residue was purified on a short column (15 × 3 cm), which was developed with hexane (to remove iodobenzene) and then with 8:1 hexane–ethyl acetate. The syrup thus obtained (0.36 g, 42%), which showed a single spot in TLC (R_f 0.66, 3:1 toluene–acetone), crystallized on storage (1 week at −14 °C) as colorless needles; mp 71–72 °C; $[\alpha]^{23}_D$ −78° (c 1.1, dichloromethane); IR (Nujol) 1755 (C=O), 735 (C—Cl) cm^{-1}; ^{13}C NMR δ 169.9 (C=O), 91.4 (C-1), 70.0 (C-3), 69.8 (C-4), 68.6 (C-5), 60.3 (C-2), 20.5 (OAc), and 17.0 (C-6).

Anal. Calcd for $C_{10}H_{14}Cl_2O_5$: C, 42.12; H, 4.95; m/z (M^+ − Cl$^·$) 249.052968. Found: C, 42.33; H, 5.11; m/z 249.053660.

3,4-Di-*O*-acetyl-2-chloro-2,6-dideoxy-β-L-glucopyranosyl Chloride (1b). Compound **1** (0.081 g, 0.38 mmol) was chlorinated in nitromethane (2 mL) under the conditions described for the preparation of **1a** and **1d**. The syrup obtained after evaporation of the solvent was purified by LC (μPorasil column, 0.78 × 30 cm, at a flow rate of 3.0 mL/min) with 8:1 hexane–ethyl acetate as solvent. The fractions containing the compound having t_R 6.6 min were pooled, evaporated, and dried at room temperature at 3.3 torr to afford a crystalline sample of **1b**: yield 9.0 mg (8%); mp 67–69 °C; $[\alpha]^{23}_D$ −45° (c 0.7, dichloromethane); IR (Nujol) 1755 (C=O), and 735 (C—Cl) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}Cl_2O_5$: m/z (M^+ − Cl$^·$) 249.052968. Found: m/z 249.053660.

3,4-Di-*O*-acetyl-2-bromo-2,6-dideoxy-α-L-gluco- and -α-L-mannopyranosyl Bromides (1e and 1f). L-Rhamnal diacetate (1, 0.856 g, 4 mmol) dissolved in carbon tetrachloride (20 mL) was treated for 10 min at 0 °C with a slight excess of bromine. Evaporation of the solvent under diminished pressure at 40 °C afforded a colorless syrup that crystallized after a few hours at −14 °C. TLC revealed the solid to be a mixture of two compounds (R_f 0.35 and 0.30, 4:1 hexane–ethyl acetate) that were separated by column chromatography (silica gel, 80 g) with 5:1 hexane–ethyl acetate. The compound having R_f 0.35 (α-L-*manno* isomer, **1f**) crystallized from ether–hexane: yield 0.138 g (9%); mp 92 °C; $[\alpha]^{22}_D$ −125° (c 0.5, dichloromethane); ^{13}C NMR δ 170.0, 169.7 (C=O), 86.0 (C-1), 72.0 (C-5), 70.3 (C-4), 68.6 (C-3), 52.3 (C-2), 20.5 (OAc), and 16.8 (C-6).

Anal. Calcd for $C_{10}H_{14}Br_2O_5$: C, 32.11; H, 3.77; m/z (M^+ − ^{79}Br$^·$) 293.002505. Found: C, 31.78; H, 3.82; m/z 293.002978. Evaporation of the later fractions from the column afforded the crystalline α-L-*gluco* isomer **1e**. Recrystallization from ether–hexane gave colorless crystals: yield 0.43 g (29%); mp 128–129 °C; $[\alpha]^{22}_D$ −283° (c 0.5, dichloromethane) (in good agreement with values reported[38] in the literature); ^{13}C NMR δ 170.0 (C=O), 89.3 (C-1), 79.3, 71.0, 69.0 (C-3,4,5), 49.1 (C-2), 20.5 (OAc), and 16.8 (C-6).

Anal. Calcd for $C_{10}H_{14}Br_2O_5$: m/z (M^+ − ^{79}Br$^·$) 293.002505. Found: m/z 293.002978.

3,4-Di-*O*-acetyl-2-chloro-2,6-dideoxy-α-L-galacto- and -β-L-talopyranosyl Chlorides (2a and 2d). 3,4-Di-*O*-acetyl-L-fucal (**2**, 0.642 g, 3 mmol) was chlorinated in carbon tetrachloride (15 mL) as described for compound 1. Evaporation of the solvent afforded a syrup that showed two main spots in TLC (R_f 0.5 and 0.3, 4:1 hexane–ethyl acetate). The mixture was separated by column chromatography (5:1 hexane–ethyl acetate). From the first fractions, the α-L-*galacto* isomer **2a** was isolated as a colorless syrup that failed to crystallize: yield 0.55 g (64%); $[\alpha]^{22}_D$ −230° (c 1.1, dichloromethane); IR (film) 1755 (C=O), 735 (C—Cl) cm^{-1}; ^{13}C NMR δ 170.2, 169.8 (C=O), 94.3 (C-1), 70.6, 69.6 (C-3,4), 68.4 (C-5), 55.6 (C-2), 20.3 (OAc), and 15.4 (C-6).

Anal. Calcd for $C_{10}H_{14}Cl_2O_5$: C, 42.12; H, 4.95; m/z (M − Cl$^·$) 249.052968. Found: C, 41.73; H, 5.25; m/z 249.052660.

Evaporation of the later fractions from the column afforded the β-L-*talo* isomer **2d**, as a colorless syrup: yield 0.068 g (8%); $[\alpha]^{23}_D$ +4.0° (c 0.4, dichloromethane); IR (film) 1755 (C=O), 730 (C—Cl) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}Cl_2O_5$: m/z (M^+ − Cl$^·$) 249.052968. Found: C, m/z 249.053660.

3,4-Di-*O*-acetyl-2-chloro-2,6-dideoxy-β-L-galactopyranosyl Chloride (2b). Chlorination of 3,4-di-*O*-acetyl-L-fucal (**2**, 50 mg) in 1,2-dichloroethane afforded a mixture of dihalides that was separated by LC (μPorasil column, 0.78 × 30 cm, at a flow rate of 3.5 mL/min) with 8:1 hexane–ethyl acetate. Fractions containing the product having t_R 11 min were pooled and evaporated to give the crystalline title compound: mp 91–93 °C; $[\alpha]^{25}_D$ −32° (c 0.2, dichloromethane).

Anal. Calcd for $C_{10}H_{14}Cl_2O_5$: m/z (M^+ − Cl$^·$) 249.052968. Found: m/z 249.053660.

3,4-Di-*O*-acetyl-2-bromo-2,6-dideoxy-α-L-galacto- and -α-L-talopyranosyl Bromides (2e and 2f). L-Fucal diacetate (**2**, 0.054 g, 0.25 mmol) dissolved in carbon tetrachloride (1.3 mL) was treated with bromine as already described for the glycal **1**. The mixture was monitored by ^{13}C NMR and separated by LC (μPorasil column, 0.78 × 30 cm, at a flow rate of 3 mL/min) with 6:1 hexane–ethyl acetate. Fractions containing the product having t_R 7.5 min were pooled and evaporated, and the α-L-*talo* isomer **2f** was obtained as a colorless syrup: yield 16 mg (17%); $[\alpha]^{22}_D$ −77° (c 1.4, dichloromethane); ^{13}C NMR δ 170.5, 169.7 (C=O), 91.6 (C-1), 47.3 (C-2), 20.3 (OAc), and 15.3 (C-6).

Anal. Calcd for $C_{10}H_{14}Br_2O_5$: m/z (M^+ − ^{79}Br$^·$) 293.002505. Found: m/z 293.003148.

The product having t_R 8.3 min was identified as the α-L-*galacto* isomer **2e**: yield 28 mg (30%); $[\alpha]^{22}_D$ −224° (c 2.0, dichloromethane); ^{13}C NMR δ 170.2, 169.6 (C=O), 88.7 (C-1), 47.0 (C-2), 20.4 (OAc), and 15.5 (C-6).

Anal. Calcd for $C_{10}H_{14}Br_2O_5$: m/z (M^+ − ^{79}Br$^·$) 293.002505. Found: m/z 293.003242.

The ^{13}C NMR signals of C-3, -4, and -5 in a mixture of **2e** and **2f** were not specifically differentiated. Their chemical shifts were 70.9, 70.7, 70.4, 70.3, 67.8, and 64.9.

Registry No. **1**, 34819-86-8; **1a**, 103321-18-2; **1b**, 103321-21-7; **1c**, 103321-20-6; **1d**, 103321-19-3; **1e**, 65784-91-0; **1f**, 103321-22-8; **2**, 54621-94-2; **2a**, 72864-45-0; **2b**, 103321-24-0; **2d**, 103321-23-9; **2e**, 103321-26-2; **2f**, 103321-25-1; **3**, 2873-29-2; **3f**, 62098-48-0; **3g**, 103475-53-2; **4**, 98044-32-7; **4f**, 103321-27-3; **4g**, 103321-28-4; **6**, 4098-06-0; **6f**, 103420-22-0; **6g**, 103420-23-1.

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Enantioselective Synthesis and Absolute Configuration of Both Enantiomers of *endo*-Brevicomin

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(1*R*,5*S*,7*S*)-(+)- and (1*S*,5*R*,7*R*)-(−)-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane ((+)- and (−)-*endo*-brevicomin, **5**) were synthesized in high enantiomeric purity in three steps starting from the (2*S*,3*S*)-(+)- and (2*R*,3*R*)-(−)-*erythro*-1-bromopentane-2,3-diol (**1**), respectively, with 60% overall yield. The key reaction is a stereoselective cycloacetalization of **1a** or **1b** with 4-(phenylsulfonyl)-2-butanone dimethyl acetal **2** or the corresponding ketone **2′**, respectively.

endo-Brevicomin is one of the attractant pheromones in the chemical communication system of several pine beetle species belonging to the genera *Dendroctonus* and *Dryocetes*.[1]

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Biological studies conducted up to now show that (+)-*endo*-Brevicomin (**5a**) is the form mainly produced by the males of *Dendroctonus* species,[2,3] *D. frontalis* (southern pine beetle), *D. ponderosae* (mountain pine beetle), *D. adjunctus* (round headed pine beetle), and *Dryocetes confusus*[3] (western balsam beetle) and *Dryocetes autographus*.[4] Very recently Vité[2] reported on the basis of field tests on the enhancing effect of the (+)-enantiomer **5a** on the southern pine beetle of both sexes, particularly in the case of the female beetles. The role of enantiomers of *endo*-brevicomin in the chemical communication of other pine beetle species, however, has not yet been clarified. In order to establish the absolute configuration of the (+)- and (−)-enantiomers **5a** and **5b**, respectively, and to present them in a purely enantiomeric form for biological studies, which are based on the indication that different insects will respond differently to enantiomers, we describe the synthesis of both enantiomers **5a** and **5b**. Apart from the racemic syntheses of *endo*-brevicomin[6,7] the optically active version was limited to Bernardi's,[8] Hatakeyama's,[10] and Mori's[9] reports.

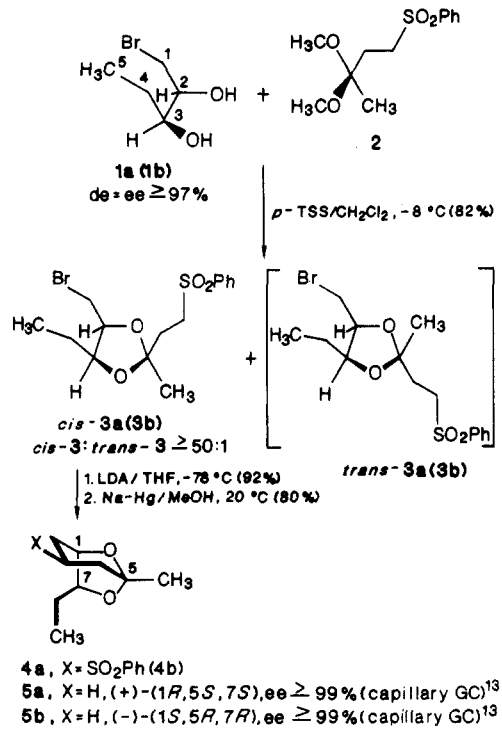
According to our results, in the former synthesis[8] the sign of the optical rotation disagrees with the configuration of **5**.

Mori[9] describes for both enantiomers of *endo*-brevicomin an enantioselective synthesis in five steps with 4.5% and 7% overall yields.

In this work, on the basis of the racemic synthesis of Meister and Scharf,[7] we have developed a method in three steps for the synthesis of the 1*R*,5*S*,7*S*-(+)-enantiomer **5a** as well as 1*S*,5*R*,7*R*-(−)-enantiomer **5b** with approximately 60% overall yield starting from the chiral building block (2*S*,3*S*)-(+)- and (2*R*,3*R*)-(−)-1-bromo-*erythro*-pentane-2,3-diol (**1a** and **1b**, respectively), which we obtained by degradation of easily accessible α-D-(+)-glucose and L-(+)-arabinose, respectively.[12]

The chiral centers C5 (C2 in **1a**) and C4 (C3 in **1a**) of α-D-(+)-glucose were incorporated into the 6,8-dioxabicyclo[3.2.1]octane skeleton of **5a** at the centers C1 and C7 and thus represent their absolute configurations. Likewise, C3 and C4 in arabinose represent the C3 and C2 centers in **1b**.

Scheme I



4a, X = SO_2Ph (4b)
5a, X = H, (+)-(1*R*,5*S*,7*S*), ee ≥ 99% (capillary GC)[13]
5b, X = H, (−)-(1*S*,5*R*,7*R*), ee ≥ 99% (capillary GC)[13]

The chiral building blocks **1a** and **1b**[10] were converted with 4-(phenylsulfonyl)-2-butanone dimethyl acetal **2** by stereoselective cycloacetalization under kinetic control at −8 °C with nearly 80% overall yield into the chiral 1,3-dioxolane systems *cis*-**3a** and *cis*-**3b**, respectively, of enantiomeric and diastereomeric purity of ≥98% determined by ^{13}C NMR analysis (Scheme I).

Under these conditions the existence of the undesired *trans*-**3a** or *trans*-**3b** was not detected by ^1H and ^{13}C NMR spectra, where the locations of the absorptions of 2-CH_3 are the deciding criteria: ^1H NMR ($CDCl_3$) cis, trans δ 1.28, 1.35; ^{13}C NMR ($CDCl_3$) cis, trans δ 23.93, 26.12.

When the cycloacetalization was accomplished with 4-(phenylsulfonyl)-2-butanone **2′** in dry chloroform under the catalytic action of dry Lewatit SC 104 resin under reflux for 8 h by means of a method of water elimination, the *cis*-**3a** product, obtained with 82% overall yield, contained the undesired diatereomer *trans*-**3a** in 15–20%.

cis-**3a** and *cis*-**3b** were separated from unreacted **1a** and **1b**, respectively, and **2** and from the byproduct **2′** by column chromatography, and its intramolecular cyclization with lithium diisopropylamide in dry tetrahydrofuran at −78 °C gave 6,8-dioxabicyclo[3.2.1]octane derivate **4** with nearly 90% yield.

The reductive desulfonation[11] of **4a** and **4b** with 6% sodium amalgam in dry methanol at room temperature yielded the (+)-(1*R*,5*S*,7*S*)-*endo*-brevicomin (**5a**) and its (−)-enantiomer **5b**, respectively, with 80% yield. ^{13}C NMR analysis of **5a** and **5b** revealed ≥97% enantiomeric purity (ee ≥99% by capillary GC).

Experimental Section

General. NMR spectra were recorded with Varian EM 390 (^1H, 90 MHz) and CFT-20 (^{13}C, 20 MHz) spectrometers with internal standard Me_4Si. IR-spectra were measured as KBr disks on a Perkin-Elmer 377 instrument. Melting points were determined with a Büchi Model 510 melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter. TLC was carried out on Merck 0.2-mm

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(13) Schurig, V., determination of enantiomeric purity by chiral-phase capillary GC.

silica gel 60 F 254 analytical aluminum plates with (A) petroleum ether–acetone (2:1), (B) hexane–toluene–ethyl acetate (6:1:3), or (C) hexane–ethyl acetate (7:3). Silica gel MN 60 (140–270 mesh, ASTM) was used for column chromatographic separations of the products.

4-(Phenylsulfonyl)-2-butanone Dimethyl Acetal (2). First 4-(phenylsulfonyl)-2-butanone (**2′**) was prepared according to the literature.[2] To its suspension (42.4 g, 0.2 mol) in 100 mL of dry methanol were added *p*-toluenesulfonic acid (0.3 g) and trimethyl orthoformate (23.3 g, 0.22 mol). This mixture was stirred until it was homogeneous and left to stand at room temperature for another 20 h. The reaction was monitored by TLC with solvent A. Subsequently the mixture was neutralized with sodium methanolate and evaporated to dryness. The crude product after crystallization from dry ether yielded 46.5 g (90%) of **2**. The spectral data (^{1}H NMR, IR) of **2** were identical with those in the literature:[7] mp 65–66 °C (lit.[7] mp 62–63 °C); R_f (solvent A) 0.43.

(2*S*,4*S*,5*S*)-(+)- and (2*R*,4*R*,5*R*)-(−)-4-(Bromomethyl)-5-ethyl-2-methyl-2-[2-(phenylsulfonyl)ethyl]-1,3-dioxolane (*cis*-3a and *cis*-3b). (1) Formation of *cis*-3 under Kinetic Control at −8 °C. To a solution of 1-bromo-*erythro*-pentane-2,3-diol[10] (**1**) (5.5 g, 0.03 mol) in 50 mL of dry methylene chloride at −8 °C were added 4-(phenylsulfonyl)-2-butanone dimethyl acetal (**2**) (9.3 g, 0.036 mol) and *p*-toluenesulfonic acid (100 mg), and this mixture was stirred at −8 °C under exclusion of moisture for 10 days. The reaction was monitored by GC (column OV 101, 1 M; 220 °C iso; N_2, H_2, air = 1 kbar/cm^2; 1 cm/min) and by TLC with solvent B. Subsequently, the reaction mixture was neutralized with solid K_2CO_3 or dry Lewatit M 600 resin and evaporated to dryness. ^{1}H and ^{13}C NMR analyses of this reaction mixture showed the absence of the undesired diasteromer *trans*-**3**. The distinct product *cis*-**3** was purified from the reactant **1** and **2** and from the byproduct 4-(phenylsulfonyl)-2-butanone (**2′**) by column chromatography over silica gel with hexane–ethyl acetate (6:4), yielding 9.3 g (80%) of pure *cis*-**3**, which can be crystallized from dry ether. ^{13}C NMR analysis or both enantiomers shows an enantiomeric purity or ≥97%. The spectral data (^{1}H NMR, ^{13}C NMR, and IR) of *cis*-**3** were identical with those in the literature:[7] mp 61.5–62.5 °C; R_f (solvent B) 0.45. Anal. Calcd for $C_{15}H_{21}BrSO_4$: C, 47.75; H, 5.61. Found: C, 47.99; H, 5.77. *cis*-**3a**: $[\alpha]^{28}_D$ +17.8° (*c* 0.97, CH_2Cl_2); $[\alpha]^{28}_{Hg,365}$ +61.9° (*c* 0.97, CH_2Cl_2). *cis*-**3b**: $[\alpha]^{28}_D$ −20.6° (*c* 0.71, CH_2Cl_2); $[\alpha]^{28}_{Hg,365}$ −64.23° (*c* 0.71, CH_2Cl_2).

(2) Formation of *cis*-3a by means of a Method of Water Elimination. A solution of **1a**[10] (3 g, 0.0164 mol) and 4-(phenylsulfonyl)-2-butanone (**2′**)[7] (5.2 g, 0.0245 mol) in 150 mL of dry chloroform containing 1.3 g of dry Lewatit SC 104 resin was refluxed for 8 h, and water was removed azeotropically. The reaction was controlled by GC (under the same conditions as before) and by TLC with solvent B. The reaction mixture was filtered off and evaporated to dryness. ^{1}H NMR analysis of this reaction mixture shows that *cis*-**3a** contains 15–20% of the undesired diasteromer *trans*-**3a**. This *cis*-**3a** was purified from the unreacted educts **1** and **2′** by chromatography over silica gel with hexane–ethyl acetate (6:4) or petroleum ether–acetone (5:1), giving 5.1 g (82%) of *cis*-**3a** which involves *trans*-**3a** in 15–20%. *cis*-**3a** could not be totally purified from *trans*-**3a** by crystallization from ether. The ^{1}H NMR spectrum of the *cis*-**3a** product was identical with that in the literature:[7] $[\alpha]^{22}_{Hg,365}$ +57.2° (*c* 1.627, CH_2Cl_2).

(1*R*,5*S*,7*S*)-(+)- and (1*S*,5*R*,7*R*)-(−)-7-Ethyl-5-methyl-3-(phenylsulfonyl)-6,8-dioxabicyclo[3.2.1]octane (4a and 4b). First a solution of lithium diisopropyl amide was prepared for the intramolecular cyclization. A mixture of dry tetrahydrofuran (300 mL) and dry diisopropyl amine (3.2 g, 0.032 mol) was treated under dry nitrogen atmosphere at −78 °C (CO_2/acetone) with 19.8 mL of *n*-butyllithium (1.6 M in hexane). After 15 min, 5.7 g (0.015 mol) *cis*-**3** was added under dry nitrogen with stirring at −78 °C and without allowing the temperature to rise; stirring was continued for 1 h. The reaction was monitored by TLC with solvent C. Subsequently, the reaction mixture was allowed to attain 0 °C and was hydrolyzed with 2.3 g of dry acetic acid. The most of the solvent was removed under reduced pressure, and the residue was extracted with ether and washed with water until neutrality. The water layer was again extracted with ether, and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. This residue was purified by chromatography over silica gel with dry pentane–ethyl acetate (8:2). The overall yield was 4.1 g (92%) of **4**, which can also be purifed by recrystallization from dry ether but with loss. ^{1}H NMR and IR spectra of **4** were identical with those in the literature:[7] mp 122.5–123.5 °C; R_f (solvent C) 0.26, (solvent B) 0.35; ^{13}C NMR ($CDCl_3$) δ 10.83 (CH_3), 22.00 (CH_2), 22.87 (CH_2 ring), 24.58 (5-CH_3), 34.59 (CH_2 ring), 56.42 ($CHSO_2Ph$), 75.27, 81.49 (2 × CHO), 105.91 (OCO), 128.89, 129.32 (ortho and meta Ph C), 133.95 (para Ch C), 136.98 (Ph C-1). Anal. Calcd for $C_{15}H_{20}SO_4$: C, 60.79; H, 6.80. Found: C, 60.71; H, 6.80. **4a**: $[\alpha]^{30}_D$ + 66.1° (*c* 1.53, CH_2Cl_2); $[\alpha]^{30}_{Hg,365}$ +209.1° (*c* 1.53, CH_2Cl_2). **4b**: $[\alpha]^{30}_D$ −69.5° (*c* 1.7, CH_2Cl_2); $[\alpha]^{30}_{Hg,365}$ −219.4° (*c* 1.7, CH_2Cl_2).

(1*R*,5*S*,7*S*)-(+)- and (1*S*,5*R*,7*R*)-(−)-7-Ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane ((+)- and (−)-*endo*-Brevicomin) (5a and 5b). To a solution of **4** (4 g, 0.0135 mol) in 240 mL of dry methanol was added at room temperature with stirring and protection from moisture 51.5 g of freshly prepared sodium amalgam (6%) in several portions. This reductive desulfonylation was monitored by TLC with solvent B and was completed within 90 min. Subsequently, the reaction mixture was filtered off and concentrated at atmospheric pressure. The residue was extracted with distilled ether and washed with water until neutrality. The aqueous layer was also extracted with distilled ether, and the combined ether extracts were dried over K_2CO_3. After removal of the solvent by distillation at atmospheric pressure the crude *endo*-brevicomin **5** was purified by chromatography on silica gel with distilled dry pentane–ether (10:1), yielding after removal of the eluting solvent under atmospheric pressure 1.7 g (80%) of the highly pure *endo*-brevicomin (**5**). Analysis of **5** by capillary GC[13] revealed ≥99% enantiomeric purity. The spectral data (^{1}H and ^{13}C NMR, IR) of **5** were identical with those published in the literature:[7,9] $n^{22.5}$ 1.4457 (lit.[9] n^{21}_D 1.4422); R_f (solvent B) 0.71. **5a**: $[\alpha]^{22}_D$ +79.5° (*c* 1.18, Et_2O); $[\alpha]^{22}_{Hg,365}$ +240.8° (*c* 1.18, Et_2O). **5b** $[\alpha]^{22}_D$ −78.9° (*c* 0.99, Et_2O); $[\alpha]^{22}_{Hg,365}$ −239.2° (*c* 0.99, Et_2O) [lit.[8] $[\alpha]^{20}_D$ −76.7° (*c* 2, Et_2O), lit.[9] $[\alpha]^{21}_D$ +78.8° (*c* 0.5, Et_2O), [lit.[10] $[\alpha]^{21}_D$ +74.6° (*c* 1.06, Et_2O)].

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