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Novel Synthetic Approach to (*S*)-Coriolic Acid

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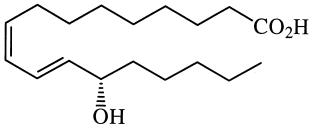
Abstract—A new synthetic approach to (*S*)-coriolic acid **1** has been developed, starting from the readily available (*E*)-1-bromo-2-trimethylsilylethene **4** and trimethylsilylacetylene **5**. A simple acylation reaction of **4**, followed by a coupling reaction of the halogenoderivative intermediate with **5** in the presence of a Pd(0) catalyst affords the monosilylated ketoenyne **7**. After desilylation of **7**, enantioselective reduction of the carbonyl group with (*S*)-BINAL-H leads to the alcohol **2** (*e.e.*=94%). A subsequent coupling reaction and stereoselective reduction of the triple bond affords the target molecule **1**.

Introduction

Coriolic acid **1** is an oxygenated unsaturated fatty acid deriving from the metabolism of linoleic acid in plants and animals and possessing interesting biological properties. Compound **1** has been isolated from rice (*Oryza sativa* L.) and shown to act as a self defense substance against rice blast disease.[1] Furthermore, coriolic acid **1** is present in bovine heart mitochondria[2] and in the sera of patients with familiar Mediterranean fever.[3] These properties have prompted numerous synthetic[4–9] and chemo-enzymatic[10–16] approaches to this valuable compound. Frequently the Wittig reaction[4] is employed between a chiral unsaturated hydroxy aldehyde and the appropriate phosphonium salt in order to generate the (*E*,*Z*)-dienyl moiety[5,6,10] or compound **1** can be conveniently obtained by the action of soybean lipoxygenase on linoleic acid followed by sodium borohydride reduction.[11–14] Alternative methodologies involve coupling reactions of chiral hydroxy vinyl halides with fatty acids containing a terminal triple bond,[7,15] or of a chiral alkynol with the appropriate (*Z*)-vinyl halide,[9] or coupling reactions of chiral (*E*)-hydroxy vinylstannanes with (*Z*)-vinyl halides.[8,16]



1 (*S*)-*Coriolic acid*

In our recent studies on the synthesis of stereodefined compounds[17] we have devised new methodologies for the synthesis of a series of natural compounds[18–23] with a conjugated polyenyl structure, starting from unsaturated silyl derivatives. Thus, we considered compound **1** as an attractive target for synthesis and now we wish to report a novel synthetic approach to (*S*)-coriolic acid.

Results and Discussion

Our overall synthesis design is summarized in a retroanalytical fashion in Scheme 1.

Thus, the disconnection of the C_8–C_9 bond leads to the chiral fragment **2**, whose stereogenic center can be obtained by enantioselective reduction of the unsaturated carbonyl compound **3**. The unsaturated moiety of the ketone **3** can be realized by employing simple silyl derivatives **4** and **5**. The key steps leading to compound **1** require a coupling reaction of the chiral fragment **2** with the appropriate halogeno acid and stereoselective reduction of the triple bond.

Accordingly, the synthesis of the alcohol **2** was performed as depicted in Scheme 2. The intermediate **6** was obtained in 99% yield, by a simple acylation reaction[24] of (*E*)-1-bromo-2-trimethylsilylethene **4** with the hexanoyl chloride/$AlCl_3$ complex, as a 70:30 mixture of compound **6a** (the bromovinylketone) and compound **6b** (the chlorovinylketone). [The acylation reaction, which should be an addition reaction of the acyl chloride, followed by an elimination reaction of trimethylsilyl chloride,[25] probably also involves the elimination of trimethylsilyl bromide.] The subsequent reaction of compound **6** with trimethylsilylacetylene **5** in the presence of a Pd(0) catalyst[26] led to the monosilylated ketoenyne **7** in 61% yield. Desilylation of compound **7** with KF/MeOH led to the ketone **3** (72% yield), which was subjected to enantioselective reduction of the carbonyl group with (*S*)-BINAL-H.[27] The (*S*)-alcohol **2** was obtained

Keywords: silicon and compounds; stereoselective synthesis; natural products.

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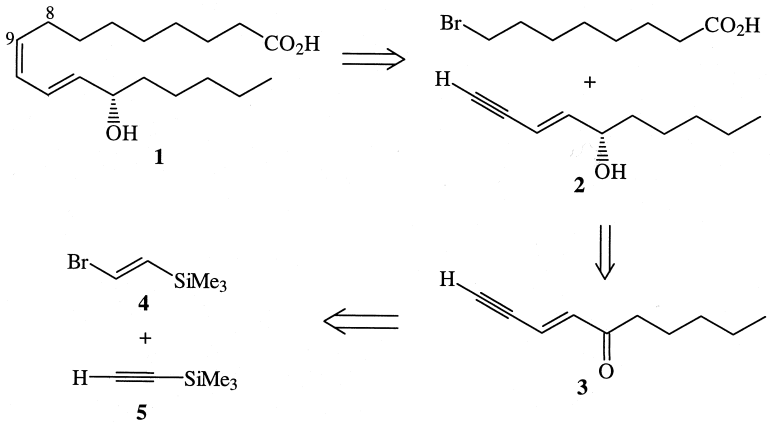
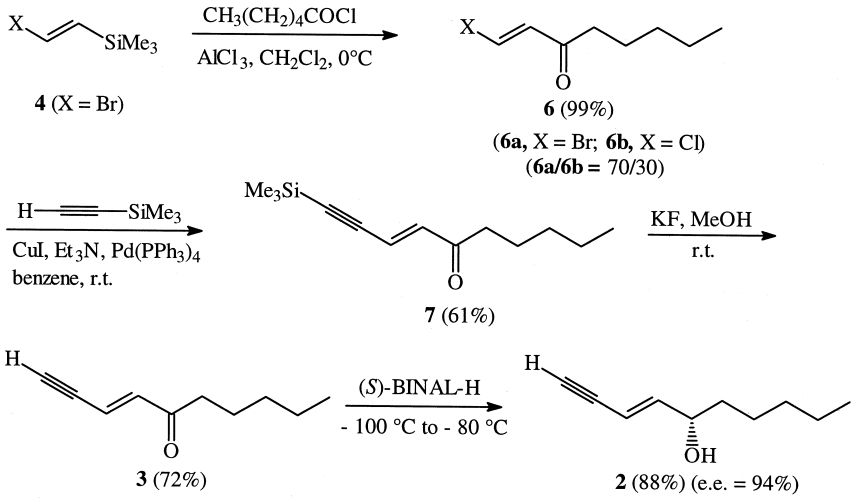
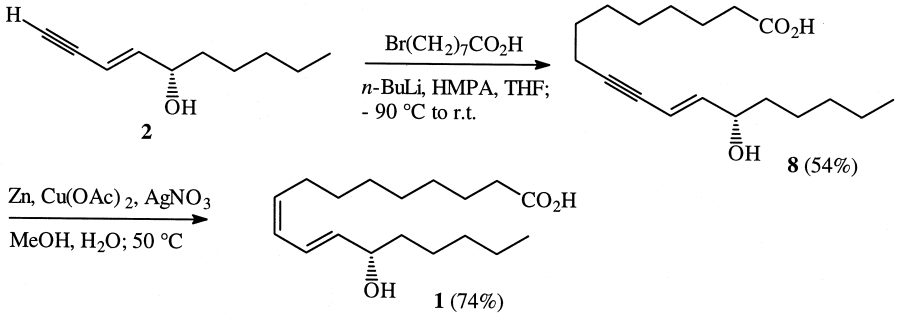


Scheme 1.



Scheme 2.



Scheme 3.

in 88% yield. The enantiomeric excess was evaluated to be 94%, by ^{1}H NMR analysis of the esters obtained by reaction of the alcohol **2** with the (*R*)-β,β,β-trifluoro-α-methoxy-α-phenylpropionyl chloride, according to Mosher's procedure.[28]

The completion of the synthetic strategy described in Scheme 1 required a coupling reaction of the (*S*)-alkynol **2** with the appropriate bromoacid[29] (Scheme 3).

The product **8** was obtained in 54% yield. Stereoselective reduction of the triple bond of the alcohol **8** with activated Zn[30] led to the target molecule **1** in 74% yield.

In conclusion, our synthetic approach to (*S*)-coriolic acid compares favorably with other procedures. A special advantage of our strategy is represented by the possibility of creating different stereoisomers, both in the reduction step of the triple bond and in the reduction of the acetylenic

ketone by the same chiral reagent, but in the opposite configuration. Moreover, the ready availability of the silyl derivatives employed and the simplicity of the operations involved are additional features making the procedure very useful.

Experimental

Macherey–Nagel silica gel (60, particle size 0.040–0.063 mm) for flash column chromatography and Macherey–Nagel aluminum sheets with silica gel 60 F_{254} for TLC were used. GC analysis was performed on a Hewlett–Packard 5890 series II gas chromatograph equipped with a SE-30 (methylsilicone, 30 m×0.25 mm id) capillary column. GC–mass-spectrometry analysis was performed on a Shimadzu GCMS-QP5000 gas chromatograph–mass spectrometer equipped with a MDN-1 capillary column (methylsilicone, 30 m×0.25 mm id). ^{1}H NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 500 MHz and on a Varian XL 200 spectrometer at 200 MHz. ^{13}C NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 125.7 MHz. IR spectra were recorded on a Perkin Elmer 1710 FT spectrometer.

1-Bromo-1(*E*)-octen-3-one (6a) and 1-chloro-1(*E*)-octen-3-one (6b). A CH_2Cl_2 solution (40 mL) of freshly distilled hexanoyl chloride (3.61 g, 26.82 mmol) was added, under nitrogen, to a cold (0°C) suspension of anhydrous $AlCl_3$ (3.58 g, 26.82 mmol) in 40 mL of CH_2Cl_2. The resulting mixture was stirred for 10 min at 0°C, then a solution of (*E*)-1-bromo-2-trimethylsilylethene **4** (4.00 g, 22.33 mmol) in 40 mL of CH_2Cl_2 was added dropwise. After complete addition, the reaction mixture was stirred at 0°C for 1 h, quenched with a saturated aqueous solution of NH_4Cl (100 mL), and extracted with ethyl acetate (3×50 mL). The organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9.5:0.5) leading to a 70:30 mixture of (*E*)-1-bromo-1-octen-3-one **6a**[15] and (*E*)-1-chloro-1-octen-3-one **6b**[31] (4.20 g, 99% yield). The mixture of **6a** and **6b** was employed for the preparation of compound **7**.

(6a)+(6b) ^{1}H NMR data (200 MHz, $CDCl_3$): δ 0.86 (t, J=6.7 Hz, 3H), 1.15–1.40 (m, 4H), 1.45–1.70 (m, 2H), 2.49 (t, J=7.4 Hz, 2H), 6.50 (d, J=13.6 Hz, vinylic H of **6b**), 6.77 (d, J=14.0 Hz, vinylic H of **6a**), 7.26 (d, J=13.6 Hz, vinylic H of **6b**), 7.50 (d, J=14.0 Hz, vinylic H of **6a**) ppm. IR (neat) ν 1700, 1682, 1585, 943 cm^{-1}.

(6a) MS *m*/*z*: 163 (2), 161 (2), 150 (67), 148 (71), 135 (99), 133 (100), 125 (27), 107 (15), 105 (14), 82 (11), 69 (15), 55 (48), 43 (82), 41 (54).

(6b) MS *m*/*z*: 125 (17), 106 (15), 104 (48), 91 (31), 89 (100), 69 (9), 63 (4), 61 (13), 55 (17), 43 (36), 41 (27).

1-Trimethylsilyl-3(*E*)-decen-1-yn-5-one (7). A solution of ethynyltrimethylsilane **5** (2.75 g, 28.00 mmol) in benzene (50 mL) was added at room temperature, under nitrogen, to a stirred mixture of **6** (4.20 g, 22.21 mmol), Et_3N (4.25 g, 42.00 mmol), CuI (0.27 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.65 g, 0.56 mmol) in benzene (70 mL). After reaction completion (7 h), the mixture was quenched with a saturated aqueous solution of NH_4Cl (100 mL), and extracted with ethyl acetate (3×50 mL). The organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The residue, containing a small amount of unreacted compound **6b** (~7%), was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9.7:0.3) affording 3.03 g (61% yield) of pure **7** as a yellow oil.

^{1}H NMR data (500 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.82 (t, J=7.0 Hz, 3H), 1.15–1.30 (m, 4H), 1.54 (quintet, J=7.4 Hz, 2H), 2.44 (t, J=7.4 Hz, 2H), 6.46 (d, J=16.0 Hz, 1H), 6.55 (d, J=16.0 Hz, 1H) ppm. ^{13}C NMR data (125.7 MHz, $CDCl_3$): δ −0.52, 13.78, 22.33, 23.60, 31.26, 41.01, 101.88, 105.38, 122.35, 137.82, 199.02 ppm. IR (neat) ν 1694, 1677, 1594, 1252, 847 cm^{-1}. MS *m*/*z* 207 (M^+−15, 22), 166 (59), 151 (100), 97 (60), 75 (32), 43 (32). Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 69.90; H, 9.80.

3(*E*)-decen-1-yn-5-one (3). 4.71 g of KF (81.04 mmol) were added at room temperature to a solution of **7** (2.575 g, 11.58 mmol) in CH_3OH (100 mL). The reaction mixture was stirred for 2 h, quenched with a saturated aqueous solution of NH_4Cl (200 mL), and extracted with ethyl acetate (3×150 mL). The organic extracts were washed with water (3×100 mL), dried over Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 9.5:0.5) led to compound **3** (1.25 g, 72% yield) as a dark yellow oil.

^{1}H NMR data (500 MHz, $CDCl_3$): δ 0.82 (t, J=7.0 Hz, 3H), 1.17–1.31 (m, 4H), 1.55 (quintet, J=7.4 Hz, 2H), 2.47 (t, J=7.4 Hz, 2H), 3.33 (s, 1H), 6.52 (s, 2H) ppm. ^{13}C NMR data (125.7 MHz, $CDCl_3$): δ 13.75, 22.30, 23.44, 31.20, 41.02, 80.66, 86.28, 121.41, 138.93, 198.85 ppm. IR (neat) ν 3304, 3256, 2102, 1694, 1599, 963 cm^{-1}. MS *m*/*z* 135 (M^+−15, <1), 121 (3), 107 (5), 94 (84), 79 (100), 66 (17), 51 (54), 43 (19), 41 (17). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.61; H, 9.46.

(*S*)-3(*E*)-decen-1-yn-5-ol (2). 6.4 mL of a 1 M solution of EtOH in THF (6.40 mmol) were added dropwise at room temperature, under nitrogen, to a stirred solution of $LiAlH_4$ in THF (1 M, 6.4 mL, 6.40 mmol). Then 25 mL of a THF solution of (*S*)-binaphthol (1.83 g, 6.40 mmol) were added dropwise at the same temperature. The resulting mixture of BINAL-H reagent[27] was stirred for 30 min at room temperature, then cooled to −100°C. A solution of **3** (0.32 g, 2.13 mmol) in THF (15 mL) was added dropwise over a period of 20 min at −100°C. The reaction mixture was stirred for 1 h at this temperature and at −80°C for an additional 1 h. After addition of 1 mL of CH_3OH at −80°C, the mixture was warmed to room temperature. Then, dilute HCl was added (50 mL) and the reaction mixture extracted with ethyl acetate (3×80 mL). The organic extracts were washed with water (100 mL), dried over Na_2SO_4 and concentrated under vacuum. *n*-Pentane (50 mL) was added to the residue and pure (*S*)-binaphthol was recovered by filtration. Finally, the organic solution was concentrated and the residue was purified by flash chromatography (silica gel, petroleum

ether/ethyl acetate 8:2) leading to compound **2**[32] (0.285 g, 88% yield) as a yellow oil. $[\alpha]_D^{20}=+16.2$ (c 2.6, chloroform).

^{1}H NMR data (500 MHz, $CDCl_3$): δ 0.84 (t, J=6.9 Hz, 3H), 1.12–1.40 (m, 6H), 1.41–1.56 (m, 2H), 2.18 (br s, 1H), 2.85 (d, J=2.2 Hz, 1H), 4.09 (broad q, J=6.3 Hz, 1H), 5.63 (ddd, J=16.0, 2.2, 1.5 Hz, 1H), 6.19 (dd, J=16.0, 5.9 Hz, 1H) ppm. ^{13}C NMR data (125.7 MHz, $CDCl_3$): δ 13.94, 22.48, 24.83, 31.59, 36.72, 71.95, 77.74, 81.66, 108.45, 147.67 ppm. IR (neat) ν 3400–3100, 2105, 958 cm^{-1}. MS *m*/*z* 109 (3), 99 (9), 96 (12), 95 (25), 81 (100), 71 (13), 55 (19), 53 (79), 51 (18), 43 (77), 41 (33).

To evaluate the enantiomeric excess of (*S*)-**2**, the Mosher's esters of (*S*)-**2** and racemic **2** were prepared according to the following procedure. To a sample of enynol **2** (0.025 g, 0.164 mmol) were added 0.083 g (0.329 mmol) of (*R*)-β,β,β-trifluoro-α-methoxy-α-phenylpropionyl chloride, pyridine (five drops) and CCl_4 (five drops). The mixture was stirred at room temperature for 2 h, then quenched with dilute HCl (10 mL) and extracted with ethyl acetate (3×10 mL). The organic extracts were washed with water (2×10 mL), dried over Na_2SO_4 and concentrated under vacuum. The crude product was subjected to ^{1}H NMR analysis and then purified by flash chromatography (yields in the range 75–81%). The derivative of racemic **2** displayed two sets of signals due to vinylic protons (ddd, δ 5.62 and 5.73, dd δ 6.05 and 6.14), the chiral-**2** derivative showed the vinylic signals of the (*S*)-ester at δ 5.73 and 6.14 (97%) and that of the (*R*)-ester at δ 5.62 and 6.05 (3%), indicating an enantiomeric excess of 94%.

13(*S*)-Hydroxy-11(*E*)-octadecen-9-ynoic acid (8). A solution of *n*-BuLi 1.4N in hexane (4.7 mL, 6.58 mmol) was added, under nitrogen, at −80°C, to a solution of **2** (0.50 g, 3.29 mmol) in THF (12 mL) and HMPA (1.72 mL, 9.87 mmol). The temperature was slowly raised to −30°C and maintained for 45 min at this temperature.[29] Then a solution of the dilithium salt of **2** was added, under nitrogen, at −90°C, to a suspension of $Br(CH_2)_7COOLi$, generated by addition of *n*-BuLi (2.4 mL, 3.29 mmol) to a cold (−90°C) solution of 8-bromooctanoic acid (0.734 g, 3.29 mmol) in THF (12 mL). After complete addition, the temperature was slowly raised to room temperature. The reaction mixture was stirred for 15 h, quenched with dilute HCl (30 mL), and extracted with ethyl acetate (3×50 mL). The organic extracts were washed with water (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 7:3) leading to compound **8** (0.523 g, 54% yield) as a pale yellow oil. $[\alpha]_D^{20}=+7.8$ (c 2.7, chloroform).

^{1}H NMR data (500 MHz, $CDCl_3$): δ 0.84 (t, J=7.0 Hz, 3H), 1.12–1.63 (m, 18H), 2.24 (td, J=7.0, 2.1 Hz, 2H), 2.29 (t, J=7.5 Hz, 2H), 4.06 (broad q, J=6.5 Hz, 1H), 5.61 (dtd, J=15.9, 2.1, 1.1 Hz, 1H), 5.98 (dd, J=15.9, 6.5 Hz, 1H), 6.2 (br s, 2H) ppm. ^{13}C NMR data (125.7 MHz, $CDCl_3$): δ 13.92, 19.27, 22.49, 24.55, 24.86, 28.48, 28.51, 28.59, 28.81, 31.65, 33.94, 36.84, 72.49, 78.49, 91.01, 110.55, 143.99, 179.37 ppm. IR (neat) ν 3600–2400, 2217, 1713, 956 cm^{-1}. MS *m*/*z* 276 (M^+ −18, <1), 205 (9), 165 (23), 151 (25), 121 (7), 107 (13), 95 (20), 91 (13), 81 (32), 71 (21), 67 (20), 55 (37), 43 (100), 41 (62). Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.61; H, 10.24.

13(*S*)-Hydroxy-9(*Z*),11(*E*)-octadecadienoic acid (1)-(*S*)-coriolic acid. Nitrogen was passed through a stirred suspension of 2 g of Zn dust (<325 mesh)[30] in 12 mL of H_2O for 15 min, and 0.2 g of $Cu(OAc)_2\cdot H_2O$ were added. Stirring was continued for 15 min, then 0.2 g of $AgNO_3$ were added and the suspension was stirred for a further 30 min. The metal was collected by vacuum filtration and washed with H_2O (2×15 mL), MeOH (2×15 mL), acetone (2×15 mL), and finally Et_2O (2×15 mL). The Et_2O–moist Zn was transferred into 8 mL of H_2O/MeOH 1:1 (v/v) and was ready for use. A solution of **8** (0.183 g 0.62 mmol) in MeOH (4 mL) was added to the suspension of activated Zn and the mixture was stirred at 50°C for 24 h, then cooled at room temperature. A saturated aqueous solution of NH_4Cl (50 mL) and ethyl acetate (50 mL) were added, and after vigorous stirring, the metal was removed by filtration and washed with ethyl acetate (30 mL). The mixture was acidified to pH 2 by adding dilute HCl (20 mL), the organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate (50 mL). The combined organic extracts were washed with water (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 7:3) leading to compound **1** (0.136 g, 74% yield) as a pale yellow oil. $[\alpha]_D=+8.7$ (c 1.22, chloroform), lit.[9] $[\alpha]_D=+9.3$ (c 1.29, chloroform).

^{1}H NMR data (500 MHz, $CDCl_3+D_2O$): δ 0.84 (t, J=6.9 Hz, 3H), 1.15–1.63 (m, 18H), 2.12 (broad q, J=7.7 Hz, 2H), 2.27 (t, J=7.4 Hz, 2H), 4.11 (q, J=6.9 Hz, 1H), 5.38 (dt, J=10.7, 7.7 Hz, 1H), 5.59 (dd, J=15.2, 6.9 Hz, 1H), 5.92 (apparent t, J=11 Hz, 1H), 6.42 (dd, J=15.2, 11.0 Hz, 1H) ppm. ^{13}C NMR data (125.7 MHz, $CDCl_3$): δ 13.93, 22.49, 24.54, 24.97, 27.51, 28.77, 28.82, 28.85, 29.31, 31.66, 33.91, 37.05, 72.81, 125.73, 127.81, 132.56, 135.53, 179.01 ppm. IR (neat) ν 3600–2400, 1713 cm^{-1}.

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