–)-2-Methyl-1,2-butanediol (**10**). Prepared as diol **9**, but starting from **4** (91 mg, 69 %). $[\alpha]_D^{20}$ = –7.5 (*c* = 1.32, $CHCl_3$). ^{1}H- and ^{13}C-NMR (see Table 1).

9α-Angeloyloxy-7β-[(2R,3S)-2,3-epoxy-2-methylbutyryloxy]-1-oxolongipin-2-ene (**14**). Acyl chloride **11** was obtained from potassium salt **5** as described in ref. 6 for angeloyl chloride. A solution of **11** (50 mg) in CCl_4-CH_2Cl_2 4:1 (10 ml) was treated with 7β-hydroxy-9α-angeloyloxy-1-oxolongipin-2-ene (**13**) (100 mg). The mixture was stirred for 48 h at 25 °C. The solvents were evaporated and the crude product was chromatographed on silica gel using CH_2Cl_2 as the eluent. The initial fractions yielded diester **14** (50 mg, 37 %). ^{1}H-NMR: δ = 5.80 (*sext*, *J* = 1.4 Hz, H-2), 2.65 (*d*, *J* = 1.4 Hz, H-4), 2.33 (*s*, H-5), 5.05 (*d/d*, *J* = 1.8/11.9 Hz, H-7), 2.22 (*d/d/d*, *J* = 3.0/11.9/14.7 Hz, H-8$_\beta$), 2.10 (*d/d/d*, *J* = 1.8/3.0/14.7 Hz, H-8$_\alpha$), 5.13 (*d/d*, *J* = 3.0 Hz, H-9), 3.11 (*d/d*, *J* = 1.4/6.7 Hz, H-11), 2.08 (*d*, *J* = 1.4 Hz, Me-12), 1.00 (*s*, Me-13), 1.08 (*s*, Me-14), 0.90 (*s*, Me-15), 3.27 (*q*, *J* = 5.5 Hz, H-3'), 1.33 (*d*, *J* = 5.5 Hz, Me-4'), 1.50 (*s*, Me-5'), 6.13 (*q/q*, *J* = 1.5/8.5 Hz, H-3"), 2.03 (*d/q*, *J* = 1.4/8.5 Hz, Me-4"), 1.98 (*d/q*, *J* = 1.4 Hz, Me-5") ppm. ^{13}C-NMR: δ = 202.69 (C-1), 122.85 (C-2), 170.52 (C-3,1'), 48.44 (C-4), 65.64 (C-5), 32.33 (C-6), 74.32 (C-7), 37.44 (C-8), 73.97 (C-9), 55.89 (C-10), 54.03 (C-11), 23.33 (C-12), 21.33 (C-13), 18.81 (C-14), 26.12 (C-15), 170.12 (C-3,1'), 57.52 (C-2'), 57.76 (C-3'), 13.47 (C-4'), 13.28 (C-5'), 167.09 (C-1"), 127.81 (C-2"), 139.08 (C-3"), 15.89 (C-4"), 20.61 (C-5") ppm. IR ($CHCl_3$): ν_{max} = 1714, 1674, 1616, 1454, 1288, 1182, 1146 cm^{-1}. UV (EtOH): λ_{max} 226 (ε 9435), λ_{max} 250 (ε 8695). $[\alpha]_D^{20}$ = + 38.1 (*c* = 1.6, $CHCl_3$). MS: m/z (%) = 430 (M^+, 2.5), 347 (2), 331 (3), 303 (4), 231 (7), 214 (14), 187 (15), 173 (14), 145 (11), 122 (10), 83 (100), 55 (58), 43 (38).

9α-Angeloyloxy-7β-[(2S,3R)-2,3-epoxy-2-methylbutyryloxy]-1-oxolongipin-2-ene (**15**). Prepared as diester **14**, but using the acyl chloride **12**, obtained from potassium salt **6**, (54 mg, 40 %). ^{1}H-NMR: δ = 5.81 (*sext*, *J* = 1.4 Hz, H-2), 2.66 (*d*, *J* = 1.4 Hz, H-4), 2.32 (*s*, H-5), 5.04 (*d/d*, *J* = 1.9/11.9 Hz, H-7), 2.23 (*d/d/d*, *J* = 3.1/11.9/14.8 Hz, H-8$_\beta$), 5.12 (*d/d*, *J* = 3.1 Hz, H-9), 3.11 (*d/d*, *J* = 1.4/6.8 Hz, H-11), 2.06 (*d*, *J* = 1.4 Hz, Me-12), 1.00(*s*, Me-13), 1.07 (*s*, Me-14), 0.91 (*s*, Me-15), 3.24 (*q*, *J* = 5.4 Hz, H-3'), 1.35 (*d*, *J* = 5.4 Hz, Me-4'), 1.49 (*s*, Me-5'), 6.12 (*q/q*, *J* = 1.4/8.6 Hz, H-3"), 2.02 (*d/q*, *J* = 1.4/8.6 Hz, Me-4"), 1.97 (*d/q*, *J* = 1.4 Hz, Me-5") ppm. ^{13}C-NMR: δ = 202.80 (C-1), 122.84 (C-2), 170.55 (C-3,1'), 48.38 (C-4), 65.62 (C-5), 32.18 (C-6), 74.32 (C-7), 37.41 (C-8), 74.18 (C-9), 55.89 (C-10), 53.99 (C-11), 23.37 (C-12), 21.34 (C-13), 18.90 (C-14), 26.29 (C-15), 170.21 (C-3,1'), 57.47 (C-2'), 58.04 (C-3'), 13.47 (C-4'), 13.36 (C-5'), 167.17 (C-1"), 128.83 (C-2"), 139.03 (C-3"), 15.83 (C-4"), 20.62 (C-5") ppm. IR ($CHCl_3$): ν_{max} = 1738, 1674, 1614, 1438, 1284, 1232, 128 cm^{-1}. UV (EtOH): λ_{max} 224 (ε 9250), λ_{max} 250 (ε 8510). $[\alpha]_D^{20}$ = + 45.3, (*c* = 1.7, $CHCl_3$). MS: m/z (%) = 430 (M^+, 6), 331 (5), 303 (6), 214 (25), 199 (22), 187 (21), 173 (20), 122 (17), 121 (13), 83 (100), 55 (50), 43 (28).

Alternative preparation of diesters **14** *and* **15**. A solution of **13** (234 mg) in CH_2Cl_2 (5 ml) was treated with CH_2Cl_2 solutions of dicyclohexylcarbodiimide (887 mg in 5 ml), *N,N*-dimethylaminopyridine (80 mg in 2

ml) and either (2*R*,3*S*)- or (2*S*,3*R*)-2,3-epoxy-2-methtylbutanoic acid (100 mg in 5 ml), at room temperature for 48 h. In each case, the reaction mixture was filtered and chromatographed on silica gel using hexane-EtOAc (97:3) followed by hexane-EtOAc (9:1) as the eluent to give **14** (250 mg, 78 %) and **15** (220 mg, 69 %), respectively.

Methyl (2R,3S)-(-)- and (2S,3R)-(+)-2,3-Epoxy-2-methylbutanoates (**16**) *and* (**17**). A solution of (2*R*,3*S*)- or (2*S*,3*R*)-2,3-epoxy-2-methylbutanoic acid (7 or **8**, respectively) (100 mg) in Et_2O (20 ml) was treated with an ethereal solution of diazomethane[16] at room temperature. After evaporation of the solvent, methyl esters **16** (91 mg, 83 %) $[\alpha]_D^{20} = -7.2$ (*c* = 7.0, $CHCl_3$) and **17** (101 mg, 90 %) $[\alpha]_D^{20} = +8.0$ (*c* = 7.0, $CHCl_3$) were obtained. ^1H- and ^{13}C-NMR (see Table 1). IR ($CHCl_3$): ν_{max} = 1725, 1454, 1312, 1156, 1104 cm^{-1}.

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