UDC 547.474.07

87. **Hikokichi Oura:** Studies on Mycolic Acid and Related Compounds. III.[1] Synthesis of α-Mycolic Acid found in Brévannes Strain of Human-type Tubercle Bacilli (1).

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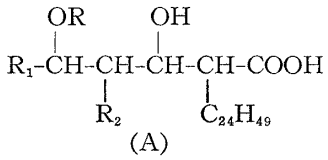
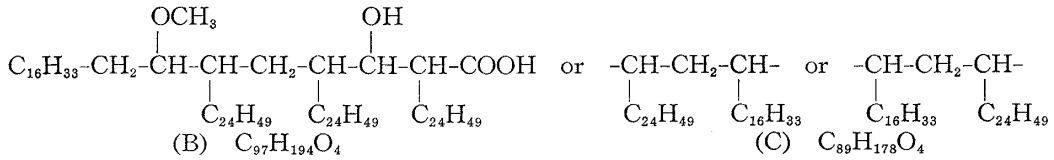
Lederer and others[2] forwarded the structure (A) for α-mycolic acid isolated from the Brévannes strain of human-type tubercle bacilli and stated, from the result of decomposition and other reactions, that it is probably a mixture of compounds in which R is hydrogen and methyl.



(A)

$R_1 + R_2 = C_{58}H_{119} \pm 5CH_2$
$R = H,\ C_{87}H_{174}O_4 \pm 5CH_2$
$R = CH_3,\ C_{88}H_{176}O_4 \pm 5CH_2$

More recently, Morgan and Polgar[3] proposed the formula (B) or (C) for mycolic acid from the result of decomposition and other reactions, and from consideration of its biogenesis.



(B) $C_{97}H_{194}O_4$ (C) $C_{89}H_{178}O_4$

On the other hand, Lederer and others[4] undertook the synthesis of mycolic acid and obtained an oily substance (I), $C_{54}H_{104}O_5$, by the reaction route shown in Chart 1. Reduction of (I) with sodium borohydride, followed by saponification with potassium hydroxide, and purification by alumina chromatography failed to afford the objective 2-hexadecyl-4-tetradecyl-3,5-dihydroxyeicosanoic acid (II), and these workers reported that the products obtained were all neutral substances.

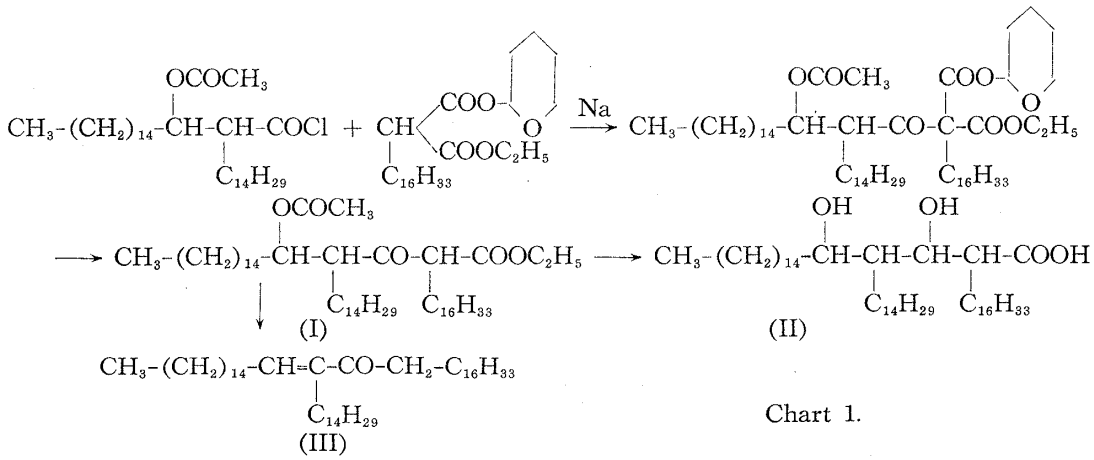
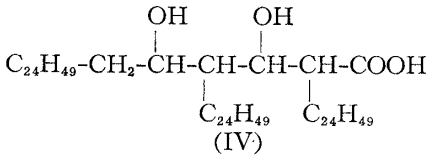


Chart 1.

Synthesis of compounds related to mycolic acids in this laboratory was described in the preceding paper[1] and the preparation of Lederer's formula (A) compound was now taken up. As a start, synthesis of 2, 4-ditetracosyl-3,5-dihydroxytriacontanoic acid (IV) was attempted.

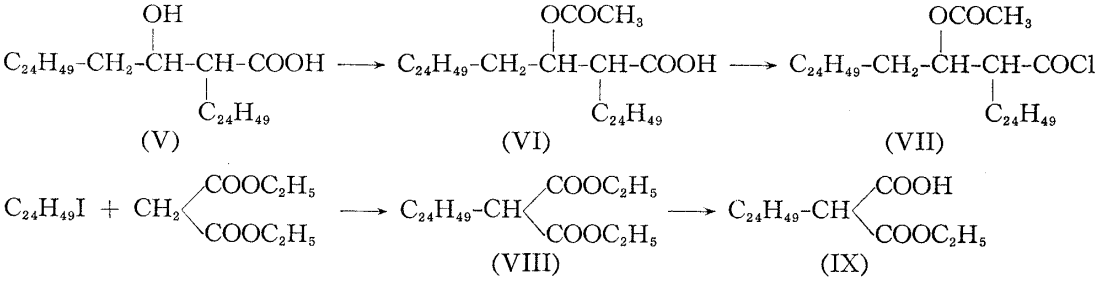
* 5 Okuda, Toyama. (大浦彦吉).

1) Part II: This Bulletin, **6**, 451(1958).
2) A. Aebi, M. E. Vilkas, E. Lederer: Bull. soc. chim. France, **1954**, 79.
3) E. D. Morgan, N. Polgar: J. Chem. Soc., **1957**, 3779.
4) U. Eisner, J. Polonsky, E. Lederer: Bull. soc. chim. France, **1955**, 212.



(IV)

The racemic compound of 2-tetracosyl-3-hydroxyoctacosanoic acid[5] (V) was acetylated with pyridine and acetic anhydride and the product therefrom was purified by chromatography over alumina. Neutral substance was removed by elution of the column with benzene and ether, and the column was developed cautiously with ether containing 0.1% of glacial acetic acid, from which 2-tetracosyl-3-acetoxyoctacosanoic acid (VI), m. p. 70~71°, was obtained. (VI) was reacted with thionyl chloride in benzene to form (VII). On the other hand, diethyl tetracosylmalonate (VIII), m. p. 54.5~55.5°, was obtained in 92% yield from tetracosyl iodide and diethyl malonate, (VIII) was hydrolyzed to its half-ester (IX), m. p. 77~78°, and derived to the tetrahydropyran ester of (IX) according to Bowman's ketone synthesis.[6]



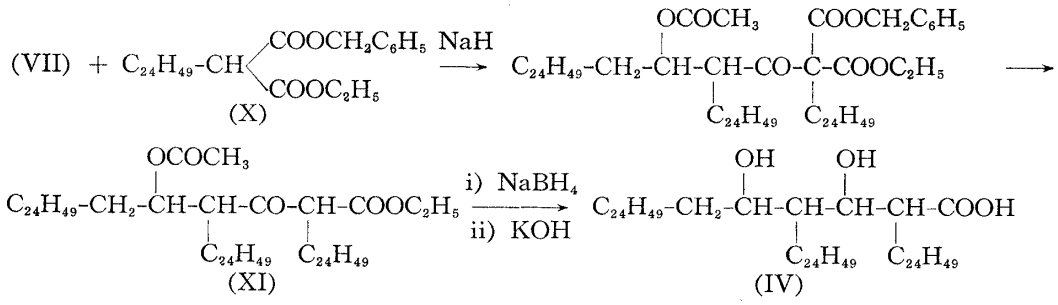
(V) (VI) (VII)

(VIII) (IX)

Attempted condensation of the pyran ester of (IX) with (VII) by standing the mixture in benzene at room temperature for 24~48 hours failed to afford the objective (XI).

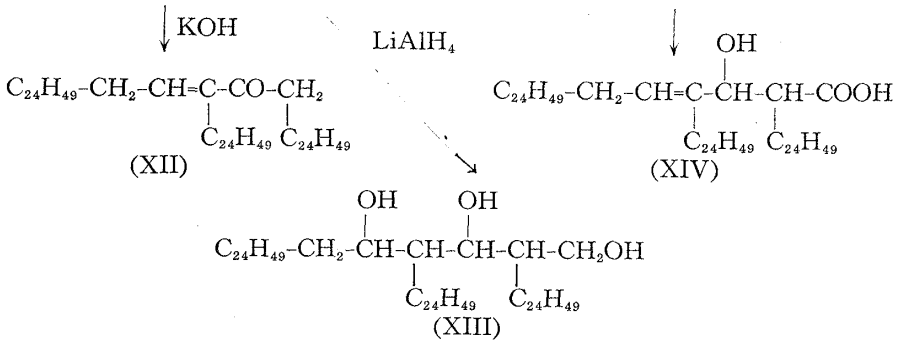
It was thought that the failure of this reaction might be due to the large molecule of the compound in this case, compared to the reactant used by Bowmann and Lederer, and the compound may not undergo condensation at ordinary temperature. Therefore, the benzyl ester (X) was used in place of the tetrahydropyran ester, and the mixture was heated in a sealed tube at 120~130° for 6 hours. The product obtained from this reaction was submitted to catalytic reduction over 10% palladium-carbon to remove the benzyl group, then decarboxylated, and the product therefrom was chromatographed twice over Florisil, from which ethyl 2,4-ditetracosyl-3-oxo-5-acetoxytriacontanoate (XI), m. p. 63~64°, was obtained in 50% yield.

When the above condensation reaction was carried out at ordinary pressure by heating at 120~130° in an oil bath for 32 hours, the yield of the product was only 20%. The reduction of the ketone group in 3-position, using palladium-carbon, was found to be not effected since the absorption for alcoholic hydroxyl was not found in the infrared absorption spectrum of (XI).



(X) (XI) (IV)

5) H. Oura, T. Makino: Yakugaku Zasshi, **78**, 141(1958).
6) R. E. Bowman, W. D. Fordham: J. Chem. Soc., **1952**, 3945.
7) R. E. Bowman: *Ibid.*, **1950**, 325.



Analytical values and molecular weight of (XI) agreed with those expected from this formula, and the structure was also confirmed through its ultraviolet spectrum (Fig. 1) exhibiting absorptions at 222, 225, 266, and 271 mμ, its infrared spectrum (Fig. 2) exhibiting characteristic absorption bands for an ester at 5.76 μ, for enolized β-keto ester at 5.99 μ, for -C=C- at 6.11 μ, and for an O-acetyl at 8.06 μ, and quantitative formation of an α,β-unsaturated ketone compound (XII), m.p. 72~72.5°, by saponification of (XI) with 2*N* ethanolic potassium hydroxide and subsequent chromatography over alumina.

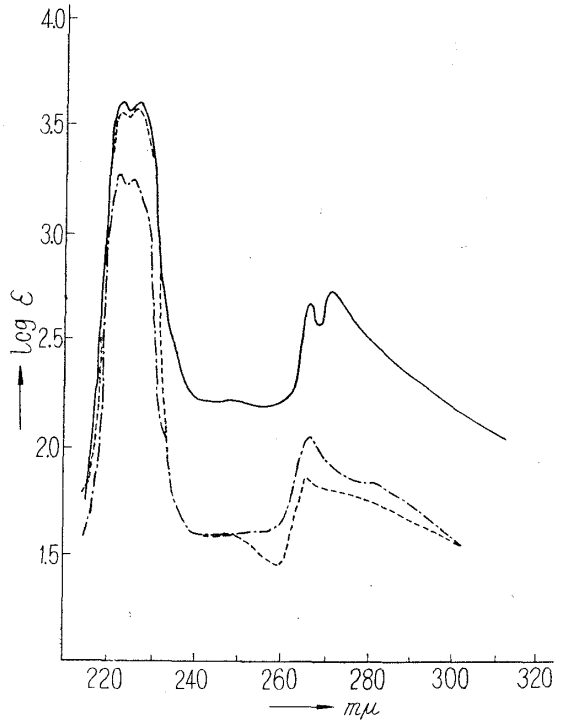


Fig. 1. Ultraviolet Spectra
—— Ethyl 2,4-ditetracosyl-3-oxo-5-acetoxy-triacontanoate (XI), m.p. 63~64°
---- α,β-Unsaturated ketone (XII), m.p. 72~72.5°
-·-· 2,4-Ditetracosyl-3-hydroxy-4-triaconten-ic acid (XIV), m.p. 75~75.5°

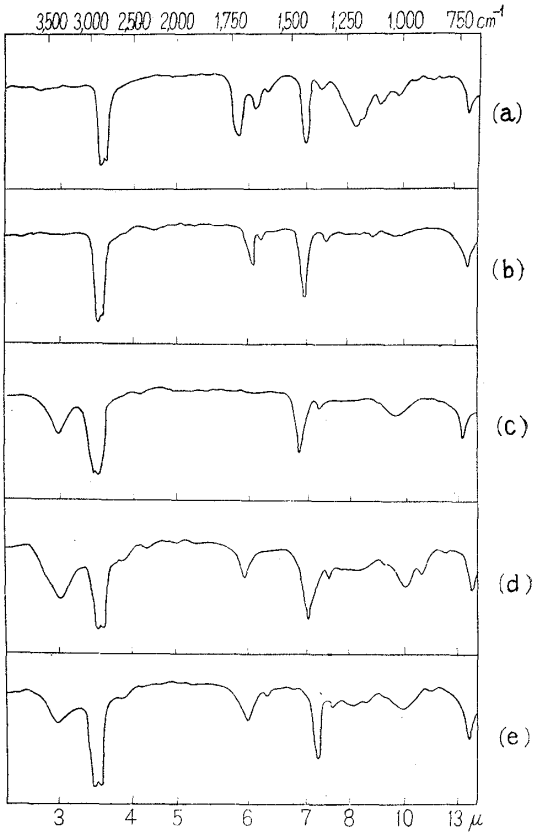


Fig. 2. Infrared Spectra (in Nujol) (Hilger H 800)
(a) Ethyl 2,4-ditetracosyl-3-oxo-5-acetoxytriacontanoate (XI), m.p. 63~64°
(b) α,β-Unsaturated ketone (XII), m.p. 72~72.5°
(c) 2,4-Ditetracosyltriacontane-1,3,5-triol (XIII), m.p. 77~79°
(d) 2,4-Ditetracosyl-3,5-dihydroxytriacontanoic acid (IV), m.p. 82.5~83.5°
(e) 2,4-Ditetracosyl-3-hydroxy-4-triacontenic acid (XIV), m.p. 75~75.5°

Reduction of (XI) with lithium aluminum hydride in ether afforded 2,4-ditetracosyltriacon-

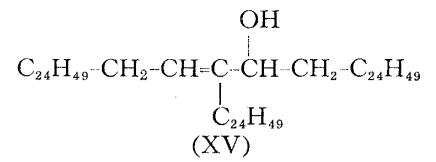
tane-1,3,5-triol (XIII), m. p. 77~79°, whose infrared spectrum exhibited only the absorption for OH at 3.0 μ (Fig. 2).

As for the reduction of the ketone at 3-position in (XI), Lederer and others[3] were not able to obtain any acid substance by reduction of (I) with sodium borohydride in dehydrated ethanol, and these workers presumed this to be due to the low reactivity of the ketone group. The same result was also obtained in this laboratory when (XI) was reacted with sodium borohydride for 8 hours in a mixture of dehydrated ethanol and dioxane, followed by saponification with potassium hydroxide and chromatography.

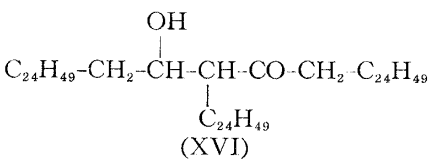
Assuming that this failure of reduction was due to steric hindrance by the presence of a long, C_{24}-alkyl chain in 2- and 4-positions, examinations were made on variety of reducing agents and reduction conditions, and it was learned that the rate of reduction with sodium borohydride was extremely slow. Use of an excess of sodium borohydride and a reaction period of 12 hours afforded 3 mg. of an acid substance from 70 mg. of (XI) and the infrared spectrum of this product exhibited a weak absorption for alcoholic hydroxyl at around 3.0 μ. The reaction period was further extended to 32 hours and saponification of the product with 1.5*N* potassium hydroxide for 8 hours gave 104 mg. of an acid substance from 400 mg. of (XI). The portion of this product eluted from chromatographic column with ether containing 2% of glacial acetic acid afforded 17 mg. of crystals which recrystallized from ether to a substance melting at 82.5~83.5°. Elemental analytical values of this substance, $C_{78}H_{156}O_4$, agreed with those calculated for (IV). Further confirmation of this structure was provided by its infrared spectrum (Fig. 2), exhibiting strong absorption for alcoholic hydroxyl at 3.0 μ and that for carboxyl at 5.87 μ, and formation of a substance of m. p. 73~75° by methylation with diazomethane, whose molecular weight determination[8] gave values agreeing with the methyl ester of (IV).

Elution of the above chromatographic column with ether containing 1% of glacial acetic acid afforded 62 mg. of crystals which melted at 75~75.5° after recrystallization from ether. The elemental analytical values of this substance agreed with those for (XIV), $C_{78}H_{154}O_3$. Since its infrared spectrum (Fig. 2) exhibited absorptions for OH at 3.0 μ, for COOH at 5.88 μ, and for -CH=CH- at 6.11 μ, and its ultraviolet spectrum (Fig. 1) exhibited absorptions at 222, 225, and 267 mμ, it was certain that this substance is 2,4-ditetracosyl-3-hydroxy-4-triacontenic acid (XIV), in which the double bond is not conjugated with the carbonyl. Considering the fact that (III) is formed from (I), and (XII) from (XI), (XIV) was formed from (IV) by facile dehydration of the hydroxyl in 5-position.

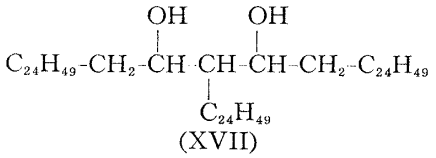
The large amount of a neutral substance obtained on the reduction of (XI) with sodium borohydride was purified by chromatography over alumina and the product was separated into four kinds of substances assumed to have the structures (XV) to (XVIII) from the results of elemental analyses, and ultraviolet and infrared spectra.



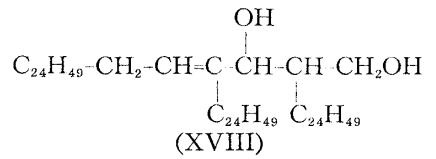
(XV)



(XVI)



(XVII)



(XVIII)

The author expresses his deep gratitude to Prof. K. Yokota, Dean of the Pharmaceutical Faculty of this University, and to Prof. T. Ishiguro of the University of Kyoto for their continued guidance and encouragement during the course of this work; and to Prof. Y. Yamamura of the University of Kyushu

8) F. H. Stodola, A. Lesuk, R. J. Anderson: J. Biol. Chem., **126**, 505(1938).

and to Dr. K. Matsui of the National Sanatorium, Toneyama Hospital, for valuable advices. The author is indebted to Miss T. Makino for technical help, to Mr. K. Okawa, Faculty of Science, University of Osaka, for infrared spectral data, and to the members of the Central Analysis Room, University of Kyoto, and to Miss M. Honda of this laboratory for elemental analyses reported herein.

Experimental (All m.p.s. uncorrected)

2-Tetracosyl-3-acetoxyoctacosanoic Acid (VI)—Five grams of the racemic compound of (V)[5] was acetylated with 60 cc. of pyridine and 50 cc. of Ac_2O, and the product was chromatographed over alumina (acid alumina obtained by treatment of Brockman's alumina with HCl). The column was eluted with benzene and Et_2O to remove neutral substances and finally eluted with Et_2O containing 0.1% of glacial AcOH. The residue obtained from this fraction was recrystallized from petr. ether to 2.8 g. of colorless crystalline powder, m.p. 70~71°. *Anal.* Calcd. for $C_{54}H_{106}O_4$ (VI): C, 79.15; H, 13.04. Found: C, 78.93; H, 12.91.

Diethyl Tetracosylmalonate (VIII)—Tetracosanoic acid[9] was esterified and the ester was reduced with $LiAlH_4$ in Et_2O, affording tetracosanol as colorless microneedles, m.p. 76~77° (the literature records m. p. 77.5°[10]) by recrystallization from acetone in 92% yield. This substance was reacted with red phosphorus and iodine and tetracosyl iodide, $b.p_{0.3}$ 211~213°, was obtained in 98% yield. This substance crystallized from acetone and melted at 54.5~55.5° (the literature[11] records $b.p_{0.35}$ 207~209°, m. p. 54.5~55.5°).

A mixture of 28.5 g. of this substance, metallic Na, and diethyl malonate in dehyd. EtOH was heated in an oil bath at 130~140° for 8 hrs. EtOH was distilled off under a reduced pressure, Et_2O was added to the residue, this was rendered acid with 10% H_2SO_4, washed with water, and dried over anhyd. Na_2SO_4. After evaporation of Et_2O, the residue was distilled *in vacuo* and 28 g. (92%) of a fraction of $b.p_{0.55}$ 240~242° was collected. Recrystallization from acetone gave colorless small needles, m.p. 54.5~55.5°. *Anal.* Calcd. for $C_{31}H_{60}O_4$: C, 74.94; H, 12.17. Found: C, 74.89; H, 12.30.

Ethyl Hydrogen Tetracosylmalonate (IX)—A solution of 8 g. of (VIII) in 1600 cc. of 96% EtOH, with calculated amount of KOH, was allowed to stand at room temperature for 10~14 days, EtOH was distilled off, and 5% Na_2CO_3 solution was added to the residue. This was extracted with benzene-hexane (1 : 1) mixture to remove the unreacted material, the aqueous and middle layer were acidified with dil. HCl, and digested with warm benzene. The product therefrom was recrystallized from hexane to colorless granules, m. p. 74~77°.

The crystals were dissolved in petr. ether and chromatographed over alumina. The column was developed with benzene and ether, and further eluted with Et_2O containing 0.2% of glacial AcOH. The product from the last elution was recrystallized from petr. ether to colorless leaflets, m.p. 77~78°. *Anal.* Calcd. for $C_{29}H_{56}O_4$: C, 74.30; H, 12.04. Found: C, 74.41; H, 12.11.

Ethyl Benzyl Tetracosylmalonate (X)—a) Dry HCl gas was bubbled through a suspension of 5 g. of (IX) in 20 cc. of benzyl alcohol, the resultant reaction mixture was extracted with Et_2O, and the product was recrystallized from acetone. This substance was dissolved in petr. ether, the solution was passed through an alumina column, and the residue from petr. ether elution was recrystallized from acetone to colorless waxy substance, m. p. 48~49°. *Anal.* Calcd. for $C_{36}H_{62}O_4$: C, 77.37; H, 11.18. Found: C, 77.51; H, 11.28.

b) A mixture of (IX) and $SOCl_2$ in benzene was reacted, sodium benzoxide was added, and subsequently worked up as in (a), giving the same result.

Ethyl 2,4-Ditetracosyl-3-oxo-5-acetoxytriacontanoate (XI)—A mixture of 3.7 g. of (VI) and excess of $SOCl_2$ in benzene was heated at 40~50° for 48 hrs. and (VII) was obtained. On the other hand, 8 g. of (X) and NaH were heated in benzene in an oil bath until H_2 gas generation was no longer observed. The two products thus obtained were sealed in a tube and heated at 120~130° for 6 hrs. The reaction mixture was then acidified with AcOH, extracted with Et_2O, and the solvent was evaporated from the extract under a reduced pressure. The residue was dissolved in 500 cc. of Et_2O : AcOEt (4 : 1) mixture and submitted to catalytic hydrogenation over 10% Pd-C until H_2-absorption no longer occurred. After removal of the catalyst by filtration, the solvent was distilled off from the filtrate, the residue was refluxed with benzene for 30 mins. to effect decarboxylation, and benzene was distilled off. The residue was chromatographed over 100 g. of Florisil and the eluant was fractionated as follows:

Fract. No.	Eluant (200 cc.)	Residue (mg.)	Fract. No.	Eluant (200 cc.)	Residue (mg.)
1	Petr. ether	25	8	Petr. ether-benzene (9 : 1)	755
2	〃 〃	350	9	〃 〃 〃	750
3	〃 〃	960	10	〃 〃 〃	840
4	〃 〃	615	11	Petr. ether-benzene (4 : 1)	805
5	〃 〃	420	12	〃 〃 〃	540
6	〃 〃	215	13	〃 〃 〃	225
7	〃 〃	150	14	Petr. ether-benzene (1 : 1)	230

9) H. Oura, *et al.*: Yakugaku Zasshi, **76**, 1433(1956).
10) R. F. Nystron, W. G. Brown: J. Am. Chem. Soc., **69**, 1197(1947).
11) P. A. Levene, F. A. Taylor: J. Biol. Chem., **59**, 905(1924).

Fract. No.	Eluant (200 cc.)	Residue (mg.)	Fract. No.	Eluant (200 cc.)	Residue (mg.)
15	Petr. ether-benzene (1 : 1)	240	17	Benzene	45
16	〃 〃	82	18	〃	21
				Total	7268 mg.

Fraction Nos. 8～16 were combined and the residue therefrom was recrystallized from Et_2O-EtOH to 2.75 g. of crystals melting at 61～62°. Yield, 50%. This product was rechromatographed over 50 g. of Florisil and the product obtained was recrystalllized twice from Et_2O-EtOH to colorless microplates, m.p. 63～64°. U. V. λ_{max}^{hexane} mμ (log ε) : 222 (3.57), 225 (3.59), 267 (2.71), 271 (2.75). *Anal.* Calcd. for $C_{82}H_{160}O_5$: C, 80.32; H, 13.15; mol. wt., 1226. Found: C, 80.82; H, 13.04; mol. wt.(Rast), 1126, 1200.

Formation of (XII) by Saponification of (XI)—A mixture of 70 mg. of (XI), 0.5 cc. of 2*N* KOH, 4 cc. of EtOH, 4 cc. of dioxane, and 5 cc. of benzene was refluxed for 6 hrs., the mixture was acidified with AcOH, and extracted with Et_2O. The residue obtained on evaporation of Et_2O was dissolved in petr. ether, chromatographed over 5 g. of alumina, and 55 mg. of a product was obtained from petr. ether eluate. Recrystallization from Et_2O-EtOH mixture afforded colorless crystalline powder, m.p. 72～72.5°, which formed needle crystals from hexane on automatic evaporation. U.V. λ_{max}^{hexane} mμ(log ε) : 222 (3.57), 225 (3.59), 266 (1.88). I. R. λ_{max}^{Nujol} μ : 6.0 (-C=C-CO-), 6.13 (-C=C-). *Anal.* Calcd. for $C_{77}H_{152}O$: C, 84.53; H, 14.01. Found: 84.45; H, 13.96.

2, 4-Ditetracosyltriacontane-1, 3, 5-triol (XIII)—(XI) was reduced with $LiAlH_4$ in Et_2O and the product was chromatographed over alumina. Residue from Et_2O eluate was recrystallized from Et_2O-EtOH mixture to colorless crystalline powder, m. p. 77～79°. *Anal.* Calcd. for $C_{78}H_{158}O_3$: C, 81.88; H, 13.92. Found: C, 82.11; H, 13.86.

2, 4-Ditetracosyl-3, 5-dihydroxytriacontanoic Acid (IV)—A solution of 400 mg. of (XI) in a mixture of 18 cc. of dioxane and 18 cc. of dehyd. EtOH, added with 200 mg. of $NaBH_4$, was refluxed for 32 hrs. To this were added 3 cc. of 1.5*N* KOH solution, 60 cc. of benzene, and 30 cc. of EtOH, and the mixture was refluxed for 8 hrs. to effect hydrolysis. The mixture was acidified with glacial AcOH, diluted with water, and extracted with Et_2O, from which 367 mg. of residue was obtained. This product was chromatographed over 20 g. of alumina and the eluate was fractionated as follows:

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc)	Residue (mg.)
1	Petr. ether (300)	34	10	Et_2O-AcOH (0.3%)	3
2	Benzene	152	11	Et_2O-AcOH (0.5%)	2
3	〃	8	12	〃	8
4	Et_2O	22	13	Et_2O-AcOH (1%)	62
5	〃	trace	14	〃	2
6	Et_2O-AcOH (0.1%)	〃	15	Et_2O-AcOH (2%)	17
7	〃	2	16	Et_2O-AcOH (3%)	1
8	Et_2O-AcOH (0.2%)	5	17	Et_2O-AcOH (5%)	trace
9	〃	2		Total	320 mg.

Residue from Fraction No. 15 was recrystallized twice from Et_2O to colorless crystalline powder, m.p. 82.5～83.5°. *Anal.* Calcd. for $C_{78}H_{156}O_4$: C, 80.89; H, 13.58. Found: C, 80.77; H, 13.86. Methyl Ester: (IV) was esterified with CH_2N_2 in Et_2O, the product was chromatographed over alumina, and recrystallized from Et_2O-Me_2CO to colorless crystalline powder, m.p. 73～75°. *Anal.* Calcd. for $C_{79}H_{158}O_4$: C, 80.95; H, 13.59; mol. wt., 1172. Found: C, 80.82; H, 13.68; mol. wt.(Rast), 1177, 1080.

2, 4-Ditetracosyl-3-hydroxy-4-triacontenic Acid (XIV)—Fraction No. 13 from the above chromatography was recrystallized twice from Et_2O to colorless crystalline powder, m. p. 75～75.5°. U. V. λ_{max}^{hexane} mμ (log ε) : 222 (3.27), 225 (3.24), 267 (2.06). *Anal.* Calcd. for $C_{78}H_{154}O_3$: C, 82.17; H, 13.62. Found: C, 82.33; H, 13.92.

Separation of the Neutral Substance: Products were collected from three experiments of $NaBH_4$-reduction, and Fraction Nos. 1～5 was rechromatographed over 40 g. of alumina, the eluate being fractionated as follows:

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc)	Residue (mg.)
1	Petr. ether	97	11	Petr. ether-benzene (3 : 1)	41
2	〃	49	12	〃	49
3	〃	15	13	〃	58
4	〃	13	14	〃	31
5	〃	6	15	Petr. ether-benzene (1 : 1)	4
6	Petr. ether-benzene (9 : 1)	44	16	〃	2
7	〃	39	17	〃	trace
8	〃	30	18	Benzene	2
9	〃	20	19	〃	trace
10	〃	15	20	Benzene-Et_2O (9 : 1) (50)	〃

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc.)	Residue (mg.)
21	Benzene-Et_2O (9 : 1) (50)	trace	25	Benzene-Et_2O (1 : 1)	2
22	Benzene-Et_2O (3 : 1)	13	26	Benzene-Et_2O (1 : 3)	15
23	〃	10	27	〃	trace
24	Benzene-Et_2O (1 : 1)	trace	28	Et_2O (100)	〃
				Total	573 mg.

Fraction No. 7: Recrystallized from Et_2O-EtOH to colorless crystalline powder, m. p. 68.5~69°. U. V. λ_{max}^{hexane}: 222 mμ (log ε 1.80). I. R. λ_{max}^{Nujol} μ: 3.01 (OH), 6.16 (-C=C-). *Anal.* Calcd. for $C_{77}H_{154}O$ (XV): C, 84.38; H, 14.16. Found: C, 83.92; H, 14.13.

Fraction No. 12: Recrystallized twice from Et_2O to colorless crystalline powder, m. p. 70~71°. U. V. λ_{max}^{hexane}: 271 mμ (log ε 2.23). I. R. λ_{max}^{Nujol} μ: 3.03 (OH), 5.85 (-CO-). *Anal.* Calcd. for $C_{77}H_{154}O_2$ (XVI): C, 83.16; H, 13.96. Found: C, 82.97; H, 14.26. Fractions Nos. 22 and 23: Recrystallized twice from Et_2O to colorless crystalline powder, m. p. 76~76.5°. I. R. λ_{max}^{Nujol}: 3.0 μ (OH). *Anal.* Calcd. for $C_{77}H_{156}O_2$ (XVII): C, 83.01; H, 14.12. Found: C, 82.81; H, 13.45

Fraction No. 26: Recrystallized from Et_2O-EtOH to colorless crystalline powder, m. p. 73.5~74°. I. R. λ_{max}^{Nujol} μ: 3.0 (OH), 6.16 (-C=C-). *Anal.* Calcd. for $C_{78}H_{156}O_2$ (XVIII): C, 83.19; H, 13.96. Found: C, 83.01; H, 14.11.

Summary

Condensation of 2-tetracosyl-3-acetoxyoctacosanoic acid chloride and ethyl benzyl tetracosylmalonate afforded ethyl 2,4-ditetracosyl-3-oxo-5-acetoxytriacontanoate whose reduction with sodium borohydride gave 2,4-ditetracosyl-3,5-dihydroxytriacontanoic acid. Preparation of their derivatives was examined.

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88. **Hikokichi Oura**: Studies on Mycolic Acid and Related Compounds. IV.[1] Synthesis of α-Mycolic Acid found in Brévannes Strain of Human-type Tubercle Bacilli. (2).

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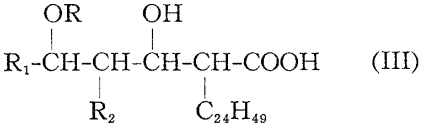
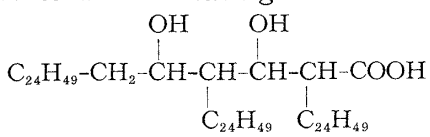
Preparation of 2,4-ditetracosyl-3,5-dihydroxytriacontanoic acid (I), $C_{78}H_{156}O_4$, and related compounds was described in the preceding paper,[1] and preparation of its homolog with four more carbons, 2-tetracosyl-4-hexacosyl-3,5-dihydroxydotriacontanoic acid (II), $C_{82}H_{164}O_4$, is described herein.



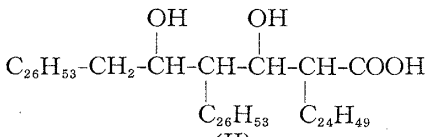
(III)

$R_1 + R_2 = C_{58}H_{118} \pm 5CH_2$
$R = H$, $C_{87}H_{174}O_4 \pm 5CH_2$
$R = CH_3$, $C_{88}H_{176}O_4 \pm 5CH_2$

Lederer, *et al.*[2] proposed the formula (III) for α-mycolic acid isolated from the Brévannes strain of human-type tubercle bacilli and stated that the acid is probably a mixture of compounds with R=H and CH_3. The molecular formula for the compound with R=H would be $C_{87}H_{174}O_4 \pm 5CH_2$, and the compound (II) taken up in the present series of work would correspond to the one having smaller number of carbon atoms in Lederer's formula.



(I)



(II)

* 5 Okuda, Toyama (大浦彦吉).

1) Part III: This Bulletin, **6**, 456 (1958).

2) A. Aebi, M. E. Vikas, E. Lederer: Bull. soc. chim. France, **1954**, 79.