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Note

Synthesis of methyl shikimate from methyl (1,3,4/2,5)-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate*,†

SEIICHIRO OGAWA‡, YASUYUKI AOKI, AND TOHEI TAKAGAKI
Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223 (Japan)

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Shikimic acid (L-**1**) was first isolated from the oriental plant *Illicium religiosum* (in Japanese, shikimi) in 1885 by Eijkmann[3]. After nearly 50 years, thanks to the pioneering works of Fischer and Dangschat[4] during the 1930's, the complete structure and absolute stereochemistry of this acid were established.

In the early 1950's, shikimic acid was shown to be a key biosynthetic intermediate in the conversion of carbohydrate into aromatic amino acids, and this discovery, stimulated renewed interest in the compound and related substances. As a result, extensive studies of the synthesis have been conducted[5]. The first total synthesis was accomplished by Smissman *et al.*[6] and McCrindle *et al.*[7] by thermal elimination reactions of the acetyl derivatives of methyl 2,3,4,5-tetrahydroxycyclohexane-1-carboxylate (DL-**3**), which was prepared from the adduct formed in the Diels–Alder reaction of (1*E*, 3*E*)-1,4-diacetoxy-1,3-butadiene with methyl acrylate or acrylic acid. The proposal of McCrindle *et al.*[7] that has the (1,2,5/3,4)-configuration was contested by Smissman and collaborators[6], but eventually confirmed by McCasland *et al.*[8] on the basis of ^{1}H-n.m.r. spectral data.

Since methyl DL-(1,3,4/2,5)-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate (DL-**6**), the 1-epimer of DL-**3**, is now readily available from the Diels–Alder adduct of furan and acrylic acid, it became of interest to assess the suitability of this compound as a precursor of methyl shikimate. We describe here a total synthesis of methyl DL- and L-shikimate by elimination reactions of the tosyl derivatives of the esters DL- and L-**6**, respectively.

The precursor, DL-**5**, was prepared in good yield by a modified procedure. Thus, treatment of methyl DL-(1,3/2)-2,3-di-*O*-acetyl-2,3-dihydroxy-4-cyclo-

* Dedicated to the memory of Hermann O. L. Fischer on the centenary of his 100th birth.
†Pseudo-Sugars, Part XVIII. For Part XVII, see ref. 1.
‡To whom correspondence should be addressed.

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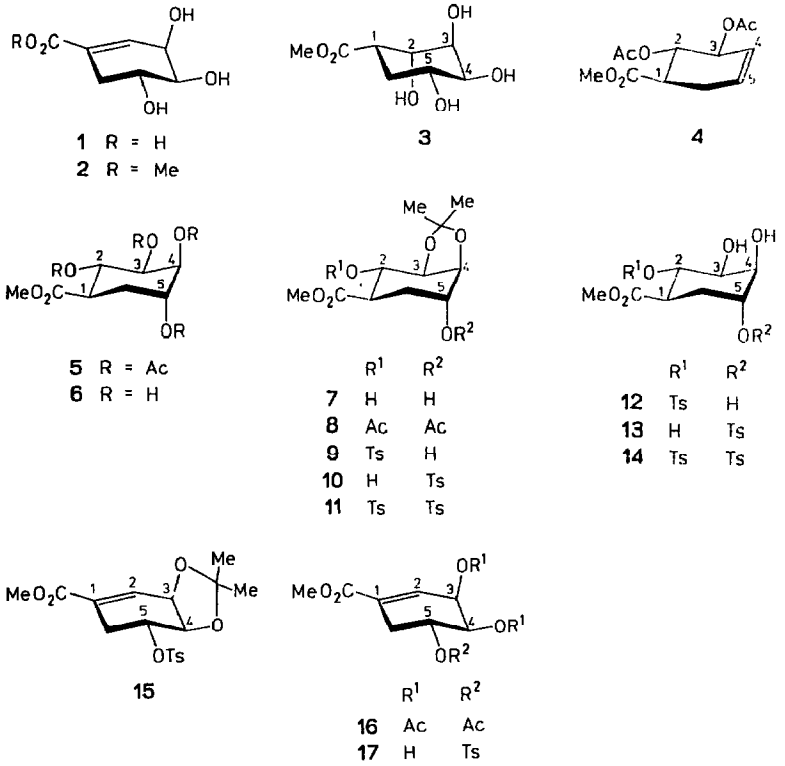

Fig. 1. The compounds described here are named and numbered according to the IUPAC-IUB 1973 Recommendations for Cyclitols (ref. 2). Thus C-1 is the reference carbon for determining configurational series (L), except in 1,2-unsaturated compounds, where the reference carbon is C-3. For convenience, only single enantiomers corresponding to methyl L-shikimate are depicted.

hexene-1-carboxylate[9] (DL-**4**) with hydrogen peroxide and formic acid at 60°, followed by acetylation with acetic anhydride and pyridine, produced DL-**5** in a quantitative yield. Diaxial opening of the intermediate 4,5-epoxide proceeded selectively with assistance from AcO-3. *O*-Deacetylation of DL-**5** with methanolic sodium methoxide gave the tetrahydroxy compound[9] DL-**6**, which was treated with 2,2-dimethoxypropane in *N,N*-dimethylformamide in the presence of *p*-toluenesulfonic acid to give 92% yield of the syrupy 3,4-*O*-isopropylidene derivative DL-**7**. Acetylation of DL-**7** in the usual way gave the diacetate DL-**8**. Selective tosylation of DL-**7** was carried out with 3.2 mol. equiv. of tosyl chloride in pyridine for 4 days at ambient temperature to give, after chromatography, a crystalline mixture of the monotosylates DL-**9** and DL-**10** (49%), and the ditosylate DL-**11** (45%). A mixture of DL-**9** and DL-**10** was treated with aqueous 80% acetic acid to give, after chromatography, the 2- (DL-**12**, 33%) and 5-tosylates (DL-**13**, 50%). The structure of DL-**12** was confirmed by the appearance of a triplet (δ 5.07, J 9 Hz) due to H-2 in the ^{1}H-n.m.r. spectrum. Treatment of DL-**12** with 0.25M methanolic sodium methoxide at ambient temperature smoothly afforded a single product identical with natural methyl shiki-

mate (t.l.c.). The compound was then isolated as the triacetate DL-**16** (94%), which was identified using an authentic sample[5e] by comparison of the ^{1}H-n.m.r. spectra.

On the other hand, deprotection of DL-**11** with aqueous acetic acid gave the hydroxy compound (DL-**14**, 84%), together with a small amount of the elimination product (DL-**17**, 9%). On reaction with sodium acetate in aqueous 2-methoxyethanol at reflux temperature, DL-**14** gave a 29% yield of methyl shikimate (DL-**2**), presumably as a result of the preferential opening of an intermediate 4,5-epoxide. Under these conditions, an aromatization seemed to occur as a side reaction and the formation of less polar components was observed by t.l.c. Compound DL-**2** was converted conventionally into crystalline DL-shikimic acid (DL-**1**; 76% yield), identical to an authentic sample[9].

Likewise, methyl L-shikimate was synthesized from L-**4** (ref. 1) by a somewhat improved procedure. When the ester L-**5**, prepared from L-**4**, was *O*-deacetylated with methanolic sodium methoxide, in addition to L-**6** (80%) L-**2** was isolated in 16% yield. Treatment of the isopropylidene derivative (L-**7**) of L-**6** with 3.8 mol. equiv. of tosyl chloride in pyridine at 60° for 2 days resulted in the elimination of the 2-tosyloxy function from the intermediate ditosylate L-**11**, giving rise to the derivative L-**15** in 82% yield. The presence of the *cis*-fused acetal ring is likely to sterically enhance the elimination reaction at C-1 and -2 (ref. 7). Removal of the protecting isopropylidene group gave the dihydroxy compound L-**17** (89%), which was then converted by treatment with sodium acetate into L-**2**, $[\alpha]_D^{24}$ − 133° (EtOH), in 40% yield. This compound was identified by comparison with an authentic sample[4a,5e].

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP capillary melting-point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 polarimeter. ^{1}H-N.m.r. spectra were recorded at 90 MHz with a Varian EM-390 spectrometer for solutions in $CDCl_3$ or CD_3OD, referenced to Me_4Si as the internal standard. T.l.c. was performed on plates coated with Silica Gel 60 F-254 (E. Merck) and silica gel column chromatography employed Wakogel C-300 (300 Mesh, Wako Co.). Organic solutions were dried over anhydrous sodium sulfate and concentrated below 40° under diminished pressure.

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetra*-O-*acetyl-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate* (DL-**5**). — A mixture of methyl DL-(1,3/2)-2,3-di-*O*-acetyl-2,3-dihydroxy-4-cyclohexene-1-carboxylate[9] (DL-**4**; 2.05 g, 8.0 mmol), 90% aqueous formic acid (20 mL), and 35% hydrogen peroxide (6 mL) was stirred for 1 h at 60°, and then concentrated. The residue was treated with acetic anhydride (10 mL) and pyridine (10 mL) overnight at ambient temperature, and concentrated. The residue was taken up in ethyl acetate (30 mL) and the solution was successively washed with M hydrochloric acid, saturated sodium hydrogencarbonate, and water, and dried. Evaporation of the solvent gave DL-**5** (3.0 g, quantitative) as a syrup. The ^{1}H-n.m.r spectrum was superimposable on that of an authentic sample[9].

Similarly, starting from the 1L enantiomer L-**4**, L-**5** was prepared quantitatively, syrup, $[\alpha]_D^{23}$ −31° (*c* 1.2, chloroform).

Anal. Calc. for $C_{16}H_{22}O_{10}$: C, 51.3; H, 5.9. Found: C, 51.2; H, 5.8.

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate* (DL-**6**). — Compound DL-**5** (2.8 g, 7.5 mmol) was treated with 0.25 M methanolic sodium methoxide (38 mL) for 1 h at ambient temperature. T.l.c. (5:1 chloroform–methanol) showed one major (R_F 0.23) and one minor spot (R_F 0.45). The mixture was neutralized with Amberlite IR-120 (H^+) resin (30 mL) and concentrated. The residue was recrystallized from ethanol to give DL-**6** (0.89 g, 58%) as prisms, R_F 0.23, m.p. 148–149°; lit.[7] m.p. 148–149°.

Similarly, L-**5** (380 mg, 1.0 mmol) gave a mixture of products, which was separated on a silica-gel column (13 g) with 8:1 chloroform–methanol as eluent. The first fraction gave methyl shikimate (L-**2**, 30 mg, 16%) as crystals, m.p. 109–110.5°, $[\alpha]_D^{23}$ −130° (*c* 0.34, ethanol); lit.[10] m.p. 113–114°, $[\alpha]_D^{20}$ 130° (EtOH). The ^{1}H-n.m.r. spectrum (CD_3OD) was superimposable on that of an authentic sample[4a,5c].

Anal. Calc. for $C_8H_{12}O_5$: C, 51.1; H, 6.4. Found: C, 51.0; H, 6.4.

The second fraction gave L-**6** (172 mg, 82%) as a syrup, $[\alpha]_D^{24}$ −7.5° (*c* 1.2, methanol). The ^{1}H-n.m.r spectrum (CD_3OD) was superimposable on that of an authentic sample[9].

Anal. Calc. for $C_8H_{14}O_6$: C, 46.6; H, 6.8. Found: C, 46.3; H, 6.9.

Methyl (1,3,4/2,5)-2,3,4,5-tetrahydroxy-3,4-O-isopropylidenecyclohexane-1-carboxylate (DL-**7**). — A mixture of DL-**6** (1.59 g, 7.7 mmol), 2,2-dimethoxypropane (10 mL), *N,N*-dimethylformamide (15 mL), and *p*-toluenesulfonic acid (60 mg) was stirred for 3 h at 60°. The mixture was then neutralized with sodium hydrogencarbonate and concentrated. The residue was taken up in ethyl acetate (30 mL) and the solution was passed through a short column of alumina. The solvent was evaporated and the residue was purified on a silica gel column (70 g) with 2:3 2-butanone–toluene as eluent to give DL-**7** (1.74 g, 92%) as a syrup, ^{1}H-n.m.r. ($CDCl_3$): δ 3.77 (s, 3 H, CH_3), 1.53, and 1.38 (2 s, each 3 H, CH_3).

Anal. Calc. for $C_{11}H_{18}O_6$: C, 53.6; H, 7.4. Found: C, 53.8; H, 7.3.

Similarly, the 1L enantiomer (L-**7**) was prepared from L-**6** in 90% yield; needles, m.p. 78–80°, $[\alpha]_D^{23}$ +43° (*c* 1, chloroform).

Anal. Found: C, 53.6; H, 7.4.

Compound DL-**7** (110 mg, 0.45 mmol) was treated with acetic anhydride (1.5 mL) and pyridine (1.5 mL) overnight at ambient temperature. The mixture was processed in a usual way and the product was crystallized from petroleum ether to give the diacetate DL-**8** (125 mg, 85%), m.p. 100–101.5°; ^{1}H-n.m.r. ($CDCl_3$): δ 3.70 (s, 3 H, CH_3), 2.10, 2.06 (2 s, each 3 H, 2 CH_3CO), 1.56, and 1.35 (2 s, each 3 H, CH_3).

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.5; H, 6.7. Found: C, 54.3; H, 6.6.

Selective tosylation of DL-**7** *in pyridine.* — A mixture of DL-**7** (0.80 g, 3.3 mmol), tosyl chloride (2.0 g, 11 mmol), and pyridine (16 mL) was stirred for 4 days at ambient temperature and then poured into ice–water. The solution was extracted

with ethyl acetate (60 mL), and the extract was washed with water and dried. Evaporation of the solvent left a syrup (1.68 g), which was fractionated on a silica-gel column (80 g) with 1:6 2-butanone–toluene as eluent. The first fraction (R_F 0.77) gave the 2,5-ditosylate DL-**11** (0.81 g, 45%) as needles, m.p. 110–112°; ^{1}H-n.m.r. ($CDCl_3$): δ 7.83, 7.35 (2 d, each 4 H, *J* 9 Hz, Ph-H), 5.10–4.65 (m, 2 H, H-2,5), 3.66 (s, 3 H, CH_3), 2.84 (td, 1 H, $J_{1,6a}$ 4.5, $J_{1,2}$ = $J_{1,6b}$ = 8.6 Hz, H-1), 2.45 (s, 6 H, 2 tosyl CH_3), 1.63, and 1.53 (2 s, each 3 H, CH_3).

Anal. Calc. for $C_{25}H_{30}O_{10}S_2$: C, 54.1; H, 5.1. Found: C, 54.5; H, 5.5.

The second fraction (R_F 0.46) gave a crystalline mixture (0.63 g, 49%) of the 2- (DL-**9**) and 5-tosylates (DL-**10**).

Anal. Calc. for $C_{18}H_{24}O_8S$: C, 54.0; H, 6.0. Found: C, 54.0; H, 6.0.

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetrahydroxy-2-*O-p-*tolylsulfonylcyclohexane-1-carboxylate* (DL-**12**) *and methyl* DL-*(1,3,4/2,5)-2,3,4,5-tetrahydroxy-5-*O-p-*tolylsulfonylcyclohexane-1-carboxylate* (DL-**13**). — A mixture (1.15 g, 2.9 mmol) of DL-**9** and DL-**10** was treated with 80% aqueous acetic acid (15 mL) for 2 h at 70°, and then concentrated. The products were eluted from a silica gel column (60 g) with 13:1 chloroform–methanol to give, in the first fraction (R_F 0.65), DL-**12** (340 mg, 33%), prisms, m.p. 137–138°; ^{1}H-n.m.r. (CD_3OD): δ 7.83, 7.42 (2 d, each 2 H, *J* 9 Hz, Ph-H), 5.06 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9 Hz, H-2), 4.77 (bq, 1 H, *J* ~4 Hz, H-5), 3.57 (s, 3 H, CH_3), 2.92 (td, 1 H, $J_{1,6ax}$ 10.5, $J_{1,6eq}$ 4.5 Hz, H-1), and 2.45 (s, 3 H, tosyl CH_3).

Anal. Calc. for $C_{15}H_{20}O_8S$: C, 50.0; H, 5.6. Found: C, 50.0; H, 5.6.

The second fraction (R_F 0.74) was DL-**13** (520 mg, 50%), prisms, m.p. 119–120.5°; ^{1}H-n.m.r. (CD_3OD): δ 7.83, 7.45 (2 d, each 2 H, *J* 9 Hz, Ph-H), 5.13 (bdt, 1 H, $J_{4,5}$ 12, $J_{5,6a}$ = $J_{5,6b}$ = 3 Hz, H-5), 3.67 (s, 3 H, CH_3), 2.48 (s, 3 H, tosyl CH_3), 2.03 (td, 1 H, $J_{1,6a}$ 9, $J_{6,6}$ 15 Hz, H-6a), and 1.70 (dt, 1 H, H-6b).

Anal. Found: C, 50.1; H, 5.6.

Methyl DL-*(3,4/5)-3,4,5-tri-*O-*acetyl-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate* (DL-**16**, *methyl* DL-*shikimate triacetate*). — Compound DL-**12** (150 mg, 0.42 mmol) was dissolved in methanol (3 mL) and the solution was treated with M methanolic sodium methoxide (1 mL) for 5 min at ambient temperature. T.l.c. (6:1 chloroform–methanol) showed a single spot migrating with the same R_F (0.40) as an authentic sample of methyl shikimate. The mixture was neutralized with M hydrochloric acid and concentrated, and the residue was acetylated in the usual way. The product was purified on a silica-gel column to give DL-**16** (123 mg, 94%) as a syrup. The ^{1}H-n.m.r. spectrum ($CDCl_3$) was superimposable on that of an authentic sample[5e].

Anal.. Calc. for $C_{14}H_{18}O_8$: C, 53.5; H, 5.8. Found: C, 53.8; H, 5.8.

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetrahydroxy-2,5-di-*O-p-*tolylsulfonylcyclohexane-1-carboxylate* (DL-**14**). — A mixture of DL-**11** (440 mg, 0.79 mmol) and 80% aqueous acetic acid (10 mL) was stirred for 8 h at 70°. T.l.c. (1:2 2-butanone–toluene) showed one major (R_F 0.42) and one minor spot (R_F 0.28). The mixture was concentrated and the residue was eluted from a silica-gel column (30 g) with 2:3

2-butanone–toluene. The first fraction gave DL-**14** (356 mg, 87%) as needles, m.p. 132–133°; ^{1}H-n.m.r. ($CDCl_3$, D_2O): δ 7.84, 7.34 (2 d, each 4 H, 2 phenyl), 5.07 (t, 1 H, $J_{1,2} = J_{2,3} = 8.2$ Hz, H-2), 4.77 (bq, 1 H, $J \sim 4$ Hz, H-5, 3.58 (s, 3 H, OCH_3), 2.71 (td, 1 H, $J_{1,6ax}$ 9.5, $J_{1,6eq}$ 4 Hz, H-1), and 2.45 (s, 6 H, 2 tosyl CH_3).

Anal. Calc. for $C_{22}H_{26}O_{10}S_2$: C, 51.4; H, 5.1. Found: C, 51.4; H, 5.1.

The second fraction was *methyl* DL-*(3,4/5)-3,4,5-trihydroxy-5-*O-p-*tolylsulfonyl-cyclohexene-1-carboxylate* (DL-**17**; 24 mg, 9%), prisms, m.p. 139.5–141.5°; ^{1}H-n.m.r. [$(CD_3)_2SO$]: δ 7.81, 7.46 (2 d, each 2 H, J 9 Hz, Ph-H), 6.70 (bs, 1 H, H-2), 4.69 (bq, 1 H, J 5 Hz, H-5), 4.27–4.10 (m, 2 H, H-3,4), 3.67 (s, 3 H, OCH_3), 2.43 (s, 3 H, tosyl CH_3), and 2.20 (bdd, 1 H, $J_{1,6a}$ 6, $J_{6,6}$ 18 Hz, H-6a).

Anal. Calc. for $C_{15}H_{18}O_7S$: C, 52.6; H, 5.3. Found: C, 52.5; H, 5.2.

Methyl DL-*(3,4/,5)-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate* (DL-**2**, *methyl* DL-*shikimate*). — A mixture of DL-**14** (200 mg, 0.39 mmol), anhydrous sodium acetate (160 mg, 2.0 mmol), and 90% aqueous 2-methoxyethanol (4 mL) was refluxed for 1.5 h, and then concentrated. The residue was acetylated in a usual way. The product was purified on a silica-gel column and then *O*-deacetylated with methanolic sodium methoxide. The product was crystallized from methanol and ethyl acetate to give DL-**2** (21 mg, 29%) as prisms, m.p. 166–168°. The ^{1}H-n.m.r. spectrum (CD_3OD) was superimposable on that of an authentic sample[5c].

Anal. Calc. for $C_8H_{12}O_5$: C, 51.1; H, 6.4. Found: C, 51.1; H, 6.3.

DL-*(3,4/5)-3,4,5-Trihydroxy-1-cyclohexene-1-carboxylic acid* (DL-**1**, DL-*shikimic acid*). — Compound DL-**2** (65 mg, 0.35 mmol) was treated with 0.35M potassium hydroxide in 4:1 methanol–water (1 mL) overnight at ambient temperature. The mixture was neutralized with Amberlite IR-120 (H^+) and the product was crystallized from ethyl acetate–methanol to give DL-**1** (46 mg, 76%) as prisms, m.p. 191–193°; lit.[7] m.p. 191–192°.

Anal. Calc. for $C_7H_{10}O_5$: C, 48.3; H, 5.8. Found: C, 48.3; H, 5.7.

Methyl 3 L-*(3,4/5)-3,4,5-trihydroxy-3,4-*O-*isopropylidene-5-*O-p-*tolylsulfonyl-1-cyclohexene-1-carboxylate* (L-**15**). — A mixture of L-**7** (170 mg, 0.70 mmol), tosyl chloride (0.50 g, 2.6 mmol), and pyridine (3 mL) was stirred for 52 h at 60°. T.l.c. (1:2 2-butanone–toluene) showed a single spot at R_F 0.72. The mixture was poured into ice–water and extracted with ethyl acetate (20 mL). The extract was washed with water, dried, and concentrated to give, after chromatography on silica gel, L-**15** (220 mg, 82%) as a syrup, $[\alpha]_D^{24}$ −52° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.83, 7.35 (2 d, each 2 H, J 9 Hz, Ph-H), 6.89 (narrow m, 1 H, H-2), 4.87–4.62 (m, 2 H, H-3,5), 4.21 (t, 1 H, $J_{3,4} = J_{4,5} = 6$ Hz, H-4), 3.79 (s, 3 H, CH_3), 2.80, 2.39 (2 dd, each 1 H, $J_{5,6a} = J_{5,6b} = 4.5$, $J_{6,6}$ 18 Hz, H-6a,b), 2.47 (s, 3 H, tosyl CH_3), 1.31, and 1.20 (2 s, each 3 H, CCH_3).

Anal. Calc. for $C_{18}H_{22}O_7S$: C, 56.5; H, 5.8. Found: C, 56.3; H, 5.8.

*Methyl 3*L-*(3,4/5)-3,4,5-trihydroxy-5-*O-p-*tolylsulfonyl-1-cyclohexene-1-carboxylate* (L-**17**). — A treatment of L-**15** (170 mg, 0.44 mmol) with 80% aqueous acetic acid (4 mL) for 1.5 h at 70° gave L-**17** (140 mg, 89%) as needles, m.p. 136.5–137.5° (from EtOH), $[\alpha]_D^{25}$ −90° (*c* 1, chloroform). The ^{1}H-n.m.r. spectrum

was superimposable on that of the racemic modification.

Anal. Calc. for $C_{15}H_{18}O_7S$: C, 52.6; H, 5.3. Found: C, 52.2; H, 5.2.

Methyl 3L-(3,4/5)-trihydroxy-1-cyclohexene-1-carboxylate (L-2, methyl L-shikimate). — Compound L-17 (105 mg, 0.31 mmol) was treated with sodium acetate (50 mg, 0.62 mmol) in 90% aqueous 2-methoxyethanol (2 mL) for 1.5 h at 120°. The mixture was processed as described for the preparation of DL-2. The product was finally purified on a silica-gel column (3 g) with 10:1 chloroform–methanol as eluent to give L-2 (23 mg, 40%) as needles, m.p. 111–112° (from ethyl acetate), $[\alpha]_D^{24}$ −133° (*c* 0.62, ethanol). The ^{1}H-n.m.r. spectrum (CD_3OD) was superimposable on that of an authentic sample[4a,5e].

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