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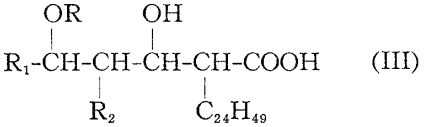
88. **Hikokichi Oura**: Studies on Mycolic Acid and Related Compounds. IV.[1] Synthesis of α-Mycolic Acid found in Brévannes Strain of Human-type Tubercle Bacilli. (2).

(*Pharmaceutical Faculty, University of Toyama**)

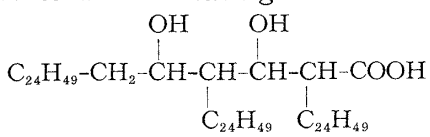
Preparation of 2,4-ditetracosyl-3,5-dihydroxytriacontanoic acid (I), $C_{78}H_{156}O_4$, and related compounds was described in the preceding paper,[1] and preparation of its homolog with four more carbons, 2-tetracosyl-4-hexacosyl-3,5-dihydroxydotriacontanoic acid (II), $C_{82}H_{164}O_4$, is described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



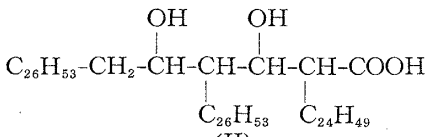
(III)

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

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)

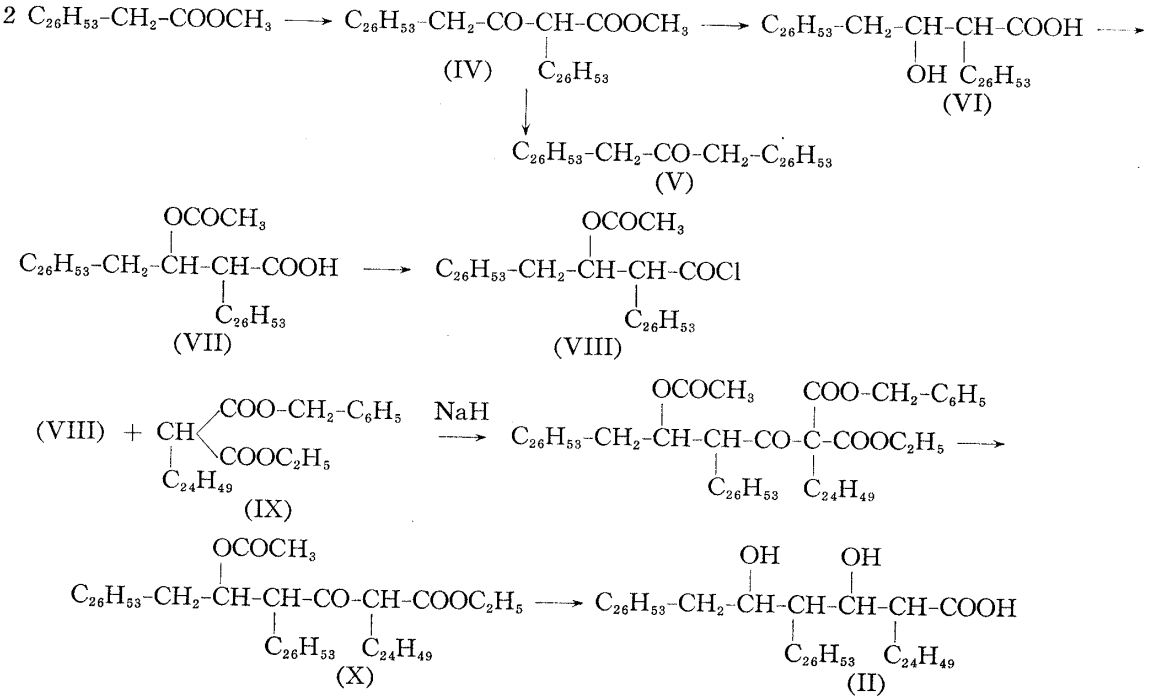
* 5 Okuda, Toyama (大浦彦吉).

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

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

Preparation of octacosanoic acid had been reported earlier.[3] In the present work, its methyl ester was reacted with sodium hydride in xylene, according to the method of Hansley,[4] at 160~170° for 24 hours, and methyl 2-hexacosyl-3-oxotriacontanoate (IV), m.p. 71~72°, was obtained in 74% yield. The yield was only 30% when reacted for 8 hours and it was found that its reaction velocity is much slower than that of methyl 2-docosyl-3-oxohexacosanoate or methyl 2-tetracosyl-3-oxoöctacosanoate.[5] Ultraviolet absorption spectrum of (IV) is shown in Fig. 1. Saponification of (IV) effected decarboxylation and a ketone compound (V), m. p. 101~102°, was obtained quantitatively, identified as its oxime.

Reduction of (IV) with sodium borohydride as in previous cases,[5] saponification, and purification through alumina chromatography afforded two isomers of 2-hexacosyl-3-hydroxytriacontanoic acid, (VIa), m. p. 93~94°, and (VIb), m. p. 89~90°. The racemic compound of (VI) was acetylated to 2-hexacosyl-3-acetoxytriacontanoic acid (VII), m. p. 74~75°, and reacted with thionyl chloride to form (VIII), which was reacted with ethyl benzyl tetracosylmalonate (IX)[1] in the presence of sodium hydride, in a sealed tube, keeping at 130~140° for 8 hours. The product therefrom was catalytically reduced over 10% palladium-charcoal, decarboxylated, and purified through chromatography over Florisil twice, from which ethyl 2-tetracosyl-4-hexacosyl-3-oxo-5-acetoxydotriacontanoate (X), m. p. 64.5~65.5°, was obtained in 31% yield.



The elemental analytical values and molecular weight of (X) agreed with theoretical values. The ultraviolet spectrum of (X) (Fig. 1) exhibited absorptions at 222, 226, 267, and 270 mμ, and its infrared spectrum (Fig. 2) showed characteristic absorptions for an ester at 5.76 μ, for β-keto ester enol at 5.99 μ, a double bond at 6.10 μ, and an O-acetyl at 7.98 μ. This curve was almost identical with that of ethyl 2,4-ditetracosyl-3-oxo-5-acetoxytriacontanoate.[1]

(X) was then reduced with sodium borohydride for 32 hours, the reaction mixture was acidified with glacial acetic acid, and extracted with benzene. The product was saponified by boiling with 1N potassium hydroxide in benzene-ethanol mixture for 5 hours, and the product was purified through alumina chromatography. The residue from a fraction eluted

3) H. Oura, J. Hase, K. Honda, S. Fukai: Yakugaku Zasshi, **76**, 1433(1956).
4) V. L. Hansley: U. S. Pat. 2,158,071(1938), 2,218,026(1940).
5) H. Oura, T. Makino: Yakugaku Zasshi, **78**, 141(1958).

with ether containing 2% of glacial acetic acid was recrystallized from ether and (II), m.p. 77.5°, was obtained in a poor yield, the amount being only 20 mg. of (II) from 1 g. of (X).

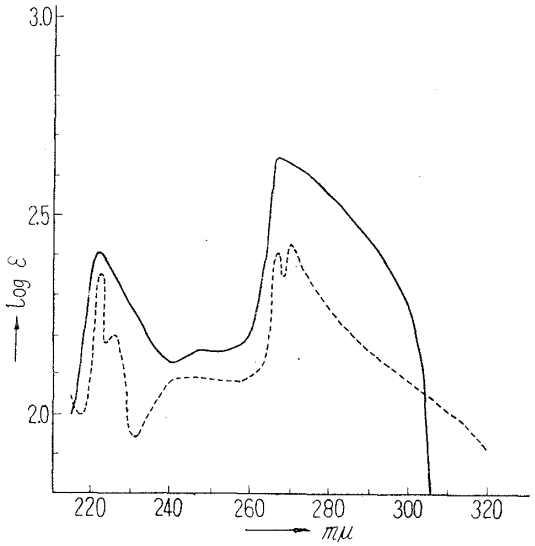


Fig. 1. Ultraviolet Spectra
—— Methyl 2-hexacosyl-3-oxotriacontanoate (IV), m.p. 71~72°.
---- Ethyl 2-tetracosyl-4-hexacosyl-3-oxo-5-acetoxydotriacontanoate (X), m.p. 64.5~65.5°

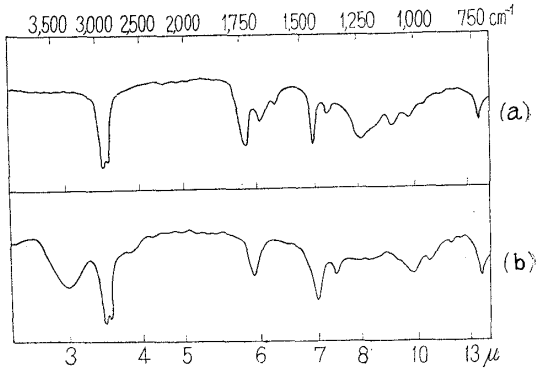
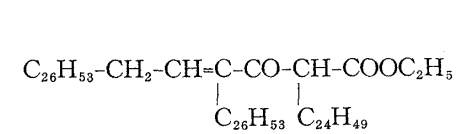


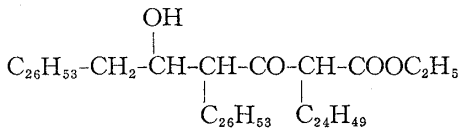
Fig. 2. Infrared Spectra (in Nujol) (Hilger H 800)
(a) Ethyl 2-tetracosyl-4-hexacosyl-3-oxo-5-acetoxydotriacontanoate (X), m.p. 64.5~65.5°
(b) 2-Tetracosyl-4-hexacosyl-3,5-dihydroxydotriacontanoic acid (II), m.p. 77.5°

It was assumed that (X) had greater steric hindrance due to larger molecule than that of ethyl 2,4-ditetracosyl-3-oxo-5-acetoxytriacontanoate.[1]

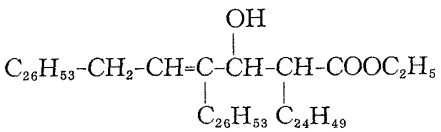
The neutral substance formed as a by-product during the reduction was separated into four kinds of compound from their ultraviolet and infrared spectra and their structures were assumed to be (XI) to (XIV):



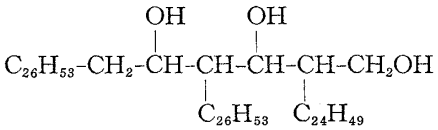
(XI)



(XII)



(XIII)



(XIV)

The properties of the mycolic acid prepared in the present work and that isolated by Lederer and others are compared in Tables I and II.

TABLE I.

	Isolated from Brévannes Strain[a]			Author's	
Mycolic acid	α	β	γ		
m.p. (°C)	56	76	57	82.5~83.5	77.5
OCH_3 (%)	1.48	1.97	1.12		
Formula	$C_{88}H_{176}O_4 \pm 5CH_2$ + $C_{87}H_{174}O_4 \pm 5CH_2$		$C_{88}H_{176}O_3$ + $C_{87}H_{174}O_3$	$C_{78}H_{156}O_4$	$C_{82}H_{164}O_4$
Functions	OH OH	OCH_3 OH	OH OCH_3	OH OH	OH OH

a) A. Aebi, J. Asselineau, E. Lederer: Bull soc. chim. biol., **35**, 661 (1953).

TABLE II.

Types of Mycolic Acids isolated from Human Strain of Tubercle Bacilli[a]

No.	Name of acid	Order of elution and strain	m. p. (°C)	Formula
1	3-Hydroxymycolanic acid	[1-R_1]	57~59	$C_{87}H_{174}O_3$
2	3-Hydroxymycolanoic acid	[2-Canetti]	62~64	$C_{87}H_{174}O_3$
3	3-Hydroxy-x-methoxymycolanoic acid	[1-Test]	55~56	$C_{88}H_{176}O_4$
4	3,x-Dihydroxymycolanoic acid	[2-R_1]	56~58	$C_{87}H_{174}O_4$
5	3-Hydroxy-x-oxomycolanoic acid	[3-R_1]	68~73	$C_{87}H_{172}O_4$
6	3-Hydroxy-x-methoxymycolanoic acid	[2-Test]	71~73	$C_{88}H_{176}O_4$
7	3,x-Dihydroxymycolanoic acid	[3-H-$_{37}$Rv]	70~72	$C_{87}H_{174}O_4$
8	3,x-Dihydroxymycolanoic acid	[5-Canetti]	81~82	$C_{87}H_{174}O_4$
9	x-Methoxymycolanoic acid	[3-Test]	59~60	$C_{88}H_{176}O_3$
10	3-Hydroxymycolanoic acid	[4-Test]	56~57	$C_{87}H_{174}O_3$

a) J. Asselineau, E. Lederer: "Chemical Structure and Biological Activity of Mycolic Acids," Ciba Foundation Symposium on Experimental Tuberculosis, **1955**, 14.

The mycolic acids (I) and (II) prepared by pure synthesis show generally higher melting point than that of natural mycolic acid, but it is interesting that the melting point of (I) is close to that of No. 8 in Table II, and that of (II), to β-mycolic acid in Table I.

The author expresses his deep gratitude to Prof. K. Yokota, Dean of this Faculty, and to Prof. T. Ishiguro of the University of Kyoto for their kind and unfailing guidance and encouragement throughout the course of this work. He is indebted to Prof. Y. Yamamura, University of Kyushu, and Dr. K. Matsui, National Sanatorium, Toneyama Hospital, for valuable advices, to Misses T. Makino and M. Sakakibara for technical assistance, to Dr. K. Okawa, Faculty of Science, University of Osaka, for infrared spectral measurements, and to the Analysis Center of the University of Kyoto and to Miss M. Honda of this Faculty for elemental analyses reported in this work

Experimental (All m.p.s uncorrected)

Methyl 2-Hexacosyl-3-oxotriacontanoate (IV)—Octacosanoic acid[3] was esterified with dehyd. MeOH and H_2SO_4 in benzene for 25~30 hrs. and the methyl ester, $b.p._{0.5}$ 235~240°, was recrystallized from acetone to crystals of m.p. 67~67.5° (m.p. 66.7°[6]). To the freshly distilled ester (12 g.) 35 cc. of dehyd xylene, 2 g. of NaH, and 1 drop of dehyd. MeOH were added, and the mixture was heated with stirring at 160~170° for 24 hrs. The cooled reaction mixture was acidified with glacial AcOH, extracted with warm ligroine (b.p. 80~100°), and the solvent was evaporated from the extract. The residue was recrystallized from hexane and afforded 8.5 g. (74%) of colorless granules, m.p. 71~72°. U. V. λ_{max}^{hexane} mμ (log ε): 222 (2.42), 267 (2.65). I. R. λ_{max}^{Nujol} μ: 5.72 (ester), 5.80 (-CO-). *Anal.* Calcd. for $C_{57}H_{112}O_3$: C, 80.99; H, 13.35; mol. wt., 845.5. Found: C, 81.06; H, 13.22; mol. wt.(Rast), 890.

Saponification of (IV); Formation of (V)—Saponification of 0.2 g. of (IV) by boiling with 2*N* ethanolic KOH for 20 hrs. and recrystallization of the product from AcOEt gave colorless leaflets, m.p. 101~102°. *Anal.* Calcd. for $C_{55}H_{110}O$: C, 83.89; H, 14.09. Found: C, 83.54; H, 13.99.

Oxime: Colorless crystalline powder, m. p. 87~89°. *Anal.* Calcd. for $C_{55}H_{111}ON$: C, 82.32; H, 13.94. Found: C, 82.49; H, 13.80.

2-Hexacosyl-3-hydroxytriacontanoic Acid (VI)—One gram of (IV) was reduced with 200 mg. of $NaBH_4$ in 50 cc. of dioxane-MeOH mixture (4:1) at 70~80° for 3 hrs. To this mixture, 2 cc. of 25% KOH solution was added, the mixture was refluxed for 2 hrs., and cooled. The crystals that precipitated out on acidification with 20% H_2SO_4 were collected by filtration and recrystallized from AcOEt to crystals of m.p. 88~91°. This substance (950 mg.) was chromatographed over 25 g. of alumina and separated into following fractions:

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc.)	Residue (mg.)
1	$CHCl_3$	110	9	Et_2O-AcOH (0.5%)	59
2	〃	78	10	〃	72
3	Et_2O	25	11	Et_2O-AcOH (1%)	56
4	〃	3	12	〃	30
5	Et_2O-AcOH (0.1%)	trace	13	Et_2O-AcOH (2%)	87
6	〃	21	14	〃	88
7	Et_2O-AcOH (0.2%)	9	15	Et_2O-AcOH (3%)	66
8	〃	14	16	〃 (200 cc.)	46
				Total	764 mg.

6) F. Francis, S. H. Piper: J. Am. Chem. Soc., **61**, 577(1938).

Fractions 7 to 11 were combined, rechromatographed over 10 g. of alumina, and the fraction obtained on elution with Et_2O containing 0.2% of AcOH was recrystallized twice from AcOEt to colorless crystalline powder (VIa), m.p. 93~94°. *Anal.* Calcd. for $C_{56}H_{112}O_3$: C, 80.70; H, 13.55. Found: C, 80.35; H, 13.37. Acetate: m.p. 75.5~76°. *Anal.* Calcd. for $C_{58}H_{114}O_4$: C, 79.56; H, 13.12. Found: C, 79.23; H, 12.94.

The fractions 12~16 were combined, rechromatographed over 10 g. of alumina, and the fraction obtained from elution with Et_2O containing 2% of AcOH was recrystallized twice from AcOEt to colorless crystalline powder (VIb), m.p. 89~90°. *Anal.* Calcd. for $C_{56}H_{112}O_3$: C 80.70; H, 13.55. Found: C, 80.45; H. 13.43.

Acetate: m.p. 74~75°. *Anal.* Calcd. for $C_{58}H_{114}O_4$: C, 79.56; H, 13.12. Found: C, 79.84; H. 13.18.

2-Hexacosyl-3-acetoxytriacontanoic Acid (VII)—The racemic compound (2.6 g.) of (VI) was acetylated with 35 cc. of pyridine and 25 cc. of Ac_2O, the product was purified through chromatography, and the residue obtained from a fraction eluted with Et_2O containing 0.2% of AcOH was recrystallized from petr. ether to colorless crystalline powder, m.p. 74~75°. *Anal.* Calcd. for $C_{58}H_{114}O_4$: C, 79.56; H, 13.12. Fonnd: C, 79.48; H, 13.01.

Ethyl 2-Tetracosyl-3-oxo-4-hexacosyl-5-acetoxydotriacontanoate (X)—(VIII) was obtained by reacting 3.37 g. of (VII) with $SOCl_2$ in benzene. Ethyl benzyl tetracosylmalonate (IX) (6 g.) was replaced with NaH and the product and (VIII) were sealed in a tube. The tube was heated at 130~140° for 8 hrs., the reaction mixture was acidified with glacial AcOH, and extracted with warm benzene. The benzene residue was treated in a usual manner and the residue was dissolved in 500 cc. of Et_2O. This solution was submitted to catalytic reduction over 10% Pd-C to effect decarboxylation and the residue was chromatographed over 100 g. of Florisil. The effluent was separated into the following fractions:

Fract. No.	Eluant (200 cc.)	Residue (mg.)	Fract. No.	Eluant (200 cc.)	Residue (mg.)
1	Petr. ether	560	11	Petr. ether-benzene (4:1)	330
2	Petr. ether-benzene (9:1)	65	12	Petr. ether-benzene (1:1)	357
3	〃	212	13	〃	373
4	〃	160	14	〃	380
5	〃	110	15	〃	200
6	〃	100	16	〃	115
7	Petr. ether-benzene (4:1)	98	17	Benzene	82
8	〃	442	18	〃	81
9	〃	437	19	〃	20
10	〃	215	20	〃	8
				Total	4345 mg.

The fractions 8 to 18 were combined and recrystallized from a mixture of a large amount of Et_2O and small amount of EtOH to 1.55 g. (31%) of a substance melting at 62~63°. This was rechromatographed over 50 g. of Florisil and the product was recrystallized from Et_2O to colorless microgranules, m.p. 64.5~65.5°. *Anal.* Calcd. for $C_{86}H_{168}O_5$ (X): C, 80.55; H, 13.21; mol. wt., 1282. Found: C, 80.39; H, 12.89; mol. wt. (Rast), 1222.

2-Tetracosyl-3,5-dihydroxy-4-hexacosyldotriacontanoic Acid (II)—To a solution of 1 g. of (X) dissolved in a mixture of 50 cc. of dioxane and 50 cc. of dehyd. EtOH, 400 mg. of $NaBH_4$ was added and the mixture was refluxed for 32 hrs. After cool, the mixture was acidified with glacial AcOH, extracted with benzene, the extract was washed with water, dried, and concentrated to about 100 cc. This concentrated solution was refluxed with 75 cc. of MeOH and 7.5 cc. of 5% KOH solution, and the product was chromatographed over 25 g. of alumina.

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc.)	Residue (mg.)
1	Benzene	340	10	Et_2O-AcOH (1%)	3
2	Et_2O	235	11	〃	8
3	〃	15	12	〃	5
4	Et_2O-AcOH (0.2%)	20	13	〃	2
5	〃	10	14	Et_2O-AcOH (2%)	20
6	Et_2O-AcOH (0.5%)	8	15	〃	6
7	〃	7	16	Et_2O-AcOH (3%) (200 cc.)	5
8	〃	10	17	Et_2O-AcOH (5%) (200 cc.)	1
9	〃	2			
				Total	697 mg.

Fraction 14 was recrystallized from Et_2O to colorless crystalline powder, m.p. 77.5°. I. R. $\lambda_{max}^{Nujol}\mu$: 3.0 (OH), 5.86 (COOH). *Anal.* Calcd. for $C_{82}H_{164}O_4$ (II): C, 81.11; H, 13.62. Found: C, 80.97; H, 13.59.

This substance was esterified with CH_2N_2 in Et_2O and the product was recrystallized from Me_2CO-Et_2O mixture to colorless waxy substance, m.p. 68~70°. *Anal.* Calcd. for $C_{83}H_{166}O_4$: C, 81.16; H, 13.62; mol. wt., 1228. Found: C, 81.02; H, 13.68; mol. wt. (Rast), 1256, 1170.

Separation of the Neutral Substances—Fractions 1 to 3 from the above chromatography were combined and rechromatographed over 20 g. of alumina, separating the effluent into following fractions:

Fract. No.	Eluant (100 cc.)	Residue (mg.)	Fract. No.	Eluant (100 cc.)	Residue (mg.)
1	Petr. ether	40	11	Petr. ether-benzene (1:1)	60
2	〃	25	12	〃	65
3	〃	20	13	〃	22
4	〃	27	14	Benzene	50
5	Petr. ether-benzene (9:1)	30	15	〃	60
6	〃	3	16	Benzene-Et_2O (3:1)	22
7	〃	2	17	〃	30
8	Petr. ether-benzene (4:1)	32	18	〃	15
9	〃	22	19	Benzene-Et_2O (1:1)	3
10	〃	27	20	〃	2
			21	Et_2O	trace
				Total	557 mg.

Fraction 1 was recrystallized from Et_2O-EtOH to colorless crystalline powder, m.p. 71~73°. U.V. λ_{max}^{hexane} mμ (log ε): 222 (2.74), 267 (2.43), 271 (2.57). I. R. λ_{max}^{Nujol} μ: 5.80 (ester), 5.88 (-CO-), 6.10 (-C=C-). *Anal.* Calcd for $C_{84}H_{164}O_3$ (XI): C, 82.55; H, 13.53. Found: C, 82.45; H, 13.73.

Fraction 12 was recrystallized from Et_2O-EtOH to colorless crystalline powder, m.p. 69~70.5°. U.V. λ_{max}^{hexane} mμ (log ε): 222 (2.64), 267 (2.34), 271 (2.40). I.R. λ_{max}^{Nujol} μ: 3.0 (OH), 5.75 (ester), 5.82 (-CO-). *Anal.* Calcd. for $C_{84}H_{166}O_4$ (XII): C, 81.35: H, 13.49. Found: C, 81.64; H, 13.83.

Fraction 14 was recrystallized from Et_2O-EtOH to colorless crystalline powder, m.p. 72~74°. U.V. λ_{max}^{hexane} mμ (log ε): 222 (2.46), 266 (1.85), 270 (2.08). I. R. λ_{max}^{Nujol} μ: 3.0 (OH), 5.75 (ester), 6.10 (-C=C-). *Anal.* Calcd. for $C_{84}H_{166}O_3$ (XIII): C, 82.41; H, 13.67. Found: C, 82.47; H, 13.82.

Fraction 18 was recrystallized from Et_2O-EtOH to colorless crystalline powder, m.p. 72.5~73°. U. V. λ_{max}^{hexane}: Nil. I. R. λ_{max}^{Nujol}: 3.0 μ (OH). *Anal.* Calcd. for $C_{82}H_{166}O_3$ (XIV): C, 82.06; H, 13.94. Found: C, 81.75; H, 13.66.

Summary

Condensation of 2-hexacosyl-3-acetoxytriacontanoic acid chloride and ethyl benzyl tetracosylmalonate gave ethyl 2-tetracosyl-3-oxo-4-hexacosyl-5-acetoxydotriacontanoate whose reduction with sodium borohydride finally afforded the objective 2-tetracosyl-3, 5-dihydroxy-4-hexacosyldotriacontanoic acid, $C_{82}H_{164}O_4$.

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89. Tetsuji Kametani, Keiichiro Fukumoto, and Yukio Nomura: Studies on the Syntheses of Heterocyclic Compounds. XLV.* Synthesis of the Methyl Derivatives of Heterocyclic Compounds by the Hydrogenolysis of their Phenylurethans from Primary Alcohol.

(*Pharmaceutical Faculty, University of Osaka***)

Many methods are known for obtaining methyl derivatives by the reduction of a hydroxyl group in primary alcohols, such as by red phosphorus and hydrogen iodide,[1,2] sodium and alcohol,[3] zinc dust distillation,[4] or sodium and ammonia,[5] but these methods

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