A nucleophilic addition ring closure [NARC]-based synthesis of (+) -nonactic acid

Benjamin Fraser and Patrick Perlmutter *

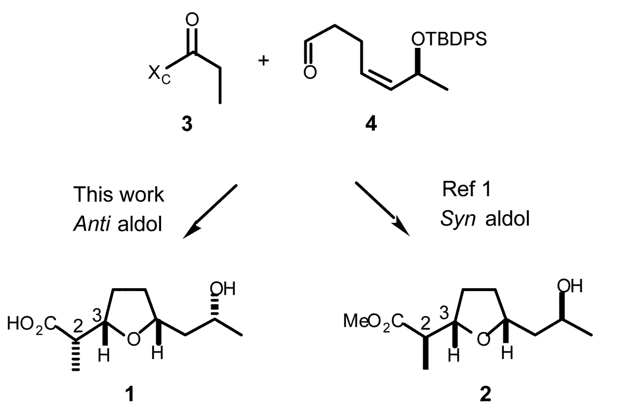
School of Chemistry, Monash University, PO Box 23, Victoria, Australia 3800.
E-mail: patrick.perlmutter@sci.monash.edu.au; Fax: 61 3 9905 4597; Tel: 61 3 9905 4522

Received (in Cambridge, UK) 9th July 2002, Accepted 17th September 2002
First published as an Advance Article on the web 21st November 2002

Nonactic acid **1** has been synthesized in 12 steps from readily available (S)-(−)-ethyl lactate in 20% overall yield. The key ("NARC") sequence in this method involved *anti*-aldol addition of acylsultam **3** with aldehyde **4** followed by intramolecular oxymercuration. The efficiency and selectivity of the *anti*-aldol reaction was found to be critically dependent upon the ratio of Lewis acid to base. The intramolecular oxymercuration was also found to be highly diastereoselective and was attributed to allylic control consistent with previous studies in our group.

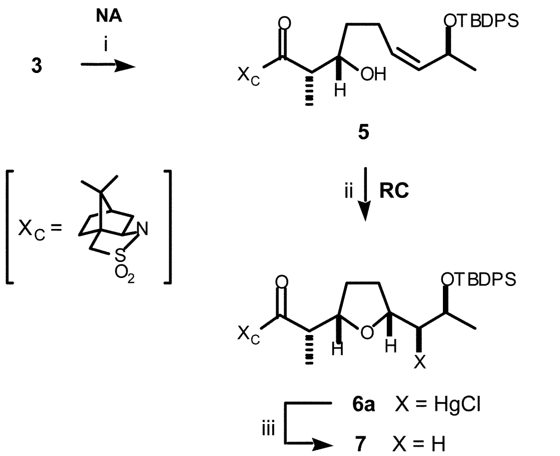
Introduction

Several years ago we reported a synthesis of certain diastereomers of methyl nonactate such as **2** below.[1] The essence of the approach involved a "NARC" sequence of *syn*-aldol addition followed by intramolecular oxymercuration. Herein we report the successful development of a set of conditions for executing a highly *anti*-selective aldol addition of **3** with **4** which provides the correct relative stereochemistry between C2 and C3 and therefore forms the basis of a total synthesis of (+)-nonactic acid (**1**).[2–16]



Results and discussion

The two key processes in this synthesis were (i) an *anti*-selective aldol reaction[17,18] and (ii) a diastereoselective intramolecular oxymercuration (Scheme 1).[1,19] The *anti*-aldol addition was achieved *via* addition of the (Z)-boron enolate of acylsultam **3**[20] to aldehyde **4**.[1] This enolate typically adds to aldehydes in a *syn*-fashion (proceeding by a closed transition state) unless an excess of Lewis acid is present (which has been proposed to divert the reaction manifold though an open transition state).[21–23] We have found that through careful manipulation of the ratio of Lewis acid to base the *anti*-aldol adduct **5** could be obtained exclusively in 83% yield. The optimum ratio of Lewis acid to base was found to be 3 : 2. Significantly, unlike most previous reports,[17,18,21–23] we were able to employ the same Lewis acid (*i.e.* diethylboron triflate †) for enolate generation and *anti*-aldol stereocontrol.[24] There was a clear requirement for free Lewis acid[25] as employing three equivalents of diethylboron triflate *and* Hünig's base gave exclusively a *syn*-adduct.[9] Further increases in Lewis acid : base ratio >1.5 yielded *anti*-aldol products but with poorer yields. Interestingly, no *syn*-addition products were observed under these conditions. (This process appears to be substrate specific as a similar aldol addition with benzaldehyde gave a mixture of diastereomeric adducts. Such substrate dependence in Lewis acid-promoted *anti*-aldols has been noted before by Heathcock and Walker[22]).



Scheme 1 *Reagents and conditions* i) Et_2BOTf, iPr_2NEt, DCM, −78 °C, 4 h, 88%. ii) $Hg(OAc)_2$, DCM, 24 h, rt, 76%. iii) Bu_3SnH, AIBN, toluene, 2 h, rt, 98%.

Hence we believe the most likely transition states for this reaction are those shown in Fig. 1. The presence of excess Lewis acid ensures that open transition states are operating. Of these, anti-periplanar transition state **I** is lower in energy than synclinal **II** due to the latter's unfavourable steric interaction

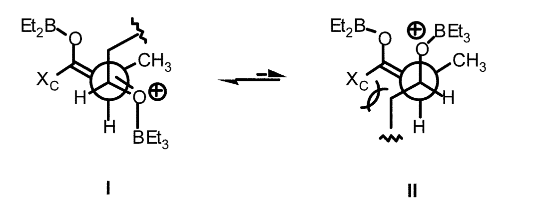


Fig. 1 Putative open transition states for the *anti*-aldol reaction.

† The IUPAC name for triflate is trifluoromethanesulfonate.

 DOI: 10.1039/b206656d

between the auxiliary and the aldehyde chain. Transition state **I** leads to the relative stereochemistry obtained.

The second key process, *i.e.* intramolecular oxymercuration, was examined next. Reaction of **5** with mercury(II) acetate provided the desired isomer, **6a**, in a 10 : 1 diastereoselectivity (Scheme 1). Unlike previous studies[1] we found that the stereoselectivity was invariant when run in more polar solvents such as acetonitrile. Purification by recrystallisation afforded pure **6a** in 76% yield. Its crystal structure is shown in Fig. 2‡. The

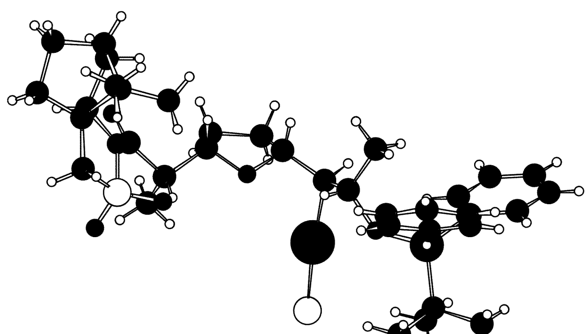
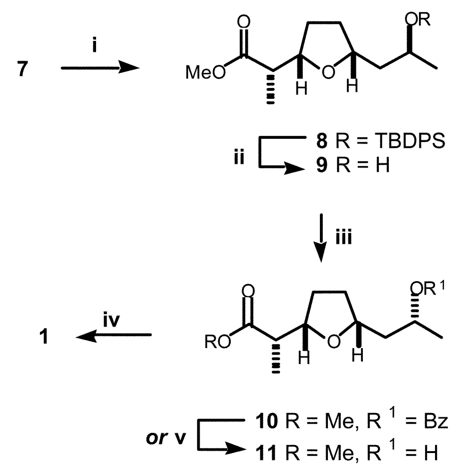


Fig. 2 X-Ray crystal structure of chloromercurio complex **6a** (the acylsultam moiety has been rotated away from the THF ring for clarity).

diastereoselectivity of this ring closure is consistent with our previous studies[1,19] of the use of a remote allylic control element in intramolecular oxymercurations. In these studies we demonstrated that the remote allylic group (in this case the OTBDPS group) controls the diastereoselectivity and the reactions are essentially insensitive to the stereochemistry of the incoming nucleophilic alcohol.

Relatively straightforward synthetic manipulations remained to complete the synthesis of nonactic acid **1**. Reductive demercuration of **6a** proceeded smoothly affording tetrahydrofuran **7** in excellent yield (97%) (Scheme 1). Removal of the chiral auxiliary under standard conditions followed by esterification with diazomethane gave the methyl ester **8** in 62% yield (Scheme 2). Desilylation of **8** with tetrabutylammonium fluoride in THF afforded alcohol **9**. A sequence of Mitsunobu inversion and ester hydrolysis following a method reported by Lee and Kim[26] yielded (+)-nonactic acid **1** in quantitative yield.



Scheme 2 *Reagents and conditions* i) a. H_2O_2, LiOH, THF–H_2O 5 : 1, 7 h; b. CH_2N_2, ether, 0 °C, 1 h, 62% over two steps ii) TBAF, THF, 24 h, rt, 79%. iii) PPh_3, benzoic acid, DEAD, rt, 18 h, 82%. iv) 30% NaOH, 24 h, rt, 100%. v) 15% NaOMe, MeOH, 18 h, rt, 95%.

‡ CCDC reference number 189550. See http://www.rsc.org/suppdata/p1/b2/b206656d/ for crystallographic files in .cif or other electronic format.

Alternatively, following the method of Warm and Vogel,[16] (+)-methyl nonactate could be prepared by treatment of benzoate **10** with 15% NaOMe in methanol. This gave (+)-methyl nonactate **11** in excellent yield (95%) without need for purification.

Experimental

General

Melting points were recorded on a Kofler hot stage apparatus and are uncorrected. Elemental microanalyses were performed by Chemical & Micro Analytical Services of the University of Otago, New Zealand. Optical rotations were measured on a PolAAr 2001 automatic polarimeter and are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on a 1600 Series Fourier Transform spectrometer and refer to thin film of liquids (neat) or paraffin (Nujol) mulls of solids between NaCl plates. Infrared band intensities of each frequency of absorption are expressed as follows: s (strong), m (medium), w (weak) or b (broad). ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AM 300 spectrometer or Varian Mercury spectrometer. Chemical shifts were recorded on the δ scale in parts per million (ppm) in $CDCl_3$. ^{13}C NMR spectra were recorded at 75 MHz on a Varian Mercury and at 75 MHz on a Bruker AM 300 spectrometer. Spectra were referenced using the solvent carbon signal as an internal standard. Mass spectra (ESI) were recorded using samples in MeOH and CH_3CN on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) for accurate mass determinations were recorded on a Bruker BioApex 47e FTMS. Silica gel used for flash chromatography was 40–63 µm (230–400 mesh) silica gel 60 (Merck No. 9385). Many of the reagents used were purchased from commercial suppliers and used as supplied. Solvents were dried by distillation from sodium–benzophenone ketyl before use.

anti-Aldol adduct (5)

Freshly distilled triflic acid (0.885 mL, 10 mmol) was added to a solution of 1 M triethylborane in hexanes (10 mL, 10 mmol) and was allowed to stir for 0.5 h at room temperature. After this time a yellow–orange colour developed and the solution appeared homogeneous. The solution was then cooled to −5 °C and a solution of the acylsultam **3** (910 mg, 3.33 mmol) in dichloromethane (10 mL) was added dropwise. Freshly distilled *N*,*N*-diisopropylethylamine (1.16 mL, 6.67 mmol) was then added dropwise whilst maintaining the temperature of −5 °C. The solution was allowed to stir for a further 0.5 h at −5 °C and then cooled to −78 °C (dry ice–acetone bath). The aldehyde **4** (2.44g, 6.67 mmol) was then added dropwise over a period of 30 min whilst maintaining the temperature below −75 °C. The solution was stirred for 1 h at −78 °C and then freshly distilled *N*,*N*-diisopropylethylamine (1 mL, 5.75 mmol) was added dropwise whilst maintaining the temperature below −75 °C. Phosphate buffer (pH 7, 10 mL) was then added dropwise to the solution again maintaining a temperature below −75 °C. After stirring for 20 min at −78 °C the solution was removed from the dry ice–acetone bath and allowed to warm to room temperature. The organic layer was separated from the aqueous layer and the aqueous layer extracted with ether (3 × 5 mL). The combined organic extracts were then washed (sat. NH_4Cl), dried ($MgSO_4$) and the solvent removed *in vacuo* to give a crude yellow oil which was subjected to flash chromatography (20% ethyl acetate–hexanes) yielding the title compound as a colourless oil (1.76 g, 83%). $[a]_D^{23}$ +42.1 (*c* 1.2, $CHCl_3$). δ_H 0.97 (s, 3H, CH_3 sultam), 1.03 (s, 9H, $OSiC(CH_3)_3$), 1.14 (s, 3H, CH_3 sultam), 1.14 (d, *J* 4.4 Hz, 3H, $OCHCH_3$), 1.16 (d, *J* 6.6 Hz, 3H, CH_3CH), 1.31–1.45 (m, 3H, CH_2 and CH sultam), 1.60–1.72 (m, 2H, CH_2 sultam), 1.82–1.95 (m, 4H, CH_2, H4 and H5), 2.02–2.14 (m, 2H, CH_2 sultam), 3.06 (quintet, *J* 6.6 Hz, 1H, H2), 3.38–3.48 (m, 1H, H3), 3.41–3.54 (ABq, *J* 13.8 Hz, 2H, CH_2SO_2), 3.88 (dd, *J* 5.1, 7.2 Hz, 1H, $CHNSO_2$), 4.52–4.61 (dquintet, *J* 6.6, 0.9 Hz, 1H, $SiOCHCH_3$), 5.08–5.17 (m, 1H, H7), 5.47–5.54 (dd, *J* 8.4, 10.8 Hz, 1H, H8), 7.32–7.45 (m, 6H, CH_{ar}), 7.64–7.7 (m, 4H, CH_{ar}). δ_C 14.5, 19.5, 20.2, 21.1, 24.0, 25.0, 26.8, 27.3, 33.3, 35.8, 38.8, 45.0, 45.8, 48.0 and 48.6, 53.4, 65.6, 66.2, 75.3, 127.5, 129.6, 134.4, 135.5, 135.9, 136.0, 175.3. IR ν/cm^{-1} 3447b, 1654b (Found: C, 67.58; H, 8.19; N, 2.33%; $C_{36}H_{51}NO_5SSi$ requires C, 67.78; H, 8.06; N, 2.20%).

Chloromercurio complex (6a)

To a solution of the aldol adduct (1.445 g, 2.27 mmol) **5** in DCM (20 mL) was added mercury(II) acetate (1.1 g, 3.45 mmol). The solution was allowed to stir at room temperature for 24 h. Brine (5 mL) was then added and the solution stirred for a further 0.5 h. The organic layer was separated from the aqueous layer and the aqueous layer extracted with further portions of ether (3 × 7 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a 10 : 1 crude solid mixture of diastereomeric chloromercurio complexes **6a** and **6b**. Recrystallisation of the crude solid from ethyl acetate–hexanes gave the major diastereomer **6a** in 76% yield. Mp 170–172 °C. $[\alpha]_D^{23}$ − 61.8 (*c* 1.06, $CHCl_3$). δ_H 0.96 (s, 3H, CH_3 sultam), 1.05 (s, 9H, $OSi(CH_3)_3$), 1.09 (d, *J* 6.8 Hz, 3H, C_2CH_3), 1.14 (d, *J* 6.0 Hz, $OCHCH_3$), 1.27 (s, 3H, CH_3 sultam), 1.32–1.45 (m, 3H, CH_2 and CH sultam), 1.52–1.76 (m, 2H, CH_2 sultam), 1.78–2.0 (m, 4H, 2 × CH_2 sultam), 2.06–2.26 (m, 4H, CH_2, H4 and H5), 2.52 (dd, *J* 2.3, 9.5 Hz, 1H, CHHg), 3.03 (quintet, *J* 6.8 Hz, 1H, H2), 3.39–3.54 (ABq, *J* 13.8 Hz, CH_2SO_2), 3.85–3.93 (dd, *J* 5.4, 5.1 Hz, 1H, $CHNSO_2$), 3.93–4.04 (m, 2H, H3 and H5), 4.11–4.17 (dq, *J* 2.3, 6.0 Hz, 1H, $SiOCHCH_3$), 7.34–7.48 (m, 6H, CH_{ar}), 7.61–7.69 (m, 4H, CH_{ar}). δ_C 14.5, 19.5, 20.2, 22.6, 26.8, 27.5, 29.8, 32.1, 33.2, 39.2, 44.9, 45.9, 48.0 and 48.6, 53.6, 65.7, 70.6, 72.2, 80.5 and 81.5, 127.7, 129.93, 133.5, 136.1, 174.5. IR ν/cm^{-1} 1684s (Found: C, 49.53; H, 5.77; N, 1.60%; $C_{36}H_{50}NO_5SSiHgCl$ requires C, 49.48; H, 6.08; N, 1.66%).

Tetrahydrofuran (7)

To a solution of the chloromercurio complex **6a** (1.8 g, 2.06 mmol) in toluene (36 mL) was added azoisobutyronitrile (36 mg, 0.205 mmol) and tributylstannane (1.4 mL, 5.14 mmol). Mercury precipitated almost immediately and the solution was allowed to stir at room temperature for 2 h and then heated to 40 °C for 1 h. Carbon tetrachloride (5 mL) was then added and the solution stirred for 1 h at room temperature. The solution was then decanted from the mercury and diluted with 25% dichloromethane–light petroleum (25 mL). The solution was then washed with 5% potassium fluoride solution (3 × 3 mL) and the organic layer dried ($MgSO_4$) and evaporated *in vacuo* giving a grey crude oil that was subjected to flash chromatography (25% ethyl acetate–hexanes) yielding the title compound as a colourless oil (1.28 g, 98%). Mp 171–172 °C. $[\alpha]_D^{22}$ − 7.2 (*c* 1.0, $CHCl_3$). δ_H 0.93 (s, 3H, CH_3 sultam), 1.04 (s, 9H, $OSi(CH_3)_3$), 1.08 (d, *J* 6 Hz, 3H, C_2CH_3), 1.09 (d, *J* 6.3 Hz, $OCHCH_3$), 1.16 (s, 3H, CH_3 sultam), 1.30–1.45 (m, 3H, CH_2 and CH sultam), 1.46–1.76 (m, 2H, CH_2 sultam), 1.78–2.0 (m, 4H, 2 × CH_2 sultam), 2.06–2.25 (m, 4H, CH_2, H4 and H5), 3.05 (m, 1H, H2), 3.37–3.50 (ABq, *J* 13.8 Hz, CH_2SO_2), 3.85–3.92 (dd, *J* 5.0, 7.8 Hz, 1H, $CHNSO_2$), 3.92–4.06 (m, 3H, H3, H5 and H8), 7.32–7.45 (m, 6H, CH_{ar}), 7.65–7.70 (m, 4H, CH_{ar}). δ_C 13.8, 19.3, 19.9, 21.2, 24.1, 25.2, 26.6, 27.1, 29.2, 30.7, 32.9, 38.4, 44.7, 46.1, 47.7 and 48.2, 53.6, 65.2, 67.7, 81.6, 127.2, 129.3, 134.2, 135.8, 174.7. IR ν/cm^{-1} 1698s, 1686s. MS *m*/*z* 660.3 (M^+ + Na) (Found: C, 67.43; H, 7.9; N 2.13%; $C_{36}H_{51}NO_5SSi$ requires C, 67.78; H, 8.06; N, 2.20%).

(+)-Methyl 8-*epi*-8-*O*-(*tert*-butyldiphenylsilyl)nonactate (8)

To a solution of the tetrahydrofuran **7** (1.2 g, 2.64 mmol) in 4 : 1 THF–water (15 mL) was added LiOH (160 mg, 6.7 mmol). The solution was cooled to 0 °C and 30% H_2O_2 solution (1.6 mL) was added dropwise maintaining the temperature at 0 °C. The solution was then allowed to warm to room temperature and stirred for 7 h. Sat. sodium sulfite (5 mL) was added and the solution stirred for 0.5 h. The solution was then acidified with 1 M HCl to pH 1, diluted with ether (10 mL). The aqueous phase was extracted with ether (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to give the crude carboxylic acid as a clear oil (~0.9 g). The crude oil was immediately dissolved up in ether (20 mL) and treated with an excess of diazomethane (2 g Diazald®). After allowing the excess diazomethane to dissipate the solvent was removed *in vacuo* to give the crude methyl ester which was purified by flash chromatography (0–20% ethyl acetate–hexane solvent gradient) yielding the title compound as a colourless oil (0.983g, 83%). $[\alpha]_D^{22}$ +3.8 (*c* 1.032, $CHCl_3$). δ_H 1.04 (s, 9H, $OSi(CH_3)_3$, 1.07 (d, *J* 3.6 Hz, 3H, C_2CH_3), 1.08 (d, *J* 7.5 Hz, $OCHCH_3$), 1.4–1.9 (m, 5H, CH_2, H4, H5 and H7), 2.43 (quintet, *J* 7.2 Hz, 1H, H2), 3.63 (s, 3H, CH_3 methyl ester), 3.93–4.01 (m, 3H, H3, H5 and H8), 7.32–7.46 (m, 6H, CH_{ar}), 7.64–7.70 (m, 4H, CH_{ar}). δ_C 13.6, 19.6, 23.8, 27.3, 28.7 and 31.5, 45.5, 51.9, 67.8, 80.3, 127.5, 129.6, 134.6, 136.0, 175.5. IR ν/cm^{-1} 1749s. MS *m*/*z* 477.4 (M^+ + Na) (Found: C, 71.47; H, 8.48%; $C_{27}H_{38}O_4Si$ requires C, 71.32; H, 8.42%).

(+)-Methyl *8-epi*-nonactate (9)

To a solution of the TBDPS ether **8** (0.446 g, 0.98 mmol) in THF (17 mL) at room temperature was added tetrabutylammonium fluoride (4.6 mL, 4.6 mmol, 1 M solution in THF). The solution was then allowed to stir at room temperature for 24 h. The solution was then diluted with ether (50 mL), dried ($MgSO_4$)and the solvent removed *in vacuo*. The residue was purified by flash chromatography (40% ethyl acetate–hexanes) yielding the title compound as a clear oil (167 mg, 79%). $[\alpha]_D^{22}$ +33.5 (*c* 1.0, $CHCl_3$) lit.[26] +32.3. δ_H 1.11 (d, *J* 7.0 Hz, 3H, C2CH$_3$), 1.16 (d, *J* 6.3 Hz, $OCHCH_3$), 1.46–1.7 (m, 4H, CH_2, H4, H5), 1.90–2.11 (m, 2H, H7), 2.48–2.58 (dq, *J* 7.0, 8.7 Hz, 1H, H2), 3.69 (s, 3H, CH_3 methyl ester), 3.91–4.01 (m, 3H, H3, H5 and H8). δ_C 13.9, 23.7, 28.9 and 32.1, 44.9, 45.6, 52.1, 68.1, 80.5, 81.9. IR ν/cm^{-1} 3518b, 1736s. MS *m*/*z* 239.1 (M^+). HRMS *m*/*z* 239.1247 calculated for $C_{11}H_{20}O_4Na^+$ 239.1259.

(+)-Methyl 8-*O*-benzoylnonactate (10)

Following the procedure of Lee and Kim[26] triphenylphosphine (177 mg, 0.67 mmol), benzoic acid (87 mg, 0.67 mmol) and the methyl ester **9** (72 mg, 0.3348 mmol) were dissolved in THF (4 mL) at room temperature. Diethyl azodicarboxylate (0.108 mL, 0.67 mmol) was then added dropwise to the solution and the initial yellow colour was lost indicating commencement of reaction. The solution was then stirred at room temperature. After 18 h the reaction was quenched with water (5 mL). The aqueous phase was extracted with ether (3 × 3 mL) and the combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting crude yellow oil was purified (12.5% ethyl acetate–hexanes) to yield the title compound as a colourless oil (87 mg, 82%). $[\alpha]_D^{21.5}$ −28.5° (*c* 1.2, $CHCl_3$) lit.[26] − 30.4. δ_H 1.09 (d, *J* 6.9 Hz, 3H, C_2CH_3), 1.36 (d, *J* 6.3 Hz, $OCHCH_3$), 1.53–2.02 (m, 5H, CH_2, H4, H5 and H7), 2.47–2.56 (dq, *J* 6.9, 7.2 Hz, 1H, H2), 3.68 (s, 3H, CH_3 methyl ester), 3.92–4.02 (m, 2H, H3 and H5), 5.18–5.28 (m, 1H, H8), 7.40–7.57 (m, 3H, CH_{ar}), 8.00–8.03 (m, 2H, CH_{ar}). δ_C 13.6, 21.0, 28.7 and 31.6, 42.9, 45.6, 51.8, 70.1, 76.6, 80.4 128.3, 129.5, 130.8, 132.7, 165.9, 175.2.

(+)-Methyl nonactate (11)

Following the procedure of Warm and Vogel[16] benzoate **10** (50 mg, 0.156 mmol) was dissolved in 10 mL of anhydrous methanol. To this solution was added 15% NaOMe in methanol (0.6 M, 2.2 mmol). The solution was allowed to stir for 18 h at room temperature. The pH was then adjusted to 5 by addition of 1 M HCl. Dichloromethane (5 mL) was then added and the aqueous phase separated from the organic phase. The aqueous phase was further extracted with dichloromethane (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The residual oil was purified by flash chromatography yielding the title compound **11** as a colourless oil in quantitative yield (34 mg). $[\alpha]_D^{24}$ +15.3 (*c* 1.2, $CHCl_3$) lit.[16] +16.1. δ_H 1.11 (d, *J* 6.9 Hz, 3H, C_2CH_3), 1.18 (d, *J* 6.3 Hz, 3H, $OCHCH_3$), 1.52–2.05 (m, 5H, CH_2, H4, H5 and H7), 2.47–2.57 (dq, *J* 6.9, 8.4 Hz, 1H, H2), 2.93 (br s, 1H, OH), 3.67 (s, 3H, CH_3 methyl ester), 3.92–4.16 (m, 2H, H3 and H5). δ_C 13.8, 23.4, 29.0 and 30.7, 42.8, 45.5, 51.9, 65.3, 77.4 and 81.2, 175.2.

(+)-Nonactic acid (1)

(+)-Methyl nonactate **11** (34 mg, 0.157 mmol) was dissolved in MeOH (1 mL) and to this solution was added methanolic NaOH (0.8 mL, 2 M NaOH in MeOH). The solution was allowed to stir for 24 h at room temperature and was then acidified to pH 2 with 0.1 M HCl. Ether was added (1 mL) and the aqueous phase was extracted with a further two portions of ether (2 × 1 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield (+)-nonactic acid in quantitative yield. $[\alpha]_D^{22}$ +9.1 (*c* 1.2 $CDCl_3$) lit.[10] +9.0 (*c* 0.15). δ_H 1.16 (d, 3H, *J* 6.9 Hz), 1.22 (d, 3H, *J* 6.3 Hz), 1.52–1.56 (m, 4H), 1.91–2.21 (m, 2H), 2.45–2.55 (m, 1H), 3.95–4.27 (m, 3H), 4.80–5.60 (br s, 2H).

References

1 A. Garavelas, I. Mavropoulos, P. Perlmutter and G. Westman, *Tetrahedron Lett.*, 1995, **36**, 463–466.
2 M. J. Arco, M. H. Trammel and J. D. White, *J. Org. Chem.*, 1976, **41**, 2075–83.
3 A. G. M. Barrett and H. G. Sheth, *J. Org. Chem.*, 1983, **48**, 5017–22.
4 P. A. Bartlett and K. K. Jernstedt, *Tetrahedron Lett.*, 1980, **21**, 1607–10.
5 P. A. Bartlett, J. D. Meadows and E. Ottow, *J. Am. Chem. Soc.*, 1984, **106**, 5304–11.
6 H. M. C. Ferraz and M. E. Payret-Arrua, *Quim. Nova*, 1998, **21**, 597–607.
7 I. Fleming and S. K. Ghosh, *Stud. Nat. Prod. Chem.*, 1996, **18**, 229–268.
8 H. Gerlach and H. Wetter, *Helv. Chim. Acta*, 1974, **57**, 2306–21.
9 T. Honda, H. Ishige, J. Araki, S. Akimoto, K. Hirayama and M. Tsubuki, *Tetrahedron*, 1992, **48**, 79–88.
10 R. E. Ireland and J. P. Vevert, *Can. J. Chem.*, 1981, **59**, 572–83.
11 P. A. Bartlett and K. K. Jernstedt, *Tetrahedron Lett.*, 1980, **21**, 1607–10.
12 P. Metz, U. Meiners, E. Cramer, R. Froehlich and B. Wibbeling, *Chem. Commun.*, 1996, 431–2.
13 G. Solladie and C. Dominguez, *J. Org. Chem.*, 1994, **59**, 3898–901.
14 K. Takatori, N. Tanaka, K. Tanaka and M. Kajiwara, *Heterocycles*, 1993, **36**, 1489–92.
15 K. Takatori, K. Tanaka, K. Matsuoka, K. Morishita and M. Kajiwara, *Synlett*, 1997, 159–160.
16 A. Warm and P. Vogel, *Helv. Chim. Acta*, 1987, **70**, 690–700.
17 R. Mahrwald, *Chem. Rev.*, 1999, **99**, 1095–1120.
18 C. Palomo, M. Oiarbide and M. Garcia, *Chem.-Eur. J.*, 2002, **8**, 37–44.
19 K. Bratt, G. Garavelas, P. Perlmutter and G. Westman, *J. Org. Chem.*, 1996, **61**, 2109–2117.
20 W. Oppolzer, J. Blagg, I. Rodriquez and E. Walther, *J. Am. Chem. Soc.*, 1990, **112**, 2767–2772.
21 H. C. Heathcock, M. M. Hansen and H. Danda, *J. Org. Chem.*, 1990, **55**, 173.
22 H. C. Heathcock and M. A. Walker, *J. Org. Chem.*, 1991, **56**, 5747–5750.
23 H. C. Heathcock and B. C. Raimundo, *Synlett*, 1995, **12**, 1213–1214.
24 W. Oppolzer and P. Lienard, *Tetrahedron Lett.*, 1993, **34**, 4321–4324.
25 D. A. Evans, J. M. Takacs, L. R. McGee, M. D. Ennis, D. J. Mathre and D. J. Bartoli, *J. Pure. Appl. Chem.*, 1981, **53**, 1109.
26 J. Lee and B. Kim, *Tetrahedron*, 1996, **52**, 571–588.