292.1861, found 292.1857. Anal. Calcd: C, 73.92; H, 9.65. Found: C, 74.38; H, 9.57.

γ-(Phenylthio)-α,β-unsaturated Aldehydes 3a–c. These compounds were prepared following the procedure of Sowerby and Coates.[6]

Compound 3a: yield 90%; mp 51–51.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 6 H), 1.4–1.8 (m, 4 H), 2.1–2.3 (m, 2 H), 3.96 (s, 2 H), 7.3 (br s, 5 H), 10.28 (s, 1 H); mass spectrum, *m/z* (relative intensity) 260 (15), 150 (100), 135 (27), 107 (21), 81 (20); accurate mass calcd for $C_{16}H_{20}OS$ 260.1235, found 260.1239. Anal. Calcd C, 73.80; H, 7.74. Found: C, 73.56; H, 7.79. DNPH, mp 179–180 °C. Anal. Calcd for $C_{22}H_{24}N_4O_4S$: C, 59.98 H, 5.49. Found: C, 59.79; H, 5.66.

Compound 3b: yield 79%, obtained as a yellow oil which crystallized upon standing in the refrigerator, mp 55–57 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 0.93 (s, 3 H), 1.13 (s, 3 H), 1.1–2.5 (m, 11 H), 3.90 (q_{AB}; δ_A 3.67, δ_B 4.12, J_{AB} = 12 Hz, 2 H), 7.24 (br s, 5 H), 9.97 (s, 1 H); mass spectrum, *m/z* (relative intensity) 328 (38), 299 (7), 218 (100), 203 (29), 175 (11), 105 (14), 91 (11), 81 (13); accurate mass calcd for $C_{12}H_{28}OS$ 328.1861, found 328.1863. Anal. Calcd: C, 76.78; H, 8.59. Found: C, 76.72; H, 8.61. DNPH, mp 173–175 °C. Anal. Calcd for $C_{27}H_{32}N_4O_4S$: C, 63.75; H, 6.34. Found: C, 63.54; H, 6.25.

Compound 3c: yield 91%; mp 89–90 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 1.07 (d, *J* = 6 Hz, 3 H), 1.5–2.6 (m, 10 H), 3.95 (q_{AB}; δ_A 3.75, δ_B 4.15, J_{AB} = 11 Hz, 2 H), 4.63 (d, *J* = 0.9 Hz, 1 H), 4.81 (d, *J* = 0.9 Hz, 1 H), 7.31 (br s, 5 H), 10.21 (s, 1 H); mass spectrum, *m/z* (relative intensity) 326 (27), 216 (100), 173 (93), 105 (17), 91 (19), 81 (16), 79 (16); accurate mass calcd for $C_{21}H_{26}OS$ 326.1704, found 326.1707. Anal. Calcd: C, 77.25; H, 8.03. Found: C, 76.93; H, 7.80. DNPH, mp 103–105 °C. Anal. Calcd for $C_{27}H_{30}N_4O_4S$: C, 64.01; H, 5.97. Found: C, 63.86; H, 5.82.

γ-(Phenylsulfinyl)-α,β-unsaturated Aldehydes 4a–c. The procedure of Leonard and Johnson[7] was followed for the preparation of these sulfoxides.

Compound 4a: yield 90%; mp 145–146 °C; ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.22 (s, 3 H), 1.6–1.8 (m, 4 H), 2.2–2.6 (m, 2 H), 3.98 (q_{AB}, δ_A 3.70, δ_B 4.23, J_{AB} = 13 Hz, 2 H), 7.6 (m, 5 H), 9.80 (s, 1 H). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.53; H, 7.36.

Compound 4b: yield 92%; mp 139–140 °C. The diastereoisomers gave practically the same NMR spectrum: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H), 0.95 (s, 3 H), 1.13 (s, 3 H), 1.3–2.6 (m, 11 H), 3.93 (q_{AB}, δ_A 3.58, δ_B 4.25, J_{AB} = 13 Hz, 2 H), 7.55 (m, 5 H), 9.95 (s, 1 H). Anal. Calcd for $C_{21}H_{28}O_2S$: C, 73.21; H, 8.19. Found: C, 73.19; H, 8.01.

Compound 4c: yield 92%, obtained as an unstable oil which proved to be a mixture of diastereoisomers. The ^{1}H NMR spectrum showed complex multiplets at δ 0.9–1.5 (CH_3), 1.5–2.7 (CH_2) and 3.2–4.5 (-$SOCH_2$), 4.70 and 4.85 (br, s, =CH_2), 7.6 (m, Ar H), 9.67 (s, -CHO) and 9.88 (s, -CHO). This material was most conveniently directly converted into **5c**.

General Procedure for the Preparation of the (Phenylthio)furans 5a–c. A solution of 7.0 mmol of the sulfoxide **4a** (1932 mg), **4b** (2408 mg), or **4c** (2394 mg) in 15 mL of acetic anhydride was stirred for 1.5 h at 110 °C under nitrogen. After cooling, the reaction mixture was poured into 80 mL of 4 N sodium hydroxide solution. The mixture was stirred for 0.5 h and extracted with ether. The ethereal solution was washed with water and brine, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography using 100 g of silica gel and an ether–petroleum ether, bp 40–60 °C mixture (0.3:99.7), as eluent.

Compound 5a: yield 70%; oil; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6 H), 1.5–1.8 (m, 4 H), 2.3–2.6 (m, 2 H), 7.1 (m, 5 H), 7.22 (s, 1 H); mass spectrum, *m/z* (relative intensity) 258 (68), 243 (100), 105 (8), 91 (9), 81 (7), 77 (8); accurate mass calcd for $C_{16}H_{18}OS$ 258.1076, found 258.1071.

Compound 5b: yield 77%; oil; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 3 H), 0.95 (s, 3 H), 1.21 (s, 3 H), 1.3–1.9 (m, 9 H), 2.6–3.0 (m, 2 H), 7.1 (m, 5 H), 7.21 (s, 1 H); mass spectrum, *m/z* (relative intensity) 326 (100), 311 (62), 201 (41), 105 (7), 91 (13), 81 (4), 77 (7), 69 (35); accurate mass calcd for $C_{21}H_{26}OS$ 326.1703, found 326.1708.

Compound 5c: yield 61%; oil; ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.06 (d, *J* = 6 Hz, 3 H), 1.2–2.9 (m, 10 H), 4.52 (d, *J* = 0.9 Hz, 1 H), 4.80 (d, *J* = 0.9 Hz, 1 H), 6.8–7.1 (m, 5 H), 7.22 (s, 1 H); mass spectrum, *m/z* (relative intensity) 324 (100), 309 (54), 200 (19), 199 (15), 105 (6), 91 (14), 81 (4), 77 (9); accurate mass calcd for $C_{21}H_{24}OS$ 324.1546, found 324.1551.

General Procedure for the Preparation of the Butenolides 6a–c. To a solution of 3 mmol of the (phenylthio)furan **5a** (774 mg), **5b** (978 mg), or **5c** (972 mg) in 3 mL of water and 50 mL of methanol was added a solution of 2 mmol of $HgCl_2$ in 3 mL of 4 N hydrochloric acid and 50 mL of methanol. This reaction mixture was stirred at room temperature for 1 to 5 days, until the hydrolysis was complete. The methanol was evaporated in vacuum at room temperature and 20 mL of water was added. The water solution was extracted with ether. The ethereal solution was washed with $NaHCO_3$ solution and with brine and dried ($MgSO_4$), and the ether was evaporated. The residue was purified by column chromatography on silica gel by using an ether–petroleum ether, bp 40–60 °C mixture (30:70), as eluent.

Compound 6a: yield 90%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 6 H), 1.5–2.4 (m, 6 H), 4.59 (s, 2 H); mass spectrum, *m/z* (relative intensity) 166 (95), 151 (100), 138 (17), 137 (18), 123 (68), 121 (30), 95 (44), 93 (48), 91 (19), 79 (18), 77 (18); accurate mass calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0994.

Compound 6b: yield 90%; mp 88–90 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H), 0.95 (s, 3 H), 1.18 (s, 3 H), 1.2–2.5 (m, 11 H), 4.58 (s, 2 H); mass spectrum, *m/z* (relative intensity) 234 (28), 219 (100), 189 (11), 163 (19), 151 (54), 123 (26), 95 (11), 91 (18), 81 (13), 79 (12), 77 (11); accurate mass calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1615. Anal. Calcd: C, 76.88; H, 9.46. Found: C, 76.88; H, 9.37.

Compound 6c:[11] yield 61%; mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H), 0.96 (d, *J* = 6 Hz, 3 H), 1.1–1.9 (m, 8 H), 2.7–2.9 (m, 2 H), 3.87 (s, 2 H), 4.54 (d, *J* = 0.9 Hz, 1 H), 4.80 (d, *J* = 0.9 Hz, 1 H); mass spectrum, *m/z* (relative intensity) 232 (96), 217 (100), 204 (18), 203 (21), 189 (22), 162 (28), 151 (29), 150 (23), 107 (33), 105 (30), 91 (42), 79 (38), 77 (28); accurate mass calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1453. Anal. Calcd: C, 77.55; H, 8.68. Found: C, 77.50; H, 8.75.

Registry No. **1a**, 1193-47-1; **1b**, 16776-05-9; **1c**, 89656-00-8; **2a**, 67218-06-8; **2b**, 89708-57-6; **2c**, 89656-01-9; **3a**, 81053-99-8; **3b**, 89656-02-0; **3c**, 89656-03-1; **4a**, 81054-00-4; **4b**, 89656-04-2; **4c**, 89656-05-3; **5a**, 89656-06-4; **5b**, 89656-07-5; **5c**, 89708-58-7; **6a**, 89656-08-6; **6b**, 1684-54-4; **6c**, 60114-23-0; $PhSCH_2Li$, 13307-75-0.

(11) The ^{1}H NMR spectrum of **6c** was in complete agreement with that kindly provided by Professor R. E. Corbett.[12]

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Synthesis of the Novel Marine Diterpenes (±)-Isocopal-12-ene-15,16-dial, (±)-14-Epiisocopal-12-ene-15,16-dial, and (±)-15-Acetoxyisocopal-12-en-16-al from Methyl Isocopalate

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Sesquiterpenes possessing two aldehyde groups, isolated from terrestrial and marine organisms,[1] showed a wide spectrum of biological activity.[2,3] A new series of tricyclic diterpenes **1**, **2**, and **3**, with an arrangement of functional groups similar and very related to those mentioned above,

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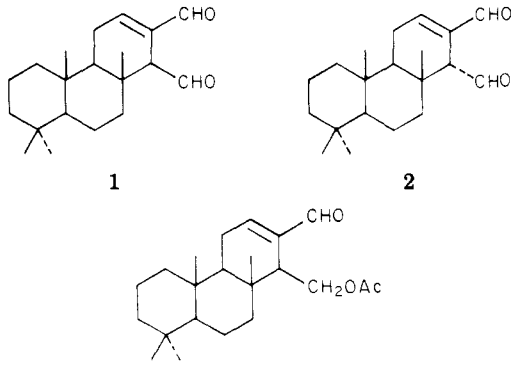


1 2

3

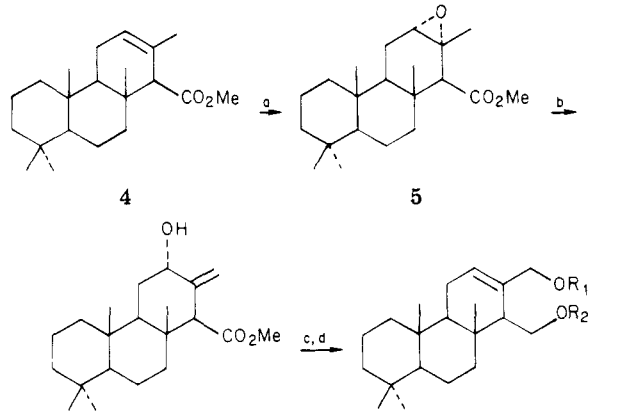
were recently isolated from *Spongia officinalis*.[4] As a continuation of our project on the synthesis of terpenoids and related products from marine origen,[5-7] we decided to study the transformation of (±)-methyl isocopalate (**4**)[8] into racemic **1**, **2**, and **3**.

We have found that treatment of the known α-epoxide **5**[5] with aluminum isopropoxide[9] in refluxing toluene afforded **6** in 60% overall yield from **4** (Scheme I). Oxidation of diol **7a** with dimethyl sulfoxide–oxalyl chloride[10] gave 79% of crystalline **1**, showing identical IR, ^1H and ^{13}C NMR, and mass spectral data to those reported for the natural product.[4] Epimerization of **1** with basic alumina in refluxing dichloromethane afforded a 1:2 mixture of **1** and **2**, from which the less polar dialdehyde **2** was isolated as a crystalline product. The IR and ^1H NMR spectral data of **2** are coincident with those reported for the natural product. Also, the γ effect of the pseudoaxial carbonyl group, in the ^{13}C NMR spectrum of **2**, shields the signal of C-11 by 5.1 ppm in comparison with the shift of the same carbon of **1**, confirming the proposed stereochemistry. For the synthesis of **3**, diol **7a** appeared to be the best choice as starting material since regioselective protection of the allylic and less hindered alcoholic function followed by acetylation of the remaining hydroxyl group, deprotection, and oxidation would give **3**. In practice, however, the use of *tert*-butyldimethylsilyl chloride and imidazole in dimethylformamide, as described previously for a related transformation,[11] led to a 1:1 mixture of mono- and disilyl ethers **7b** and **7c**. Acetylation of **7b** gave the acetate **7d**, which was hydrolyzed with acetic acid in aqueous tetrahydrofuran to hydroxy acetate **7e**. Finally, manganese dioxide oxidation of **7e** afforded the oily product **3**. The IR, ^1H NMR, and mass spectral data of synthetic **3** are in good agreement with those reported for the natural product, and further, the ^{13}C NMR spectrum shows the expected signals supporting the proposed structure.

Experimental Section

Melting points were determined on an Ernst Leitz hot-stage microscope and are uncorrected. IR spectra were measured with a Beckman Acculab 8 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at 80.13 and 20.15 MHz, respectively, on a Bruker WP 80 SY spectrometer, in $CDCl_3$ solutions. The carbon shifts of **2** and **3** were assigned by comparison with the reported data of **1**[4] and analysis of the single-frequency off-resonance decoupled (SFORD) spectra and the generated CH/CH_3 and CH_2/q subspectra by spin–echo sequence utilizing the proton-flip method (APT).[12] Silica gel GF_{254} (type 60) was utilized for TLC, and spots were visualized by staining with anisaldehyde–sulfuric acid.[13]

Scheme I[a]



4 5 6

7a, $R_1 = R_2 = H$
b, $R_1 = t\text{-BuMe}_2Si$; $R_2 = H$
c, $R_1 = R_2 = t\text{-BuMe}_2Si$
d, $R_1 = t\text{-BuMe}_2Si$; $R_2 = OCCH_3$
e, $R_1 = H$; $R_2 = OCCH_3$

[a] (a) $mCPBA/CH_2Cl_2$; (b) $Al(i\text{-PrO})_3$/toluene/reflux; (c) H_2SO_4 (6 N)-dioxane (1:13); (d) $LiAlH_4/Et_2O$.

(±)-Methyl Isocopalate (4) and Its Epoxide 5. These products were prepared as described in ref 5.

(±)-Methyl 12α-Hydroxyisocopal-13(16)-en-15-oate (6). To a stirred solution of **5** (340 mg, 1.02 mmol) in toluene (34 mL) was added aluminum isopropoxide (204 mg, 2.91 mmol), and the mixture was heated at reflux under N_2. After 24 h at this temperature, the mixture was cooled and Et_2O (15 mL) was added. The organic solution was then washed with aqueous 30% NaOH (4 × 30 mL) and brine, dried (Na_2SO_4), and evaporated. The residue upon chromatographic purification gave starting material **5** (30 mg, 9%) and **6** (250 mg, 73%). Crystallization of **6** from hexane afforded material with a melting point of 152–154 °C [lit.[7] mp 155–156 °C].

(±)-Isocopal-12-ene-15,16-diol (7a). This product was prepared as described in ref 7.

(±)-Isocopal-12-ene-15,16-dial (1). To a stirred solution of oxalyl chloride (0.1 mL, 0.11 mmol) in CH_2Cl_2 (2.5 mL) at −60 °C, in a careful dried system, was added a solution of Me_2SO (0.24 mL) in CH_2Cl_2 (1 mL) dropwise. After 10 min of stirring, a solution of **7a** (100 mg, 0.3 mmol) in CH_2Cl_2 (4 mL) was also added dropwise, and the stirring was continued for 4 h at the same temperature. TEA (0.6 mL) was then added. After 15 min, the reaction mixture was allowed to reach room temperature; H_2O (3 mL) was then added and the solution stirred for 10 additional min. The CH_2Cl_2 phase was separated and the aqueous layer extracted with more CH_2Cl_2 (3 × 10 mL). The combined organic extracts were then washed successively with dilute HCl, H_2O, aqueous 10% $NaHCO_3$, and brine, dried (Na_2SO_4), and evaporated. Application of this product (92 mg) to a column of silica gel and elution with hexane and mixtures of hexane–EtOAc afforded pure **1**: 78 mg, 79%; melting point 130–135 °C [lit.[4] mp 139–142 °C]; IR (KBr) 2940–2865, 1720, 1680, 1480, 1400, 1185, 1100, 850 cm^{-1}; ^1H NMR δ 0.83, 0.88, 0.93 and 0.95 (s, C-4, C-8

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and C-10 Me), 2.83 (br s, H-14), 7.12 (br s, H-12), 9.45 (s, H-16), 9.54 (d, J = 4 Hz, H-15); mass spectrum, m/e (relative intensity) 302 (M^+, 2), 274 (29), 259 (23), 177 (8), 135 (10), 121 (100), 107 (18), 95 (21), 69 (28), 55 (15); ^{13}C NMR δ 39.6 (t, C-1), 18.1[a] (t, C-2), 41.6[b] (t, C-3), 32.9 (s, C-4), 56.2 (d, C-5), 17.9[a] (t, C-6), 41.0[b] (t, C-7), 36.9 (s, C-8), 56.7 (d, C-9), 37.4 (s, C-10), 24.1 (t, C-11), 153.7 (d, C-12), 138.6 (s, C-13), 60.7 (d, C-14), 198.1 (d, C-15), 192.5 (d, C-16), 15.5[c] (q, C-17), 33.0 (q, C-18), 21.4 (q, C-19), 15.9[c] (q, C-20). (Assignments with superscripts a–c may be reversed.)

(±)-14-Epiisocopal-12-ene-15,16-dial (2). Basic alumina (500 mg) was added to a stirred solution of 1 (100 mg) in CH_2Cl_2 (40 mL). After 8 h of heating at reflux, the mixture was filtered and the solvent evaporated. Chromatography of the crude product over silica gel with hexane and with mixtures of hexane and increasing amounts of EtOAc resulted in the recovery of starting material 1 (25 mg, 25%) and the isolation of the crystalline dialdehyde **2**: 58 mg, 58%; mp 105–110 °C [lit.[4] mp 115–118 °C]; IR (KBr) 2945–2890, 1735, 1695, 1475, 1400, 1225, 1115, 1000 cm^{-1}; ^1H NMR δ 0.83, 0.85, 0.93 (s, C-4, C-8 and C-10 Me), 3.26 (m, H-14), 7.08 (m, H-12), 9.40 (s, H-16), 9.83 (d, J = 2.4 Hz, H-15); ^{13}C NMR δ 39.3 (t, C-1), 18.1 (t, C-2), 41.3 (t, C-3), 32.9 (s, C-4), 56.1 (d, C-5), 18.1 (t, C-6), 37.9 (t, C-7), 37.0 (s, C-8), 48.8 (d, C-9), 37.6 (s, C-10), 24.5 (t, C-11), 153.5 (d, C-12), 136.7 (s, C-13), 58.3 (d, C-14), 202.0 (d, C-15), 192.5 (d, C-16), 22.4 (q, C-17), 33.0 (q, C-18), 21.5 (q, C-19), 15.1 (q, C-20).

(±)-15-Acetoxyisocopal-12-en-16-al (3). To a stirred solution of **7a** (100 mg, 0.3 mmol) and imidazole (155 mg, 2.2 mmol) in DMF (3 mL) at 0 °C and under N_2 was added *tert*-butyldimethylsilyl chloride (120 mg, 0.6 mmol). After 5 min of stirring at 0 °C and 20 min at room temperature, the mixture was poured into Et_2O (50 mL) and washed with H_2O (50 mL). The organic extract was then dried (Na_2SO_4) and evaporated. Chromatography of the residue (150 mg) over silica gel with hexane and with mixtures of hexane and increasing amounts of EtOAc afforded pure **7c**: [65 mg, 38%; ^1H NMR δ 0.046 (s, 6 H, SiMe), 0.063 (s, 6 H, SiMe), 0.78 and 0.82 (s, C-4, C-8, and C-10 Me), 0.89 (s, $SiCMe_3$), 0.92 (s, $SiCMe_3$), 3.44–3.88 (m, 2 H, $-CH_2OSi-$), 4.20 (br s, 2 H, $-CH_2OSi-$), 5.79 (br s, H-12)] and **7b** [54 mg, 40%; ^1H NMR δ 0.097 (s, 6 H, SiMe), 0.76, 0.82, and 0.88 (s, C-4, C-8, and C-10 Me), 0.90 (s, $SiCMe_3$), 3.77 (br s, 2 H, $-CH_2OH$), 4.07 (d, J = 12 Hz, H-15), 4.36 (d, J = 12 Hz, H-15), 5.69 (br s, H-12).

The monosilyl ether **7b** (54 mg) was treated with Ac_2O (0.6 mL), TEA (3 mL), and DMAP (10 mg) overnight at room temperature. The mixture was then poured into H_2O (30 mL) and extracted. The Et_2O extracts were washed with aqueous 10% Na_2CO_3 and H_2O, dried (Na_2SO_4), and evaporated. The crude product, purified by a short column chromatography, afforded pure **7d**: 50 mg, 85%; ^1H NMR δ 0.097 (s, 6 H, SiMe), 0.76 and 0.88 (s, C-4, C-8, and C-10 Me), 0.90 (s, $SiCMe_3$), 2.04 (s, OCMe), 3.85 (br s, CH_2OAc), 3.91 (d, H-15), 4.14 (d, H-15), 5.80 (br s, H-12).

Without further purification **7d** (50 mg) was hydrolyzed with a mixture of THF:HOAc:H_2O (1:3:1) (10 mL) for 9 h at room temperature. The mixture was then poured into H_2O (20 mL) and extracted with Et_2O. The combined organic extracts were washed with aqueous 10% $NaHCO_3$ and H_2O, dried (Na_2SO_4), and evaporated. The crude product was purified by a short column chromatography, yielding **7e** (30 mg, 81%); ^1H NMR δ 0.79, 0.82, 0.88, and 0.89 (s, C-4, C-8, and C-10 Me), 2.06 (s, OCMe), 3.78–4.69 (complex m, 4 H, H-15 and H-16), 5.83 (br s, H-12).

A mixture of **7e** (30 mg, 0.08 mmol) and active MnO_2 (900 mg), dried as prescribed by Goldman,[14] in benzene (40 mL) was stirred for 18 h. After filtration of the mixture through a Celite pad, the filtrate and washings were concentrated to dryness. Chromatography of the residue on silica gel with EtOAc–hexane afforded **3** (20 mg, 69%) as an oily product: IR ($CHCl_3$) 3940, 2860, 1740, 1695, 1470, 1380, 1100 cm^{-1}; ^1H NMR δ 0.83, 0.87, and 0.97 (s, C-4, C-8, and C-10 Me), 1.94 (s, OCMe), 4.30–4.75 (AB part of an ABX system, 2 H, H-15), 6.90 (br s, H-12), 9.42 (s, H-16); mass spectrum, m/e (relative intensity) 347 ($(M + 1)^+$, 15), 303 (30), 287 (28), 286 (28), 271 (35), 192 (90), 177 (95), 105 (60), 95 (70), 91 (99), 81 (100); ^{13}C NMR δ 39.7 (t, C-1), 18.3 (t, C-2), 41.6 (t, C-3), 33.2 (s, C-4), 56.1 (d, C-5), 18.4 (t, C-6), 41.2 (t, C-7), 36.0 (s, C-8), 53.7 (d, C-9), 36.0 (s, C-10), 23.8 (t, C-11), 153.0 (d, C-12), 139.8 (s, C-13), 49.1 (d, C-14), 59.9 (t, C-15), 193.9 (d, C-16), 15.8 (q, C-17), 33.0 (q, C-18), 21.5 (q, C-19), 15.3 (q, C-20), 170.7 and 21.5 (OCMe).

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A Practical Synthesis of Racemic Vinylglycine from (*Z*)-2-Butene-1,4-diol

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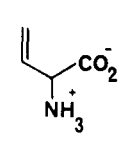
β,γ[1] and γ,δ-Unsaturated[2,3] amino acids belong to a growing class of natural products that possess biological activity both as irreversible enzyme inhibitors[4,5] and as antibiotics.[6,7] This class of compounds has held long-standing interest[8–11] among chemists. In particular, the total synthesis of vinylglycine 1 has received the most



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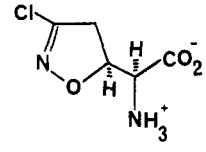

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attention.[8,10] During our efforts toward a total synthesis[12] of acivicin (**2**),[13] an antitumor, antimetabolite from fermentation broth of *Streptomyces sviceus*, we developed a practical synthesis of racemic vinylglycine using a synthetic route that holds considerable promise for a commercial synthesis of this amino acid.

Recently, Bartlett and Barstow[14] elegantly demonstrated the application of the ester–enolate Claisen rearrangement of α-amino acid derivatives to the synthesis of natural γ,δ-unsaturated amino acids. In contrast, our synthetic strategy toward the β,γ-unsaturated amino acid 1 is centered upon the well-documented[15] [3,3] sigmatropic rear-

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