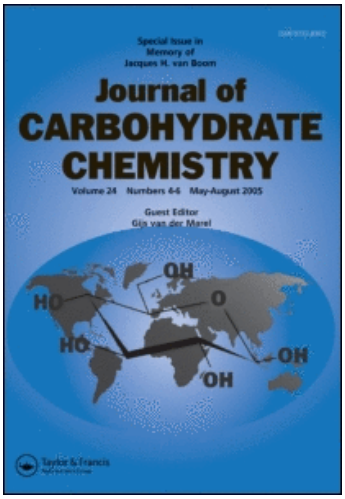

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Yadav, J. S. , Mysorekar, Sudha V. , Pawar, Sushma M. and Gurjar, M. K.(1990) 'Synthesis of (3R, 4R)-1, 2-Divinylglycol and its Unsymmetrical Derivatives : An Application to the Synthesis of R-(+)-α-Lipoic Acid', Journal of Carbohydrate Chemistry, 9: 2, 307 — 316
To link to this Article: DOI: 10.1080/07328309008543834
URL: http://dx.doi.org/10.1080/07328309008543834

J. CARBOHYDRATE CHEMISTRY, 9(2&3), 307-316 (1990)

SYNTHESIS OF (3R,4R)-1,2-DIVINYLGLYCOL AND ITS UNSYMMETRICAL DERIVATIVES : AN APPLICATION TO THE SYNTHESIS OF R-(+)-α-LIPOIC ACID

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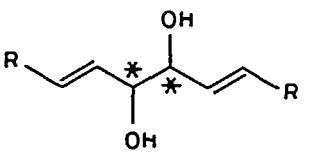
Received July 7, 1989 - Final Form November 29, 1989

ABSTRACT

The synthesis of (3R,4R)-divinylglycol (1) and some of its unsymmetrical derivatives has been described starting from D-mannitol. 1 has been converted into R-(+)-α-lipoic acid.

INTRODUCTION

1,2-Divinylglycols of the type 1 have drawn considerable attention in recent years as useful building blocks[1] because of the presence of C_2 symmetry. The ease with which one of the vinyl groups could be functionalized in the presence of the other indeed led to the synthesis of various natural products.[1] However, it appeared to us that the synthesis of 1 in



1 R = H

optically pure[2,3] form would be most appropriate if carried out without resorting to stereocontrolled asymmetric reactions. In this report we describe the chiral synthesis of (R,R)-divinylglycol (1) and some of its unsymmetrical derivatives from D-mannitol.

RESULTS AND DISCUSSION

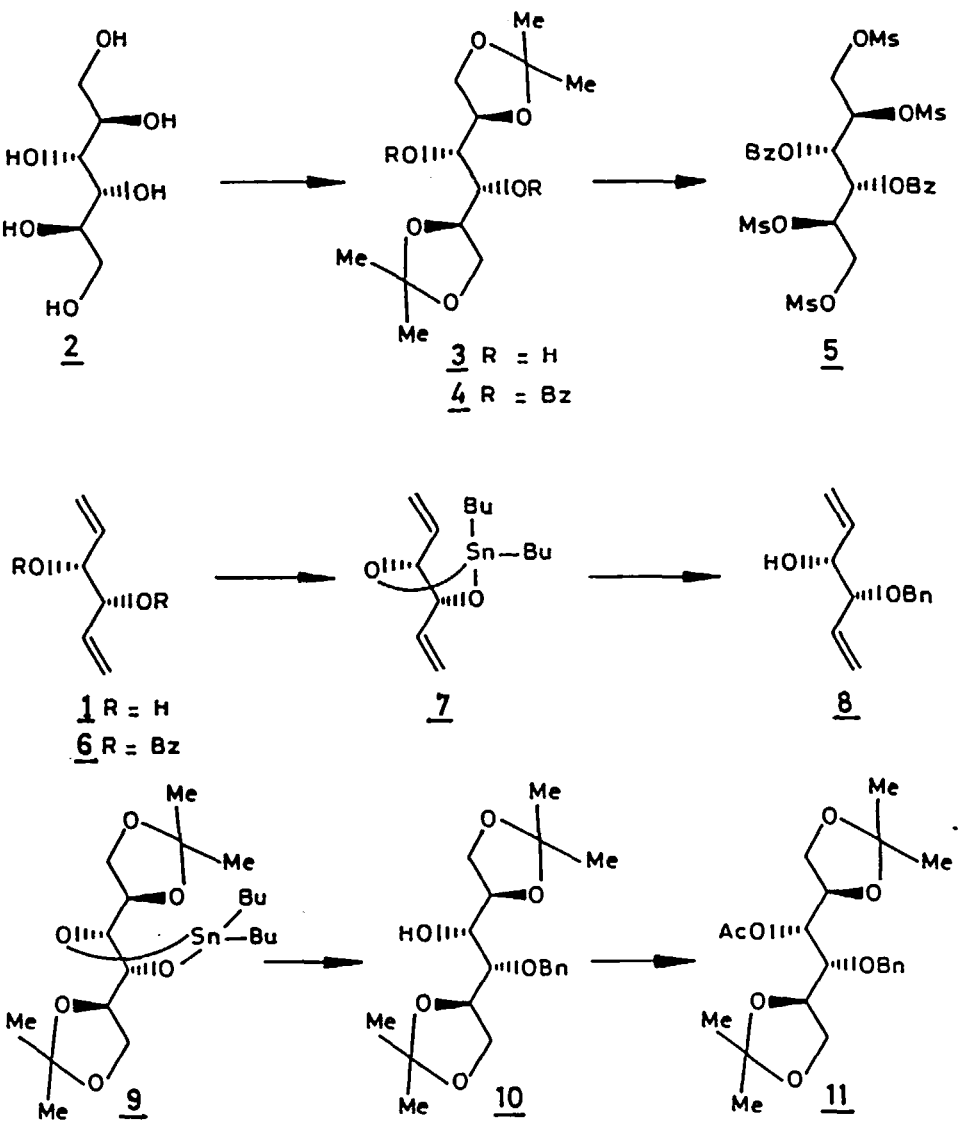
The readily obtainable 1,2:5,6-di-O-isopropylidene-D-mannitol (3)[4] having C_2 symmetry, was chosen as the starting material. Compound 3 was conventionally benzoylated with a mixture of benzoyl chloride-pyridine to afford the 3,4-dibenzoate 4. Subsequent hydrolysis of 4 with 50% aqueous acetic acid on a boiling water bath gave the tetrol derivative which, with mesyl chloride-pyridine afforded the tetramesylate (5) in 80% yield. Treatment of 5 with sodium iodide-zinc dust in refluxing N,N'-dimethylformamide[5] for 2 h followed by debenzoylation with methanolic sodium methoxide furnished (R,R)-divinylglycol (1) in 56% yield. The ^{1}H NMR spectrum of 1 was consistent with the assigned structure (Scheme 1).

Selective mono-O-alkylation of the vicinal glycol through O-stannylene acetal[6] with alkyl halides is the key reaction in several natural product syntheses. Apparently, the substrates with C_2 axis of symmetry provide one product during this reaction.[7] Thus, 1 was converted into the corresponding dibutylstannylene acetal (7) and reacted without delay with 1.2 eq. of benzyl bromide in DMF to furnish 8 in 77% yield.

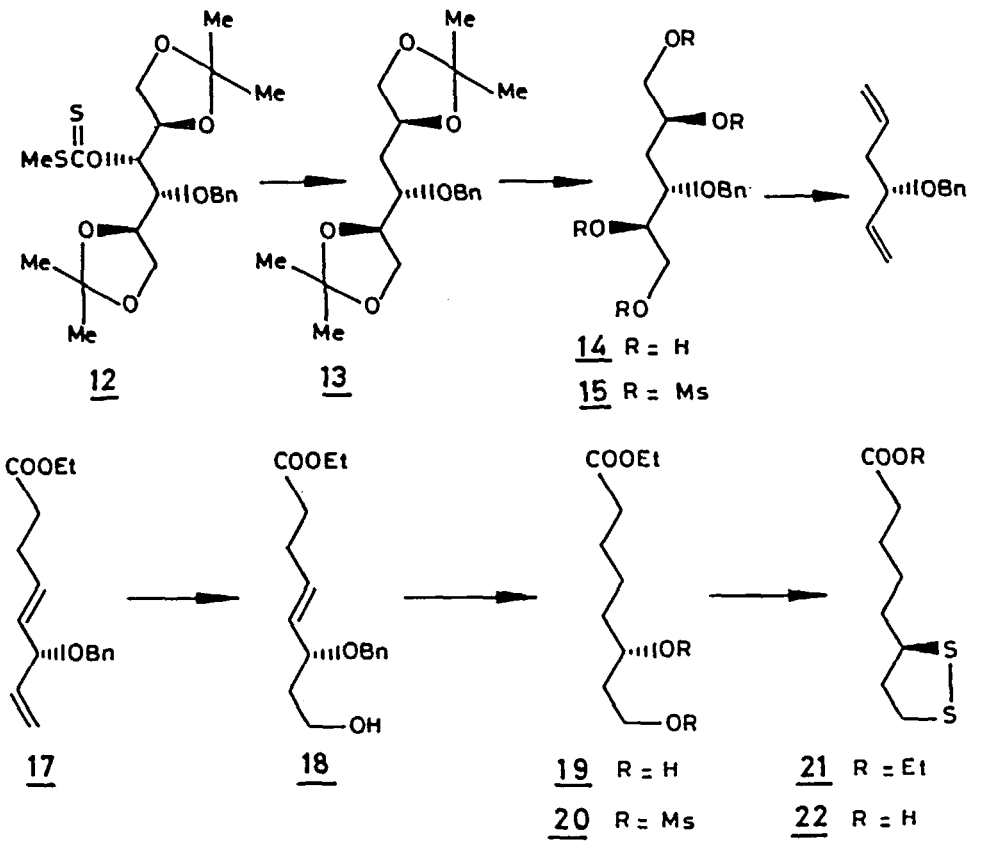
In alternate approach towards 8, D-mannitol (2) was transformed into the monobenzylated derivative (10)[1c] via the corresponding stannylene acetal (9). After protecting the OH group of 10 as an acetate (11), the later compound was subjected to: i) isopropylidene hydrolysis, ii) mesylation, iii) reaction with sodium iodide-zinc in DMF and iv) deacetylation to afford 8 in a 36% overall yield (Scheme 1).

Deoxygenation of the hydroxyl group present in 8 was effected by the Barton-McCombie reaction.[8] For example, 8 was successively treated with sodium hydride-carbon disulfide-methyl iodide in THF to afford the dithiocarbonate derivative (12). Subsequent reaction of 12 with freshly prepared tri-n-butyltin hydride in toluene containing AIBN for 7 h gave the product 13 in 60% yield. Its structure was assigned from its ^{1}H NMR spectrum which revealed the characteristic signals for H-4,4' at δ 1.5. Conversion of 13 into (S)-3-benzyloxyhexa-1,5-diene (16) was effected as described above for 1 via the intermediates 14 and 15 (Scheme 2).

The ready availability of 8 prompted us to explore its transformation into R-(+)-α-lipoic acid[9] (22), a cofactor in biochemical[10] decarboxylation of α-keto acids. Thus, the Claisen ester rearrangement (Scheme 3) of 8 with excess triethyl orthoacetate and a catalytic amount of propionic acid



at 145 °C gave the diene ester (17) in 81% yield. Selective hydroboration-oxidation of the terminal double bond in 17 was accomplished with 9-BBN to afford 18 which on exhaustive hydrogenation over palladium on charcoal effected simultaneously the hydrogenation of the double bond and debenzylation to give the diol 19 in 70% yield. Transformation of 19 into R-(+)-α-lipoic acid (22) was effected by the procedure of Golding et al.[11] according to which the derived dimesylate derivative 20 was heated with sodium sulfide-



sulfur in DMF to give ethyl R-(+)-α-lipoate (21). Hydrolysis of 21 with alkali gave R-(+)-α-lipoic acid (22) whose ^{1}H NMR spectral and $[\alpha]_D$ values were comparable with those reported.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 683 or 1310 spectrometer. ^{1}H NMR were recorded on a Varian FT-80A or Jeol PMX-90 spectrometer, using TMS as internal standard. Mass spectra were recorded on a CEC-21-110B double focussing mass spectrometer operating at 70eV using the direct inlet system. Optical rotations were measured with a Jasco Dip 181 digital polarimeter.

(R,R)-3,4-Dibenzoyloxyhexa-1,5-diene (6). A mixture of 4[12] (8.0 g, 17 mmol) and 50% aqueous acetic acid (80 mL) was heated on a boiling water

bath for 4 h. The reaction mixture was concentrated and traces of acetic acid were removed by codistillation with toluene to give the tetrol which was treated with methanesulfonyl chloride (6.6 mL) in the presence of pyridine (8 mL) and methylene chloride (40 mL). After 4 h at room temperature the reaction mixture was worked up to give 5 (9.6 g, 80%) which was used as such for the next reaction.

Compound 5 (8.5 g, 12 mmol), sodium iodide (14.4 g, 96 mmol) and dry DMF (75 mL) were heated under reflux with stirring. Activated zinc dust (6.3 g, 96 mmol) was introduced gradually. After refluxing for 2 h the reaction mixture was diluted with water (150 mL) and ether (100 mL) and filtered. The organic layer was separated and the aqueous layer was repeatedly extracted with ether. The combined ethereal layer was successively washed with 10% aqueous sodium thiosulfate, water, then dried and concentrated. The residue was purified on a column of silica gel with light petroleum-ethyl acetate (5:1) as eluent to give 6 (2.35 g, 60%) as an oil : $[\alpha]_D$ +13.1° (c 3.3, chloroform); ^{1}H NMR ($CDCl_3$) δ 5.3-5.6 (m, 6H, 2xCH_2=, 2xCH-O), 5.8-6.4 (m, 2H, 2xCH=), 7.6 (m, 6H, arom), 8.2 (m, 4H, arom); IR ($CHCl_3$) 1720 cm^{-1} (COPh); Mass m/z 161 (M^+/2), 122, 105 (100%).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.53; H, 5.63. Found : C, 74.02; H, 5.45.

(R,R)-1,5-Hexadien-3,4-diol (1). Compound 6 (2.25 g, 7 mmol) in methanol (20 mL) was treated with sodium metal (10 mg) for 16 h. The reaction mixture was deionized with Amberlite resin, filtered and concentrated to afford crude 1 which was purified on a short column of silica gel with light petroleum-ethyl acetate (1:1) as eluent to afford 1 (0.74 g, 93%) as an oil : $[\alpha]_D$ +32.6° (c 0.98, chloroform); IR (film) 3350 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 3.5 (b.s, 2H, 2xOH), 4.0 (dd, 2H, 2xCH-OH), 5.2-5.5 (m, 4H, 2xCH_2=), 5.8-6.1 (m, 2H, 2xCH=); Mass m/z 57 (M^+/2).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found : C, 62.63; H, 8.62.

(R,R)-4-Benzyloxyhexa-1,5-dien-3-ol (8). A solution of 1 (0.68 g, 6 mmol) and di-n-butyltin oxide (1.42 g, 5.7 mmol) in dry toluene (20 mL) was heated under reflux with azeotropic removal of water for 3 h. The reaction mixture was concentrated and then treated with DMF (10 mL) and benzyl bromide (0.83 mL, 6.6 mmol) at 100 °C for 4 h. It was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, dried and concentrated to afford a residue which was chromatographed

on a column of silica gel by using light petroleum-ethyl acetate (2:1) as eluent to give **8** (0.92 g, 77% based on recovered **1**) as an oil : $[\alpha]_D$ +2.9° (c 1.2, chloroform); ^{1}H NMR ($CDCl_3$): δ 3.8 (t, 1H, H-3), 4.2 (t, 1H, H-4), 4.6 (AB-q, 2H, CH_2Ph), 5.2-5.5 (m, 4H, 2xCH_2=), 5.7-6.0 (m, 2H, 2xCH=), 7.4 (s, 5H, Ph); Mass m/z 147, 91 (100%), 57.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found : C, 76.11; H, 7.58.

4-O-Benzyl-1,2:5,6-di-O-isopropylidene-D-mannitol (10). **3** (5.24 g, 20 mmol) and di-n-butyltin oxide (4.72 g, 19 mmol) were heated under reflux in dry toluene (75 mL) for 3 h and then concentrated to dryness in vacuo. The resulting stannylene acetal (**9**) was treated with DMF (25 mL) and benzyl bromide (2.75 mL, 22 mmol) at 100 °C for 4 h. After the usual work up the residue was chromatographed on a column of silica gel with light petroleum-ethyl acetate (2:1) to give **10** (5.38 g, 76% based on recovered **3**) as an oil : $[\alpha]_D$ + 2.8° (c 1.5, chloroform); IR (film) 3425 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 1.3, 1.35 (2s, 12H, 4xCH_3), 3.9-4.1 (m, 7H), 4.2 (dd, 2H, CH_2-OBn), 4.7 (AB-q, 2H, CH_2Ph), 7.3 (s, 5H, Ph); Mass m/z 352 (M^+), 337, 91 (100%).

Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.77; H, 8.01. Found : C, 64.32; H, 7.74.

3-O-Acetyl-4-O-benzyl-1,2:5,6-di-O-isopropylidene-D-mannitol (11). Compound **10** (5.15 g, 14 mmol) was acetylated with acetic anhydride (2 mL) and pyridine (4 mL) in a conventional manner to give **11** (5.36 g, 90%) as an oil : $[\alpha]_D$ +30.6° (c 1.15, chloroform); IR (film) 1745 cm^{-1} ($COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.35 (2s, 6H, 2xCH_3), 1.43 (s, 6H, 2xCH_3), 2.1 (s, 3H, OAc), 3.9-4.1 (m, 7H), 4.2 (dd, 1H, H-4), 4.8 (Ab-q, 2H, CH_2Ph), 7.4 (s, 5H, Ph); Mass m/z (M^+), 379, 235, 91 (100%).

Anal. Calcd for $C_{21}H_{30}O_7$: C, 63.96; H, 7.67. Found : C, 63.61; H, 7.52.

(R,R)-4-Benzyloxyhexa-1,5-dien-3-ol (8). Compound **11** (5.11 g, 12 mmol) was heated on a boiling water bath with 50% aqueous acetic acid (50 mL) for 4 h to afford the tetrol derivative which, without purification was subjected to mesylation with mesyl chloride (4.7 mL, 60 mmol) and pyridine (6 mL) in methylene chloride (25 mL) to give the tetramesylate (7.1 g, 81%). This compound was treated with sodium iodide-zinc-DMF in accordance with the above procedure, followed by Zemplen deacetylation to give **8** (1.3 g, 56%) identical with the product prepared earlier.

3-O-Benzyl-1,2:5,6-di-O-isopropylidene-4-O-[(s-methylthio)thiocarbonyl]-D-mannitol (12). To a solution of **10** (4.0 g, 11.36 mmol) in tetrahydrofuran (20 mL) under nitrogen was added sodium hydride (50% oil dispersion, 0.70 g, 29.16 mmol). After 1.5 h, carbon disulfide (1.2 g, 17.07 mmol) was introduced, followed after 20 min by methyl iodide (3.04 g, 21.3 mmol). The reaction mixture was stirred for 24 h and then decomposed with methanol. The residue obtained after evaporation of the solvent, was chromatographed on a silica gel column with ethyl acetate-light petroleum (1:8) as eluent to afford **12** (3.0 g, 60%) as an oil : $[\alpha]_D$ +49.5° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.30, 1.41 (2s, 12H, 4xCH_3), 2.55 (s, 3H, S-Me), 3.8-4.15 (m, 7H), 4.35 (dd, 1H, H-3), 4.75 (AB-q 2H, CH_2-Ph), 6.1 (dd, 1H, H-4), 7.23 (s, 5H, Ph).

Anal. Calcd for $C_{21}H_{30}O_6S_2$: C, 57.01; H, 6.83. Found : C, 56.80; H, 6.80.

3-O-Benzyl-4-deoxy-1,2:5,6-di-O-isopropylidene-D-mannitol (13). Compound **12** (3.0 g, 6.78 mmol), AIBN (5 mg) and tri-n-butyltin hydride (2.37 g, 8.14 mmol) were refluxed in toluene (30 mL) under nitrogen. After 7 h the reaction mixture was concentrated and chromatographed on a column of silica gel using ethyl acetate-light petroleum (1:7) to give **13** (1.36 g, 60%) as an oil : $[\alpha]_D$ -18.4° (c 1, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.9, 1.0 (2s, 12H, 4xCH_3), 1.2-1.8 (m 2H, H-4,4'), 3.9-4.35 (m, 7H), 4.85 (AB-q, 2H, CH_2Ph), 7.25 (s, 5H, Ph).

Anal. Calcd for $C_{19}H_{28}O_5$: C, 67.83; H, 8.39. Found : C, 67.82; H, 8.33.

3-O-Benzyl-4-deoxy-1,2:5,6-tetra-O-mesyl-D-mannitol (15). Compound **13** (1.0 g, 2.97 mmol) in 50% aqueous acetic acid (7 mL) was heated on a boiling water bath for 2 h to furnish the tetrol which was treated with pyridine (10 mL) and methanesulfonyl chloride (5 mL) for 3 h to give, after the usual work up, a syrup which was chromatographed on a column of silica gel using ethyl acetate-light petroleum (1:1) to afford **14** (1.2 g, 90%) as an oil : $[\alpha]_D$ -2.8° (c 1.13, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.8-2.2 (m, 2H, H-4,4'), 3.0 (s, 12H, 4xOMs), 4.25-4.8 (m, 7H), 5.1 (AB-q, 2H, CH_2Ph), 7.2 (s, 5H, Ph).

Anal. Calcd for $C_{17}H_{28}O_{13}S_4$: C, 35.92; H, 4.96. Found : C, 35.72; H, 4.81.

3-Benzyloxyhexa-1,5-diene (16). A mixture of **15** (1.0 g, 2.13 mmol), sodium iodide (2.56 g, 17.09 mmol) and zinc dust (1.25 g, 19.23 mmol) in dry DMF was heated under reflux for 2 h affording a residue which when purified on a column of silica gel using ethyl acetate-light petroleum (1:5) furnished **16** (0.20 g, 50%) as an oil : $[\alpha]_D$ -36° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 2.4 (m, 2H, H-4,4'), 3.8 (m, 1H, H-3), 4.5 (AB-q, 2H, CH_2Ph), 4.9-6.05 (m, 6H, 2xCH=CH_2), 7.2 (s, 5H, Ph).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found : C, 82.74; H, 8.2.

(R)-Ethyl 6-Benzyloxy-4,7-octadienoate (17). A mixture of **8** (1.0 g, 5 mmol), triethyl orthoacetate (6.5 mL, 35 mmol) and propionic acid (0.5 mL) was heated to 145 °C for 2 h. The excess triethyl orthoacetate was removed under reduced pressure and the residue was dissolved in ethyl acetate and the solution washed with sodium bicarbonate, brine, then dried and concentrated. The product was chromatographed over silica gel using light petroleum-ethyl acetate (8:1) as eluent to furnish **17** (1.12 g, 81%) as an oil : $[\alpha]_D$ +10.9° (c 2.7, chloroform); IR (film) 1710 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, $CH_2\underline{CH_3}$), 2.4 (distorted d, 4H, 2xCH_2), 4.2 (q, 2H, OEt), 4.3 (m, 1H, CH-OBn), 4.55 (s, CH_2Ph), 5.1-6.4 (m, 5H, CH= & CH_2=), 7.3 (s, 5H, Ph).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found : C, 73.91; H, 8.20.

(R)-Ethyl 6-Benzyloxy-8-hydroxyoct-4-enoate (18). Compound **8** (0.82 g, 3 mmol) and 9-BBN (0.44 g, 3.6 mmol) were heated for 2 h at 60 °C under nitrogen. To the resulting gummy syrup, the solution of sodium acetate (0.8 g in 2 mL water) was added followed by 30% H_2O_2 (2 mL). After stirring for 1.5 h at room temperature, the solution was extracted with ethyl acetate, washed with brine, dried and concentrated. The residue was purified by column chromatography on silica gel with light petroleum-ethyl acetate (1:1) as eluent, to give **18** (0.71 g, 81%) as an oil : $[\alpha]_D$ +5.2° (c 1.04, chloroform); IR ($CHCl_3$) 3300 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, $CH_2\underline{CH_3}$), 1.6-1.9 (m, 2H, CH_2), 2.4 (distorted d, 4H, 2xCH_2), 3.8 (t, 2H, CH_2OH), 3.9-4.1 (m, 1H, CH-OBn), 4.2 (q, 2H, OEt), 4.5 (AB-q, 2H, CH_2Ph), 5.3-5.85 (m, 2H, CH=CH), 7.4 (s, 5H, Ph).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found : C, 69.22; H, 8.10.

(S)-Ethyl 6,8-Dihydroxyoctanoate (19). Compound 18 (0.60 g) and palladium on charcoal (0.06 g) in ethyl acetate (15 mL) was hydrogenated at atmospheric pressure and room temperature for 4 h and the mixture then filtered. The filtrate was concentrated to give a residue which was chromatographed on silica gel using light petroleum-ethyl acetate (1:3) as eluent to yield 19 (0.32 g, 76%) as an oil : IR ($CHCl_3$) 3200-3400 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.3 (t, 3H, $CH_2\underline{CH_3}$), 1.45-1.90 (m, 8H, 4xCH_2), 2.3 (t, 2H, CH_2-CO), 3.6-3.9 (m, 3H, CH_2OH, CH-OH), 4.1 (q, 2H, OEt); Mass m/z 204 (M^+).

(S)-Ethyl 6,8-Dimesyloxyoctanoate (20). A solution of 19 (0.20 g, 1 mmol) and triethylamine (0.56 mL, 4 mmol) in dry methylene chloride (5 mL) was treated with methanesulfonyl chloride (0.24 mL, 3 mmol) for 3 h to give a crude product which was purified by a short column of silica gel using light petroleum-ethyl acetate (8:1) to afford 20 (0.32 g, 90%) as an oil : $[\alpha]_D$ +16.4° (c 0.83, chloroform), lit.[10b] $[\alpha]_D$ +17.0° (c 1, chloroform); IR ($CHCl_3$) 1715 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H, $CH_2\underline{CH_3}$), 1.45-2.4 (m, 10H, 5xCH_2), 3.0 (s, 6H, 2xOMs), 4.1 (q, 2H, OEt), 4.32 (t, 2H, CH_2-OMs), 4.9 (m, 1H, CH-OMs).

Anal. Calcd for $C_{12}H_{24}O_8S_2$: C, 39.98; H, 6.71. Found : C, 39.65; H, 6.54.

R-(+)-Ethyl α-Lipoate (21). A solution of 20 (0.29 g, 0.8 mmol), powdered sodium sulfide monohydrate (80 mg, 0.8 mmol) and sulfur (26 mg, 0.8 mmol), in dry DMF (3 mL) was heated at 90 °C for 24 h. The mixture was then poured on ice and the aqueous mixture extracted with ethyl acetate. The organic layer was washed with brine, dried and concentrated to give a residue which was chromatographed over silica gel using light petroleum as the eluent to afford 21 (0.13 g, 70%) as an oil : $[\alpha]_D$ +60.2° (c 0.81, chloroform); lit.[10b] $[\alpha]_D$ +61.0° (c 0.3, chloroform); IR ($CHCl_3$) 1710 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 1.25 (t, 2H, $CH_2\underline{CH_3}$), 1.5-1.9 (m, 8H, 4xCH_2), 2.3 (t, 2H, CH_2-CO), 3.15 (t, 2H, CH_2-S), 3.55 (m, 1H, CH-S), 4.1 (q, 2H, OEt); Mass m/z 234 (M^+).

R-(+)-α-Lipoic Acid (22). Compound 21 (0.11 g, 0.5 mmol) in ethanol (5 mL) was hydrolyzed with 0.1 M aqueous KOH (6 mL) in accordance with the literature procedure to yield 22 (50 mg, 76% based on recovered 21) as a semi-solid : $[\alpha]_D$ +92.4° (c 0.62, benzene), lit.[10c] $[\alpha]_D$ +107° (c 0.82, benzene); IR ($CHCl_3$) 1700 cm^{-1} (acid); ^1H NMR ($CDCl_3$) δ 1.5-1.9 (m, 8H,

4xCH_2), 2.4 (t, 2H, CH_2-CO), 3.15 (t, 2H, CH_2-S), 3.55 (m, 1H, CH-S), 8.1 (b.s, 1H, COOH).

REFERENCES

1. a) J. Mulzer, Nachr. Chem. Techn. Lab., 32, 798 (1984) and references cited therein; b) U. Kufner and R. R. Schmidt, Synthesis, 1060 (1985) and references cited therein; c) R. R. Schmidt and K. Frische, Liebigs Ann. Chim., 209 (1988) and references cited therein.

2. a) Preliminary communication : A. V. Rama Rao, S. V. Mysorekar, M. K. Gurjar and J. S. Yadav, Tetrahedron Lett., 28, 2183 (1987); b) M. K. Gurjar and S. M. Pawar, Indian J. Chem. Sect. B, 26, 55 (1987).

3. H. C. Brown, P. K. Jadhav and K. S. Bhat, J. Am. Chem. Soc., 110, 1535 (1988).

4. G. J. F. Chittenden, Carbohydrate Res., 84, 350 (1980).

5. M. Kinoshita and Y. Suzuki, Bull. Chem. Soc. Japan, 50, 2375 (1977).

6. S. David and S. Hanessian, Tetrahedron, 41, 643 (1985).

7. N. Nagashima and M. Ohno, Chem. Letters, 141 (1987).

8. D. H. R. Barton and W. B. Motherwell, Pure Appl. Chem., 53, 15 (1981).

9. a) L. J. Reed, J. C. Gunsalus, B. G. DeBusk and C. S. Hornberger, Science, 114, 93 (1951); b) H. Seigel, Angew. Chem. Int. Ed. Engl., 21, 389 (1982).

10. a) J. D. Elliott, J. Steele and W. S. Johnson, Tetrahedron Lett., 26, 2535 (1985); b) A. V. Rama Rao, K. Garyali, M. K. Gurjar and T. Ravindranathan, Carbohydrate Res., 148, 51 (1986); c) P. C. B. Page, C. M. Rayner and I. O. Sutherland, J. Chem. Soc. Chem. Commun., 1408 (1986); d) A. V. Rama Rao, A. V. Purandare, E. R. Reddy and M. K. Gurjar, Synthetic Commun., 17, 1095 (1987); e) R. B. Menon, M. A. Kumar and T. Ravindranathan, Tetrahedron Lett., 28, 5313 (1987); f) M. H. Brookes, B. T. Golding and A. T. Hudson, J. Chem. Soc. Perkin Trans. I, 9 (1988).

11. M. H. Brookes, B. T. Golding, D. A. Howes and A. T. Hudson, J. Chem. Soc. Chem. Commun., 1051 (1983).

12. B. R. Baker and H. S. Sachdev, J. Org. Chem., 28, 2135 (1963).

IICT Communication No.2337