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Article

Asymmetric Synthesis of *exo*-Isobrevicomin and *exo*-Brevicomin *via* Conjugated Addition of Primary Alkyl Iodides to α,β-Unsaturated Ketones

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(-)-*exo*-Isobrevicomina (**1**) e (+)-*exo*-brevicomina (**2**) são substâncias voláteis produzidas pelos besouros machos *Dendroctonus ponderosae*, os quais habitam árvores do gênero Pinus encontradas no hemisfério norte, freqüentemente causando a morte dos hospedeiros. Objetivando a obtenção desses feromônios de agregação, que apresentam a estrutura 6,8-dioxabiciclo[3.2.1]octano, as estratégias sintéticas utilizadas nesse trabalho tiveram como etapas-chaves a di-hidroxilação assimétrica de Sharpless e a adição conjugada, promovida pela liga Zn(Cu) em meio aquoso e acelerada por ultra-som. A adição conjugada dos acetonídeos **13** e **14** às respectivas cetonas insaturadas (metil-vinil-cetona e etil-vinil-cetona) gerou os adutos **15** e **16**. A ciclização intramolecular catalisada dos compostos **15** e **16** com ácido fosfotungstico ($H_3PW_{12}O_{40}$) forneceu a *exo*-isobrevicomina (**1**) e a *exo*-brevicomina (**2**).

(-)-*exo*-Isobrevicomin (**1**) and (+)-*exo*-brevicomin (**2**) are volatile substances produced by males of the beetles *Dendroctonus ponderosae*, which inhabit pine trees found in the northern hemisphere, frequently causing the death of their host. In order to obtain these aggregation pheromones, which present the 6,8-dioxabicyclo[3.2.1]octane structure, the synthetic strategies utilized in this work had as key steps the Sharpless asymmetric dihydroxylation and the conjugated addition, promoted by the Zn(Cu) couple in aqueous medium and accelerated by ultrasound. The conjugated addition of acetonides **13** and **14** to the respective unsaturated ketones (methyl vinyl ketone and ethyl vinyl ketone) furnished the adducts **15** and **16**. The intramolecular catalyzed cyclization of compounds **15** and **16** with phosphotungstic acid ($H_3PW_{12}O_{40}$) produced *exo*-isobrevicomin (**1**) and *exo*-brevicomin (**2**).

Keywords: Isobrevicomin, brevicomin, 6,8-dioxabicyclo[3.2.1]octane, aggregation pheromones, conjugate addition

Introduction

Mountain pine beetles, *Dendroctonus ponderosae*, are destructive pests which cause damage to coniferous forests in the northern hemisphere. The interest in chemical communication systems of insect species, coupled with their economic influence, has stimulated biological activity and synthetic studies.[1]

The isolation and the first synthesis of (-)-*exo*-isobrevicomin (**1**), (1*S*,5*R*,7*S*)-5-ethyl-7-methyl-6,8-dioxabicyclo[3.2.1]octane, and the respective hydroxylated derivatives were reported by Francke and co-workers[2] in 1996. Further alternative strategies for the preparation of this compound were reported by Mori and co-workers[3] in 1997, and by Taniguchi and co-workers[4] in 1998. Compound **1** is a new naturally occurring isomer of (+)-*exo*-brevicomin (**2**), with opposite absolute configuration at the stereogenic centers, produced by males of the beetles *Dendroctonus ponderosae*.

As the major volatile component of several bark beetle species, (+)-*exo*-brevicomin (**2**), (1*R*,5*S*,7*R*)-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane, prepared by diverse synthetic methodologies, has been described quite frequently in the literature.[1,5] The strategy most commonly used for the syntheses of compounds **1** and **2** involves the conversion of *E*-7-nonen-3-ones and *E*-6-nonen-2-ones into their chemical equivalent intermediates (epoxy or dihydroxy derivatives) by means of enzymatic or enantioselective transformations, followed by intramolecular acetalization.[1,2] Despite compound **2** existing in nature as a pure enantiomer, it has been shown that its racemate is potent enough for practical applications.[1-4]

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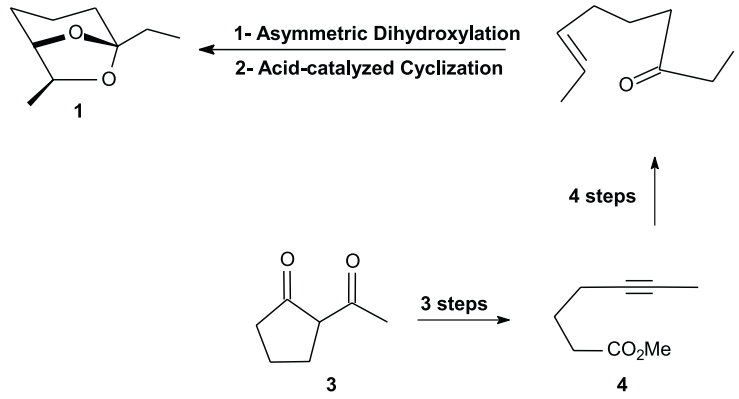


Scheme 1. Synthesis of *exo*-Isobrevicomin (**1**) from ethanoyl-cyclopentanone

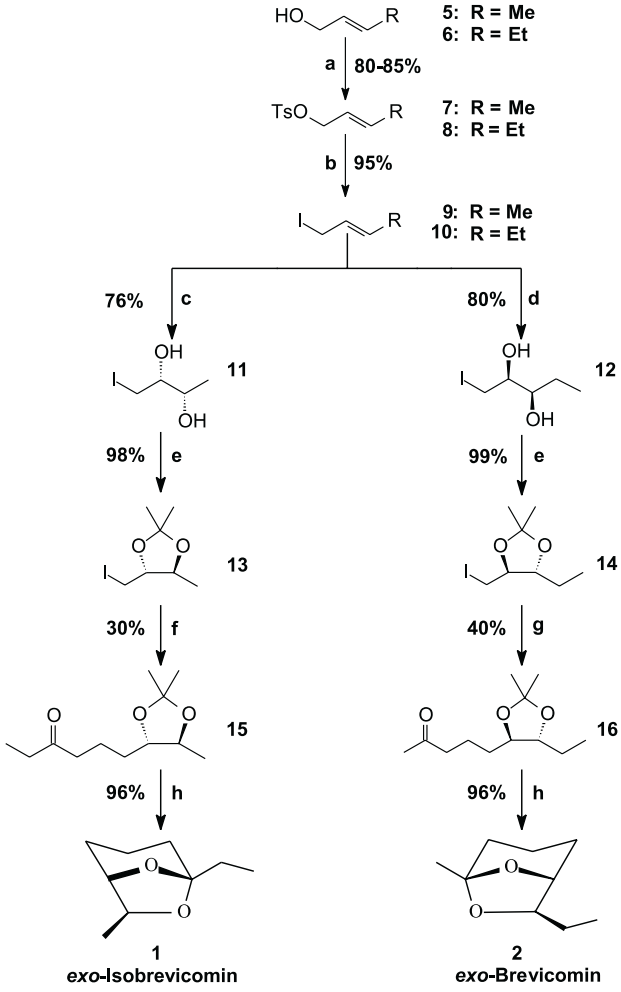
Our interest in the preparation of bicyclic acetal (**1**) arose from its recent isolation and syntheses.[1,2-4] We have been involved with the syntheses of some acyclic pheromones[6,7] from acyl-cyclopentanones **3**. The acetylenic ester **4**, obtained as the key intermediate, can be transformed into the natural product **1** (Scheme 1).

Although the route described in Scheme 1 had involved inexpensive starting materials and could have led to homochiral products, it was quite long. Therefore, we have developed a new sequence which is shorter and leads to optically active products[7] (Scheme 2).

In this alternative path, the conjugate addition reactions (**paths f** and **g**) were definitely considered as key steps in furnishing the desired products **1** and **2.**

Experimental

Unless otherwise specified, all reagents and solvents were used as received from the commercial suppliers. Organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure on a rotatory evaporator. Chromatographic purifications were conducted by flash[8] or "dry-column" flash chromatography[9] on silica gel (Merck, 60 Å, 230-400 mesh). Melting points were determined on a Kofler block and are uncorrected. A Bransonic ultrasonic cleaner (Model 1210 ; 47 ± 6 KHz) was used to conduct heterogeneous reactions. Infrared spectra of liquid samples (neat films) and solids (KBr disks) were recorded on a Bomem Hartmann & Braun (MB-100) spectrometer. Routine ^1H NMR spectra were obtained on a VARIAN EM-390 (90 MHz) spectrometer, while the high resolution ^1H and ^{13}C NMR spectra were registered on a Bruker ARX200 (200/50 MHz) spectrometer and on a Bruker ARX400 (400/100 MHz) spectrometer. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. GC-EIMS (70 eV) analyses were carried out on a PERKIN ELMER Q-MASS 910 spectrometer, containing the DB-17 capillary column (30



a) *p*-TsCl, KOH, Et_2O, -10 °C, 1.5 h; b) NaI, acetone, 25 °C, 16 h; c) AD-mix-α, $MeSO_2NH_2$, $NaHCO_3$, *t*-BuOH:H_2O (1:1), 0 °C, 15 h; d) AD-mix-β, $MeSO_2NH_2$, $NaHCO_3$, *t*-BuOH:H_2O (1:1), 0 °C, 15 h; e) 2,2-dimethoxy-propane, PPTS, 25 °C, 5 h; f) EVK, Zn(Cu), EtOH:H_2O (7:3), ultrasound, 25 °C, 2 h; g) MVK, Zn(Cu), EtOH:H_2O (7:3), ultrasound, 25 °C, 2 h; h) $H_3PW_{12}O_{24}$ cat., CH_2Cl_2, 25 °C, 4h.

Scheme 2. Synthesis of *exo*-Isobrevicomin (**1**) and *exo*-Brevicomin (**2**)

m x 0.25 mm x 0.25 mm). GC analyses were carried out on a VARIAN STAR 3400 CX, utilizing DB-WAX and Chirasil-DEX CB capillary columns (30 m x 0.25 mm x 0.25 mm).

*(E)-But-2-en-1-yl p-toluenesulfonate (**7**)*

To a stirred solution of the (*E*)-but-2-en-1-ol (**5**) (3.4 mL, 40 mmol), *p*-toluenesulfonyl chloride (9.6 g, 50 mmol) in dry ether (40 mL), cooled at -10 ºC and under anhydrous conditions, was added pulverized potassium hydroxide 85% (4.5 g, 80 mmol). The reaction mixture was stirred for 1-2 h, diluted with brine (20 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined extract was washed with water (30 mL), diluted HCl (30 mL) and a saturated solution of $NaHCO_3$ (30 mL). Drying and evaporation of solvent gave a colorless liquid (7.7 g, 85%), which was used in the next step; IR ν_{max}/cm^{-1} 3030, 1674, 1598, 1358, 1189 (film); ^{1}H NMR (90 MHz, CCl_4) δ 1.60 (d, *J* 6.0 Hz, 3H), 2.37 (s, 3H), 4.27 (d, *J* 6.0 Hz, 2H), 5.12-5.87 (m, 2H), 7.19 (d, *J* 9.0 Hz, 2H), 7.63 (d, *J* 9.0 Hz, 2H).

*(E)-Pent-2-en-1-yl p-toluenesulfonate (**8**)*

It was prepared from (*E*)-pent-2-en-1-ol (**6**), as described in the above method, giving a colorless liquid (7.7 g, 80%), which was utilized in the next reaction without further purification; IR ν_{max}/cm^{-1} 3033, 1671, 1598, 1359, 1189 (film); ^{1}H NMR (90 MHz, CCl_4) δ 0.85 (t, *J* 7.5 Hz, 3H), 1.70-2.10 (m, 2H), 2.39 (s, 3H), 4.30 (d, *J* 6.0 Hz, 2H), 5.08-5.88 (m, 2H), 7.21 (d, *J* 9.0 Hz, 2H), 7.63 (d, *J* 9.0 Hz, 2H).

*(E)-1-Iodo-but-2-ene (**9**)*

Anhydrous sodium iodide (6.0 g, 40 mmol) was added to (*E*)-but-2-en-1-yl *p*-toluenesulfonate (**7**) (7.7 g, 34 mmol) in anhydrous acetone (40 mL). After stirring at room temperature for 16 h, the mixture was diluted with ice/water (10 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic phase was washed with dilute solution of $Na_2S_2O_3$ (30 mL), saturated solution of $NaHCO_3$ (2 x 30 mL) and brine (30 mL). Drying and evaporation of solvent furnished a crude dark brown liquid that was purified by "dry-column" flash chromatography, eluting with petroleum ether, to afford a brownish liquid (5.9 g, 95%); IR ν_{max}/cm^{-1} 3024, 1658, 961 (film); ^{1}H NMR (90 MHz, CCl_4) δ 1.61 (t, 3H), 3.50-4.00 (m, 2H), 5.30-5.90 (m, 2H); GC/EIMS (70 eV) *m/z* 182 (M^+, 13.8%), 127 (34), 55 (100).

*(E)-1-Iodo-pent-2-ene (**10**)*

It was obtained from (*E*)-pent-2-en-1-yl *p*-toluenesulfonate (**8**) (7.7g, 32 mmol), as described above, affording a brownish liquid (5.98 g, 95%); IR ν_{max}/cm^{-1} 3027, 1655, 961 (film); ^{1}H NMR (90 MHz, CCl_4,) δ 0.99 (t, *J* 7.5 Hz, 3H), 1.57-2.35 (m, 2H), 3.60-4.00 (m, 2H), 5.20-6.00 (m, 2H).

*(2R,3S)-1-Iodo-butane-2,3-diol (**11**)*

AD-mix-α® (4.2 g) was added to a solution of (*E*)-1-iodo-but-2-ene (**9**) (0.55 g, 3 mmol), methanesulfonamide (0.29 g, 3 mmol) and sodium bicarbonate (0.76 g, 9 mmol) in *t*-butanol:water (1:1, 30 mL), and stirred at 0 ºC for 15 h. The reaction was quenched with sodium sulfite (4.5 g), stirred for 15 min at 0 ºC and for 10 min at room temperature, and then extracted with CH_2Cl_2 (3 x 25 mL). The combined extracts were washed with brine, dried and concentrated to furnish a yellowish solid. The crude solid was recrystallized from *n*-hexane/ethyl acetate (4:1) and purified by "dry-column" flash chromatography (*n*-hexane:ethyl acetate, 3:1), yielding a white solid (0.49 g, 76%); m.p. 61-63 ºC; IR ν_{max}/cm^{-1} 3311, 1145, 1050 (KBr); ^{1}H NMR (200 MHz, CD_3OD) δ 1.15 (d, *J* 6.5 Hz, 3H), 3.12-3.24 (m, 1H), 3.34-3.46 (m, 2H), 3.80 (dq, *J* 4.5 and 6.5 Hz, 1H); ^{13}C NMR (50 MHz, CD_3OD) δ 9.5, 19.5, 70.4, 76.7.

*(2S,3R)-1-Iodo-pentane-2,3-diol (**12**)*

Using the same conditions as described above, compound **12** was synthesized from olefin **10** (0.59 g, 3 mmol) utilizing, in this case, the AD-mix-β® (4.2 g) to obtain a white solid (0.55 g, 80%); m.p. 65-67 ºC; IR ν_{max}/cm^{-1} 3641, 3236, 1149, 1054 (KBr); ^{1}H NMR (200 MHz, CD_3OD) δ 0.96 (t, *J* 7.5 Hz, 3H), 1.39-1.63 (m, 2H), 3.19 (dd, *J* 6.9 and 10.0 Hz, 1H), 3.36 (dd, *J* 5.2 and 10.0 Hz, 1H), 3.50-3.59 (m, 2H); ^{13}C NMR (50 MHz, CD_3OD) δ 9.5, 11.0, 27.4, 75.4, 75.5.

*(4R,5S)-4-Iodomethyl-2,2,5-trimethyl-[1,3]-dioxolane (**13**)*

To a solution of compound **11** (0.86 g, 4 mmol) in anhydrous CH_2Cl_2 (30 mL) under argon was added 2,2-dimethoxy-propane (0.5 mL, 4 mmol) and pyridinium *p*-toluenesulfonate (0.1 g, 0.4 mmol). After stirring for 5 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with brine (20 mL). Drying and evaporating afforded a colorless liquid that was purified by "dry-column" flash chromatography, eluting with *n*-hexane/ethyl acetate (9:1), to obtain a colorless liquid (1.0 g, 98%); IR ν_{max}/cm^{-1} 1455, 1379, 1241, 1097 (film); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35 (d, *J* 6.0 Hz, 3H), 1.42 (d, *J* 0.6 Hz, 3H), 1.43 (d, *J* 0.6 Hz, 3H), 3.25 (d, *J* 5.2

Hz, 1H), 3.26 (d, *J* 5.2 Hz, 1H), 3.56 (dt, *J* 5.2 and 7.5 Hz, 1H), 3.88 (dq, *J* 6.0 and 7.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.0, 18.5, 27.2, 27.5, 77.4, 81.0, 108.6; GC/EIMS (70 eV) *m/z* 241 (M-CH_3, 100%), 181 (11), 127 (9), 85 (27).

*(4R,5S)-4-Ethyl-5-iodomethyl-2,2-dimethyl-[1,3]-dioxolane (**14**)*

Starting from compound **12** (0.92 g, 4 mmol) and using the same conditions described in the previous method, compound **14** was prepared as a colorless liquid (1.07 g, 99%); IR ν_{max}/cm^{-1} 1458, 1379, 1238, 1033 (film); ^{1}H NMR (200 MHz , $CDCl_3$) *d* 1.03 (t, *J* 7.5 Hz, 3H), 1.41 (d, *J* 0.6 Hz, 3H), 1.44 (d, *J* 0.6 Hz, 3H), 1.55-1.78 (m, 2H), 3.13-3.34 (m, 2H), 3.62-3.78 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) *d* 6.3, 10.0, 26.4, 27.4, 27.6, 79.4, 82.6, 108.9; GC/EIMS (70 eV) *m/z* 255 (M-CH_3, 100%), 195 (53), 85 (88), 59 (49).

*(4S',5S')-6-(2,2,5-Trimethyl-[1,3]-dioxolan-4-yl)-hexan-3-one (**15**)*

Freshly distilled ethyl vinyl ketone (0.4 mL, 3.9 mmol) was added to a suspension of acetonide **13** (0.77 g, 3 mmol), activated zinc[10] (Aldrich, 0.248 g, 3.8 mmol) and copper iodide (0.83 g, 4.4 mmol) in ethanol/water (21 mL/9 mL). The reaction mixture was irradiated with ultrasound for 2 h under argon and then diluted with brine (10 mL). After filtration over diatomaceous earth and extracting with CH_2Cl_2 (3 x 30 mL), the organic phase was washed with brine. Usual work-up gave a yellowish liquid, which was purified by "dry-column" flash chromatography (*n*-hexane:ethyl acetate, 9:2) furnishing a colorless liquid (0.19 g, 30%); IR ν_{max}/cm^{-1} 1718, 1239, 1182, 1103 cm^{-1} (film); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* 7.3 Hz, 3H), 1.24 (d, *J* 6.0 Hz, 3H), 1.36 (s , 3H); 1.38 (s, 3H), 1.42-1.59 (m, 2H), 1.63-1.80 (m, 2H), 2.42 (q, *J* 7.3 Hz, 2H), 2.46 (t, *J* 7.2 Hz, 2H), 3.50 (dt, *J* 4.0 and 8.0 Hz, 1H), 3.70 (dq, *J* 6.0 and 8.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.8, 17.5, 20.5, 27.2, 27.3, 31.6, 35.9, 42.1, 76.7, 82.2, 107.8; GC/EIMS (70 eV) *m/z* 199 (M-CH_3, 11%), 139 (16), 127 (4), 112 (13), 86 (27), 57 (100).

*(4R',5R')-5-(5-Ethyl-2,2-dimethyl-[1,3]-dioxolan-4-yl)-pentan-2-one (**16**)*

Compound **16** was prepared using the same conditions as above, from compound **14** (0.81 g, 3 mmol) and methyl vinyl ketone (0.32 mL, 3.9 mmol), yielding a colorless liquid (0.26 g, 40%); IR ν_{max}/cm^{-1} 1718, 1241, 1170, 1102 (film); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* 7.4 Hz, 3H), 1.36 (s, 6H), 1.40-1.62 (m, 4H), 1.62-1.84 (m, 2H), 2.13 (s, 3H), 2.47 (t, J 7.3 Hz, 2H), 3.54 (dt, *J* 4.4 and 8.0 Hz, 1H), 3.60 (dt, *J* 3.5 and 8.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.5, 20.5, 25.6, 27.1, 29.9, 32.1, 43.4, 80.3, 81.9, 107.5, 208.6; GC/EIMS (70 eV) *m/z* 199 (M-CH_3, 54%), 139 (59), 98 (79), 81 (100).

*(1S,5R,7S)-5-Ethyl-7-methyl-6,8-dioxabicyclo[3.2.1]octane (**1**)*

A solution of adduct **15** (0.17 g, 0.8 mmol) and $H_3PW_{12}O_{40}$ (0.23 g, 0.08 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with water (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and the organic phase washed with brine (20 mL). After drying and evaporation of the solvent, it was obtained a yellowish liquid that was purified by "dry-column" flash chromatography (*n*-hexane:ethyl acetate, 9.5:0.5) to afford a colorless liquid (0.12 g, 96%); IR ν_{max}/cm^{-1} 1463, 1363, 1239, 1182, 1015 (film); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* 7.5 Hz, 3H), 1.18 (d, *J* 6.2 Hz, 3H), 1.47-1.95 (m, 8H), 4.04 (s large, 1H), 4.21 (q, *J* 6.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.3, 17.1, 21.7, 28.1, 30.6, 33.5, 75.6, 80.0, 110.0; GC/EIMS (70 eV) *m/z* 156 (M^+, 7%), 112 (16), 100 (45), 71 (19), 57 (100).

*(1R,5S,7R)-7-Ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane (**2**)*

Using the same conditions as above, compound **2** was prepared as a pale liquid (0.12 g, 96%); IR ν_{max}/cm^{-1} 1461, 1382, 1239, 1174, 1033 (film); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* 7.4 Hz, 3H), 1.40 (s, 3H), 1.41-1.94 (m, 8H), 3.92 (t, *J* 6.5 Hz, 1H), 4.12 (s large, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.8, 17.2, 25.1, 28.0, 28.6, 35.0, 78.3, 81.2, 107.7; GC/EIMS (70 eV) *m/z* 156 (M^+, 8%), 114 (100), 98 (46), 85 (96).

Results and discussion

In this novel synthesis of *exo*-isobrevicomin (**1**) and *exo*-brevicomin (**2**), (*E*)-but-2-en-1-ol (**5**) and (*E*)-pent-2-en-1-ol 95% (**6**), purchased from Aldrich as a 95:5 mixture of *E*:*Z* isomers, were converted by the method already described[11] into their respective tosylated derivatives **7** and **8** in 85 and 80% yield, respectively. The next step, involving a nucleophilic substitution with NaI in anhydrous acetone permitted, in almost quantitative yields, the preparation of iodide derivatives **9** and **10**, whose respective *E*:*Z* compositions (98:2 and 95:5) were characterized by gas chromatography (DB-WAX). The asymmetric catalytic *cis*-dihydroxylation of the double

bonds of **9** and **10**, mediated by the commercially available Sharpless reagents (AD-mix-α® and AD-mix-β®),[12] which have already been used to synthesize the (-)-*exo*-isobrevicomin (**1**),[3,4] (+)-*exo*-brevicomin (**2**) and respective *endo* isomer[13], furnished the corresponding diols **11** and **12**, in 76–80% yield. Since compounds **9** and **10** were also primary halides, the dihydroxylation reaction was carried out under buffered conditions by the addition of $NaHCO_3$ in order to avoid the formation of an epoxy intermediate.[12] Purification by recrystallization and column flash chromatography enhanced the diastereomeric purity of diols **11** and **12** (92:8 and 94:6 ratios, respectively, by chiral gas chromatography on Chirasil-DEX CB). The absolute configuration for **11** and **12** was suggested based on a related transformation reported by Sharpless and co-workers with (*E*)-crotyl chloride.[12] The acetonides **13** and **14**, obtained quantitatively by the classical method (2,2-dimethoxy-propane and PPTS),[14] were submitted to conjugate addition, promoted by Zn/Cu couple, with ethyl or methyl vinyl ketones under ultrasonic radiation.[15] The proposed mechanism for the reaction of these adducts has been discussed as involving a free radical formed in the aqueous medium.[16] For the primary halide compounds, several studies have confirmed their low reactivity in the coupling reaction and poor yields have resulted from the generation of side products.[16,17] The intramolecular acetalization of adducts **15** and **16** was catalysed by the heteropoly acid, phosphotungstic acid, a catalyst that has been underutilized for carrying out organic reactions in heterogeneous and homogenous systems, although it has been applied in some industrial and academic cases.[18-20] *exo*-Isobrevicomin (**1**) and *exo*-brevicomin (**2**) were synthesized from adducts **15** and **16** in 96% yield. Involving six steps, the overall yields for the natural products **1** and **2** were 17 and 23%, respectively, based on the starting materials **5** and **6**. The spectrometric data (IR, ^{1}H and ^{13}C NMR, GC/MS) of these both compounds were compared to those reported in the literature.

The chemical methodology described herein has enabled us to prepare compounds **1** and **2** and should be readily adapted to prepare isomers and higher homologues.

Acknowledgments

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