The Synthesis of Dimethyl *dl*-3-Ethyl-4-methyl-1,2-cyclopentanedicarboxylates[1]

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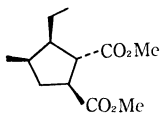
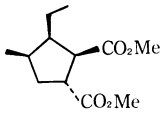
The four 3,4-*cis*-stereoisomers of dimethyl *dl*-3-ethyl-4-methyl-1,2-cyclopentanedicarboxylates (**1a**, **1b**, **1c**, and **1d**) have been synthesized and their configurations established. A comparison of the spectral data and the GLC behaviors has shown that the corresponding ester, one of the key degradation products of ikarugamycin, has the *r*-1, *t*-2, *c*-3, *c*-4-configuration (**1a**). The *r*-1, *t*-2, *c*-3, *t*-4-stereoisomer (**1f**) has also been prepared.

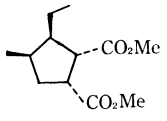
Ikarugamycin[2] is an antibiotic with a unique *as*-hydrindacene skeleton. On permanganate oxidation followed by esterification it yielded a monocyclic ester **1**, $C_8H_{14}(CO_2Me)_2$, along with a number of esters.[2b] The structure of the ester **1** was determined as dimethyl 3-ethyl-4-methyl-1,2-cyclopentanedicarboxylate by spectral data and the concomitant formation of dimethyl 2-ethyl-3-methylglutarate.[2b] Furthermore, the *r*-1, *t*-2, *c*-3, *c*-4 stereochemistry was suggested by the facts: the configuration of the ethyl and methyl groups in the isolated dimethyl 2-ethyl-3-methylglutarate was *erythro*, and the base-catalyzed equilibration of the ester **1** resulted in the recovery of **1** as the major product.[2b]



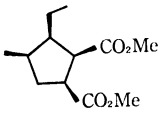
1a



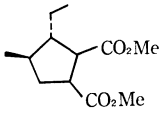
1b



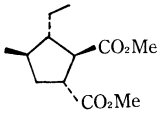
1c



1d

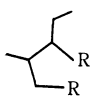


1e



1f

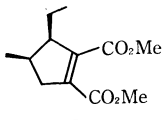
Since the ester **1** contained four of the nine asymmetric carbons in ikarugamycin, it became necessary to unequivocally confirm the relative configuration of the ester **1** through its synthesis. We describe here the synthesis and the stereochemistry of the four isomeric 3,4-*cis*-3-ethyl-4-methyl-1,2-cyclopentanedicarboxylates (**1a**, **1b**, **1c**, and **1d**). Two 3,4-*trans*-stereoisomers (**1e** and **1f**) were also prepared.



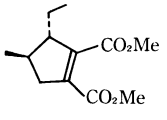
2a: R=CO_2H
2b: R=CH_2OH
2c: R=CH_2OTs
2d: R=CH_2CN
2e: R=CH_2CO_2H
2f: R=$CHBrCO_2Me$

There have been extensive works on the synthesis of nepetic acids, 3-methyl-1,2-cyclopentanedicarboxylic acids.[3] However, none of them seemed applicable for the synthesis of 3,4-disubstituted 1,2-cyclopentanedicarboxylic acids. The cyclization reaction by McDonald and Reitz[4] appeared to be the most convincing method for our purpose. As the starting material was chosen 2-ethyl-3-methylglutaric acid (**2a**) which was prepared by a known method[5] as a mixture (1 : 2 ratio) of *erythro*- and *threo*-isomers.

Lithium aluminum hydride reduction of the acid **2a** gave a diol **2b**. The corresponding ditosylate (**2c**) was treated with sodium cyanide in dimethyl sulfoxide to yield a dinitrile **2d**, which was then hydrolyzed with potassium hydroxide in aqueous ethylene glycol to give a dicarboxylic acid **2e**. Bromoesterification[6] of **2e** yielded a dibromo diester **2f**, whose structure was confirmed by the mass spectrum and elemental analysis (see Experimental). The cyclization of **2f** with sodium hydride in *N*,*N*-dimethylformamide[4] proceeded smoothly, giving the two expected cyclopentene derivatives **3a** and **3b** in 5 : 7 ratio. They were separated without difficulty by chromatography on silver nitrate impregnated silica gel followed by preparative gas-liquid chromatography (GLC). In order to confirm the relative configurations of the ethyl and methyl groups in the esters (**3a** and **3b**), the latter (**3b**) was submitted to ozonolysis and yielded *threo*-2-ethyl-3-methylglutaric acid.[7]



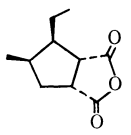
3a



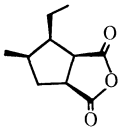
3b

Hydrogenation of the unsaturated 3,4-*cis*-ester (**3a**) proved to be very difficult. However, this was overcome by repeating hydrogenation in acetic acid over platinum oxide. The products, free of unsaturated esters, were separated by preparative GLC, giving three saturated esters **1d**, **1a**,[8] and **1e**[8] in 33, 7, and 13% yields, respectively.

On equilibration by heating with methanolic sodium methoxide, the ester **1d** disappeared to give the isomeric ester **1a** as the major product, along with two new esters **1b** and **1c** (ratio of **1a**, **1b**, and **1c**; 89 : 2 : 9). This indicates that the isomer **1a** has the most stable *r*-1, *t*-2, *c*-3, *c*-4-configuration.[9]



4a



4b

The two isomeric 1,2-*cis*-esters (**1c** and **1d**) were also prepared *via* their anhydrides (**4a** and **4b**) as follows. The ester **1d** was equilibrated, hydrolyzed, and then

treated under reflux with acetic anhydride containing *p*-toluenesulfonic acid. Preparative GLC of the product afforded the 2,3-*trans*-anhydride (**4a**) and the 2,3-*cis*-anhydride (**4b**) in 4: 1 ratio. Methanolysis of **4a** and **4b** followed by esterification with diazomethane gave the corresponding esters (**1c** and **1d**), respectively. Thus, the second most stable isomer **1c** must have the *r*-1, *c*-2, *t*-3, *t*-4-configuration and the least stable isomer **1d** the *r*-1, *c*-2, *c*-3, *c*-4-configuration.

The remaining isomer whose configuration was to be confirmed was then the *r*-1, *t*-2, *t*-3, *t*-4-ester (**1b**). It was prepared from the anhydride **4b** by essentially the same method as used for the preparation of *t*-3-methyl-*r*-1, *t*-2-cyclopentanedicarboxylic acid.[10] The anhydride (**4b**) was converted to a mixture of half methyl esters, which was equilibrated with base and esterified. The product consisted mostly of the ester **1b** which was isolated in 50% yield by preparative GLC.

Thus, all of the four stereoisomers of dimethyl 3,4-*cis*-3-ethyl-4-methyl-1,2-cyclopentanedicarboxylates were prepared with high purities and their stereochemistry established.

Consequently, the isomer **1e**, obtained by the catalytic hydrogenation of **3a** (described above), must have 3,4-*trans*-configuration.[8] In fact, equilibration of **1e** yielded predominantly the sixth isomer **1f** whose stereochemistry was most likely *r*-1, *t*-2, *c*-3, *t*-4.

A comparison of the IR and NMR spectra and retention times on GLC showed that the ester **1**, obtained from ikarugamycin, was identical with the synthetic sample of dimethyl *c*-3-ethyl-*c*-4-methyl-*r*-1,*t*-2-cyclopentanedicarboxylate (**1a**).

Experimental

The IR spectra were taken on a JASCO IR-S spectrophotometer and the UV spectra on a Perkin-Elmer 202 UV-VIS spectrophotometer. The NMR spectra were recorded on Nihondenshi JNM-C60H and 4H-100 spectrometers using CCl_4 as the solvent; the chemical shifts are given in ppm relative to the internal TMS, and the coupling constants given in Hz. The mass spectra were obtained with a Hitachi RMU-6D spectrometer, operating with an ionization energy of 70 eV. The preparative gas-liquid chromatography (GLC) were carried out on a Varian 1828-4 instrument, using a column packed with 10% OV-17 on Chromosorb W at 170 °C.

Synthesis of Dimethyl 2,6-Dibromo-3-ethyl-4-methylpimelate (2f). *(a) 3-Ethyl-4-methyl-1,5-pentanediol (2b)*: A solution of 2-ethyl-3-methylglutaric acid (**2a**: 17.4 g) in ether (100 ml) was added dropwise during 2 h to a stirred suspension of lithium aluminum hydride (11.2 g) in ether (200 ml) at 0 °C. The mixture was stirred at room temperature for an additional 4 h. After cooling to 0 °C ethyl acetate (20 ml) and then water were carefully added. After 1 h a mixture of ice-water (150 ml) and concd sulfuric acid (45 ml) was added and the mixture was extracted with ether (600 ml). The ether extract was washed with saturated sodium hydrogen carbonate solution and saturated sodium chloride solution, and dried over magnesium sulfate. Evaporation of the solvent afforded 12.2 g (83%) of a colorless oil, $\nu_{max}^{CHCl_3}$ 3670, 3600—3200 cm^{-1}.

(b) Ditosylate (2c) of 2b: To a stirred solution of *p*-toluenesulfonyl chloride (38.2 g) in pyridine (70 ml) at 0 °C was added dropwise a solution of the diol **2b** (12.1 g) in pyridine (20 ml) during 20 min. After standing at 5 °C for 18 h the mixture was poured into ice-water (200 ml) and extracted with chloroform (500 ml). The chloroform extract was washed with concd hydrochloric acid (100 ml) and water, and then dried over sodium sulfate. Evaporation of the solvent gave 31.9 g (84%) of a colorless oil, $\nu_{max}^{CHCl_3}$ 1603, 1360, 1170 cm^{-1}. The crude ditosylate was immediately used for the next experiment without a further purification.

(c) 3-Ethyl-4-methylpimelonitrile (2d): A mixture of the ditosylate **2c** (31.9 g) and sodium cyanide (10.3 g) in dimethyl sulfoxide (350 ml) was heated with stirring at 100 °C for 2 h under an atmosphere of nitrogen. After cooling the mixture was poured into a solution of ammonium chloride (40 g) in water (400 ml) and extracted with dichloromethane (800 ml). The dichloromethane extract was washed throughly with water and dried over sodium sulfate. Removal of the solvent gave a reddish residue, which was distilled to furnish 8,7 g (76%) of **2d** as a pale pink oil: bp 132—155 °C/3 mmHg; $\nu_{max}^{CCl_4}$ 2260, 1427 cm^{-1}; *m/e* 165 (M^++1), 163 (M^+−1). Found: C, 73.22; H, 10.27; N, 17.06%. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06%.

(d) 3-Ethyl-4-methylpimelic Acid (2e): A mixture of the nitrile **2d** (9.8 g) and potassium hydroxide (32 g) in ethylene glycol (225 ml)–water (25 ml) was heated with stirring at 110 °C for 16 h. After cooling the mixture was poured into ice-water (200 ml) and extracted with benzene (200 ml). The aqueous layer was acidified with concd hydrochloric acid (60 ml) and extracted throughly with chloroform (600 ml). The chloroform extract was washed with water and dried over sodium sulfate. Evaporation of the solvent left 7.3 g (62%) of **2e** as a pale yellow viscous oil, $\nu_{max}^{CHCl_3}$ 1713 cm^{-1}. which was used for the next experiment without a further purification.

(e) Dimethyl 2,6-Dibromo-3-ethyl-4-methylpimelate (2f): The dicarboxylic acid **2e** (8.7 g) was heated with thionyl chloride (20 ml) under reflux for 2 h and then bromine (5 ml) was added dropwise to the mixture at 90 °C during 1 h. After heating the mixture for 17 h at 90 °C, it was cooled, poured into methanol (60 ml), and kept for 1 h at room temperature. The mixture was then diluted with water and extracted with ethyl acetate (250 ml). The ethyl acetate extract was washed successively with saturated sodium hydrogen sulfite solution, saturated sodium hydrogencarbonate solution, water, and then saturated sodium chloride solution. The extract was dried over sodium sulfate and the solvent evaporated under reduced pressure. The reddish residue was distilled to give 12.3 g of a pale brown oil, bp 153—171 °C/4 mmHg, which was then chromatographed on silica gel (200 g). Elution with hexane–ether (6: 1) gave 9.4 g (38%) of **2f** as a pale yellow oil: $\nu_{max}^{CCl_4}$ 1753 cm^{-1}; *m/e* 359, 357, 355 (M^+−OMe), 309, 307 (M^+−Br). Found: C, 37.18; H, 4.29%. Calcd for $C_{12}H_{16}O_4Br_2$: C, 37.52; H, 4.20%.

Dimethyl cis- *and* trans-*3-ethyl-4-methyl-1-cyclopentene-1,2-dicarboxylates (3a and 3b).* To a stirred solution of sodium hydride (55% mineral oil dispersion; 445 mg) in *N,N*-dimethylformamide (8 ml) at 0 °C was added dropwise a solution of the dibromodiester **2f** (1.97 g) in *N,N*-dimethylformamide (8 ml). The mixture was stirred at 0 °C for 1 h and at room temperature for another 2 h. Aqueous 10% potassium hydroxide (10 ml) was then added and the mixture was stirred at 0 °C for 1 h and at room temperature for 14 h. The mixture was extracted with ether to remove the mineral oil and the ether extract was washed with water. The combined aqueous layer was acidified with 6M hydrochloric acid and extracted with ethyl acetate (200 ml). The ethyl acetate extract was washed throughly with water, saturated sodium chloride solution, and dried over sodium sulfate. Evaporation of the solvent gave a mixture of dicarboxylic acid, which was then

esterified with diazomethane and the product distilled to yield a mixture (966 mg) of **3a** and **3b**, bp 150 °C/6 mmHg. The unsaturated esters were roughly separated by column chromatography on 13% silver nitrate impregnated silica gel (18 g) with hexane–ethyl acetate (6: 1) as an eluent. Further purification by preparative GLC furnished 283 mg (25%) of **3a** and 392 mg (35%) of **3b** as colorless oil.

*Unsaturated 3,4-*cis*-Dimethyl Ester (3a)*: $\nu_{max}^{CCl_4}$ 1728, 1642 cm^{-1}; λ_{max}^{MeOH} 235 nm (ε 6300); *m/e* 226 (M$^+$), 195, 166; δ 0.91 (3H, t, 6.8), 1.01 (3H, d, 6.3), 1.5 (2H, m), 2.2—3.1 (4H, m), 3.65 (3H, s), 3.68 (3H, s). Found: C, 63.40; H, 8.14%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

*Unsaturated 3,4-*trans*-Dimethyl Ester (3b)*: $\nu_{max}^{CCl_4}$ 1727, 1646 cm^{-1}; λ_{max}^{MeOH} 235 nm (ε 5700); *m/e* 226 (M$^+$), 195, 166; δ 0.90 (3H, t, 6.8), 1.10 (3H, d, 6.9), 1.3—2.7 (6H, m), 3.64 (3H, s), 3.65 (3H, s). Found: C, 63.84; H, 7.93%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

*Ozonolysis of Unsaturated 3,4-*trans*-Dimethyl Ester (3b).* The ester **3b** (72 mg) in dichloromethane (4 ml) was saturated with ozone (5 min) at −70 °C. To it 10% sodium hydroxide (2 ml) and 35% hydrogen peroxide (2 ml) were added, and the mixture was vigorously stirred for 20 hr at room tem perature. After extraction with ether the aqueous layer was acidified with 6 M hydrochloric acid and extracted with ether (30 ml). The crude acid (49 mg) obtained was crystallized from ether–hexane, giving 21 mg (38%) of *threo*-2-ethyl-3-methylglutaric acid, mp 98—99 °C. The IR spectrum of this acid was identical with that of an authentic sample, mp 99—100 °C.[7]

*Catalytic Hydrogenation of Unsaturated 3,4-*cis*-Dimethyl Ester (3a): Preparation of Dimethyl Esters 1a, 1d, and 1f.* A solution of **3a** (123 mg) in acetic acid (5 ml) was hydrogenated for 40 h in the presence of platinum oxide (57 mg). The catalyst was filtered and the acetic acid was evaporated under reduced pressure. Although the oil obtained was free of the starting material **3a** (GLC), it contained isomeric unsaturated ester(s) (IR and mass spectra). Therefore, it was again hydrogenated for 12 h in acetic acid (4 ml) over platinum oxide (54 mg). The resulting mixture of saturated esters was separated by preparative GLC into three dimethyl esters, **1a**, **1d**, and **1e**.

Dimethyl c-*3-Ethyl*-c-*4-methyl*-r-*1*, t-*2-Cyclopentanedicarboxylate (1a)*: 8.8 mg (7%); $\nu_{max}^{CCl_4}$ 1742 cm^{-1}; *m/e* 228 (M$^+$), 168,109; δ 0.87 (3H, d, 6.8), 0.90 (3H, t, 7.0), 1.2—2.4 (6H, m), 2.81 (1H, t, 8.0), 3.11 (1H, ddd, 9.0, 8.0, 7.2), 3.61 (3H, s), 3.62 (3H, s). Found: C, 62.73, H, 9.20%. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83%.

Dimethyl c-*3-Ethyl*-c-*4-methyl*-r-*1*, c-*2-Cyclopentanedicarboxylate (1d)*: 40.9 mg (33%); $\nu_{max}^{CCl_4}$ 1746 cm^{-1}; *m/e* 228 (M$^+$), 168, 109; δ 0.93 (3H, d, 5.8), 0.95 (3H, t, 7.5), 1.4 (2H, m), 1.9—2.5 (4H, m), 2.82 (1H, m), 3.10 (1H, t, 6.6), 3.60 (6H, s).

*3,4-*trans*-Dimethyl Ester (1e)*: 16.2 mg (13%); $\nu_{max}^{CCl_4}$ 1742 cm^{-1}; *m/e* 228 (M$^+$), 168, 109; δ 1.02 (3H, d, 5.9), 1.02 (3H, t, 7.1), 1.0—2.5 (6H, m), 3.2 (2H, m), 3.62 (6H, s).

Base-catalyzed Equilibration of 1d Formation of Dimethyl Esters 1a, 1b, and 1c. A solution of **1d** (72 mg) in 1 M sodium methoxide–methanol (5 ml) was heated under reflux for 8 h. The methanol was removed under reduced pressure, the residue was acidified with 6 M hydrochloric acid and extracted with ethyl acetate (30 ml). The ethyl acetate extract was dried over sodium sulfate and concentrated to give an oil, from which three dimethyl esters, **1a**, **1b**, and **1c**, were isolated by preparative GLC.

r-*1*, t-*2*, c-*3*,c-*4-Dimethyl Ester (1a)*: 36.9 mg (51%).

r-*1*, t-*2*, t-*3*, t-*4-Dimethyl Ester (1b)*: 0.8 mg (1%) (described later).

Dimethyl t-*3-Ethyl*-t-*4-methyl*-r-*4*,c-*2-cyclopentanedicarboxylate (1c)*: 3.8 mg (5%): $\nu_{max}^{CCl_4}$ 1747 cm^{-1}; *m/e* 228 (M$^+$), 168, 109; δ 0.85 (3H, d, 7.0), 0.93 (3H, t, 7.2), 1.2—1.7 (3H, m), 2.0—2.5 (3H, m), 2.72 (1H, dd, 10.0, 8.4), 3.10 (1H, dt, 10.0, 8.0), 3.58 (3H, s), 3.59 (3H, s).

Acid Anhydrides 4a and 4b. Preparation of Dimethyl Esters 1c and 1d. The diester **1d** (40 mg) was heated with 1 M sodium methoxide–methanol (5 ml) under reflux for 12 h. Water (1 ml) was added and the mixture was heated under reflux for an additional 2 h. The methanol was evaporated, the aqueous solution was acidified with 6 M hydrochloric acid and extracted with ethyl acetate (50 ml). The ethyl acetate extract was dried over sodium sulfate and evaporated to dryness, yielding a mixture of dicarboxylic acids (33 mg). The oily mixture was dissolved in xylene (1 ml), to which acetic anhydride (1 ml) and *p*-toluenesulfonic acid (3 mg) were added. The mixture was heated at 140 °C for 14 h and then concentrated under reduced pressure. The residue was subjected to preparative GLC, giving two isomeric acid anhydrides **4a** and **4b**

t-*3-Ethyl*-t-*4-methyl*-r-*1*, c-*2-Cyclopentanedicarboxylic Anhydride (4a)*: 11.2 mg (35%); $\nu_{max}^{CCl_4}$ 1865, 1791 cm^{-1}; *m/e* 182 (M$^+$), 154, 140, 110, 81; δ 0.96 (3H, d, 5.6), 1.02 (3H, t, 6.0), 1.0—2.5 (6H, m), 2.9—3.6 (2H, m).

c-*3-Ethyl*-c-*4-methyl*-r-*1*, c-*2-Cyclopentanedicarboxylic Anhydride (4b)*: 2.5 mg (8%); $\nu_{max}^{CCl_4}$ 1865, 1790 cm^{-1}; *m/e* 182 (M$^+$), 154, 140, 110, 81; δ 0.82 (3H, d, 6.3), 1.05 (3H, t, 7.0), 1.1—2.6 (6H, m), 2.9—3.8 (3H, m).

The *r*-1, *c*-2, *t*-3, *t*-4-acid anhydride (**4a**; 9.7 mg) was treated with methanol followed by diazomethane. Purification by preparative GLC gave 8.4 mg (69%) of the corresponding dimethyl ester (**1c**). A similar treatment of the *r*-1, *c*-2, *c*-3, *c*-4-anhydride (**4b**) yielded the corresponding ester (**1d**).

Preparation of r-*1*, t-*2*, t-*3*, t-*4-Dimethyl Ester (1b)*. A solution of *r*-1, *c*-2, *c*-3, *c*-4-acid anhydride (**4b**; 27.3 mg) in methanol (1 ml) was heated under reflux for 1 h. Evaporation of the methanol gave a mixture of monocarboxylic acids, $\nu_{max}^{CCl_4}$ 1744, 1706 cm^{-1}. It was heated with 1 M sodium methoxide–methanol (2 ml) under reflux for 2 h. The methanol was evaporated, the residue was acidified with dil hydrochloric acid, and extracted with ethyl acetate. The extract was dried over sodium sulfate and evaporated to dryness, leaving an oil, which was esterified with diazomethane. A mixture of the dimethyl esters **1a** and **1b** was formed, which was separated by preparative GLC, yielding 17.2 mg (50%) of *dimethyl* t-*3-ethyl*-t-*4-methyl*-r-*1*, t-*2-cyclopentanedicarboxylate (1b)* in 97% purity (contaminated by 3% of **1a**): $\nu_{max}^{CCl_4}$ 1742 cm^{-1}; *m/e* 228 (M$^+$), 168, 109; δ 0.89 (3H, t, 6.8), 0.92 (3H, d, 6.8), 1.3 (2H, m), 1.85 (2H, m), 2.2 (2H, m), 3.3 (2H, m), 3.64 (3H, s), 3.66 (3H, s). A mixture (3.4 mg) of **1a** and **1b** was also obtained.

Base-catalyzed Equilibration of 1e: Preparation of Dimethyl Ester 1f. The 3,4-*trans*-dimethyl ester **1e** (11.3 mg) was equilibrated in the same way as used for the equilibration of **1d**. Preparative GLC of the resulting mixture gave 5.3 mg (47%) of *dimethyl* c-*3-ethyl*-t-*4-methyl*-r-*1*, t-*2-cyclopentanedicarboxylate (1f)*: $\nu_{max}^{CCl_4}$ 1743 cm^{-1}; *m/e* 228 (M$^+$), 168, 109; δ 0.90 (3H, t, 6.8), 1.02 (3H, d, 6.0), 1.1—2.2 (6H, m), 2.5—3.3 (2H, m), 3.63 (3H, s), 3.64 (3H, s). A mixture (0.8 mg) of **1f** and other isomers was also obtained.

References

1) A brief accout of this research has appeared in Ref. 2c.

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