Stereoselective Synthesis of (−)-(1*R*,1′*R*,5′*R*,7′*R*)-1-Hydroxy-*exo*-brevicomin and (+)-*exo*-Brevicomin from 3,4,6-Tri-*O*-acetyl-D-glucal

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Stereoselective syntheses of (−)-(1*R*,1′*R*,5′*R*,7′*R*)-1-hydroxy-*exo*-brevicomin (**1**) and (+)-*exo*-brevicomin (**2**) were accomplished from 3,4,6-tri-*O*-acetyl-D-glucal (**5**; *Schemes 2* and *3*). Chemoselective reduction, *Grignard* reaction, *Barton–McCombie* deoxygenation, and ketalization were used as key steps.

Introduction. – Several species of bark beetles infect pine trees resulting in the destruction of millions of trees causing great ecological and economic damage [1]. Brevicomins consisting of the 6,8-dioxabicyclo[3.2.1]octane system are components of the attracting pheromone system of several bark-beetle species belonging to the genera *Dendroctonus* and *Dryocoetes*. (−)-(1*R*,1′*R*,5′*R*,7′*R*)-1-Hydroxy-*exo*-brevicomin[1]) (**1**; *Fig.*) [2] has been identified in the volatiles of the male mountain-pine beetle, *Dendroctonus ponderosae*, whereas (+)-*exo*-brevicomin (**2**; *Fig.*) has been reported to be an aggregation pheromone produced by the Western-pine beetle, *Dendroctonus brevicomis* [3]. Since pheromones have great importance in the fields as communication systems of insects, the synthesis of brevicomins attracted great attention of synthetic chemists [4].

(–)-1-Hydroxy-*exo*-brevicomin (**1**)[1]) (+)-*exo*-Brevicomin (**2**)

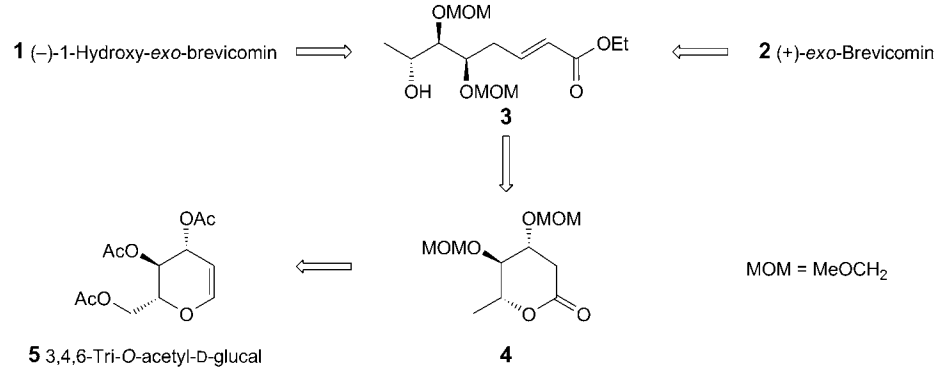
Figure. *Structures of brevicomins*

Results and Discussion. – Within our recently initiated program on the synthesis of the natural lactones cryptopyranmoscatone B1 [5a] and A1 [5b], and synargentolide A [5c] from the chiral-pool compound 3,4,6-tri-*O*-acetyl-D-glucal (= 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*aralino*-hex-1-enitol), we now devised a stereoselective total synthesis for 1-hydroxy-*exo*-brevicomin **1** and (+)-*exo*-brevicomin (**2**). The chiral

[1]) Trival atom numbering; for systematic names, see *Exper. Part.*

centers present in 3,4,6-tri-*O*-acetyl-D-glucal will perfectly match those of the target molecules. The retrosynthetic analysis revealed that **1** and **2** (*Scheme 1*) could be achieved from a common intermediate **3**, which is accessible from the known lactone **4** prepared in turn from the commercially available 3,4,6-tri-*O*-acetyl-D-glucal (**5**) by sequential reactions as shown in our earlier reports [5b,c].

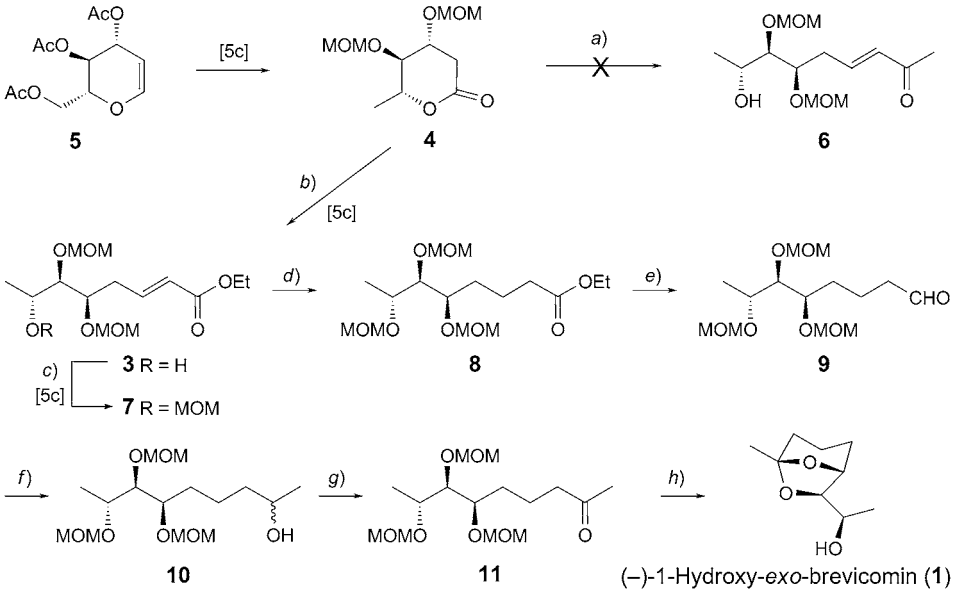
Scheme 1. *Retrosynthetic Analysis for Brevicomins*



In a first attempt to synthesize **1**, lactone **4** [5c] was reduced to the lactol with diisobutylaluminium hydride (DIBAL-H) at $-78°$ in dry CH_2Cl_2, which without purification was subjected to *Wittig* olefination with stabilized 1-(triphenylphosphoranylidene)propan-2-one ($Ph_3P{=}CHCOMe$) in refluxing toluene (*Scheme 2*); but several attempts failed to give the required open-chain α,β-unsaturated methyl ketone **6**. Therefore, **4** was converted to the known α,β-unsaturated ester **3** [5c] with the stabilized C_2 ylide ethyl (triphenylphosphoranylidene)acetate. The resulting hydroxy ester **3** carrying the three requisite stereogenic centers was protected as a methoxymethyl (MOM) ether to give **7** [5c] in 90% yield. Reduction of the C=C bond with $NaBH_4$ in the presence of $NiCl_2$ [6] gave the saturated ester **8** in 94% yield, which was reduced with DIBAL-H to aldehyde **9**. The latter was converted to methyl ketone **11** by a two-step procedure involving a *Grignard* reaction with MeMgBr (→**10**) followed by oxidation with *Dess–Martin* periodinane. Treatment of **11** with a trace of aqueous 2N HCl at room temperature for 2 h resulted in methoxymethyl ether cleavage and subsequent intramolecular ketalization to afford the target molecule 1-hydroxy-*exo*-brevicomin **1**.

The synthesis of (+)-*exo*-brevicomin (**2**) started from the intermediate ester **3** (*Scheme 3*). Removal of the secondary OH group was achieved by means of the *Barton–McCombie* deoxygenation reaction [7]. Thus, xanthate ester **13**, readily obtained in 92% yield on treatment of **12** with NaH, CS_2, and MeI, was deoxygenated with tributylstannane (Bu_3SnH) in the presence of a catalytic amount of 2,2′-azobis[2-methylpropanenitrile] (AIBN) to furnish **14** in 85% yield. The latter was reduced to aldehyde **15** with DIBAL-H, which was converted to methyl ketone **17** by the same two-step procedure as described above (*Grignard* reaction and *Dess–Martin* oxidation. Treatment of **17** with a trace of aqueous 2N HCl at room temperature for 5 h in MeOH

Scheme 2



a) 1. DIBAL-H, CH_2Cl_2, −78°; 2. Ph_3P=CHCOMe, toluene, reflux, 24 h. *b*) 1. DIBAL-H, CH_2Cl_2, −78°; 2. Ph_3P=CHCOOEt, benzene, reflux, 4 h, 87%. *c*) Methoxymethyl chloride ($MeOCH_2Cl$ = MOMCl; 1.5 equiv.), EtN^iPr_2 (3 equiv.), 0° to r.t., CH_2Cl_2, 8 h; 90%. *d*) $NaBH_4$ (1.2 equiv.), $NiCl_2$ (0.2 equiv.), MeOH, 0° to r.t., 30 min; 94%. *e*) DIBAL-H (1.2 equiv.), CH_2Cl_2, −78°, 2 h, 95%. *f*) MeMgBr (1.5 equiv.), dry THF, 0° to r.t., 1 h, 81%. *g*) *Dess–Martin* periodinane (2 equiv.), dry CH_2Cl_2, 0° to r.t., 2 h; 80%. *h*) Aq. 2N HCl, MeOH, 5 h, 37%.

2 h resulted in methoxymethyl ether cleavage and subsequent ketalization to afford the target molecule (+)-*exo*-brevicomin (**2**).

Conclusion. – In summary, the total synthesis of the natural pheromones (1*R*,1′*R*,5′*R*,7′*R*)-1-hydroxy-*exo*-brevicomin (**1**) and (+)-*exo*-brevicomin (**2**) were achieved in a highly stereoselective way from 3,4,6-tri-*O*-acetyl-D-glucal (**5**) as the chiral starting material.

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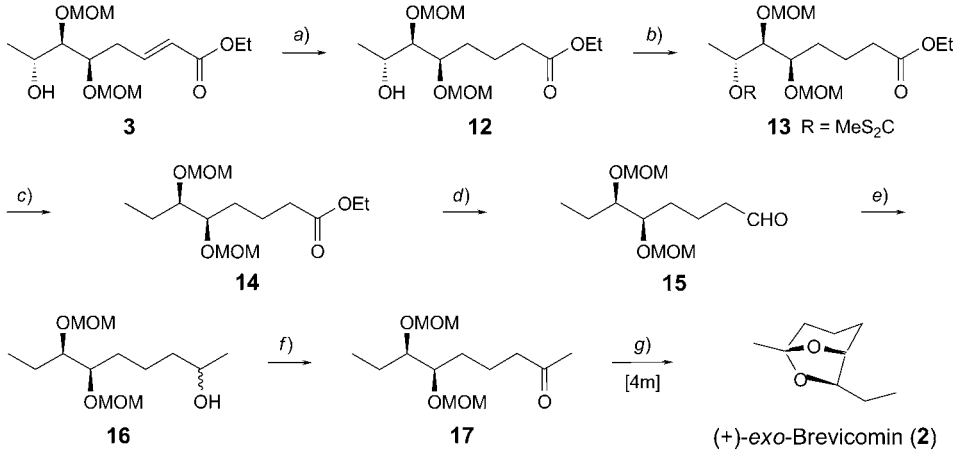
Experimental Part

General. Reactions were conducted under N_2 in anh. solvents such as CH_2Cl_2, THF, and AcOEt. (TLC monitoring). Yields refer to chromatographically and spectroscopically (^{1}H- and ^{13}C-NMR) homogeneous material. Air sensitive reagents were transferred by syringe or double-ended needle. Column chromatography (CC): silica gel (SiO_2; 60–120 mesh) supplied by *Acme Chemical Co.*, India. TLC: *Merck-60-F_{254}* SiO_2 plates; hexanes (b.p. 60–80°) as eluent detection under UV light. Optical rotation: *Jasco-DIP-370* polarimeter. IR Spectra: *Thermo Nicolet Nexus 670* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Varian FT-400* and *Bruker-UXNMR-FT-300* (*Avance*) spectrometers; in $CDCl_3$; δ

Scheme 3



a) $NaBH_4$ (1.2 equiv.), $NiCl_2$ (0.2 equiv.), MeOH, 0° to r.t., 30 min, 94%. *b*) NaH (2 equiv.), CS_2, (4 equiv.), MeI (8 equiv.), THF, 0° to r.t., 4 h; 86%. *c*) Bu_3SnH, 2,2′-azobis[2-methylpropanenitrile) (AIBN), dry toluene, reflux, 30 min; 85%. *d*) DIBAL-H (1.2 equiv.), CH_2Cl_2, −78°, 2 h; 95%. *e*) MeMgBr (1.5 equiv.), dry THF, 0° to r.t., 1 h; 81%. *f*) *Dess–Martin* periodinane (2 equiv.), dry CH_2Cl_2, 0° to r.t., 2 h; 80%. *g*) Aq. 2N HCl, MeOH, 5 h, 36%.

in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *ES-MSD* spectrometers (*Agilent Technologies*); at 70 eV; in *m*/*z*.

*Ethyl (5*R,*6*R,*7*R*)-5,6,7-Tris(methoxymethoxy)octanoate* (**8**). To a soln. of compound **7** [5c] (0.27 g, 0.77 mmol) in MeOH (10 ml) were added $NiCl_2$ (18 mg, 0.15 mmol) and $NaBH_4$ (35 mg, 0.9 mmol), slowly at 0°, and the mixture was stirred at 0° for 30 min. Then the residue was removed by filtration, and washed twice with MeOH and the combined filtrate concentrated: **8** (0.23g, 94%). $[\alpha]_D^{25} = +22.9$ ($c = 0.4$, $CHCl_3$). IR (KBr): 2936, 1735, 1382, 1150, 1031, 917. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.82–4.64 (*m*, 6 H); 4.13 (*q*, *J* = 7.17, 14.35, 2 H); 3.91–3.82 (*m*, 1 H); 3.71–3.59 (*m*, 2 H), 3.42 (*s*, 3 H); 3.40 (*s*, 3 H); 3.38 (*s*, 3 H); 2.38–2.30 (*m*, 2 H); 1.82–1.60 (*m*, 4 H); 1.29–1.21 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.2; 97.5; 96.9; 95.0; 80.6; 77.7; 73.1; 60.1; 55.9; 55.8; 55.3; 34.1; 30.8; 20.7; 15.9; 14.1. ESI-MS: 375 ([*M* + Na]$^+$).

*(6*R,*7*R,*8*R*)-6,7,8-Tris(methoxymethoxy)nonan-2-ol* (**10**). To a stirred soln. of **8** (0.2 g, 0.56 mmol) in dry CH_2Cl_2 (10 ml) was added 1.6M DIBAL-H in hexane (0.42 ml, 2.95 mmol), dropwise within 2 min under N_2 at −78°. After stirring for 2 h at −78°, dry MeOH (2 ml) was added, and the mixture was allowed to warm to r.t. Sat. aq. sodium potassium tartarate soln. (5 ml) was added, and the resulting mixture was stirred vigorously until the two layers were separated. The aq. layer was extracted with additional CH_2Cl_2 (2 × 10 ml) and the combined org. phase washed with H_2O and brine, dried (Na_2SO_4), and concentrated: crude aldehyde **9**, which was used for the next step without further purification.

To a stirred soln. of **9** in dry THF (10 ml) at 0°, 3M MeMgBr in Et_2O (0.3 ml, 0.9 mmol) was added dropwise. After the addition was completed, the mixture was stirred at r.t. for 1 h, and then the reaction was quenched with sat. aq. NH_4Cl soln. The aq. layer was extracted with AcOEt (2 × 10 ml), the combined org. phase washed with H_2O and brine, dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2, 20% AcOEt/hexane): diastereoisomer mixture **10** (0.15 g, 81%). Viscous liquid. $[\alpha]_D^{25} = +14.7$ ($c = 0.4$, $CHCl_3$). IR (KBr): 3489, 2935, 1459, 1306, 1149, 1031, 917, 764. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.83–4.64 (*m*, 6 H); 3.92–3.77 (*m*, 2 H); 3.72–3.59 (*m*, 2 H); 3.42 (*s*, 3 H); 3.41 (*s*,

3 H); 3.38 (*s*, 3 H); 3.00 (br. *s*, 1 H); 1.78–1.41 (*m*, 6 H); 1.27–1.18 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 97.6; 97.0; 95.0; 80.6; 78.1; 73.1; 67.7; 56.0; 55.9; 55.4; 39.2; 31.4; 23.5; 21.3; 15.9. ESI-MS: 347 ($[M+Na]^+$).

*(6*R*,7*R*,8*R*)-6,7,8-Tris(methoxymethoxy)nonan-2-one* (**11**). To a soln. of diastereoisomer mixture **10** (0.1 g, 0.3 mmol) in dry CH_2Cl_2 (5 ml), *Dess–Martin* periodinane DMP (0.26 g, 0.61 mmol) and $NaHCO_3$ (0.1 g, 1.2 mmol) were added at 0° under N_2. The turbid soln. was allowed to warm to r.t. and stirred for 2 h. The mixture was diluted with CH_2Cl_2 (10 ml), quenched with sat. aq. $NaHCO_3$ soln. (5 ml) and sat. aq. $Na_2S_2O_3$ soln. (5 ml) and vigorously stirred until a clear solution was formed. The aq. layer was extracted with CH_2Cl_2 (2 × 10 ml), the combined org. phase were washed with brine (1 × 10 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2, 20% AcOEt/hexane): **11** (0.07 g, 80%). Viscous liquid. $[\alpha]_D^{25} = +24.7$ ($c = 0.6$, $CHCl_3$). IR: 2932, 1715, 1447, 1365, 1149, 1031, 917. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.83–4.61 (*m*, 6 H); 3.91–3.81 (*m*, 1 H); 3.70–3.58 (*m*, 2 H); 3.42 (*s*, 3 H); 3.40 (*s*, 3 H); 3.38 (*s*, 3 H); 2.52–2.42 (*m*, 2 H); 2.21–2.12 (*m*, 3 H); 1.77–1.42 (*m*, 4 H); 1.23 (*d*, $J = 6.42$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 208.6; 97.6; 97.0; 95.0; 80.6; 77.9; 73.1; 56.0 (*d*, 2 C); 55.4; 43.5; 30.8; 29.8; 19.5; 16.0. ESI-MS: 345 ($[M+Na]^+$).

*(α*R*,1*S*,5*R*,7*R*)-α,5-Dimethyl-6,8-dioxabicyclo[3.2.1]octane-7-methanol* (*=(−)-(1*R*,1′*R*,5′*R*,7′*R*)-1-Hydroxy*-exo-*brevicomin*; **1**). To a soln. of **11** (30 mg. 0.09 mmol) in MeOH (2 ml) was added 3N HCl (0.02 ml) at r.t. After the completion of the reaction (5 h), the mixture was neutralized with solid $NaHCO_3$, after which the volatiles were evaporated. The resultant residue was partitioned between AcOEt and H_2O, the org. layer dried (Na_2SO_4) and concentrated, and the crude product purified by CC (SiO_2, hexane/AcOEt 75:25): pure **1** (6 mg, 37%). $[\alpha]_D^{25} = +16.0$ ($c = 0.3$, $CHCl_3$). IR (KBr): 3447, 2924, 1717, 1457, 1382, 1236, 1036, 843, 765. ^{1}H-NMR (500 MHz, (D_6)acetone): 4.44–4.41 (*m*, 1 H); 3.71–3.66 (*m*, OH); 3.62 (*d*, $J = 7.55$, 1 H); 3.47–3.39 (*m*, 1 H); 1.90–1.80 (*m*, 1 H); 1.77–1.69 (*m*, 1 H); 1.61–1.52 (*m*, 3 H); 1.48–1.42 (*m*, 1 H); 1.29 (*s*, 3 H); 1.15 (*d*, $J = 6.6$, 3 H). ^{13}C-NMR (75 MHz, (D_6)acetone): 109.3; 85.8; 78.0; 70.0; 36.6; 29.7; 26.2; 21.1; 18.9. ESI-MS: 195 ($[M+Na]^+$).

*Ethyl (5*R*,6*R*,7*R*)-7-Hydroxy-5,6-bis(methoxymethoxy)octanoate* (**12**). As described for **8**, with **3** (0.3 g, 0.85 mmol) in MeOH (10 ml), $NiCl_2$ (20 mg, 0.16 mmol), and $NaBH_4$ (39 mg, 1.0 mmol): **12** (0.25 g, 94%). IR (KBr): 2936, 1735, 1382, 1150, 1031, 917. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.81–4.65 (*m*, 4 H); 4.15 (*q*, $J = 6.79$, 2 H); 4.06–3.83 (*m*, 1 H); 3.77–3.52 (*m*, 2 H); 3.43 (*s*, 3 H); 2.35 (*t*, $J = 6.79$, 2 H); 1.90–1.50 (*m*, 4 H); 1.32–1.18 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 173.2; 98.2; 97.0; 84.6; 78.3; 66.7; 60.2; 56.0 (2 C); 34.1; 30.0; 20.9; 18.9; 14.1. ESI-MS: 331 ($[M+Na]^+$).

*Ethyl (5*R*,6*R*,7*R*)-5,6-Bis(methoxymethoxy)-7-[(methylthio)thioxomethoxy]octanoate* (**13**). To a soln. of NaH (0.05 g, 2.08 mmol) in anh. THF (10 ml), alcohol **12** (0.35 g, 1.1 mmol) in anh. THF (10 ml) was added at 0° and stirred at r.t. for 0.5 h. To this mixture, CS_2 (0.3 ml, 4.9 mmol) and MeI (0.6 ml, 9.6 mmol) were added at 0°. The mixture was stirred at r.t. for 3 h. After completion of the reaction, the reaction was quenched at 0° by slow addition of crushed ice. The temp. was raised to r.t., the aq. layer washed with CH_2Cl_2 (2 × 25 ml), the combined org. phase dried (Na_2SO_4) and concentrated and the residue purified by CC (SiO_2, AcOEt/hexane 1:20): **13** (0.39 g, 86%). Liquid. $[\alpha]_D^{25} = +71.6$ ($c = 0.7$, $CHCl_3$). IR (KBr): 2933, 1733, 1224, 1150, 1033, 919, 863. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.90–5.81 (*m*, 1 H); 4.77–4.65 (*m*, 4 H); 4.13 (*q*, $J = 6.79$, 14.35, 2 H); 3.96–3.91 (*m*, 1 H); 2.39–2.29 (*m*, 2 H); 1.85–1.52 (*m*, 4 H); 1.42 (*d*, $J = 6.04$, 3 H); 1.26 (*t*, $J = 6.79$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 215.2; 173.3; 97.5; 96.9; 80.4; 79.3; 77.8; 60.3; 56.1 (*d*, 2 C); 34.2; 30.6; 20.9; 19.0; 14.7; 14.3. ESI-MS: 416 ($[M+NH_4]^+$).

*Ethyl (5*R*,6*R*)-5,6-Bis(methoxymethoxy)octanoate* (**14**). A suspension of **13** (0.35 g, 0.8 mmol), Bu_3SnH (0.8 ml, 2.85 mmol), and AIBN (15 mg, 0.09 mmol) in anh. toluene (20 ml) was heated under reflux for 30 min.Then the mixture was cooled and concentrated, and the residue purified by CC (SiO_2, AcOEt/hexane 1:33): **14** (0.21 g, 84%). Colorless liquid. $[\alpha]_D^{25} = +15.5$ ($c = 0.5$, $CHCl_3$). IR (KBr): 2936, 1735, 1460, 1375, 1150, 1104, 1036, 918, 763. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.72–4.64 (*m*, 4 H); 4.13 (*q*, $J = 7.55$, 14.35, 2 H); 3.64–3.57 (*m*, 1 H); 3.54–3.47 (*m*, 1 H); 3.39 (*s*, 6 H); 2.83–2.29 (*m*, 2 H); 1.82–1.59 (*m*, 4 H); 1.56–1.42 (*m*, 2 H); 1.25 (*t*, $J = 6.79$, 3 H); 0.96 (*t*, $J = 7.55$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.4; 96.3 (2 C); 80.6 (2 C); 78.6; 60.1; 55.6; 34.2; 29.3; 22.6; 21.3; 14.1; 10.0. ESI-MS: 310 ($[M+NH_4]^+$).

*(6*R*,7*R*)-6,7-Bis(methoxymethoxy)nonan-2-ol* (**16**). As described for **10**, with **14** (0.17 g, 0.58 mmol), CH_2Cl_2 (5 ml), and 1.6M DIBAL-H in hexane (0.43 ml, 3.0 mmol): crude aldehyde **15** which was used for the next step without further purification.

As described for **10**, with 3M MeMgBr in Et_2O (0.34 ml, 1.03 mmol) **15**, and THF (5 ml): diastereoisomer mixture **16** (0.12 g, 80%). Viscous liquid. $[\alpha]_D^{25} = +7.7$ ($c = 0.4$, $CHCl_3$). IR (KBr): 3445, 2935, 1462, 1375, 1104, 1035, 916, 770. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.73–4.66 (*m*, 4 H); 3.86–3.76 (*m*, 1 H); 3.64–3.56 (*m*, 1 H); 3.55–3.48 (*m*, 1 H); 3.40 (*s*, 6 H); 1.76–1.40 (*m*, 6 H); 1.20 (*d*, $J = 6.04$, 3 H); 0.96 (*t*, $J = 7.55$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 96.7 (*d*, 2 C); 80.7; 78.9; 67.7; 55.6 (2 C); 39.3; 29.8; 23.4; 22.7; 20.5; 10.2. ESI-MS: 282 ($[M + NH_4]^+$).

*(6*R*,7*R*)-6,7-Bis(methoxymethoxy)nonan-2-one* (**17**). As described for **11**, with diastereoisomer mixture **16** (0.07 g, 0.26 mmol), CH_2Cl_2 (10 ml), *Dess–Martin* periodinane (0.22 g, 0.51 mmol), and $NaHCO_3$ (0.09 g, 1.0 mmol): **17** (0.055 g, 79%). Viscous liquid. $[\alpha]_D^{25} = +11.0$ ($c = 0.3$, $CHCl_3$). IR (KBr): 2932, 1714, 1458, 1365, 1149, 1035, 917. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.72–4.64 (*m*, 4 H); 3.63–3.55 (*m*, 1 H); 3.55–3.47 (*m*, 1 H); 3.39 (*s*, 6 H); 2.50–2.43 (*m*, 2 H); 2.14 (*s*, 3 H); 1.76–1.54 (*m*, 4 H); 1.53–136 (*m*, 2 H); 0.96 (*t*, $J = 7.55$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 208.7; 96.9 (2 C); 80.7; 78.9; 55.7; 43.7; 29.6; 29.3; 22.7; 20.1; 10.3. ESI-MS: 280 ($[M + NH_4]^+$).

*(1*R*,5*S*,7*R*)-7-Ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane* (=*(+)*-exo-*Brevicomin*; **2**). As described for **1**, with **17** (20 mg. 0.07 mmol), MeOH (2 ml), and 3N HCl 0.02 ml) CC (hexane/AcOEt) gave pure **2** (4 mg, 36%). $[\alpha]_D^{25} = +5.0$ ($c = 0.1$, $CHCl_3$). IR (KBr): 2923, 2853, 1743, 1462, 1377, 1154, 722. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.78–3.84 (*m*, 3 H); 3.76–3.70 (*m*, 1 H); 2.11–1.99 (*m*, 2 H); 1.91–1.80 (*m*, 2 H); 1.71–1.62 (*m*, 4 H); 1.43 (*s*, 3 H); 0.95 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 106.5; 96.9; 80.70; 78.9; 29.9; 29.3; 22.7; 20.1; 10.3. ESI-MS: 156 (M^+).

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