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TETRAHEDRON: *ASYMMETRY*

Diastereoselective protonation of dienols: a formal approach to zaragozic acid C side chain

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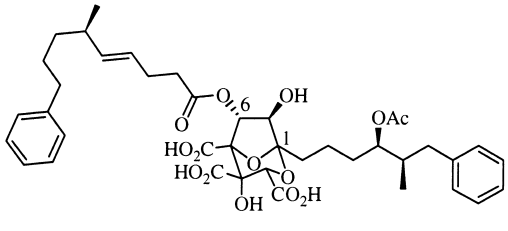
Abstract

The 2-methyl 5-phenylpropanal precursor of the side chain of zaragozic acid C has been prepared in 83% ee through the diastereoselective protonation of a photodienol generated in situ by irradiation of an α,β-unsaturated ester, bearing, as a chiral moiety, the diacetone D-glucose group. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Zaragozic acids (squalestatins) display inhibition of squalene synthase, an enzyme which catalyzes, in the metabolic pathway for the production of cholesterol, the conversion of farnesyl pyrophosphate into squalene.[1] Due to their biological activities, they have been the subject of intensive studies.[2] From a structural point of view, they possess the same bicyclic core but differ by the length and substitution of the side chains attached to carbon-1 or fixed on oxygen-6. In the case of the C-derivative, this latter chain possesses one asymmetric center (Scheme 1).



Zaragozic acid C

Scheme 1.

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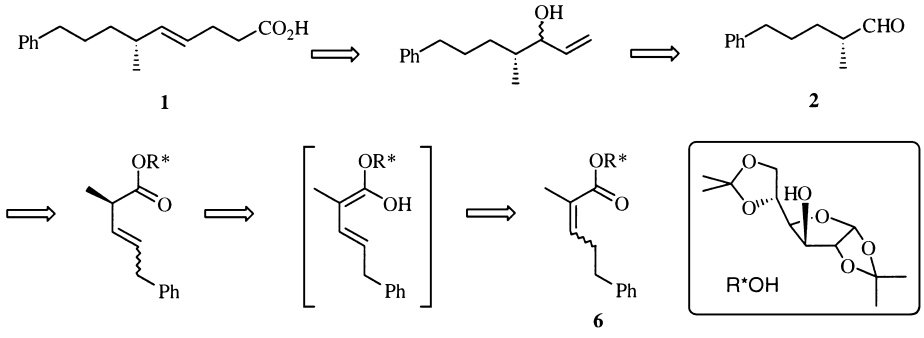
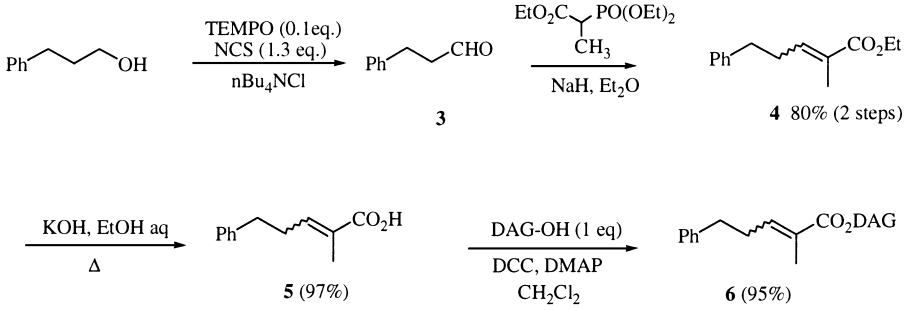
Its synthesis has already been achieved twice by the Claisen–Ireland rearrangement of an allylic ester prepared from aldehyde **2**. This chiral compound was obtained either by diastereoselective alkylation using Evans' oxazolidinone[2b] or from a chiral epoxyalcohol.[3] We report herein on an alternative approach based on the asymmetric protonation[4] of an enol intermediate produced during photodeconjugation of an optically active ester **6** (Scheme 2).



Scheme 2.

2. Results and discussion

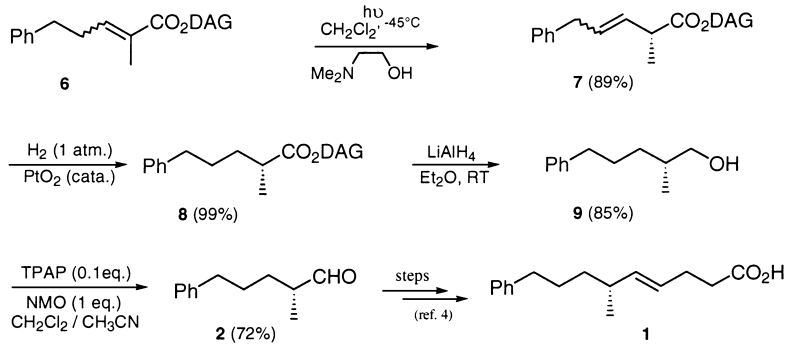
The synthesis of the chiral α,β-unsaturated ester **6** (R*OH=diacetone-D-glucose), prepared in a few steps is depicted in Scheme 4. TEMPO catalyzed oxidation of 3-phenylpropanol using *N*-chlorosuccinimide (NCS) as co-oxidant[5] afforded aldehyde **3** which was used without further purification (Scheme 3). Condensation with triethyl phosphonopropionate using a Wittig–Horner reaction[6] led to ethyl α,β-unsaturated ester **4** (*E*:*Z*, 80:20) which was saponified to unsaturated acid **5** by treatment with KOH in aqueous ethanol.[7] Esterification to DAG ester **6** was conveniently achieved using DCC activation.[8]



Scheme 3.

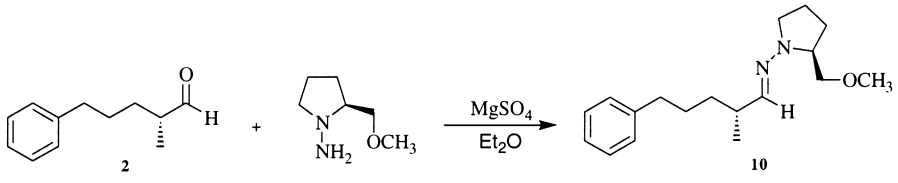
Irradiation at 254 nm of **6** was then performed at −45°C in methylene chloride in the presence of only catalytic amounts of *N*,*N*-dimethylaminoethanol (0.1 equiv.) as already reported in previous work[3] (Scheme 4). It is generally assumed that under UV activation, a photochemical *E*/*Z* isomerization first takes place between the two α,β-unsaturated esters leading to a photochemical equilibrium. Then, the *Z*-isomer (and only the *Z*) could undergo a photochemical sigmatropic hydrogen shift which affords a photodienol with a defined configuration around the prochiral center C_2. Finally, this intermediate can be converted to the β,γ-unsaturated isomer by means of a proton source (typically the aminoalcohol).

Therefore, the *E*/*Z* ratio of the starting material has no influence on the path and the efficiency of the process.



Scheme 4.

Compound **7** was thus isolated in good yield (89%) as an unseparable mixture of *Z* and *E* geometric isomers (ratio=45:55). The C=C double bond was quantitatively hydrogenated over PtO_2 in 4 h, without over-reduction of the phenyl ring. According to NMR analyses performed in chloroform and in the presence of a few drops of d_6-benzene,[9] a diastereoselectivity of 93% was measured. It is interesting to note that this high value was apparently obtained whatever the configuration of the C_3=C_4 double bond of the dienol. Finally, saturated ester **8** was converted into chiral aldehyde (*R*)-**2** by reduction with $LiAlH_4$ in ether, followed by a TPAP oxidation.[10] The enantioselectivity of this compound was first estimated to be near 90% by ^{1}H NMR performed in the presence of Eu(hfc)$_3$ as the shift reagent.[11,12] In order to find a much more confident value, chiral aldehyde **2** was transformed into chiral SAMP[13] hydrazone **10** (Scheme 5). The racemic aldehyde **2**, easily prepared in 3 steps from ester **4**, was also transformed into SAMP hydrazone **10**. By comparing the two ^{1}H NMR spectra, the selectivity for aldehyde **2** obtained from the photochemical method was directly measured by integration of the methyl signal (one doublet for each enantiomer) and reached a value of 83%. The *R*-configuration of the new stereogenic center has been attributed by comparing the signs of optical rotation for **9** and **2** with those of the literature.[3] Furthermore, the protonation occurred in accordance with a previously established model exhibiting similar substrates.[4]



Scheme 5.

While **2** has already been converted into acid **1**[3] in a three-step sequence, a formal synthesis of zaragozic C acid side chain has been thus achieved in 83% ee using, as a key step, the highly diastereoselective photodeconjugation of α,β-unsaturated ester **6** bearing as a chiral moiety the cheap and readily available diacetone D-glucose (DAGOH).[14] This approach to zaragozic C acid side chain, therefore, represents a new application of asymmetric protonations as an alternative procedure to creating stereogenic centers in the α position of carboxylic functionalities.

3. Experimental

The NMR spectra were recorded in $CDCl_3$ or d_6-benzene using a Bruker AC 250 instrument. FT-IR spectra were carried out in $CHCl_3$ on an IR MIDAC spectrometer. Mass spectra were obtained on a D-300 JEOL apparatus at the UFR Pharmacy at the University of Reims. Optical rotations were measured on a Perkin–Elmer 241 spectrometer. Elemental analyses were determined on a CHN 2400 Perkin–Elmer apparatus. Flash chromatographies[15] were performed on silica gel 60 (40–63 mesh).

*3.1. 3-Phenylpropanal: **3***

To a solution of 3-phenylpropanol (5.04 g, 37 mmol) in methylene chloride (350 ml) was successively added TEMPO (0.58 g, 3.7 mmol), tetrabutylammonium chloride (1.03 g, 3.7 mmol) and an aqueous solution (350 ml) of $NaHCO_3$ (0.5 M) and K_2CO_3 (0.05 M). Under strong agitation and at room temperature, NCS (9.88 g, 74.0 mmol) was added in one portion. After 15 h, the two phases were separated and the aqueous solution was extracted with methylene chloride (2×200 ml). The organic layers were washed with brine (2×100 ml), dried over $MgSO_4$ and concentrated. The compound was used without further purification. ^{1}H NMR: 2.74 (dt, 2H, 1.4 and 7.3 Hz), 2.96 (t, 2H, 7.3 Hz), 7.17–7.32 (m, 5H), 9.81 (t, 1H, 1.4 Hz). ^{13}C NMR: 28.1, 45.2, 126.3, 128.3, 128.6, 141.1, 201.5. IR ν: 3030, 2935, 2885, 1713, 1605, 1495, 1455, 1290, 1215, 1080, 1030.

*3.2. Ethyl 2-methyl-5-phenyl pent-2-enoate: **4***

To a suspension of sodium hydride (0.82 g, 20.6 mmol) in diethylether (160 ml) was added dropwise ethyl 2-diethylphosphonopropionate (4.91 g, 20.6 mmol) in the same solvent (10 ml). After 1 h at room temperature was slowly added a solution of crude 3-phenylpropanal **3** (2.52 g, 18.7 mmol) in the same solvent (10 ml). The reaction mixture was stirred overnight at room temperature and carefully hydrolyzed with brine. After extraction with ether (3×100 ml), the crude product was purified by flash chromatography (eluent AcOEt:PE, 2:98) to give **4** (3.23 g, 14.8 mmol) as a mixture of geometric isomers *E*:*Z*, 80:20. 80% (2 steps). ^{1}H NMR: *E*-isomer: 1.30 (t, 3H, 7.25 Hz), 1.80 (s, 3H), 2.50 (q, 2H, 7.3 Hz), 2.76 (t, 2H, 7.3 Hz), 4.20 (q, 2H, 7.25 Hz), 6.83 (dt, 1H, 1.5 Hz and 7.30 Hz), 7.15–7.40 (m, 5H). *Z*-isomer: 1.30 (t, 3H, 7.25 Hz), 1.80 (s, 3H), 2.50 (q, 2H, 7.3 Hz), 2.76 (t, 2H, 7.3 Hz), 4.20 (q, 2H, 7.25 Hz), 5.97 (dt, 1H, 1.5 Hz and 7.3 Hz), 7.15–7.40 (m, 5H). ^{13}C NMR: *E*-isomer: 14.1, 30.4, 34.6, 60.2, 125.9, 128.2, 128.3, 140.7, 141.1, 141.3, 168.0. IR ν: 2935, 1715, 1655, 1455, 1265. MS: m/z (%): 218 ($M^{+\cdot}$, 100), 173 (59), 144 (32), 129 (21), 120 (33), 117 (39), 104 (35). Anal. calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.37; H, 8.86.

*3.3. 2-Methyl-5-phenyl pent-2-enoic acid: **5***

Ethyl ester **4** (3.20 g, 14.6 mmol) diluted in ethanol (5 ml) was added to a solution of potassium hydroxide (1.23 g, 22.05 mmol) in ethanol (95 ml) and water (5 ml). The mixture was heated for 3 h at reflux, cooled to room temperature, half-concentrated under vacuum and acidified with a 2 N sulfuric acid solution. After extraction with hexanes, the organic phase was dried over $MgSO_4$, filtered and concentrated. The resulting oil was purified by flash chromatography over silica giving **5** (2.69 g, 14.1 mmol); 97%. ^{1}H NMR: *E*-isomer: 1.77 (s, 3H), 2.50 (q, 2H, 7.25 Hz), 2.75 (t, 2H, 7.25 Hz), 6.95 (dt, 1H, 1.5 Hz and 7.30 Hz), 7.15–7.35 (m, 5H). *Z*-isomer: 1.77 (d, 3H, 1.1 Hz), 2.50 (q, 2H, 7.25 Hz), 2.75 (t, 2H, 7.25 Hz), 6.15 (dt, 1H, 1.1 Hz and 7.25 Hz), 7.10–7.35 (m, 5H). ^{13}C NMR: *E*-isomer: 11.9, 30.7,

34.5, 126.1, 127.7, 128.4, 141.0, 143.8, 173.4. IR ν: 3030, 2930, 2554, 1695, 1645, 1425, 1285. MS: m/z (%): 190 ($M^{+\cdot}$, 100), 172 (53), 144 (18), 127 (24), 126 (30), 117 (37), 115 (37), 104 (42), 143 (23). Anal. calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.79; H, 7.90.

*3.4. (1,2;5,6-Di-*O*-isopropyliden-α-*D*-glucofuranose-3-*O*-yl) 2-methyl-5-phenyl pent-2-enoate:* ***6***

To a solution of acid **5** (1.75 g, 9.2 mmol) in methylene chloride were successively added DMAP (0.34 g, 2.8 mmol) and diacetone D-glucose (2.39 g, 9.2 mmol). The reaction mixture was cooled to 0°C and a solution of dicyclohexylcarbodiimide (1.89 g, 9.2 mmol) in CH_2Cl_2 was added dropwise. After stirring for 5 min at 0°C, the cooling bath was removed and the mixture stirred overnight at room temperature. Urea was filtered off and the solvent removed by evaporation under reduced pressure. Compound **6** (3.76 g, 8.7 mmol) was obtained pure by flash chromatography (eluent hexanes:ethyl acetate, 90:10); 95%. ^{1}H NMR: *E*-isomer: 1.27 (s, 3H), 1.29 (s, 3H), 1.40 (s, 3H), 1.52 (s, 3H), 1.77 (s, 3H), 2.49 (q, 2H, 7.25 Hz), 2.75 (t, 2H, 2.75 Hz), 3.94–4.30 (m, 4H), 4.50 (d, 1H, 3.4 Hz), 5.27 (d, 1H, 2.7 Hz), 5.87 (d, 1H, 3.8 Hz), 6.80 (tq, 1H, 7.25 Hz and 1.5 Hz), 7.11–7.33 (m, 5H). ^{13}C NMR: *E*-isomer: 12.3, 25.2, 26.2, 26.7, 30.6, 34.6, 67.2, 72.6, 76.3, 79.9, 83.3, 105.0, 109.2, 112.2, 126.1, 127.9, 128.3, 128.4, 140.9, 142.4, 166.5. IR ν: 2990, 2935, 1720, 1655, 1455, 1380, 1265, 1165, 1030. MS: m/z (%): 432 ($M^{+\cdot}$, 77), 417 (85), 374 (19), 273 (22), 173 (91), 160 (18), 145 (87), 129 (27), 114 (53), 113 (75), 109 (100). $[\alpha]_D^{23}$=−28.0 (*c* 0.5, CH_2Cl_2). Anal. calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.63; H, 7.72.

*3.5. (1,2;5,6-Di-*O*-isopropyliden-α-*D*-glucofuranose-3-*O*-yl) 2-methyl-5-phenyl pent-3-enoate:* ***7***

To a solution of DAG ester **6** (10 mmol) in methylene chloride (50 ml) was added *N*,*N*-dimethylethanolamine and placed around a quartz Dewar in which a short wavelength OSRAM lamp was disposed. The irradiation was carried out at −45°C. After total disappearance of the starting material (thin-layer chromatography control), the solvent was removed by rota-evaporation. The deconjugated ester was purified by flash chromatography (eluent AcOEt:petrol ether, 5:95); 89%. ^{1}H NMR: [*E*+*Z* mixture]: 1.20–1.42 (m, 9H), 1.39 (s, 3H), 1.50 (s, 3H), [3.37 (d, 6.5 Hz) and 3.45 (d, 6 Hz), 2H], [3.18 (dq) and 3.60 (dq), 1H], 3.90–4.25 (m, 4H), [4.42 (d, 1.4 Hz) and 4.46 (d, 1.4 Hz), 1H], [5.28 (d, 2.7 Hz) and 5.32 (d, 2.7 Hz), 1H], 5.48–5.70 (m, 2H), [5.85 (d, 3.7 Hz) and 5.87 (d, 3.8 Hz), 1H], 7.11–7.31 (m, 5H). ^{13}C NMR [mixture *E*+*Z*]: [17.1, 17.7], 25.2, 26.2, 26.6, 26.7, [33.6, 38.7], [38.3, 42.8], [67.5, 76.4], [72.1, 72.2], 76.0, [80.2, 80.3], 83.4, 105.2, [109.2, 112.2], 126.9, 128.8, [128.9, 129.6], [130.5, 131.3], 139.9, 166.5. IR ν: 2995, 2940, 1745, 1605, 1455, 1380, 1215, 1155, 1080, 1030. MS: m/z (%): 432 ($M^{+\cdot}$, 13), 417 (30), 374 (8), 273 (8), 145 (100), 129 (40), 117 (53), 145 (100), 129 (42), 117 (55). Anal. calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.70; H, 7.66.

*3.6. (1,2;5,6-Di-*O*-isopropyliden-α-*D*-glucofuranose-3-*O*-yl) 2-methyl-5-phenyl pentanoate:* ***8***

A solution of ester **7** (0.40 g, 0.92 mmol) in ether (15 ml) was hydrogenated over PtO_2 with hydrogen (balloon, 1 atm) for 3 h. After filtration over Celite and washing with ether, compound **8** (0.40 g, 0.92 mmol) was obtained; 99%. ^{1}H NMR: 1.16 (d, 3H, 6.8 Hz), 1.22 (s, 3H), 1.30 (s, 3H), 1.37 (s, 3H), 1.51 (s, 3H), 1.55–1.80 (m, 4H), 2.49 (tq, 1H, 6.5 Hz and 6.8 Hz), 2.60 (t, 2H, 7.25 Hz), 3.90–4.12 (m, 4H), 4.17 (t, 1H, 3.8 Hz), 4.40 (d, 1H, 3.8 Hz), 5.27 (d, 1H, 1.9 Hz), 5.82 (d, 1H, 3.8 Hz), 7.11–7.32 (m, 5H). ^{13}C NMR: *E*-isomer: 16.9, 25.1, 26.2, 26.7, 28.8, 33.2, 35.6, 39.5, 67.4, 72.3, 75.7, 80.1, 83.4, 105.1, 109.3, 112.2, 125.8, 128.3, 141.9, 175.0. IR ν: 2935, 2860, 1740, 1455, 1380, 1215, 1180, 1015. MS: m/z (%): 434 ($M^{+\cdot}$, <5), 419 (100), 376 (98), 361 (10), 318 (12), 301 (17), 275 (35), 213 (17), 175 (53), 174

(59), 147 (98), 127 (33), 113 (57). $[\alpha]_D^{23}$=−27.8 (*c* 1.0, CH_2Cl_2). Anal. calcd for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.48; H, 7.89.

3.7. 2-Methyl-5-phenyl pentanol: ***9***

To a suspension of LAH (53 mg, 1.38 mmol) in ether (50 ml) was added a solution of **8** at 0°C in the same solvent (5 ml). The resulting mixture was stirred for 4 h and carefully hydrolyzed with a saturated aqueous solution of ammonium chloride (10 ml). The aqueous layer was then extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Alcohol **9** was purified by flash chromatography (eluent hexanes:AcOEt, 10:90); 85%. ^{1}H NMR: 0.95 (d, 3H, 6.5 Hz), 1.11–1.28 (m, 1H), 1.34–1.40 (s, OH), 1.41–1.56 (m, 1H), 1.60–1.80 (m, 3H), 2.60 (t, 2H, 7.2 Hz), 3.50 (dd, 2H, 6.5 and 10.3 Hz), 7.15–7.35 (m, 5H). ^{13}C NMR: 16.5, 28.8, 32.8, 35.7, 36.2, 68.2, 125.7, 128.3, 128.4, 142.6. IR ν: 3350, 2930, 2860, 1604, 1455, 1380, 1030. MS: m/z (%): 178 ($M^{+\cdot}$, 56), 161 (30), 160 (96), 145 (19), 131 (57), 120 (33), 118 (56), 117 (91), 115 (30), 105 (100), 104 (68), 103 (41). $[\alpha]_D^{21}$=+10.3 (*c* 1.0, CH_2Cl_2). Anal. calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 80.51; H, 10.73.

3.8. 2-Methyl-5-phenyl pentanal: ***2***

To a solution of alcohol **9** (0.14 g, 0.75 mmol) in methylene chloride (1.6 mmol) was successively added 4 Å MS (0.40 g) and NMO (0.27 g, 1.19 mmol). The resulting mixture was cooled to 0°C and TPAP (0.024 g, 0.040 mmol) was added in one portion. The temperature was kept to 0°C for 5 min and then allowed to reach room temperature. After 2 h, the crude mixture was filtered over a small pad of silica, eluting with CH_2Cl_2. After concentration, the aldehyde **2** was purified by flash chromatography (eluent hexanes:AcOEt, 99:1); 72%. Data in accordance with those of literature.[3] ^{1}H NMR: 1.10 (d, 3H, 6.7 Hz), 1.15–1.50 (m, 2H), 1.60–1.80 (m, 2H), 2.28–2.42 (m, 1H), 2.65 (t, 2H, 7.2 Hz), 7.10–7.35 (m, 5H), 9.61 (d, 1H, 1.9 Hz). ^{13}C NMR: 13.3, 28.7, 30.1, 35.8, 46.2, 125.9, 128.3, 141.9, 204.9. $[\alpha]_D^{23}$=−11.4 (1.0, CH_2Cl_2). Lit.[4]: $[\alpha]_D^{23}$=−14.6 (*c* 23.0, heptane).

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