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Enzymatic Resolution of (±)-γ-Cyclohomogeraniol and Conversion of its (*S*)-Isomer to (*S*)-γ-Coronal, the Ambergris Odorant†

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Abstract—Enzymatic acetylation of (±)-γ-cyclohomogeraniol[2-(2′,2′-dimethyl-6′-methylenecyclohexyl)ethanol] with vinyl acetate in the presence of lipase AK yielded the acetate of its (*R*)-isomer, leaving its (*S*)-isomer intact. The (*S*)-isomer was chemically converted to (*S*)-γ-coronal[2-methylene-4-(2′,2′-dimethyl-6′-methylenecyclohexyl)butanal], the ambergris odorant. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Most of the naturally occurring sesquiterpenes and degraded carotenoids are optically active. Enantiomerically pure building blocks 'useful for their synthesis' must therefore be secured, and preferably should be of versatile utility. Enzymatic asymmetric reactions are becoming more important for this purpose,[2] in addition to chemical asymmetric reactions. In 1991, Mori and Puapoomchareon reported the preparation of the enantiomers of **A** (Scheme 1) by enzymatic resolution of its racemate.[3] They converted **A** to **B**, which proved it a versatile building block for sesquiterpenes and degraded carotenoids.[2] Incidentally, Noyori and his co-workers recently synthesized **A** by their asymmetric hydrogenation method.[4] The present paper describes the direct enzymatic resolution of (±)-γ-cyclohomogeraniol[2-(2′,2′-dimethyl-6′-methylenecyclohexyl)ethanol, **1**] isomeric to **B**, and the conversion of (*S*)-**1** to (*S*)-γ-coronal [2-methylene-4-(2′,2′-dimethyl-6′-methylenecyclohexyl)-butanal, **2**], the ambergris odorant.[5] Optically active **1** is envisaged as a multi-purpose building block for terpene synthesis. The existing syntheses of optically active **1** or its corresponding acid by Kurth et al.,[6] Mori and Tamura,[7] and by Vidari et al.[8] are lengthy and inefficient.

Results and Discussion

At the beginning, it was uncertain whether (±)-**1** could be resolved successfully by enzyme catalysis, because the stereogenic center of **1** is separated from the terminal hydroxy group by two methylene groups. Nevertheless, so as to test the feasibility, the substrate (±)-**1** was prepared by the method of Kawanobe et al.[9] in about 30% overall yield based on (±)-**3** (seven steps) (Scheme 2).

Enzymatic resolution of (±)-**1** with hydrolytic enzymes was then investigated.[10] After some experimentation, asymmetric acetylation of (±)-**1** with vinyl acetate in the presence of lipases was found to give optically active (*R*)-(−)-acetate (**4**), leaving optically active (*S*)-(+)-**1** intact.[7,8] Examination of 13 different enzymes including lipase MY (Meito Sangyo), lipase AF (Nagase), lipase A, AK and PS (Amano), and pig liver esterase (Sigma) revealed lipase AK to be the enzyme of choice, when used at 0–4 °C with 1.5 equiv of vinyl acetate in hexane in the presence of MS 4 Å. In preparative experiments, partially resolved (*S*)-(+)-**1** obtained by the enzyme treatment was further acetylated twice enzymatically to give (*S*)-(+)-**1** of 97.8% ee (estimated by GLC analysis on a chiral stationary phase) in 16% yield from (±)-**1**. The partially resolved (*R*)-(−)-**4** was then hydrolyzed with sodium hydroxide, and the resulting (*R*)-(−)-**1** was enzymatically acetylated to give (*R*)-(−)-**4** of increased enantiomeric purity. This enantiomerically enriched acetate (*R*)-(−)-**4** was again hydrolyzed, and the resulting alcohol (*R*)-(−)-**1** was enzymatically acetylated. Thus obtained further enriched (*R*)-(−)-**4** was hydrolyzed with base to give (*R*)-(−)-**1** of 98.0% ee in 18% yield from (±)-**1**. Although tedious, the above described enzymatic resolution procedure afforded both the enantiomer of **1** in gram-scale.

The resolved alcohol (*S*)-**1** was converted to (*S*)-γ-coronal (**2**) as shown in Scheme 2. Accordingly, (*S*)-**1** was tosylated, and the resulting tosylate (*S*)-**5** was

Key words: Enzyme and enzyme reactions; natural products; resolution; terpenes and terpenoids.

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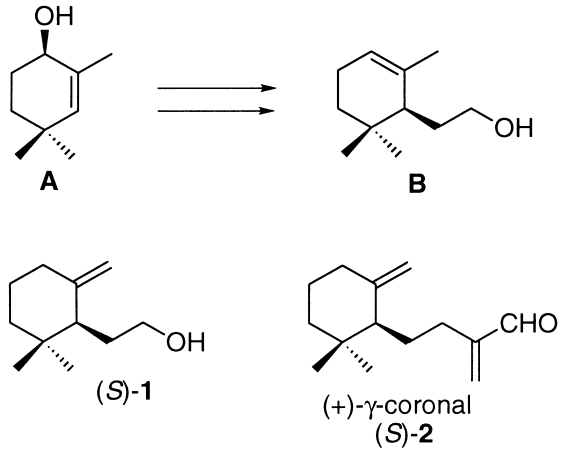
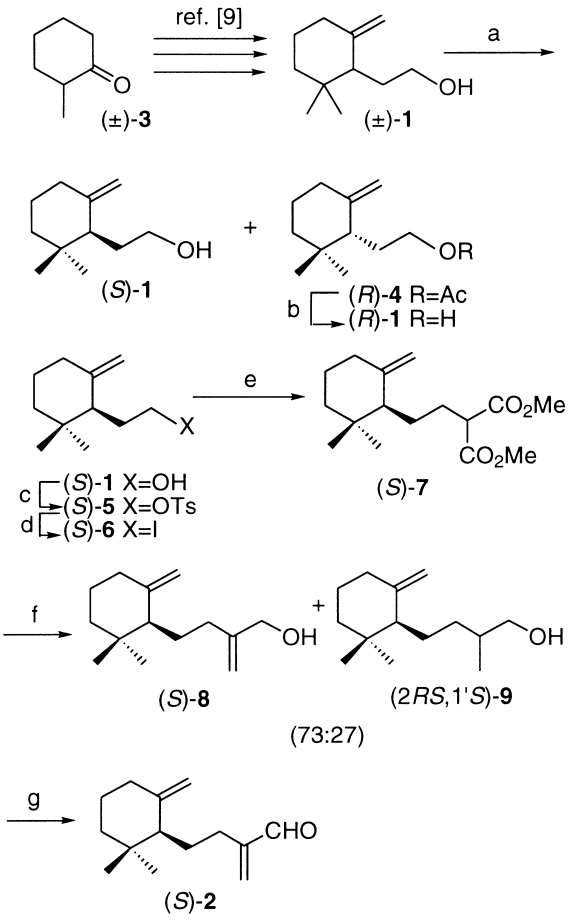
treated with sodium iodide to give (*S*)-**6**. Alkylation of dimethyl malonate with (*S*)-**6** furnished (*S*)-**7**, whose sodio enolate was reduced with lithium aluminum hydride to give a mixture of (*S*)-**8** and (2*RS*,1′*S*)-**9** in a ratio of 73/27.[11] The byproduct **9** could not be removed at this stage, and the mixture was oxidized with activated manganese dioxide. Subsequent chromatographic purification of the product cleanly separated the aldehyde (*S*)-**2** from the non-oxidized alcohol **9**. The desired ambergris odorant (*S*)-γ-coronal (**2**), $[\alpha]_D^{23} = +4.80$ ($CHCl_3$), was obtained in 28% overall yield based on (*S*)-**1** (five steps).



Scheme 1. Structures of the chiral building blocks and (+)-γ-coronal.



Scheme 2. Synthesis of (+)-γ-coronal. (a) $CH_2=CHOAc$ (1.5 equiv), Lipase AK (Amano, 20 wt%), MS 4 Å, hexane, 0–4 °C, 19 h, repeated three times [16% of (*S*)-**1** (97.8% e.e); 18% of (*R*)-**1** after hydrolysis (98.0% e.e.)]; (b) NaOH, MeOH, H_2O, rt, 30 min; (c) TsCl, C_5H_5N, 0–4 °C, 12 h; (d) NaI, Me_2CO, reflux, 4 h [93% based on (*S*)-**1**]; (e) $CH_2(CO_2Me)_2$, NaH, THF, reflux, 21 h (70%); (f) NaH, MeO-$(CH_2)_2$OMe, reflux, 6 h; then cool (0–5 °C), $LiAlH_4$, reflux, 15 min (59%); (g) MnO_2, CH_2Cl_2 room temp., 15 min (72%).

Another synthesis of (*S*)-γ-coronal (**2**) was recently reported by Tanimoto and Oritani[12] by starting from (*S*)-γ-cyclogeranyl bromide.

Conclusion

Both enantiomers of 2-(2′,2′-dimethyl-6′-methylenecyclohexyl)ethanol (**1**) were obtained by enzymatic kinetic resolution of (±)-**1** with lipase AK and vinyl acetate. The utility of the enantiomers of **1** in terpene synthesis was illustrated by converting (*S*)-**1** to (*S*)-γ-coronal (**2**), the ambergris odorant. Derivation of other sesquiterpenes from the enantiomers of **1** will be reported in due course.

Experimental

General methods

IR: Hitachi Perkin Elmer 1640. ^{1}H NMR: Jeol JNM-EX 90A (90 MHz), Bruker DPX 300 (300 MHz), (TMS at $\delta_H = 0.00$ or $CHCl_3$ at $\delta_H = 7.26$ as an internal standard). ^{13}C NMR: Bruker DPX 300 (75.5 MHz), ($CDCl_3$ at $\delta_C = 77.0$ as an internal standard). MS: Jeol JMS-SX 102A and Hitachi M-80B. Optical rotation: Jasco DIP-1000. CC: Merck Kieselgel 60 Art 1.07734.

First enzymatic resolution of (±)-γ-cyclohomogeraniol (1). To a solution of (±)-**1** (2.50 g, 14.9 mmol) in hexane (100 mL), powdered MS 4 Å (2.50 g), distilled vinyl acetate (1.90 mL, 22.3 mmol) and lipase AK (Amano, 500 mg) were added, and the reaction mixture was stirred for 19 h at 0–4 °C. The mixture was filtered through a Celite pad. The filter cake was washed with ethyl acetate. After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (25 g, hexane/ethyl acetate, 150/1) to afford 1.31 g (50%) of the partially resolved (*R*)-**4**. The obtained (*R*)-**4** was treated with 2.5 M sodium hydroxide solution in methanol (10 mL) at rt for 30 min to afford 1.00 g (40%) of the partially resolved (*R*)-**1** as colorless oil. Further elution (hexane/ethyl acetate, 50/1) gave 1.21 g of the partially resolved (*S*)-**1** (48%) as colorless oil. The partially resolved (*R*)-**1**; $[\alpha]_D^{23}$ −12.9 (*c* 1.00, $CHCl_3$). Its IR and ^{1}H NMR spectra were identical with those of (±)-**1**. The enantiomeric purity of this (*R*)-**1** was shown to be 49.0% ee by GLC analysis: GLC [column: Chirasil DEX® CB 0.25 mm×25 m, 1 min at 80 °C + 3 °C/min; Carrier gas: He, press (110 kPa)], $t_R = 24.65$ min [74.5%, (*R*)-**1**], $t_R = 24.94$ min [25.5%, (*S*)-**1**]. The partially resolved (*S*)-**1**;$[\alpha]_D^{23}$ + 10.4 (*c* 1.00, $CHCl_3$). Its IR and ^{1}H

NMR spectra were identical with those of (±)-1. The enantiomeric purity of this (*S*)-**1** was shown to be 41.0% ee by GLC analysis: GLC (the same conditions as above), $t_R = 24.72$ min [29.5%, (*R*)-**1**], $t_R = 24.94$ min [70.5%, (*S*)-**1**]. This was employed in the second resolution step without further purification.

Second enzymatic resolution of the partially resolved (*S*)-1. In almost the same manner as described above, the partially resolved (*S*)-**1** (1.20 g, 7.20 mmol) was treated with powdered MS 4 Å (1.20 g), distilled vinyl acetate (0.93 mL, 10.8 mmol) and lipase AK (210 mg) in hexane (50 mL) for 13 h at 0–4 °C to give 360 mg (32%) of the impure acetate **4** and 700 mg (58%) of the second (*S*)-**1**. $[\alpha]_D^{23}$ +19.1 (*c* 1.00, $CHCl_3$). The enantiomeric purity of (*S*)-**1** was shown to be 81.8% ee by GLC analysis: $t_R = 24.82$ min [9.1%, (*R*)-**1**], $t_R = 25.00$ min [90.9%, (*S*)-**1**]. This was employed in the third resolution without further purification.

Second enzymatic resolution of the partially resolved (*R*)-1. In almost the same manner, the partially resolved (*R*)-**1** (1.00 g, 5.95 mmol) was treated with powdered MS 4 Å (1.00 g), distilled vinyl acetate (0.77 mL, 8.92 mmol) and lipase AK (200 mg) in hexane (43 mL) for 21 h at 0–4 °C to give 640 mg (64%) of the acetate (*R*)-**4** and 280 mg (28%) of impure **1**. The obtained (*R*)-**4** was treated with 2.5 M sodium hydroxide solution in methanol (5 mL) at rt for 30 min to afford 601 mg (60% based on the starting material in the second resolution) of the second (*R*)-**1**. $[\alpha]_D^{23}$ −23.4 (*c*1.00, $CHCl_3$). The enantiomeric purity of (*R*)-**1** was shown to be 84.6% ee by GLC analysis: $t_R = 24.90$ min [92.3%, (*R*)-**1**], $t_R = 25.16$ min [7.7%, (*S*)-**1**]. This was employed in the third resolution without further purification.

Third enzymatic resolution of the second (*S*)-1. In almost the same manner, the second (*S*)-**1** (700 mg, 4.17 mmol) was treated with powdered MS 4 Å (700 mg), distilled vinyl acetate (0.54 mL, 6.25 mmol), and lipase AK (150 mg) in hexane (30 mL) for 24 h at 0–4 °C to give 215 mg (38%) of the impure acetate **4** and 390 mg (56%) of (*S*)-**1**. $[\alpha]_D^{23}$ +26.3 (*c* 1.00, $CHCl_3$). < ref 7: $[\alpha]_D^{21}$ +26.6 (*c* 1.04, $CHCl_3$); ref 8: $[\alpha]_D^{20}$ +24.0 (*c* 0.025, CH_2Cl_2) >. The enantiomeric purity of (*S*)-**1** was shown to be 97.8% ee by GLC analysis: $t_R = 25.05$ min [1.10%, (*R*)-**1**], $t_R = 25.24$ min [98.9%, (*S*)-**1**].

Third enzymatic resolution of the second (*R*)-1. In almost the same manner, the second (*R*)-**1** (600 mg, 3.57 mmol) was treated with powdered MS 4 Å (450 mg), distilled vinyl acetate (0.46 mL, 5.36 mmol) and lipase AK (90 mg) in hexane (30 mL) for 13 h at 0–4 °C to give 324 mg (68%) of the acetate (*R*)-**4** and 182 mg (30%) of impure **1**. The obtained (*R*)-**4** was treated with 2.5 M sodium hydroxide solution in methanol (4 mL) at rt for 30 min to afford 360 mg (60% based on the starting material in the third resolution) of (*R*)-**1**. $[\alpha]_D^{23}$ −26.7 (*c* 1.00, $CHCl_3$). < ref 8: $[\alpha]_D^{20}$ −24.4 (*c* 2, CH_2Cl_2). > The enantiomeric purity of (*R*)-**1** was shown to be 98.0% ee by GLC analysis: $t_R = 25.07$ min [99.0%, (*R*)-**1**], $t_R = 25.24$ min [1.0%, (*S*)-**1**].

2-(2′,2′-Dimethyl-6′-methylenecyclohexyl)ethyl tosylate-[(*S*)-5]. To an ice-cooled solution of (*S*)-**1** (1.30 g, 7.73 mmol) in dry pyridine (30 mL), tosyl chloride (1.54 g, 8.06 mmol) was added, and the reaction mixture was stirred for 12 h at 0–4 °C. It was then diluted with water and extracted several times with diethyl ether. The combined ethereal extracts were washed with 1 M hydrochloric acid, water and brine, and dried with anhydrous sodium sulfate. Removal of the solvent in vacuo gave 2.45 g (quant.) of crude (*S*)-**5**: IR (film) ν 1645 (m, C=C), 1600 (m, Ar), 1360 (s, O=S=O), 1175 cm^{-1} (s, O=S=O); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.78 (3H, s, 2′-CH_3), 0.88 (3H, s, 2′-CH_3), 1.02–2.12 (9H, m, 2, 3′, 4′, 5′-H_2, 1′-H), 2.44 (3H, s, Ar-CH_3), 3.80–4.15 (2H, m, 1-H_2), 4.40 (1H, br. d, *J* = 1.8 Hz, C=C$H_a$$H_b$), 4.68 (1H, br. s, C=C$H_a$$H_b$), 7.30 (2 H, d, *J* = 8.4 Hz, Ar-*H*), 7.79 (2 H, d, *J* = 8.4 Hz, Ar-*H*). This was employed in the next step without further purification.

2-(2′,2′-Dimethyl-6′-methylenecyclohexyl)ethyl iodide[(*S*)-6]. To a solution of the crude (*S*)-**5** in dry acetone (40 mL), sodium iodide (1.40 g, 9.30 mmol) was added, and the reaction mixture was stirred and heated under reflux for 4 h. After cooling to the rt, the mixture was poured into water and extracted several times with pentane. The combined extracts were washed with water, a saturated aqueous sodium hydrogen carbonate solution and brine, and dried with anhydrous sodium sulfate. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (15.0 g, pentane) to give 1.17 g (93%) of (*S*)-**6** as colorless oil: n_D^{24} 1.4873; $[\alpha]_D^{23}$ +4.8 (*c* 0.98, $CHCl_3$); IR (film) ν 1645 (m, C=C), 890 cm^{-1} (m, C=CH_2); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.83 (3H, s, 2′-CH_3), 0.93 (3H, s, 2′-CH_3), 1.20–2.10 (9H, m, 2, 3′, 4′, 5′-H_2,1-H), 2.78–3.42 (2H, m, CH_2I), 4.62 (1H, br. d, *J* = 2.0 Hz, C=C$H_a$$H_b$), 4.81 (1 H, m, C=C$H_a$$H_b$). This was employed in the next step without further purification.

Dimethyl 2-(2′,2′-dimethyl-6′-methylenecyclohexyl)ethylmalonate[(*S*)-7]. To an ice-cooled mixture of sodium hydride (26 mg, 0.64 mmol, 60% mineral oil suspension) in anhydrous tetrahydrofuran (0.5 mL) was added dimethyl malonate (100 mg, 0.75 mmol) in anhydrous tetrahydrofuran (0.5 mL). Then the reaction mixture was allowed to warm to rt. A solution of (*S*)-**6** (148 mg, 0.53 mmol) in anhydrous tetrahydrofuran (1 mL) was added and the mixture was heated under reflux. After stirring for 21 h, it was cooled to rt, diluted with water, and extracted several times with diethyl ether. The combined extracts were washed with water, a saturated aqueous ammonium chloride solution and brine, and dried with anhydrous magnesium sulfate. After evaporation in vacuo, the residue was chromatographed on silica gel (3.0 g, hexane/ethyl acetate, 100/1) to afford 105 mg (70%) of (*S*)-**7** as colorless oil: n_D^{23} 1.4670; $[\alpha]_D^{24}$ +4.57 (*c* 0.94, $CHCl_3$); IR (film) ν 1755 (s, C=O), 1735 (s, C=O), 1645 (m, C=C), 890 cm^{-1} (m, C=CH_2); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.73–0.97 (6H, m, 2′-CH_3), 1.10–2.20 (11 H, m, 1, 2, 3′, 4′, 5′-H_2,1′-H), 3.37 [1 H, t, *J* = 8.5 Hz, C*H*(CO_2Me)$_2$], 3.73 (6 H, s, OCH_3), 4.58 (1 H, m, C=C$H_a$$H_b$), 4.77 (1 H, m, C=C$H_a$$H_b$); Anal

calcd for $C_{16}H_{26}O_4$ (282.4): C, 68.06; H, 9.28. Found: C, 68.24; H, 8.89.

4-(2′,2′-Dimethyl-6′-methylenecyclohexyl)-2-methylene-1-butanol[(*S*)-8] contaminated with (2*RS*,1′*S*)-9. To a solution of (*S*)-**7** (82 mg, 0.29 mmol) in 1,2-dimethoxyethane (1.0 mL), sodium hydride (18 mg, 0.45 mmol, 60% mineral oil suspension) was added, and the mixture was heated under reflux for 6 h. Then it was cooled to 0–5 °C. Lithium aluminum hydride (40 mg, 0.87 mmol) was added, and the mixture was heated under reflux for 15 min. It was then cooled to rt, diluted with diethyl ether, and the excess reagent was destroyed by cautious addition of water. The mixture was filtered through a Celite pad. The filter cake was washed with tetrahydrofuran. The combined filtrate and washings were concentrated in vacuo, and the residue was chromatographed on silica gel (2.0 g, hexane/ethyl acetate, 50/1) to give 37 mg (59%) of a mixture of (*S*)-**8** and (2*RS*,1′*S*)-**9** as colorless oil. Determination of the ratio of (*S*)-**8** and (2*RS*,1′*S*)-**9**; GLC (column: TC WAX 0.53 mm × 15 m, 1 min at 80 °C, +5 °C/min; Carrier gas: He, press (110 kPa), t_R = 13.81 min [27%, **9**], t_R = 14.78 min [73%, **8**]. The purity of (*S*)-**8** was estimated to be 73%. IR (film) ν 3320 (br s, OH), 1645 (s), 890 cm^{-1} (s, C = CH_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (3H, s, 2′-CH_3), 0.92 (3H, s, 2′-CH_3), 1.24–1.42, 1.42–1.75 and 1.99–2.04 (total 12 H, m, 3, 4, 3′, 4′, 5′-H_2,1′-H, OH), 4.07 (2 H, s, 1-H_2), 4.55 (1 H, br. s, 6′-C = C$H_a$$H_b$), 4.77 (1 H, br s, 6′-C = C$H_a$$H_b$), 4.87 (1 H, br. s, 2-C = C$H_a$$H_b$), 5.01 (1 H, br. s, 2-C = C$H_a$$H_b$). This was employed in the next step without further purification.

4-(2′,2′-Dimethyl-6′-methylenecyclohexyl)-2-methylene-butanal [γ-coronal(*S*)-2]. To a stirred solution of (*S*)-**8** and (2*RS*, 1′*S*)-**9** (30 mg, 0.14 mmol) in dry dichloromethane (2 mL), activated manganese dioxide (900 mg) was added at rt. The mixture was stirred for 15 min, and then filtered through a Celite pad. The filter cake was washed with ethyl acetate. The combined filtrate and washings were concentrated in vacuo, and the residue was chromatographed on silica gel (500 mg, hexane/ethyl acetate, 50/1) to give 21 mg (72%) of (*S*)-**2** as a colorless oil: n_D^{23} 1.4543; $[\alpha]_D^{23}$ +4.80 (*c* 0.70, $CHCl_3$); ref 12: $[\alpha]_D^{26}$ +4.9 (*c* 1.2, $CHCl_3$); ref 5: $[\alpha]_D$ +2.5 (*c* 1.2, $CHCl_3$); IR (film) ν 3065 (w, C-H), 2930 (s), 2865 (s), 1695 (s, C = O), 1645 (m, C = C), 1450 (m), 940 (m), 890 cm^{-1} (m, C = CH_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (3 H, s, 2′-CH_3), 0.91 (3 H, s, 2′-CH_3), 1.19–1.23, 1.40–1.76 and 1.95–2.29 (11 H, m, 3′, 4′, 5′, 3, 4-H_2, 1′-H), 4.59 (1 H, s, 6′-C = C$H_a$$H_b$), 4.80 (1 H, s, 6′-C = C$H_a$$H_b$), 5.97 (1 H, s, 2-C = C$H_a$$H_b$), 6.25 (1 H, s, 2-C = C$H_a$$H_b$), 9.53 (1 H, s, CHO); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 24.0, 25.1, 26.7, 27.2, 28.7, 32.7, 35.2, 36.6, 54.2, 109.8, 134.3, 149.2, 151.2, 195.2; EIMS *m*/*z* (% rel int.): 206 (8), 191 (10), 173 (16), 163 (12), 145 (18), 137 (22), 123 (23), 109 (43), 95 (62), 81 (74), 69 (100), 55 (48), 41 (90), 27 (27); HRMS: Found 206.1672; Anal. calcd for $C_{14}H_{22}O$, 206.1670. The ^{1}H NMR data were in good accord with those reported in ref 12.

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