75. Enantiomeric 3,7-Dimethylocta-1,7-dienes as Useful Chiral Building Blocks

A New Access to Both Optical Antipodes of Natural (*E*)-3,7-Dimethyloct-2-ene-1,8-diol and (*E*)-3,7-Dimethyloct-2-ene-1,8-dicarboxylic Acid

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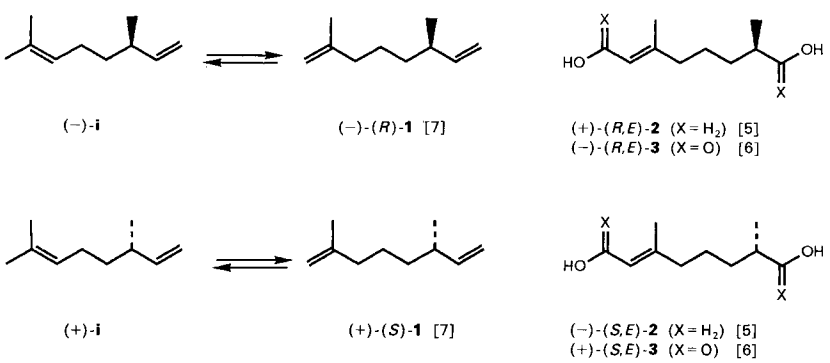
Ozonolysis of the easily available monoterpenoids (−)-**1** and (+)-**1** leads in high yield to the keto-aldehydes (−)-**4** and (+)-**4**, which serve as convenient intermediates for efficient new routes to both optical antipodes of the naturally occurring octene-diol (*E*)-**2** (*Monarch* butterfly secretion product) and octene-dicarboxylic acid (*E*)-**3** (*Callosobruchus chinensis* sex pheromone). All steps proceed with almost complete retention of configuration, ensuring the synthesis of the target compounds with high optical purity.

Introduction. – Despite tremendous progress in the development of efficient methologies for asymmetric synthesis in recent years [1], the classical approach based on judicious exploitation of cheap and abundantly available chiral building blocks has lost none of its general importance. Especially, where the starting material originates from monoterpenoid sources, this concept additionally benefits from the ready availability of both optical antipodes and their often high optical purity [2].

The previous syntheses of enantiomerically pure ipsdienols [3] and β-necrodols [4], both from (−)-α-pinene (*ee* $\geqslant$ 96%), are typical examples of this strategy.

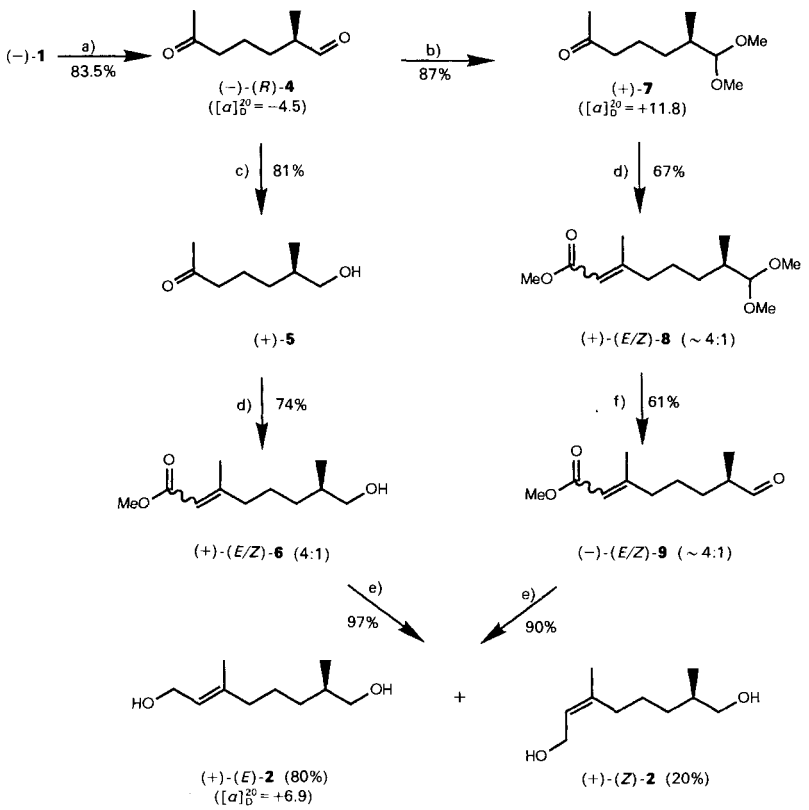
Scheme 1



Continuing our efforts in this field, we have now developed a simple access to natural (*E*)-**2**[1]) [5] and (*E*)-**3**[1]) [6] in both enantiomeric forms using the readily accessible monoterpenoids (–)-**1** and (+)-**1** [7] as chiral building blocks (*Scheme 1*).

Structurally, both natural products, (*E*)-**2** and (*E*)-**3**, are distinguished by the presence of a chiral centre at C(7), a fact which is uncommon in related plant terpenes. Their direct enantioselective preparation from existing chiral building blocks is, therefore, not obvious and, indeed, all previously reported syntheses of optically active (*E*)-**2** and (*E*)-**3** [8–10] have made use of asymmetric synthetic methods. Whilst having successfully led to the assignment of the absolute configurations at C(7), these methods, however, suffer from either low enantioselectivity [9] or poor chemical yield [8] [10].

Scheme 2



a) 1) O_3, MeOH, –70°, 2) Me_2S, 20°, 24 h. b) MeOH, TsOH, 20°, 30 min. c) $NaBH_4$, EtOH/CH_2Cl_2 (~2:1), –70°. d) $(MeO)_2POCH_2COOMe$, NaH, HMPA; $(i\text{-}Pr)_2O$ [14]. e) $LiAlH_4$, Et_2O, 0°. f) HCOOH, H_2O, 20°.

[1]) Diol (*E*)-**2** has been identified as a major component in the secretion products of the *Monarch* butterfly, *Danaus chrysippus*, [5] and the diacid (*E*)-**3** as a pheromone of the *Azuki* bean weevil, *Callosobruchus chinensis* L. [6]. The absolute configurations of the naturally occurring compounds are still undetermined. (*E*)-**3** was found to display specific activity as a sex pheromone in both enantiomeric forms [8] and has, therefore, attracted much attention for bioassay applications in pest control.

Our approach to (*E*)-**2** and (*E*)-**3** (*Schemes 2* and *3*) establishes the chiral centre at C(7) in an enantiospecific manner by ozonolysis of the vinyl group of the stereochemically well-defined dienes (−)-**1** and (+)-**1** [7]. We further take advantage of the fact that, under the same conditions, the second C=C bond in (−)-**1** and (+)-**1** is simultaneously cleaved, affording keto-aldehydes (−)-**4** and (−)-**4** as convenient precursors for the preparation of both optical antipodes of diol (*E*)-**2** and diacid (*E*)-**3**.

Results. – The starting dienes, (−)-**1** ($\alpha_D = -9.8$; ~ 80% ee[2]) and (+)-**1** ($\alpha_D = +10$; ~ 82% ee[2]), were obtained by fractional distillation of the commercially available equilibrium mixtures of (−)-**1** and (+)-**1** with the isomeric (−)- and (+)-3,7-dimethylocta-1,6-dienes ((−)-**i** $\alpha_D = -9.5$ and (+)-**i** $\alpha_D = +10$[3]), see *Scheme 1*) as reported previously by *Rienäcker* [7].

Treatment of (−)-**1**[4]) and (+)-**1** in MeOH with excess O_3 at −70° to complete conversion (GC) followed by reduction with Me_2S resulted in a high yield of the keto-aldehydes (−)-**4** ($\alpha_D = -4.5$) and (+)-**4** ($\alpha_D = +4.7$; 84% dist. yield). Their further conversion to the target compounds (*E*)-**2** and (*E*)-**3** was studied in detail only for the (*R*)-series using (−)-(*R*)-**4** as starting material, and is summarised in *Schemes 2* and *3*.

The synthesis of the enantiomeric diol (+)-(*E*)-**2** (*Scheme 2*) was accomplished by two different routes. In the first approach, (−)-(*R*)-**4** was chemoselectively reduced with $NaBH_4$ at low temperature [13], to afford the hydroxy-ketone (+)-**5** ($[\alpha]_D^{20} = +9.0$) in 81% yield. A subsequent *Horner-Wittig* reaction [14] using trimethyl phosphonoacetate in $(i\text{-Pr})_2O$ in the presence of NaH afforded the diastereoisomeric esters (+)-(*E*)-**6** and (+)-(*Z*)-**6** as a ~ 4 : 1 mixture in 74% yield. Reduction with $LiAlH_4$ gave a 4:1 mixture of diols (+)-(*E*)-**2** and (+)-(*Z*)-**2** in 97% yield. Purification of (+)-(*E*)-**2** ($[\alpha]_D^{20} = +6.9$ ($CHCl_3$)) was effected by distillation and chromatography (*cf. Exper. Part*).

Execution of this three-step procedure on a multigram scale readily allowed the preparation of (+)-(*E*)-**2** in 45% overall yield from (*R*)-**4**. The same result was obtained by application of this reaction sequence for the preparation of the antipodal diol, (−)-(*E*)-**2** ($[\alpha]_D = -7.2$) from (*S*)-**4**.

The optical purity of (+)-(*R*)- and (−)-(*S,E*)-**2** was determined by ^{1}H-NMR spectroscopy[2]) and found to be practically the same as that of the starting material (ee ~ 85% ± 5%), indicating that all steps of our reaction scheme proceeded with almost complete retention of configuration.

In the second approach to (+)-(*E*)-**2** (*cf. Scheme 2*), (*R*)-**4** was first transformed into its dimethyl acetal (+)-**7** (87% yield) which underwent a *Horner-Wittig* reaction (*vide supra*) to give the diastereoisomeric esters (+)-(*E*)-**8** and (+)-(*Z*)-**8** as a ~ 4:1 mixture in 67% yield. Subsequent deprotection of (+)-(*E*/*Z*)-**8** afforded the corresponding esters (−)-(*E*/*Z*)-**9** (61% yield) and reduction with $LiAlH_4$ then furnished a 4:1 mixture (+)-(*E*)-**2**/(+)-(*Z*)-**2** (90% yield). The rotations of (+)-(*E*)-**2** ($[\alpha]_D^{20} = +6.3$) and (+)-(*Z*)-**3** ($[\alpha]_D^{20} = +7.3$) obtained by this route correspond well with those of the former approach, confirming that the chiral centre also remained unaffected in the course of these transformations.

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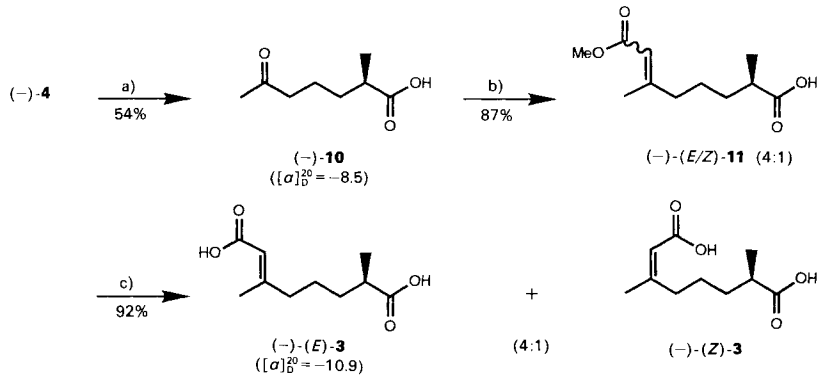
[2]) The enantiomeric excesses (ee) of (+)-**1** and (−)-**1** are in agreement with the ee values determined (for (+)-**2** and (−)-**2**) by ^{1}H-NMR spectroscopy using Eu(hfbc)$_3$ as chiral shift reagent.

[3]) The availability of (+)-**i** and (−)-**i** of high optical purity (≥ 98%) is assured by their reported synthesis from citronellol [11] or α-pinene [12] [7].

[4]) Samples of dienes (−)-**1** and (+)-**1**, still containing some (−)-**i** and (+)-**i**, may be used in the ozonolysis.

Scheme 3



a) $AgNO_3$, EtOH, H_2O, 20°. b) $(MeO)_2POCH_2COOMe$, NaH, $(i\text{-}Pr)_2O$, HMPT [14]. c) NaOH, MeOH, 20°.

The synthesis of the two enantiomers of *callosobruchusic acid*, (−)-(*E*)-**3** and (+)-(*E*)-**3**, is presented in *Scheme 3* (depicted for (−)-(*E*)-**3**). It starts with the oxidation of (*R*)-**4** to the keto-acid (−)-**10**, using $AgNO_3$ [15]; although proceeding in only moderate yield (54%), this method directly afforded (*R*)-**10** in high chemical purity with practically no loss of optical activity (*vide infra*). Subsequent submission of (−)-**10** to the *Horner-Wittig* olefination [14] then gave the diastereoisomeric acid esters as a 4:1 mixture, (−)-(*E*)-**11** and (−)-(*Z*)-**11**, in 87% yield.

Saponification of the esters to a 4:1 mixture (−)-(*E*)-**3**/(−)-(*Z*)-**3** (92% yield) and isolation of (−)-(*E*)-**3** ((*R*)-*callosobruchusic acid* [6] [8]) was readily achieved by HPLC combined with recrystallisation from hexane/EtOH. Our sample of (−)-(*E*)-**3** thus obtained (m.p. 92°; 30% overall yield from (*R*)-**4**) had $[\alpha]_D^{20} = -10.9$ ($CHCl_3$), indicating an optical purity of ~ 85% ([8]: $[\alpha]_D^{20} = -11.75$ ($CHCl_3$)). In a similar manner, (+)-(*E*)-**3** ($[\alpha]_D^{20} = +10.2$ ($CHCl_3$)) was prepared from (+)-**4** ($[\alpha]_D^{20} = +4.7$). The structures of all new compounds described in this work were unambiguously assigned from inspection of their ^1H- and ^{13}C-NMR spectra (*cf. Exper. Part*) and, for (*E*)-**2**/(*Z*)-**2** and (*E*)-**3**/(*Z*)-**3**, further confirmed by spectral comparison with authentic samples [8] [9].

In conclusion, we have shown that our access to the naturally occurring monoterpenoids (*E*)-**2** and (*E*)-**3** is thus well-suited for the synthesis of both enantiomers with high optical purity[3]) and favourably competes with other known procedures.

We are indebted to Dr. *R.L. Snowden* and Dr. *A.F. Thomas* for helpful advice, and Mrs. *B. Mayor-Frei* for technical assistance.

Experimental Part

General. Apparatus and conditions as described in [4]. B.p. and m.p. are uncorrected. *Starting material:* commercially available (−)-(*R*)- and (+)-(*S*)-3,7-dimethylocta-1,6-diene ((−)-**i**, $[\alpha]_D^{20} = -9.5$, and (+)-**i**, $[\alpha]_D^{20} = +10$; *Fluka AG*) were refluxed with catalytic amounts of TsOH in a 2-m distillation column under 30–40 Torr as reported [7]. The lower-boiling (−)-(*R*)- and (+)-(*S*)-3,7-dimethylocta-1,7-dienes ((−)-**1**, $[\alpha]_D^{20} = -9.8$ ($CHCl_3$), and (+)-**1**, $[\alpha]_D^{20} = +10.0$; b.p. 70°/40 Torr) were isolated from the head fractions by re-distillation.

Preparation of (−)-(R)- and (+)-(S)-2-Methyl-6-oxoheptanal ((−)-**4** and (+)-**4**). A soln. of (−)-**1** (20 g, 145 mmol) in MeOH (200 ml) was ozonised at −70°, until the blue colour persisted and (−)-**1** disappeared. Ar gas was passed through the soln. for 5 min, and Me_2S (20 ml) was added dropwise under stirring. Then, the temp. was allowed to attain 20°, and stirring was continued for 18 h. The solvent was removed *i.v.*, and the residue was distilled to give 17.2 g (84%) of (−)-**4**. B.p. 82–85°/8 Torr. $[\alpha]_D^{20} = -12.4$ (neat), $[\alpha]_D^{20} = -4.5$ (6% in $CHCl_3$). IR (film): 2700, 1710. ^{1}H-NMR: 1.11 (*d*, *J* = 7, 3 H); 2.12 (*s*, 3 H); 9.62 (*d*, *J* = 2, 1 H). MS: 142 (1, M^+), 124 (5), 114 (5), 109 (3), 99 (3), 84 (28), 71 (47), 58 (58), 43 (100).

Enantiomeric (+)-**4** was obtained from (+)-**1** by this treatment, with $[\alpha]_D^{20} = +4.7$ in 80% yield (for (±)-**4**, see [16]).

(+)-(R)-7-Hydroxy-6-methylheptan-2-one ((+)-**5**). $NaBH_4$ (2 g, 52 mmol) was dissolved in EtOH (45 ml), and CH_2Cl_2 (105 ml) was added. The mixture was cooled to −78°, and (−)-**4** (10 g, 70.4 mmol) was added dropwise. After stirring for 2 h, distilled CH_3CHO (10 ml) was added and the mixture allowed to warm to r.t. The resulting soln. was diluted with CH_2Cl_2, washed with 10% aq. NaOH soln., concentrated, and distilled to give 8.2 g (81%) of (+)-**5**. B.p. 105°/0.05 Torr. $[\alpha]_D^{20} = +9.0$ (4.7% in $CHCl_3$); $[\alpha]_D^{20} = +10.2$ (5.1% in EtOH). IR (film): 3410, 1710, ^{1}H-NMR: 0.9 (*d*, *J* = 6, 3 H); 2.15 (*s*, 3 H); 3.08 (*s*, 1 H, OH); 3.43 (*d*, *J* = 6, 2 H). MS: 144 (0, M^+), 126 (2), 111 (7), 83 (7), 71 (35), 58 (71), 43 (100).

Enantiomeric (−)-**5** was obtained from (+)-**1** by this method in 80% yield. $[\alpha]_D^{20} = +4.6$ ($CHCl_3$) (for (±)-**5**, see [17]).

Methyl (+)-(R,E/Z)-8-Hydroxy-3,7-dimethyloct-2-enoate ((E/Z)-**6**). To a soln. of hexamethylphosphoric triamide (HMPT; 6.3 g), NaH (1.54 g, 64 mmol), and $(i\text{-}Pr)_2O$ (65 ml) under Ar, trimethyl phosphonoacetate (11.6 g, 62.6 mmol, *Fluka*) was added under stirring. Then, stirring was continued for 30 min. Hydroxy-ketone **5** (8.8 g, 61 mmol) was added dropwise, and the mixture was heated under reflux for 2 h. The mixture was poured into ice, extracted with Et_2O, washed with brine, evaporated, and distilled to give 9.1 g (74.2%) of (*E*/*Z*)-**6**. B.p. 95–105°/0.04 Torr. ((*E*)-**6**/(*Z*)-**6** ~ 79:21; $[\alpha]_D^{20} = +8.2$ ($CHCl_3$)). The spectral properties of an isolated sample of (*E*)-**6** were identical with those given in [10].

(+)-(R,E)- and (+)-(R,Z)-3,7-Dimethyloct-2-ene-1,8-diol ((+)-(*E*)-**2**/(+)-(*Z*)-**2**). a) *From (E/Z)-***6**. The 80:20 mixture (*E*)-**6**/(*Z*)-**6** (9.1 g, 46 mmol) in Et_2O (50 ml) was added dropwise to a suspension of $LiAlH_4$ (2.0 g, 53 mmol) in Et_2O (100 ml). The mixture was heated under reflux for 2 h and, after cooling to r.t., treated by successive dropwise addition of 2 ml of H_2O, 2 ml of 10% NaOH-soln. (15%), and 6 ml of H_2O [18]. After filtration, the solvent was removed *i.v.*, and the residue was distilled to give 7.6 g (97%) of (*E*)- and (*Z*)-**2** (ratio ~ 4:1). B.p. 110–120°/0.04 Torr. The two isomers were separated by prep. GC.

(*Z*)-**2** (*Peak 1*): $[\alpha]_D^{20} = +8.1$ (1.6% in $CHCl_3$). ^{1}H-NMR: 0.90 (*d*, *J* = 6, 3 H); 1.73 (*s*, 3 H); 3.42 (*d*, *J* = 6, 2 H); 4.05 (*d*, *J* = 7, 2 H); 5.4 (*t*, *J* = 7, 1 H). MS: 172 (9, M^+), 154 (1), 139 (3), 121 (13), 107 (17), 96 (50), 81 (46), 71 (100), 55 (41), 41 (47).

(*E*)-**2** (*Peak 2*): $[\alpha]_D^{20} = +6.9$ (3.9% in $CHCl_3$). ^{1}H-NMR: 0.89 (*d*, *J* = 6, 3 H); 1.65 (*s*, 3 H); 3.42 (*d*, *J* = 6, 2 H); 4.12 (*d*, *J* = 7, 2 H); 5.4 (*t*, *J* = 7, 1 H).

The optical purity was determined by ^{1}H-NMR ($Eu(hfbc)_3$) to be 85%.

b) *From (E/Z)-***9**. Treatment of (*E*/*Z*)-**9** (5 g) with $LiAlH_4$ (0.5 g) in Et_2O as described in *a* gave (*E*/*Z*)-**2** (90% yield; (*E*)/(*Z*) ~ 4:1).

(+)-(R)-7,7-Dimethoxy-6-methylheptan-2-one ((+)-**7**). A soln. of (−)-**4** (1 g, 7 mmol), MeOH (10 ml), and TsOH (20 mg) was stirred for 30 min at r.t. The mixture was diluted with Et_2O, washed with 10% aq. $NaHCO_3$ soln. and brine, concentrated *i.v.*, and distilled to give 1.15 g (87%) of (+)-**7**. B.p. 150° (oven temp.) $[\alpha]_D^{20} = +11.8$ (1% in $CHCl_3$). IR (film): 1700. ^{1}H-NMR: 0.91 (*d*, *J* = 6, 3 H); 2.15 (*s*, 3 H); 3.35 (*s*, 6 H); 4.04 (*d*, *J* = **6**, 1 H). MS: 188 (0, M^+), 125 (3), 107 (3), 98 (8), 75 (100), 43 (19).

Methyl (+)-(R,E/Z)-8-Dimethoxy-3,7-dimethyloct-2-enoate ((+)-(*E*)-**8**/(+)-(*Z*)-**8**). Compound (+)-**7** (7.9 g, 42 mmol) was treated with trimethyl phosphonoacetate (15.6 g, 85.5 mmol) as described before to give a 7.0 g (68%) mixture of (+)-(*E*/*Z*)-**8** (4:1). B.p. 85°/0.2 Torr. The two isomers were separated by prep. GC.

(*Z*)-**8** (*Peak 1*, ~ 20%): $[\alpha]_D^{20} = +7.2$ (7.3% in $CHCl_3$). IR (film): 1705. ^{1}H-NMR: 0.91 (*d*, *J* = 6, 3 H); 1.9 (split *s*, 3 H); 3.35 (*s*, 6 H); 3.67 (*s*, 3 H); 4.02 (*d*, *J* = 6, 1 H); 5.62 (br. *s*, 1 H). MS: 244 (0, M^+), 181 (3), 149 (3), 114 (19), 98 (32), 85 (29), 75 (100), 55 (24), 41 (14).

(*E*)-**8** (*Peak 2*, ~ 80%): $[\alpha]_D^{20} = +12.5$ (8% in $CHCl_3$). IR (film): 1705. ^{1}H-NMR: 0.90 (*d*, *J* = 6, 3 H); 2.17 (br. *s*, 3 H); 3.32 (*s*, 6 H); 3.67 (*s*, 3 H); 4.02 (*d*, *J* = 6, 1 H); 5.67 (br. *s*, 1 H). MS: 244 (0, M^+), 212 (2), 180 (4), 149 (3), 98 (47), 85 (37), 75 (100), 55 (26), 41 (13).

Methyl (−)-(R,E)- and (−)-(R,Z)-3,7-Dimethyl-8-oxooct-2-enoate- ((*E*)-**9** and (*Z*)-**9**). A soln. of (*Z*)-**8** (529 mg), H_2O (1 ml), and HCOOH (1 ml) was stirred at r.t. overnight. The mixture was diluted with Et_2O (100 ml) and washed with aq. 10% NaOH soln. and brine, concentrated, and distilled to give 262 mg (61%) of (*Z*)-**9**. B.p.

150°/0.2 Torr. $[\alpha]_D^{20} = -9.5$ (9.2% in $CHCl_3$). IR ($CDCl_3$): 2700, 1705. ^{1}H-NMR: 1.16 (*d*, *J* = 6, 3 H); 1.92 (br. *s*, 3 H); 3.65 (*s*, 3 H); 5.7 (br. *s*, 1 H); 9.61 (*d*, *J* = 2, 1 H). MS: 198 (0, $M^{+\cdot}$), 180 (2), 166 (22), 127 (33), 114 (39), 95 (100), 81 (53), 67 (52), 55 (59), 41 (61).

(*E*)-**8** (1.01 g) was treated similarly to give 465 mg (56%) of (*E*)-**9**. B.p. 150°/0.01 Torr. $[\alpha]_D^{20} = -4.8$ (9.2% in $CHCl_3$). IR ($CDCl_3$): 2700, 1700. ^{1}H-NMR: 1.12 (*d*, *J* = 7, 3 H); 2.16 (split *s*, 3 H); 3.65 (*s*, 3 H); 5.67 (*m*, 1 H); 9.6 (*d*, *J* = 2, 1 H). MS: 198 (0, $M^{+\cdot}$), 180 (1), 166 (18), 127 (26), 114 (37), 95 (100), 81 (57), 67 (53), 55 (77), 41 (72).

*(−)-(*R*)-2-Methyl-6-oxoheptanoic Acid* ((−)-**10**). A soln. of NaOH (25 g) in H_2O (300 ml) was added, within 1 h, to a vigorously stirred suspension of (−)-**4** (14.2 g, 100 mmol), $AgNO_3$ (50 g, 294 mmol) in H_2O (200 ml), and EtOH (80 ml). The mixture was allowed to stand overnight. The filtered soln. was washed with Et_2O, acidified with aq. 5N HCl soln., and extracted with Et_2O. The org. phase was evaporated and the residue distilled to give 8.5 g (54%) of (−)-**10**. B.p. 120°/0.04 Torr. $[\alpha]_D^{20} = -8.5$ (1.3% in $CHCl_3$). IR (film): 1700. ^{1}H-NMR: 1.2 (*d*, *J* = 6, 3 H); 2.17 (*s*, 3 H); 9.4 (br. *s*, 1 H). MS: 158 (1, $M^{+\cdot}$); 141 (9), 129 (23), 113 (13), 102 (33), 73 (36), 55 (23), 43 (100).

*(−)-(*R,E*)-3,7-Dimethyl-2-octene-1,8-dicarboxylic Acid* (Callosobruchusic Acid; (*E*)-**3**) *and Its (−)-(*R,Z*)-Isomer* ((Z)-**3**). The acid (−)-**10** (3.4 g, 21.5 mmol) was treated with trimethyl phosphonoacetate (5 g, 27.5 mol) as described to give 4.0 g (87%) of isomeric esters **11** (b.p. 140°/0.04 Torr; ratio: 73% (*E*): 27% (*Z*)). This mixture was saponified by refluxing for 1 h with a soln. of NaOH (1.5 g) in EtOH (50 ml). The solvent was removed *i.v.* and the residue dissolved in H_2O (200 ml), washed with Et_2O, acidified with 10% aq. HCl soln., and extracted with Et_2O. The solvent was removed *i.v.* to give 3.7 g of (*E*/*Z*)-**3** (80:20). The two isomers were separated by column chromatography (silica gel (150 g), EtOH/cyclohexane 2:1).

(*E*)-**3**: $[\alpha]_D^{20} = -10.9$ (7.6% in $CHCl_3$). M.p. 92° (pentane/Et_2O). ^{1}H-NMR: 1.2 (*d*, *J* = 7, 3 H); 2.18 (*s*, 3 H); 5.7 (*s*, 1 H); 11.0 (*s*, 2 H). MS: 200 (0, $M^{+\cdot}$), 182 (3), 164 (35), 136 (100), 111 (65), 95 (87), 81 (63), 67 (63), 55 (78), 41 (87).

(*Z*)-**3**: $[\alpha]_D^{20} = -11.0$ (2% in $CHCl_3$). ^{1}H-NMR: 1.2 (*d*, *J* = 7, 3 H); 1.91 (split *s*, 3 H); 5.68 (*s*, 1 H); 10.3 (br. *s*, 2 H). MS: 200 (0, $M^{+\cdot}$), 182 (5), 164 (32), 136 (95), 111 (70), 95 (82), 81 (52), 67 (67), 55 (72), 41 (100).

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