CHEMISTRY OF UNSYMMETRICAL QUARTERNARY CARBON COMPOUNDS III.[1] SYNTHESIS OF (−)-DIMETHYL 2-CYANO-2-METHYLSUCCINATE AND DETERMINATION OF ITS ABSOLUTE CONFIGURATION.

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(*Received January 5, 1973*)

(−)-Dimethyl 2-cyano-2-methylsuccinate ((−)-IIIa) was synthesized from menthyl cyanoacetate ((−)-I), and the absolute configuration of which was elucidated as (S)-configuration by chemical correlation to the known (R)(+)-β-methylterbic acid ((R)(+)-VII). (−)-Dimethyl 2-carbamoyl-2-methylsuccinate ((−)-IV) and (−)-methyl 3-methyl-2,5-dioxo-3-pyrrolidinecarboxylate ((−)-V) are also confirmed as belonging to (S)-configuration and (+)-3-(1-hydroxy-1-methylethyl)-3-methyl-2,5-pyrrolidinedione ((+)-VI) is belonging to (R)-configuration.

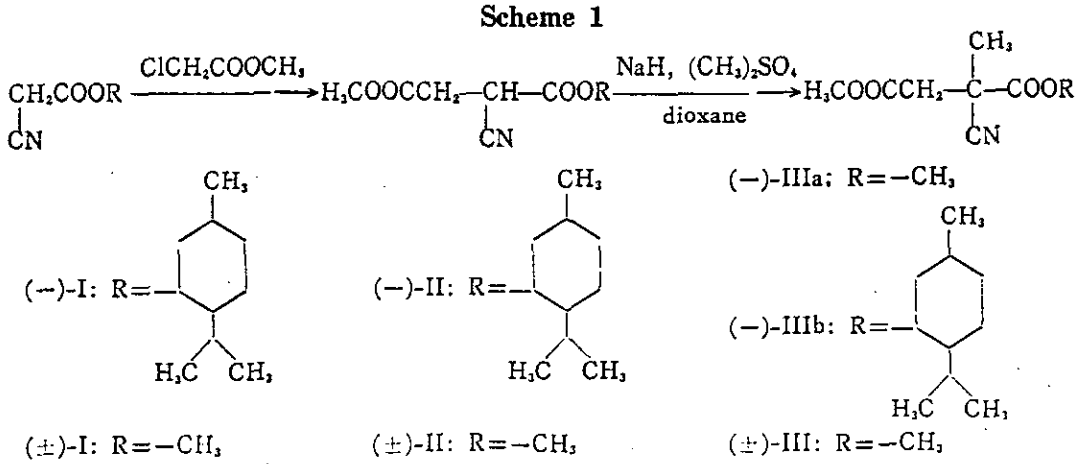
Preliminary experiments on racemic compounds are also described.

(−)-Dimethyl 2-cyano-2-methylsuccinate (IIIa), carrying a cyano group on the optically active quarternary carbon at α position to the carbonyl group, is a valuable compound for preparing various optically active quarternary carbon compounds. However the absolute configuration of IIIa is still undefined.

In the course of the studies on the relationship between chemical structure and biological activities, using several unsymmetrical quarternary carbon compounds having only one asymmetric carbon, it became necessary to establish clearly the absolute configuration of IIIa.

The preparation of (−)-IIIa is shown in Scheme 1.

Scheme 1



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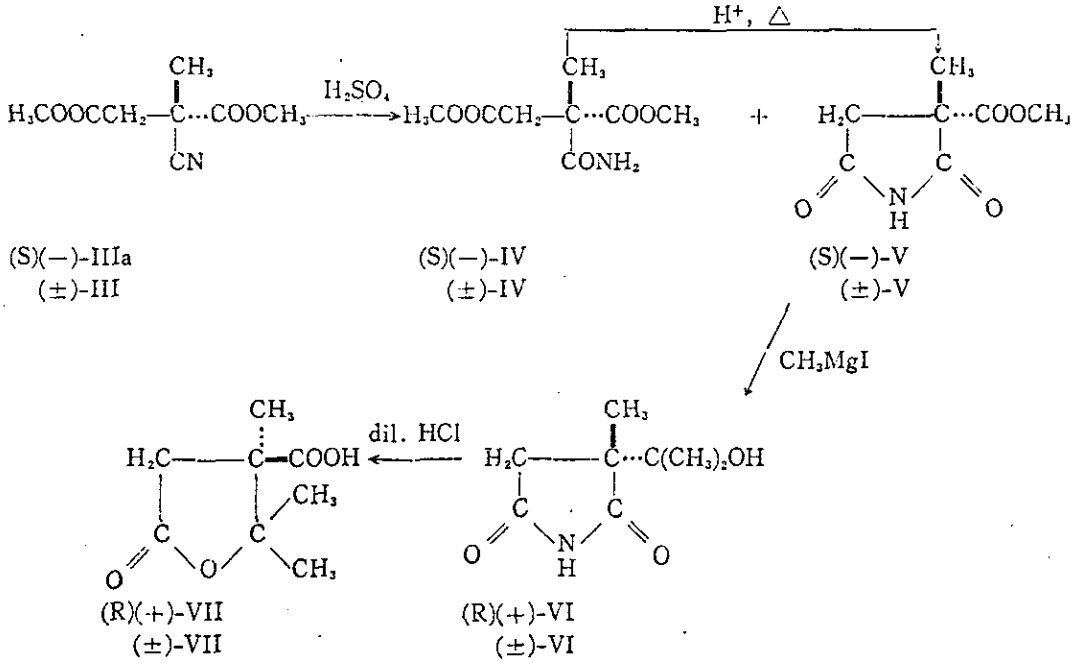
Menthyl cyanoacetate ((−)-I), $[\alpha]_D^{26}$ −46.7° (Benzene), prepared from ester exchange reaction of ethyl cyanoacetate and (−)-menthol in the presence of catalytic amount of *p*-toluenesulfonic acid, was alkyllated with methyl chloroacetate to give (−)-methyl 3-cyano-3-menthoxycarbonylpropionate ((−)-II), $[\alpha]_D^{17}$ −54.2° (Benzene), in a 45% yield from (−)-I. Methylation of (−)-II with dimethylsulfate gave (−)-methyl 3-cyano-3-menthoxycarbonylbutyrate ((−)-IIIb) in a 29% yield, $[\alpha]_D^{18}$ −49.7° (Benzene), after purification by column chromatography and fractional distillation under reduced pressure.

(−)-IIIb was saponified by KOH in absolute methyl alcohol and the potassium salt was reesterified with dimethylsulfate to give (−)-dimethyl 2-cyano-2-methylsuccinate ((−)-IIIa), $[\alpha]_D^{25}$ −1.92° (MeOH), in a 26.7% yield from (−)-IIIb.

Establishment of the absolute configuration of (−)-IIIa was undertaken by its chemical correlation to (+)-β-methylterbic acid, which was derived from (R)(−)-2-isopropyl-2-methylsuccinic acid ((R)(−)-VIII)[2] whose absolute configuration has been already determined by the quasiracemate technique[2] and X-ray diffraction method[3].

The correlation is shown in Scheme 2.

Scheme 2



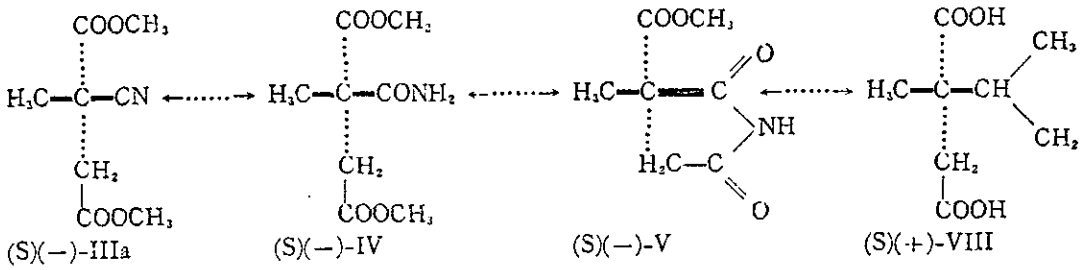
Dimethyl ester (−)-IIIa was hydrolyzed with concentrated sulfuric acid[4] to give a mixture of (−)-dimethyl 2-carbamoyl-2-methylsuccinate ((−)-IV), $[\alpha]_D^{23}$ −2.05° (MeOH), and (−)-methyl 3-methyl-2,5-dioxo-3-pyrrolidinecarboxylate ((−)-V), $[\alpha]_D^{20}$ −13.2° (MeOH), in 54% and 20% yield from (−)-IIIa respectively. (−)-IV was cyclized to (−)-V by refluxing in xylene with catalytic amount of *p*-toluenesulfonic acid in a 96% yield.

The Grignard reaction of (−)-V with excess amount of methylmagnesium iodide[5] gave (+)-3-(1-hydroxy-1-methylethyl)-3-methyl-2,5-pyrrolidinedione ((+)-VI), $[\alpha]_D^{19}$ +14.1° (MeOH)*, in a 36% yield. (+)-VI was then hydrolyzed with 18% of hydrochloric acid to give (+)-β-methylterbic acid ((+)-VII), $[\alpha]_D^{17}$ +8.8° (Acetone), in a 20% yield from (+)-VI.

Compound (+)-VII, $[\alpha]_D^{25}$ +38.5° (Acetone), has been prepared by Porath[5] from (R)(−)-2-isopropyl-2-methylsuccinic acid ((R)(−)-VIII) and the absolute configuration of (+)-VII was established as (R)-configuration.

This result, as shown in Scheme 3, established unequivocally that the (−)-IIIa used in this correlation has (S)-configuration.

Scheme 3



During the correlation, (−)-IV, (−)-V and (+)-VI, containing an asymmetric quarternary carbon at α position to the carbonyl group, were also determined that (−)-IV and (−)-V are belonging to (S)-configuration and (+)-IV is belonging to (R)-configuration.

Preliminary experiments with racemic compounds, and product identification using infrared and nuclear magnetic resonance spectra are described in detail in the experimental section.

EXPERIMENTAL**

Menthyl cyanoacetate ((−)-I)

A mixture of 32 *g* (0.20 mole) of (−)-menthol, 11.3 *g* (0.10 mole) of ethyl cyanoacetate and catalytic amount of *p*-toluenesulfonic acid was heated under reflux for 15 hours. The reaction mixture was fractionally distillated under reduced pressure giving crude (−)-I as a yellow oil, bp 155–159° (10 *mm*Hg). Crude (−)-I was

* Mutarotation, from $[\alpha]_D^{18.5}$ −2.083° (MeOH) to $[\alpha]_D^{3}$ +14.1° (MeOH), was observed during the optical activity measurement of (+)-VI.

** All melting points and boiling points were uncorrected. IR spectra were measured using Spectrometers, Model DS-402 and Model IR-S, Japan Spectroscopic Co., Ltd. NMR spectra measurements were performed using Spectrometers, Model 3H-60 (60 Mc), Japan Electro Optics Lab. and Model HA-100 (100 Mc), Varian Associates. Optical activities were determined with Yanagimoto Photo Direct Reading Polarimeter, Model OR-20. Gas chromatographic analysis were performed using Yanagimoto Gas Chromatograph Model GCG-3D.

recrystallized from petroleum ether to give pure (−)-I (14.5 *g*, 49%) as a colorless needles, mp 85-86°, $[\alpha]_D^{32}$ −46.7° (c=1.960, benzene). IR (KBr, cm^{-1}): 2260 (nitrile CN), 1736 (ester C=O). *Anal.* Calcd. for $C_{13}H_{21}O_2N$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.36; H, 9.42; N, 6.60.

(±)-Dimethyl 2-cyanosuccinate ((±)-II, R=−CH_3)

To a suspension of 24 *g* (0.50 mole) of NaH (50% oil suspension) in 800 *ml* of anhydrous benzene was added 55 *g* (0.50 mole) of methyl cyanoacetate in 200 *ml* of anhydrous benzene under water bath cooling and stirred for 3 hours, then the bath temperature was raised to 50° to complete the reaction. 55 *g* (0.50 mole) of methyl chloroacetate in 200 *ml* of anhydrous benzene was added to the mixture and refluxed under stirring for 3 hours. The reaction mixture was washed with 100 *ml* of 10% of hydrochloric acid then with 100 *ml* of water and the benzene layer was dried with anhydrous sodium sulfate. After evaporrtion of benzene, the residue was submitted to fractional distillation to give (±)-II, 27.9 *g* (32%), bp 132-136° (8-10 *mm* Hg) as a yellow oil. Gas chromatographic analysis (high vacuum silicon grease, 2 *m*, 215°, He, flow rate 40 *ml/min.*) showed a single peak whose retention time was 2.1 minutes. IR (liquid film, cm^{-1}): 2250 (nitrile CN), 1735 (ester C=O). *Anal.* Calcd. for $C_7H_9O_4N$: N, 8.18. Found: N, 8.32.

(−)-Methyl 3-cyano-3-menthoxycarbonylpropionate ((−)-II, R=menthyl)

To a suspension of 4.1 *g* (0.094 mole) of NaH (50% oil suspension) in 160 *ml* of anhydrous dioxane was added the crystal of 16.5 *g* (0.074 mole) of (−)-I under water bath cooling and stirred for 3 hours, then the bath temperature was raised to 60°. 8 *g* (0.074 mole) of methyl chloroacetate in 80 *ml* of anhydrous dioxane was added successively and heated to reflux under stirring for 3 hours. After evaporation of the solvent, the residue was submitted to fractional distillation to give crude (−)-II as a yellow oil (13 *g*), bp 175° (5 *mm* Hg). Crude (−)-II was purified by column chromatography over silica gel (eluted with benzene) and each fraction was checked by gas chromatography (5% SE-30 on diasolid L, 3 *m*, 223°, He, flow rate 55 *ml/min.*). Fractions with retention time at 3 minutes were collected and the residue, after evaporation of the solvent, was submitted to fractional distillation to give (−)-II as a yellow oil (9.8 *g*, 45%), bp 173-175° (5 *mm* Hg), $[\alpha]_D^{17}$ −54.2° (c=2.4284, benzene). IR (liquid film, cm^{-1}): 2250 (nitrile CN), 1740 (ester C=O). *Anal.* Calcd. for $C_{16}H_{25}O_4N$: C, 65.06; H, 8.53; N, 4.74. Found: C, 65.35; H, 8.40; N, 5.01.

(±)-Dimethyl 2-cyano-2-methylsuccinate ((±)-III, R=−CH_3)

2.5 *g* (0.11 *g*-atom) of Na metal was dissolved in 200 *ml* of absolute MeOH. To which 17.6 *g* (0.10 mole) of (±)-II in 100 *ml* of absolute MeOH was added under water bath cooling and stirred for 30 minutes. Then 14.3 *g* (0.12 mole) of dimethylsulfate in 60 *ml* of absolute MeOH was added and heated to reflux under stirring for 2 hours.

80 *ml* water, after evaporation of the solvent, was added to the residue and the aqueous solution was extracted with 100 *ml* of ether for 3 times. The organic layer was dried with anhydrous sodium sulfate. A yellow oil, obtained by filtration and evaporation of the above solution, was submitted to fractional distillation giving (±)-III as a colorless oil (9 *g*, 42.4%), bp 95-97° (3 *mm* Hg). IR (liquid film, cm^{-1}): 2250 (nitrile CN), 1740 (ester C=O). *Anal.* Calcd. for $C_8H_{11}O_4N$: C, 51.88; H, 5.99; N, 7.56. Found: C, 51.68; H, 6.01; N, 7.57.

(−)-Methyl 3-cyano-3-menthoxycarbonylbutyrate ((−)-IIIb, R=menthyl)

To a suspension of 2.4 *g* (0.05 mole) of NaH (50% oil suspension) in 100 *ml* of anhydrous dioxane was added 12.2 *g* (0.041 mole) of (−)-II in 80 *ml* of anhydrous dioxane under water bath cooling and stirred for 1 hour, then 6.3 *g* (0.05 mole) of dimethylsulfate in 60 *ml* of anhydrous dioxane was added and heated to reflux for 3.5 hours. To the residue, after evaporation of the solvent, 200 *ml* of ether was added and the etheral solution was washed with 100 *ml* of water, 100 *ml* of 5% of hydrochloric acid then with 100 *ml* of water respectively. The ether solution was dried with anhydrous sodium sulfate. A yellow oil (13 *g*), obtained by filtration and evaporation of above solution, was purified by column chromatography over silica gel (eluted with benzene) and each fraction was checked by gas chromatography (5% silicon DC-QF-1 on chromosorb W, 3 *m*, 200°, He, flow rate 65 *ml/min.*). Fractions with retention time at 5.5 minutes were collected and the residue, after evaporation of solvent, was submitted to fractional distillation to give (−)-IIIb as a yellow oil (4.0 *g*, 29%), bp 137-147° (0.1 *mm* Hg), $[\alpha]_D^{18}$ −49.7° (c=2.3860, benzene). IR (liquid film, cm^{-1}): 2242 (nitrile CN), 1740 (ester C=O). *Anal.* Calcd. for $C_{17}H_{27}O_4N$: C, 65.99; H, 8.80; N, 4.53. Found: C, 66.17; H, 8.92; N,4.45.

(−)-Dimethyl 2-cyano-2-methylsuccinate ((−)-IIIa, R=CH_3)

To a solution of 16 *g* (0.287 mole) of potassium hydroxide in 400 *ml* of absolute MeOH was added 40 *g* (0.13 mole) of (−)-IIIb and the reaction mixture was heated under reflux for 2.5 hours. The potassium salt, after cooling, was added 66 *g* (0.52 mole) of dimethylsulfate in 100 *ml* of absolute MeOH, then whole mixture was heated under reflux for 2 hours. This solution, after neutrallized with saturated sodium bicarbonate solution, was evaporated under reduced pressure. The residue was extracted with benzene and the benzene layer was dried with anhydrous sodium sulfate. (−)-IIIa was obtained by filtration of the above solution and by fractional distillation to give a colorless oil, 6.4 *g* (26.7%), bp 110-115° (5 *mm* Hg), $[\alpha]_D^{25}$ −1.92° (c=8.3200, MeOH). IR (liquid film, cm^{-1}): 2240 (nitrile CN), 1750 (ester C=O). NMR (60 Mc, τ value, in CCl_4): 8.40 (singlet, 3H, C—CH_3), 7.15 (singlet, 2H, C—CH_2—CO—), 6.30 (singlet, 3H, $COOCH_3$), 6.20 (singlet, 3H, $COOCH_3$). *Anal.* Calcd. for $C_8H_{11}O_4N$: C, 51.88; H, 5.99; N, 7.56. Found: C, 52.09; H, 5.95; N, 7.76.

(±)-Dimethyl 2-carbamoyl-2-methylsuccinate ((±)-IV)

30 *g* (0.162 mole) of (±)-III was added onto 30 *ml* of concentrated sulfuric acid under ice-water cooling and the reaction mixture was heated on water bath at 80° for 30 minutes. The ice-water solution, after poured the reaction mixture on to ice, was extracted with 4 times of 100 *ml* of ether and the ether solution was dried with anhydrous sodium sulfate. A brown oil, obtained by filtration and evaporation of the ether solution, was purified by column chromatography over silicagel (eluted with isopropyl ether) to give (±)-IV (14.1 *g*, 39.5%) and (±)-methyl 3-methyl-2,5-dioxo-3-pyrrolidinecarboxylate ((±)-V) (2.9 *g*, 11%) respectively.

(±)-IV was purified by recrystallization from benzene to give a white crystal, mp 84-85°. IR (KBr, cm^{-1}): 3400, 3260, 3200 (amide NH), 1740 (ester C=O), 1675, 1575 (amide C=O). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.22 (singlet, 3H, C—CH_3), 6.65 (singlet, 2H, C—CH_2—CO—), 6.05 (singlet, 3H, $COOCH_3$), 5.95 (singlet, 3H, $COOCH_3$). *Anal.* Calcd. for $C_8H_{13}O_5N$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.40; H, 6.30; N, 6.80.

(±)-V was purified by recrystallization from isopropyl ether several times to give a white crystal, mp 99.5-100.5°. IR (KBr, cm^{-1}): 3200, 3080 (imide NH), 1760, 1715 (ester and imide C=O). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.20 (singlet, 3H, C—CH_3), 6.65 (quartet, 2H, C—CH_2—CO—, J=20 Hz), 5.93 (singlet, 3H, $COOCH_3$). *Anal.* Calcd. for $C_7H_9O_4N$: C, 49.12; H, 5.30; N, 8.18. Found: C, 49.14; H, 5.34; N, 8.09.

(±)-Methyl 3-methyl-2,5-dioxo-3-pyrrolidinecarboxylate ((±)-V)

A mixture of 3.5 *g* (0.017 mole) of (±)-IV and catalytic amount of *p*-toluenesulfonic acid in anhydrous xylene was heated under reflux for 4 hours. The residue, after evaporation of xylene, was purified by column chromatography over silica gel (eluted with isopropyl ether) to give (±)-V (2.6 *g*, 89%) as a white solid. Pure (±)-V was obtained by recrystallization from isopropyl ether as a white crystal, mp 99-100°. The IR (KBr) and NMR (in D_2O) spectra were superimposable on that of (±)-V, obtained by direct hydrolysis of (±)-III, and mixed melting point measurement of these two crystals showed no depression.

(−)-Dimethyl 2-carbamoyl-2-methylsuccinate ((−)-IV)

6.4 *g* (0.035 mole) of (−)-IIIa was dissolved in 6.5 *ml* of concentrated sulfuric acid under ice-water cooling and treated as same as in the case of (±)-III to give (−)-IV (3.8 *g*, 54%), mp 83-84°, $[\alpha]_D^{26}$ −2.05° (c=1.4630, MeOH) and (−)-V (1.2 *g*, 20%) mp 97-98°, $[\alpha]_D^{20}$ −13.2° (c=3.3460, MeOH) respectively. Analytical sample of (−)-IV was obtained by recrystallization from isopropyl ether several times to give a white crystal, mp 85°, IR (KBr, cm^{-1}): 3420, 3280, 3220 (amide NH), 1749 (ester C=O), 1763, 1573 (amide C=O). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.23

(singlet, 3H, C—CH_3), 6.71 (singlet, 2H, C—CH_2—CO—), 6.04 (singlet, 3H, $COOCH_3$), 5.90 (singlet, 3H, $COOCH_3$). *Anal.* Calcd. for $C_8H_{13}O_5N$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.51; H, 6.37; N, 6.85.

Pure (−)-V was also obtained by recrystallization from isopropyl ether as a white crystal, mp 101-102°. IR (KBr, cm^{-1}): 3220, 3100 (imide NH), 1765, 1723 (ester and imide C=O). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.19 (singlet, 3H, C—CH_3), 6.68 (quartet, 2H, C—CH_2—CO—, J=20 Hz), 5.95 (singlet, 3H, $COOCH_3$). *Anal.* Calcd. for $C_7H_9O_4N$: C, 49.12; H, 5.30; N, 8.18. Found: C, 49.38; H, 5.30; N, 8.36.

(−)-Methyl 3-methyl-2, 5-dioxo-3-pyrrolidinecarboxylate ((−)-V)

3.5 *g* (0.017 mole) of (−)-IV was cyclized as that described in the case of (±)-IV to give (−)-V, (2.8 *g*, 96%), mp 98-99°, $[\alpha]_D^{20}$ −4.65° (c=2.880, MeOH). The IR (KBr) and NMR (in D_2O) spectra were superimposable with that of (−)-V, mentioned above. Mixed melting point measurement showed no depression in these two crystals.

(±)-3-(1-Hydroxy-1-methylethyl)-3-methyl-2, 5-pyrrolidinedione ((±)-VI)[5]

To a solution of 2.0 *g* (0.017 mole) of (±)-V in 20 *ml* of tetrahydrofurane, under ice-water cooling, was added 80 *ml* of methylmagnesium iodide etheral solution, prepared from 0.86 *g* (0.035 *g*-atom) of magnesium and 5.0 *g* (0.035 mole) of methyliodide, and the reaction mixture was stirred at room temperature for 6 hours then heated under reflux for 1 hour. To which 10 *ml* of saturated ammonium chloride solution was added to decompose the complex and the whole mixture was extracted with 50 *ml* of ether for 3 times and the etheral layer was dried with anhydrous sodium sulfate. A yellow oil, obtained by filtration and evaporation of the above organic solution, was purified by column chromatography over silica gel (eluted with ether) to give crude (±)-VI as a white solid (0.50 *g*, 25%). Crude (±)-VI was recrystallized from isopropyl ether several times to give pure (±)-VI, (0.34 *g*, 17%), mp 139-140°. IR (KBr, cm^{-1}): 3320, 3240 (OH and NH), 1768, 1710 (imide C=O), 1165 (OH). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.37 (singlet, 9H, C—CH_3), 6.87 (quartet, 2H, C—CH_2—CO—, J=20 Hz). *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.22; H, 7.71; N, 8.17.

(+)-3-(1-Hydroxy-1-methylethyl)-3-methyl-2, 5-pyrrolidinedione ((+)-VI)

1.4 *g* (0.0082 mole) of (−)-V* in 18 *ml* of anhydrous tetrahydrofurane, under ice-water cooling, was reacted with Grignard reagent (prepared from 0.60 *g* (0.024 *g*-atom) of magnesium and 3.5 *g* (0.024 mole) of methyliodide) in 55 *ml* of ether. The whole mixture was heated under reflux for 1.5 hour then the complex was decomposed with 20 *ml* of saturated ammonium chloride solution and treated as same as in the case of (±)-VI to give a yellow oil. (+)-VI (0.50 *g*, 36%), mp 133-134°, was

* A mixture of (−)-V with optical activity $[\alpha]_D^{20}$ −4.65° (c=2.880, MeOH) (0.84 *g*) and $[\alpha]_D^{26}$ −13.2° (c=3.3420, MeOH) (0.56 *g*) was used.

purified by column chromatography over silica gel (eluted with ether). Mutarotation of (+)-VI was obserbed during the optical activity measurement in MeOH solution. Thus, the optical activity was changed from $[\alpha]_D^{18.5}$ −2.083° (c=1.0560, MeOH) to $[\alpha]_D^{19}$ +14.12° (c=1.0560, MeOH). Further observation was not attempted. The analytical sample was obtained by severed by several recrystallization from isopropyl ether to give pure (+)-VI, mp 135-137°, $[\alpha]_D^{18.5}$ +2.76° (c=1.8120, MeOH). IR (KBr, cm^{-1}): 3320, 3240 (OH and NH), 1768, 1710 (imide C=O), 1165 (OH). NMR (60 Mc, τ value, in D_2O, DSS as internal standard): 8.36 (singlet, 9H, C—CH_3), 6.85 (quartet, 2H, C—CH_2—CO—, J=20 Hz). *Anal.* Calcd. for $C_8H_{11}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.44; H, 7.52; N, 8.38.

(±)-β-Methylterbic acid ((±)-VII)

0.30 *g* (0.00175 mole) of (±)-VI was dissolved in 20 *ml* of 18% of hydrochloric acid and heated to reflux for 2 hours. The residue, after evaporation of the solution, was recrystallized several times from water to give pure (±)-VII (0.05 *g*, 17%), mp 207-208° (decomp.) (lit.[2] mp 204-205° (decomp.)). IR (KBr, cm^{-1}): 1735 (C=O), 1190, 1150 (O—CO). IR (DMSO, cm^{-1}): 1770 (lactone C=O), 1710 (acid C=O). NMR (100 Mc, τ value, in D_2O, DSS as internal standard): 8.65 (singlet, 3H, C—CH_3) 8.6 (singlet, 3H, C—CH_3), 8.5 (singlet, 3H, C—CH_3), 7.08 (quartet, 2H, C—CH_2—CO—, J=18 Hz). *Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 56.16; H, 6.98.

(+)-β-Methylterbic acid ((+)-VII)

0.27 *g* (0.0016 mole) of (+)-VI* was dissolved in 6 *ml* of 18% of hydrochloric acid and heated to reflux for 3 hours. The residue, after evaporated to dryness under reduced pressure, was recrystallized from water to give (+)-VII (0.03 *g*, 11%), mp 207° (decomp.), $[\alpha]_D^{17}$ +8.82° (c=0.4760, acetone) (lit.[2] mp 218-220° (decomp.), $[\alpha]_D^{25}$ +38.5° (c=0.2597, acetone)). IR (DMSO, cm^{-1}): 1770 (lactone C=O), 1710 (acid C=O). *Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.80; H, 7.02.

ACKNOWLEDGEMENT

Part of this work was performed in Faculty of Pharmaceutical Sciences, University of Tokyo, Japan. The author wishes to thank Dr. S. Yamada, Professor of Faculty of Pharmaceutical Sciences, University of Tokyo, and his staff, Dr. K. Achiwa, Dr. K. Koga and Dr. S. Terashima, for their helpful suggestion and for performance of spectral measurements and elementary analyses.

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* A mixture of (+)-VI with optical activity $[\alpha]_D^{16}$ +12.3° (c=1.1840, MeOH) (0.070*g*) and $[\alpha]_D^{18}$ +2.76° (c=1.8120, MeOH) (0.20 *g*) was used.

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