Summary

Methyl 4,6-benzylidene-β-D-glucosaminide hydrochloride (III) was synthesized by a new method. Deamination of (III) with sodium nitrite in weak acetic acidity resulted in facile cleavage of glycosidic bond and simultaneous dehydration between C-2 and C-5 positions to form 2,5-anhydro-4,6-benzylidene-D-mannose. On the other hand, deamination of methyl 2-amino-4,6-benzylidene-2-desoxy-α-D-altroside hydrochloride (V) with sodium nitrite afforded methyl 2,3-anhydro-4,6-benzylidene-α-D-alloside (VI) without any change in glycosidic bond. The mechanisms of these deamination reactions were discussed.

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53. Zen-ichi Horii, Yasumitsu Tamura, Kunihiko Tanaka, and Takefumi Momose: Studies on Oxytetracycline and Related Compounds. X.*1 Synthesis of Terranaphthoic Acid.

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In previous papers concerning synthetic studies on the degradation products of oxytetracycline, the syntheses of 7-hydroxy-3-methylphthalide,[1] 6-acetylsalicylic acid,[2] decarboxyterracinoic acid,[3] and terracinoic acid[4] were described. The present report describes the synthesis of terranaphthoic acid.

Terranaphthoic acid is one of the most important degradation products of oxytetracycline and its chemical structure was shown to be 1,8-dihydroxy-4-methyl-3-naphthoic acid by Hochstein *et al.*[5] It would be interesting to synthesize terranaphthoic acid and to confirm the chemical structure by direct comparison of natural terranaphthoic acid with the synthetic material, because terranaphthoic acid plays an important role in the structural determination of oxytetracycline. However, its synthesis has not yet been accomplished.

As an exploratory experiment for the synthesis of terranaphthoic acid, the preparation of 1-hydroxy-4-methyl-3-naphthoic acid, i.e. 8-desoxyterranaphthoic acid, was carried out starting from 2-ethoxycarbonyl-3-methylindan-1-one. Based on this preliminary experiment, attempt was made to synthesize terranaphthoic acid from 2-ethoxycarbonyl-7-methoxy-3-methylindan-1-one and the acid (1,8-dihydroxy-4-methyl-3-naphthoic acid) was obtained without any difficulty during the course of processing.

Synthesis of 1-Hydroxy-4-methyl-3-naphthoic Acid (8-Desoxyterranaphthoic Acid)

2-Ethoxycarbonyl-3-methylindan-1-one (IIIa) and its 7-methoxy derivative (IIIb) were

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1) Z. Horii, K. Okumura, Y. Tamura: Yakugaku Zasshi, **73**, 526(1953); F. A. Hochstein, R. Pasternack: J. Am. Chem. Soc., **73**, 5008(1951); **74**, 3905(1952); S. Kushner, J. H. Bothe, J. Morton, J. Petisi, J. H. Williams: *Ibid.*, **74**, 3710(1952).

2) Z. Horii, Y. Tamura, K. Okumura, H. Kugita: Yakugaku Zasshi, **74**, 466(1954); R. Kuhn, K. Dury: Chem. Ber., **84**, 848(1951).

3) L. H. Conover: J. Am. Chem. Soc., **75**, 4017(1953); Z. Horii, Y. Tamura, H. Kugita, K. Okumura: Yakugaku Zasshi, **74**, 150(1954).

4) Y. Tamura: Yakugaku Zasshi, **76**, 739(1956).

5) F. A. Hochstein, P. P. Regna, K. J. Brunings, R. B. Woodward: J. Am. Chem. Soc., **74**, 3706(1952); F. A. Hochstein, *et al.*: *Ibid.*, **75**, 5455(1953).

preferred as the starting materials for the present work, and various methods were considered for the preparation of these compounds.

The Dieckmann reaction of diethyl ester (IIa) of 3-(2-carboxyphenyl)butyric acid, which was prepared from 3-methylindan-1-one through its 2-bromo and 2-cyano derivatives, gave (IIIa) in 49% yield. In a previous work,[6] (IIIa) was obtained in 23% yield by the condensation of 3-methylindan-1-one (Ia) with ethyl carbonate in benzene in the presence of sodium ethoxide. It was now found that the yield of (IIIa) of 64% was improved by using sodium hydride in ether in place of sodium ethoxide in benzene and this procedure provided the most convenient method for the preparation of (IIIa). Reaction of (IIIa) with ethyl bromoacetate by means of sodium ethoxide in boiling benzene gave ethyl 1-oxo-2-ethoxycarbonylindane-2-acetate (IVa), which was converted into (2-carboxy-α-methylbenzyl)succinic acid (Va) by refluxing with hydrous ethanolic solution of potassium hydroxide.

The trimethyl ester (VIa), obtained by the treatment of (Va) with diazomethane in ether, was subjected to the Dieckmann reaction with sodium in boiling toluene, yielding dimethyl 1-oxo-4-methylnaphthalene-2,3-dicarboxylate (VIIa). In this Dieckmann reaction, the procedure using sodium in toluene afforded a better yield compared with other procedures using sodium, sodium ethoxide, or sodium hydride in benzene.

Refluxing of (VIIa) with 20% hydrochloric acid resulted in hydrolysis and decarboxylation, affording 3-carboxy-1-oxo-4-methyl-1,2,3,4-tetrahydronaphthalene, m.p. 167°, which was not depressed when mixed with a sample of the compound prepared by intramolecular cyclization[7] of (α-methylbenzyl)succinic anhydride. (VIIa) was brominated with bromine in a mixture of chloroform and ether, and subsequently dehydrobrominated by heating with 2,4,6-collidine, thus giving dimethyl 1-hydroxy-4-methylnaphthalene-2,3-dicarboxylate (VIIIa). The naphthalene derivative here obtained was hydrolysed and decarboxylated by refluxing with 20% hydrochloric acid for 15 hours to give a compound of m.p. 203~207°, which was characterized as 1-hydroxy-4-methyl-3-naphthoic acid (IXa) by its failure to depress the melting point of a sample prepared according to the method of Haworth[8] from (α-methylbenzylidene)succinic acid.

Synthesis of Terranaphthoic Acid

Ethyl 1-oxo-7-methoxy-3-methylindan-2-carboxylate (IIIb : $R'=C_2H_5$), which was prepared by ester condensation of 7-methoxy-3-methylindan-1-one with ethyl carbonate in the presence of sodium hydride, was converted by reaction with ethyl bromoacetate to ethyl 1-oxo-2-ethoxycarbonyl-7-methoxy-3-methylindane-2-acetate (IVb). By refluxing (IVb) with diluted ethanolic solution of potassium hydroxide for 2 hours, (α-methyl-2-carboxy-3-methoxybenzyl)succinic acid (Vb) was obtained. The trimethyl ester (VIb) of (Vb), obtained by treatment of (Vb) with diazomethane, was subjected to the Dieckmann reaction with sodium in boiling toluene, yielding diethyl 1-oxo-8-methoxy-4-methyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (VIIb). Bromination of (VIIb) with bromine in a mixture of chloroform and ether, and subsequent dehydrobromination by heating with 2,4,6-collidine gave diethyl 1-hydroxy-8-methoxy-4-methylnaphthalene-2,3-dicarboxylate (VIIIb). Boiling of (VIIIb) with 48% hydrobromic acid at 130° for 2.5 hours yielded (IXb) as yellowish tan crystals of m.p. 232~233°, which showed the same melting point, and ultraviolet and infrared spectra as those of terranaphthoic acid[5] (m.p. 233~235°) derived from oxytetracycline.

The authors wish to thank Dr. F. A. Hochstein of the Research Laboratories of Chas. Pfizer and Co., Inc., for his kindness in supplying a copy of the infrared spectrum of terranaphthoic acid derived from oxytetracycline.

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7) R. S. Urban, E. M. Beavers : J. Am. Chem. Soc., **76**, 3042(1954).
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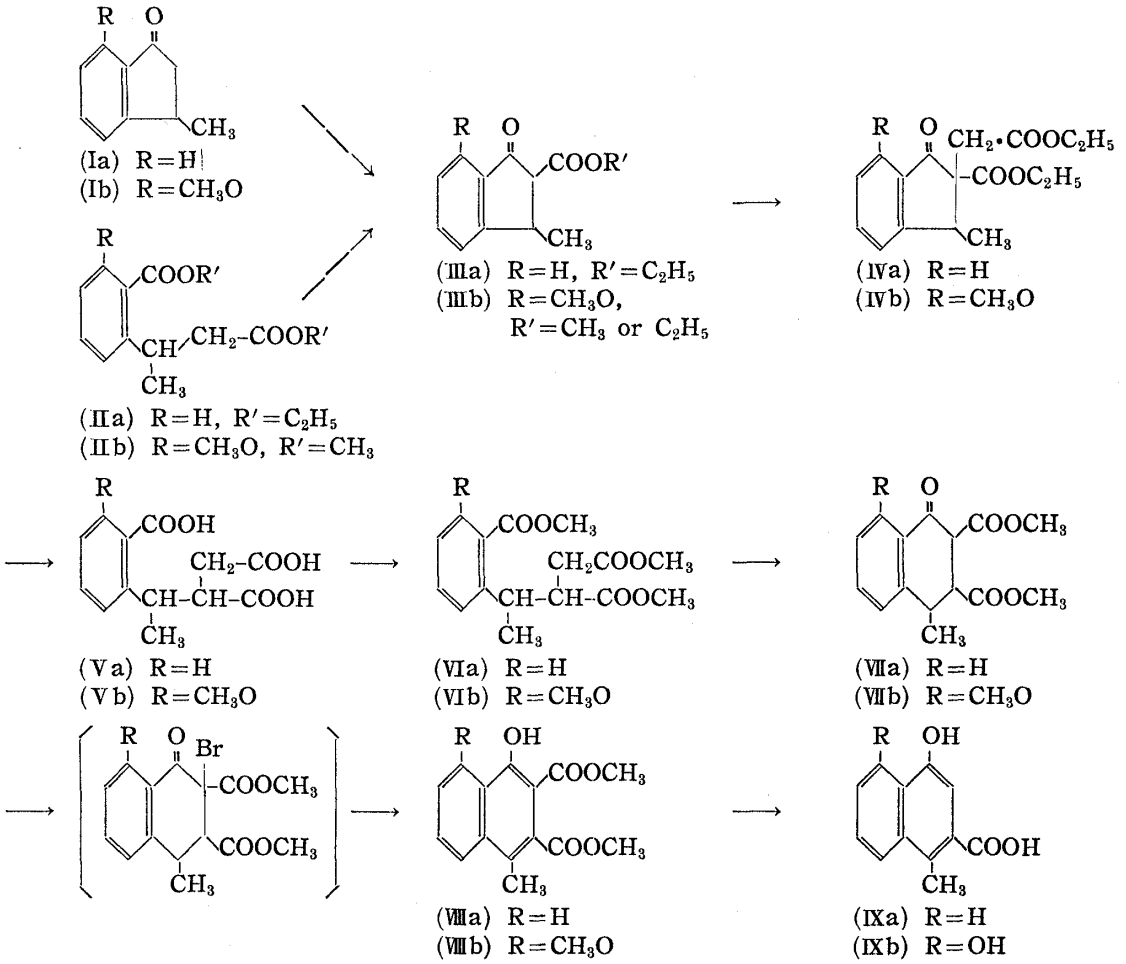


Experimental

2-Ethoxycarbonyl-3-methylindan-1-one (IIIa)—a) From Ethyl 3-(2-Ethoxycarbonylphenyl)butyrate (IIa) : A suspension of NaOEt in anhyd. Et_2O was prepared by mixing 0.45 g. of powdered Na, 0.9 g. anhyd. EtOH, and 20 cc. of anhyd. Et_2O at room temperature and allowing to stand over night. A solution of 5 g. of ethyl 3-(2-ethoxycarbonylphenyl)butyrate (IIa) in 5 cc. of anhyd. Et_2O was added to the above suspension with stirring. After keeping at room temperature for 40 hr., the reaction mixture was refluxed for 6 hr., a mixture of ice and HCl was added, and the ethereal layer was extracted with dil. NaOH solution until the ethereal layer showed no coloration (red-purple) to $FeCl_3$. The combined alkaline extract was acidified with a mixture of ice and conc. HCl, and again extracted with Et_2O. The Et_2O extract was washed with satd. $NaHCO_3$ solution and water, and dried over anhyd. Na_2SO_4. The solvent was removed and the residue was distilled under reduced pressure. The main fraction consisted of 2 g.(49%) of a yellow liquid, b.$p_{0.01}$ 102~103°.

Semicarbazone : m.p. 138~139°. *Anal.* Calcd. for $C_{14}H_{17}O_3N_3$: C, 61.08; H, 6.22. Found : C, 61.35; H, 6.20. Another experiment identical to the above except for the use of Na as condensation agent in benzene in place of NaOEt in Et_2O gave the same result.

b) From 3-Methylindan-1-one (Ia) : A mixture of 50.8 g. of diethyl carbonate, 200 cc. of anhyd. Et_2O, and NaH was stirred under reflux and a solution of 31.4 g. of 3-methylindan-1-one (Ia) and 100 cc. of anhyd. Et_2O was added dropwise during the course of 45 min. The reaction mixture was stirred under reflux for an additional 1 hr., followed by standing overnight at room temperature, and finally poured into a mixture of ice and AcOH. The organic solvent layer was separated, washed successively with water, satd. $NaHCO_3$ solution, and water, and then dried over anhyd. Na_2SO_4. The solvent was removed and the residue was distilled under reduced pressure, giving 30 g.(64%) of a yellow oil, b.$p_{0.4}$ 131~134°.

Ethyl 1-Oxo-7-methoxy-3-methylindan-2-carboxylate (IIIb)—a) From Methyl 3-(2-Methoxycarbonyl-3-methoxyphenyl)butyrate (IIb) : A solution of 5 g. of methyl 3-(2-methoxycarbonyl-3-methoxyphenyl)butyrate (IIb) in 15 cc. of anhyd. benzene was added to the suspension of NaOEt in anhyd. benzene prepared from 0.44 g. of powdered Na, 20 cc. of anhyd. benzene, and 0.61 g. of dehyd. MeOH. The reaction mixture was stirred under reflux for 6 hr., poured into a mixture of ice and HCl, and

treated by the same procedure as described for the preparation of (IIIa) from (IIa). The yield of (IIIb) was 2.7 g.(61.4%), b.$p_{0.5}$ 145~150°. This gave a deep purple $FeCl_3$ reaction.

b) From 7-Methoxy-3-methylindan-1-one (Ib): 7-Methoxy-3-methylindan-1-one (Ib) (30 g.) was dissolved in 200 cc. of anhyd. Et_2O and the solution was worked up with a mixture of 8.2 g. of NaH, 100 cc. of anhyd. Et_2O, and 40 g. of Et_2CO_3, under the same condition as described for the preparation of (IIIa) from (Ia). The yield of (IIIb) was 30.5 g.(72%), b.$p_{0.25}$ 140~160°. *Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45. Found: C, 68.68; H, 6.55.

This compound gave a deep purple coloration with $FeCl_3$.

Ethyl 1-Oxo-2-ethoxycarbonyl-3-methylindan-2-acetate (IVa)—A benzene solution (300 cc.) of 33.5 g. of (IIIa) was added dropwise to the suspension of NaOEt in benzene (prepared by standing a mixture of 3.55 g. of powdered Na, 200 cc. of anhyd. benzene, and 7.1 g. of EtOH) followed by refluxing for 2 hr. A solution of 31 g. of ethyl bromoacetate in 100 cc. of anhyd. benzene was added and the reaction mixture was stirred under reflux for 6 hr. When cool, water was added and the benzene layer was dried. Removal of the solvent and distillation of the residue under reduced pressure gave 37 g.(70%) of a light yellow viscous oil, b.$p_{0.3}$ 150~168°. *Anal.* Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.36; H, 6.60.

Ethyl 1-Oxo-2-ethoxycarbonyl-7-methoxy-3-methylindan-2-acetate (IVb)—A solution of 30 g. of (IIIb; $R'=C_2H_5$) in 250 cc. of anhyd. benzene was added to the suspension of NaOEt in anhyd. benzene (prepared from 2.8 g. of powdered Na, 5.6 g. of anhyd. EtOH, and 200 cc. of anhyd. benzene). The reaction mixture was allowed to react with 30 g. of ethyl bromoacetate in 100 cc. of anhyd. benzene under the same condition as described for the preparation of (IVa) in the preceding experiment. The yield was 34 g.(84%) of a light yellow viscous oil, b.$p_{0.15}$ 184°. *Anal.* Calcd. for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 65.05; H, 6.47.

(IIIb) ($R'=CH_3$) was also prepared by the same procedure as for (IIb) ($R'=CH_3$).

(2-Carboxy-α-methylbenzyl)succinic Acid (Va)—A mixture of 19.5 g. of (IVa) in a solution of 24 g. of KOH, 15 cc. of water, and 50 cc. of EtOH was heated under reflux for 1 hr. After evaporation of EtOH under reduced pressure, a mixture of ice and HCl was added to the reaction mixture and this mixture was extracted with AcOEt. The extract was shaken with satd. $NaHCO_3$ solution and the alkaline extract was again acidified with a mixture of ice and HCl, followed by extraction with AcOEt. The extract solution was washed, dried, and the solvent was removed, giving 14 g. (82%) of white crystals. Recrystallization from AcOEt-petr. benzine afforded white crystals, m.p. 179.5~180.5°. *Anal.* Calcd. for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30. Found: C, 58.92; H, 5.38.

(2-Carboxy-3-methoxy-α-methylbenzyl)succinic Acid (Vb)—A mixture of 16.3 g. of (IVb) in a solution of 17 g. of KOH, 100 cc. of water, and 32 cc. of EtOH was heated under reflux for 1 hr. and then treated by the same procedure as described for the preparation of (Va). The yield was 10 g. (69%) of white crystals (from AcOEt-petr. benzine), m.p. 184~187°. *Anal.* Calcd. for $C_{14}H_{16}O_7$: C, 56.75; H, 5.44. Found: C, 56.38; H, 5.36.

Dimethyl (2-Methoxycarbonyl-α-methylbenzyl)succinate (VIa)—Excess of CH_2N_2 was passed through an ice-cooled suspension of 10 g. of (Va) in 70 cc. of anhyd. Et_2O until solid of (Va) dissolved. After standing overnight in an ice-box, glacial AcOH was added to decompose excess of CH_2N_2 and the whole solution was washed successively with satd. $NaHCO_3$ solution and water, and dried over anhyd. Na_2SO_4. After evaporation of Et_2O, the residue was distilled under reduced pressure, b.$p_{0.1}$ 168~170°. The yield was 7.9 g.(68%). *Anal.* Calcd. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.45; H, 6.42.

Dimethyl (2-Methoxycarbonyl-3-methoxy-α-methylbenzyl)succinate (VIb)—64 g.(75%) of (VIb) was obtained from 7.5 g. of (Vb) by the same procedure as described for the preparation of (VIa). Light yellow oil, b.$p_{0.15}$ 178~179°. This oil solidified to white crystals of m.p. 92.5°, as recrystallized from EtOH. *Anal.* Calcd. for $C_{17}H_{22}O_7$: C, 60.34; H, 6.55. Found: C, 60.64; H, 6.33.

Dimethyl 1-Oxo-4-methyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (VIIa) and 4-Oxo-1-methyl-1,2,3,4-tetrahydro-2-naphthoic Acid—To a suspension of 0.7 g. of powdered Na in 10 cc. of anhyd. benzene, a benzene solution (15 cc.) of 9.3 g. of (VIa) was added, the reaction mixture was stirred in a stream of N_2 under reflux for 2.5 hr., cooled, and a mixture of ice and HCl was added. The benzene layer was extracted with ice-cold 1% KOH solution until the $FeCl_3$ reaction of the benzene layer became negative. The combined alkaline extract was acidified with a mixture of ice and HCl, and extracted with AcOEt. The AcOEt extract was washed successively with satd. $NaHCO_3$ solution and water, and dried over anhyd. Na_2SO_4. After evaporation of the solvent, the residue was distilled under reduced pressure. Colorless oil, b.$p_{0.1}$ ca. 145°, solidified on trituration with Et_2O, yielding white crystals of m.p. 104° when recrystallized from EtOH. Yield, 5.5 g.(66%). *Anal.* Calcd. for $C_{15}H_{14}O_5$: C, 65.21; H, 5.84. Found: C, 65.59; H, 5.59.

This compound (VIIa) was heated under reflux with 20% HCl for 12 hr. When cool, the reaction mixture was extracted with AcOEt and the extract was shaken with satd. $NaHCO_3$ solution. The alkaline solution thus obtained was acidified with a mixture of ice and HCl, providing 0.3 g. of

light brown crystals. The mother liquor, from which crystals were filtered off, was extracted with AcOEt and this extract yielded an additional 1.3 g. of crystals. The combined crude crystals were recrystallized three times from benzene-petr. benzine, yielding white crystals of m.p. 167°, which was not depressed when mixed with a sample of 4-oxo-1-methyl-1,2,3,4-tetrahydro-2-naphthoic acid prepared by ring closure of (α-methylbenzyl)succinic anhydride. *Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.68.

Dimethyl 1-Oxo-4-methyl-8-methoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (VIIb)—A mixture of 5.7 g. of (VIb), 0.4 g. of powdered Na, and 20 cc. of toluene was stirred under reflux in a stream of N_2 for 3.5 hr. The reaction mixture was treated under the same condition as described for the preparation of (VIIa) in the preceding experiment. Yield, 2 g.(37%) of light yellow crystals of m.p. 92~93° as crystallized from EtOH. *Anal.* Calcd. for $C_{16}H_{18}O_6$: C, 62.71; H, 5.92. Found: C, 62.65; H, 5.97.

Dimethyl 1-Hydroxy-4-methylnaphthalene-2,3-dicarboxylate (VIIIa)—A solution of 1.04 g. of Br_2 in 5 cc. of $CHCl_3$ was added dropwise at 5~10° to a solution of 1.8 g. of (VIIa) in 5 cc. of $CHCl_3$ and 10 cc. of Et_2O. Stirring was continued at room temperature for 2.5 hr., the reaction mixture was washed with water, and dried over anhyd. Na_2SO_4. Evaporation of Et_2O afforded the colorless vitreous bromide.

This crude bromide was heated with 10 g. of 2,4,6-collidine on a water bath. When cool, Et_2O was added to complete the precipitation of 2,4,6-collidine hydrobromide, which was filtered off, and Et_2O solution was washed successively with water and dil. HCl to remove 2,4,6-collidine completely, and again with water. After drying over anhyd. Na_2SO_4, Et_2O was evaporated and 1.6 g. of brown crystals so obtained was recrystallized from EtOH with activated carbon, affording colorless crystals, m.p. 121~122°. Yield, 1 g.(56%). This gave a deep blue $FeCl_3$ reaction. *Anal.* Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 66.04; H, 5.32.

Dimethyl 1-Hydroxy-4-methyl-8-methoxynaphthalene-2,3-dicarboxylate (VIIIb)—A reaction of 1 g. of (VIIb) in 5 cc. of anhyd. $CHCl_3$ and 10 cc. of anhyd. Et_2O with 0.5 g. of Br_2 in 3 cc. of $CHCl_3$ afforded 1.2 g. of vitreous bromide, which was subjected to dehydrobromination with 8 g. of 2,4,6-collidine by the same procedure as described for the preparation of (VIIIa). Yield, 0.5 g.(50%) of white crystals, m.p. 122~123°. *Anal.* Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.33; H, 5.27.

1-Hydroxy-4-methyl-3-naphthoic Acid (IXa)—(VIIIa)(0.5 g.) was heated under reflux with 15 cc. of 20% HCl for 15 hr. When cool, the reaction mixture was extracted with AcOEt and the extract was shaken with satd. $NaHCO_3$ solution. The alkaline solution was acidified with a mixture of ice and HCl, yielding 0.15 g. of light brown crystals. The mother liquor was extracted with AcOEt and the extract was concentrated to give an additional 0.15 g. of crystals. The combined crystals were recrystallized from water, giving m.p. 203~207°, which was not depressed when mixed with a sample prepared by ring closure of (α-methylbenzylidene)succinic acid. *Anal.* Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.50; H, 4.79.

The reaction with HBr in place of HCl gave the same result.

1,8-Dihydroxy-4-methyl-3-naphthoic Acid (Terranaphthoic Acid) (IXb)—(VIIIb)(0.3 g.) was heated with 15 cc. of 48% HBr at 130° for 2.5 hr. in N_2 stream. The reaction mixture was extracted with AcOEt and the extract was shaken with satd. $NaHCO_3$ solution. The alkaline solution was acidified with conc. HCl, giving brown crystals. Two recrystallizations from water furnished yellow-tan needles of m.p. 232~233°(decomp.)(reported[5] m.p. 234~235°). Yield, 130 mg.(60%). U. V. (Fig. 1) $\lambda_{max}^{0.01N\ HCl\text{-}EtOH}$ mμ (log ε): 234(4.60), 312(3.79), 343(3.69). I. R. (Fig. 2) $\lambda_{max}^{dioxane}$ μ: 3.3 (center of a broad band), 5.85. *Anal.* Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.83; H, 4.51.

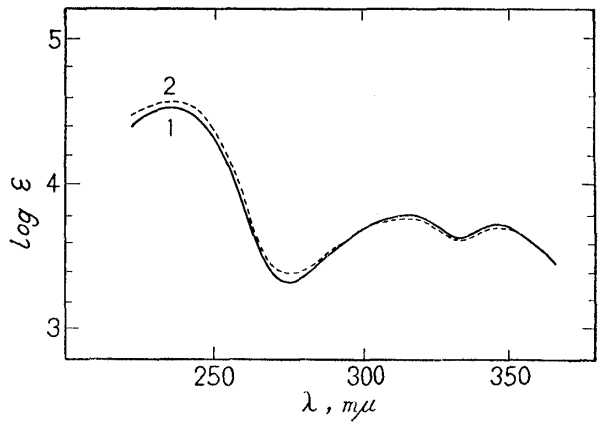


Fig. 1. Ultraviolet Spectra of Terranaphthoic Acid in Acid-EtOH
1. synthetic 2. natural

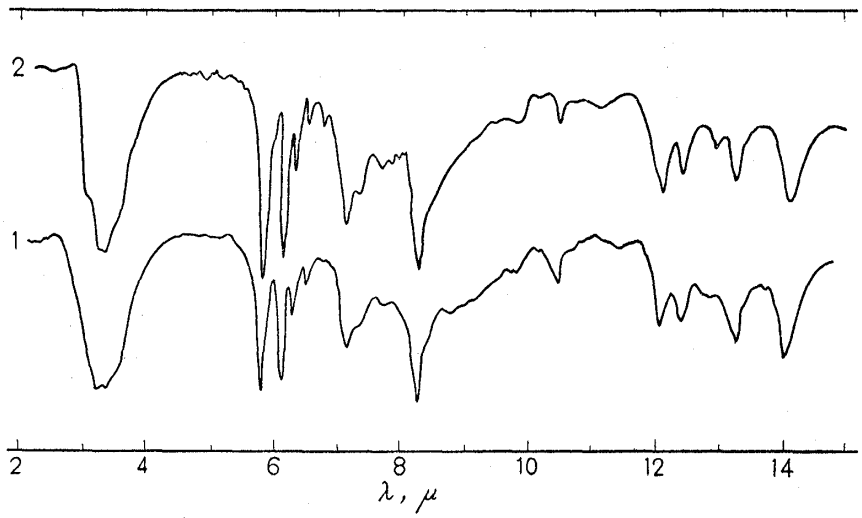


Fig. 2. Infrared Spectra of Terranaphthoic Acid in Dioxane
1. synthetic 2. natural

Summary

Terranaphthoic acid, a degradation product of oxytetracycline, was synthesized and the structure proposed by Hochstein, *et al*[5]. for this compound was thereby confirmed.

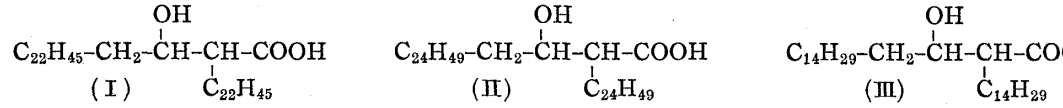
(Received September 15, 1958)

UDC 547.473.1 : 544.621

54. Hikokichi Oura*: Studies on Mycolic Acid and its Related Compounds. V.[1] Deuteration and Infrared Spectra of 2-Tetracosyl-3-hydroxyoctacosanoic Acid.

(*Pharmaceutical Faculty, University of Toyama*)

In the first paper of this series,[2] synthesis of 2-docosyl-3-hydroxyhexacosanoic acid (I) and 2-tetracosyl-3-hydroxyoctacosanoic acid (II), the characteristic structural portion of mycolic acid, was reported. Later, two substances from each of (I) and (II) were separated; α-compound, m.p. 91~92.5°, and β-compound, m.p. 86~88°, from (I), and α-compound, m.p. 92~92.5°, and β-compound, m.p. 87~89°, from (II). From their elementary analytical data, acetates, and infrared absorption spectra, it was assumed that these compounds are diastereoisomers.



In the present series of work, the α- and β-compounds of (II) were deuterated and their infrared absorption spectra were measured, by which some interesting observations were gained.

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1) Part IV: This Bulletin, **6**, 462(1958).
2) H. Oura, T. Makino: Yakugaku Zasshi, **78**, 141(1958).