proton), 5.47 (m, 1 H, $W_{1/2}$ = 7 Hz, 6α proton), and 6.01 ppm (1 H, C_4-vinyl proton; no optical activity over the range 250–450 mμ.

d-**17β-Acetoxy-13β-ethyl-6β,10β-dihydroxygon-4-en-3-one** (*d*-**XVIIIb**).—The fraction eluted from the silica gel column shown to contain the dihydroxylated transformation product XVIIIa by thin layer chromatography was evaporated under vacuum and acetylated with acetic anhydride–pyridine in the usual manner. After recrystallization from hexane–diethyl ether, there was obtained 7 mg of the 17β-monoacetate *d*-XVIIIb, mp 174–176°; uv λ_{max} 233 mμ (ε 13,800); $\lambda_{max}^{0.066\ N\ NaOH}$ 238 (ε 5600) and 275 mμ (ε 2300); ir $\tilde{\nu}_{max}^{KBr}$ 3320 (br), 1730, 1680, and 1630 cm^{-1}; $\tilde{\nu}_{max}^{CCl_4}$ 3630, 3480 (br), 1730, and 1670 cm^{-1}; ORD $[\alpha]_{430}$ +65°, $[\alpha]_{375}$ −308°, $[\alpha]_{362}$ −356°, $[\alpha]_{336}$ +600°. An insufficient sample was available for combustion analyses.

Chromatographic Relationships.—Chromatographic data showing homolog relationships between certain products are given in order as follows: gas chromatographic relative retention times on 3% QF-1, followed by thin layer chromatographic relative mobilities using ethyl acetate for irrigation with hydroxy steroids and ethyl acetate–chloroform (1:1) for irrigation with steroid acetates. Mobility data are expressed in terms of *dl*-Ia as unity for estranes and in terms of *dl*-IIa as unity for the 13β-ethylgonane homologs, except for the thin layer mobility data on the acetates, where *dl*-Ib served as unit marker for the estranes and *dl*-IIb for the 13β-ethylgonanes. A homologous relationship is demonstrated for those pairs showing the same retention data and thin layer mobility data, both as the free alcohols and as the acetates. Mobility data follow: *dl*-Ia, 1.00, 1.00; *dl*-IIa, 1.00; 1.00; *d*-IIIa, 1.30, 0.84; *dl*-XIVa, 1.33, 0.86; *d*-Va, 1.77, 0.52; *d*-XVa, 1.83, 0.49; *dl*-VIIa, 1.46, 0.65; *dl*-XVIa, 1.52, 0.69; *l*-VIIIa, 1.93, 0.32; *l*-XVIIa, 2.06, 0.31; *dl*-VIa, 3.21, 0.36; *d*-XVIIIa, 3.21, 0.31; *dl*-IVa, 1.93, 0.36; *l*-IXa, 2.22, 0.52; *dl*-Ib, 1.63, 1.00; *dl*-IIb, 1.71, 1.00; *d*-IIIb, 2.13, 0.64; *dl*-XIVb, 2.14, 0.63; *d*-Vb, 3.27, 0.61; *d*-XVb, 3.58, 0.56; *dl*-VIIb, 3.44, 0.97; *dl*-XVIb, 3.44, 0.97; *l*-VIIIb, 3.08, 0.75; *l*-XVIIb, 3.08, 0.75; *dl*-VIb, 2.98, 0.39; *d*-XVIIIb, 4.89, 0.34; *dl*-IVb, 4.87, 0.78; *l*-IXa, 3.67, 0.54.

Registry No.—*dl*-Ia, 5972-58-7; *dl*-IIa, 793-54-4; *d*-IIIb, 21317-53-3; *d*-IVa, 4075-17-6; *dl*-IVa, 21317-55-5; *d*-IVb, 21317-56-6; *dl*-IVb, 21317-57-7; *d*-Va, 2162-37-0; *d*-Vb, 21317-59-9; *d*-VIa, 21317-60-2; *dl*-VIa, 21317-61-3; *dl*-VIb, 21317-62-4; *dl*-VIIa, 21317-63-5; *d*-VIIb, 21317-64-6; *l*-VIIIb, 21317-65-7; *dl*-IIb, 21317-66-8; *l*-IXa, 21317-67-9; *dl*-IXa, 21317-68-0; *l*-IXb, 21317-69-1; *l*-XI, 21317-70-4; *l*-XII, 21317-71-5; *dl*-XIII, 21317-72-6; *dl*-XIVa, 6615-05-0; *dl*-XIVb, 6615-06-1; *d*-XVa, 21317-75-9; *d*-XVb, 21317-76-0; *dl*-XVIb, 6615-11-8; *l*-XVIIa, 21321-83-5; *l*-XVIIb, 21321-84-6; *d*-XVIIIb, 21321-85-7; *l*-XIX, 21321-86-8.

Acknowledgment.—The authors are indebted to Dr. Bruno Jirgenson, M. D. Anderson Hospital, Houston, for generous aid in recording optical rotatory dispersion, and to Dr. Edward S. Lewis, Rice University, Houston, for aid in obtaining proton spectra; to Drs. J. de Flines and A. F. Marx, Royal Netherlands Fermentation Industries, Delft, and to Dr. W. F. Johns, G. D. Searle Co., Chicago, for reference steroid samples; and to Dr. Rudolph Wiechert, Schering AG, Berlin, for generous supplies of racemic 13β-ethylgonane samples.

Synthesis of Racemic Phytosphingosine and the *lyxo* Isomer

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Received February 20, 1969

dl-erythro-2-Benzylamino-3-hydroxy-4-ethylenedioxyoctadecanoic acid (**15**), prepared from *dl-trans*-2,3-epoxy-4-ethylenedioxyoctadecanoic acid (**14**) and benzylamine, was converted into methyl *dl-erythro*-2-benzylamino-3-hydroxy-4-oxooctadecanoate hydrochloride (**19**). The ester hydrochloride **19** was reduced with lithium aluminum hydride to yield *dl*-2-benzylamino-1,3,4-trihydroxyoctadecane (**20a,b**), and, from the *dl-ribo* isomer (**20a**), racemic phytosphingosine (**25a**) was obtained by catalytic hydrogenolysis. The same compound **25a** and the diastereoisomeric *dl-lyxo* compound (**25b**) were prepared from *dl*-2-benzylamino-3,4-dihydroxyoctadecanoic acids (**23a,b**) and their lactones (**24a,b**) by reduction with lithium aluminum hydride followed by hydrogenolysis.

In 1963, Carter and Hendrickson[1] established by degradative studies that phytosphingosine was D-*ribo*-2-amino-1,3,4-trihydroxyoctadecane,[2] and the syntheses of this optically active aminotriol from sphingosine[3] and sugars[4] have been published. Also, a total synthesis to prepare the stereoisomers of racemic 2-amino-1,3,4-trihydroxyoctadecane has been reported,[5] but the configurations of the products were not defined. The present paper describes the syntheses of racemic phytosphingosine and its *lyxo* isomer.

The process is based on the method described previously for a synthesis of racemic dihydrosphingosine,[6] *i.e.*, on the stereospecific reaction of *dl-trans* glycidic acid with benzylamine to yield *dl-erythro*-2-benzylamino-3-hydroxy acid.

1-Bromo-2-hexadecanone (**3**) was prepared from *n*-pentadecanoyl chloride (**1**) by treatment with diazomethane followed by gaseous hydrogen bromide. The reaction of the α-bromo ketone **3** with 2 mol equiv of carbomethoxymethylenetriphenylphosphorane in boiling benzene[7] gave methyl 4-oxo-*trans*-2-octadecenoate (**4**). That the keto ester **4** has the *trans* configuration was proved by the infrared absorption spectrum and by an independent synthesis from 4-ethylenedioxy-*trans*-2-octadecenoic acid (**8**). This ketal acid **8** was prepared

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(2) For the historical aspects of the isolation and the structure determination of phytosphingosine, see, J. Gigg, R. Gigg, and C. D. Warren, *J. Chem. Soc., C*, 1872 (1966), and references cited therein.

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(4) (a) R. Gigg, C. D. Warren, and J. Cunningham, *Tetrahedron Lett.*, 1303 (1965); ref 2; (b) J. Gigg and R. Gigg, *J. Chem. Soc., C*, 1876 (1966); (c) R. Gigg and C. D. Warren, *ibid.*, 1879 (1966).

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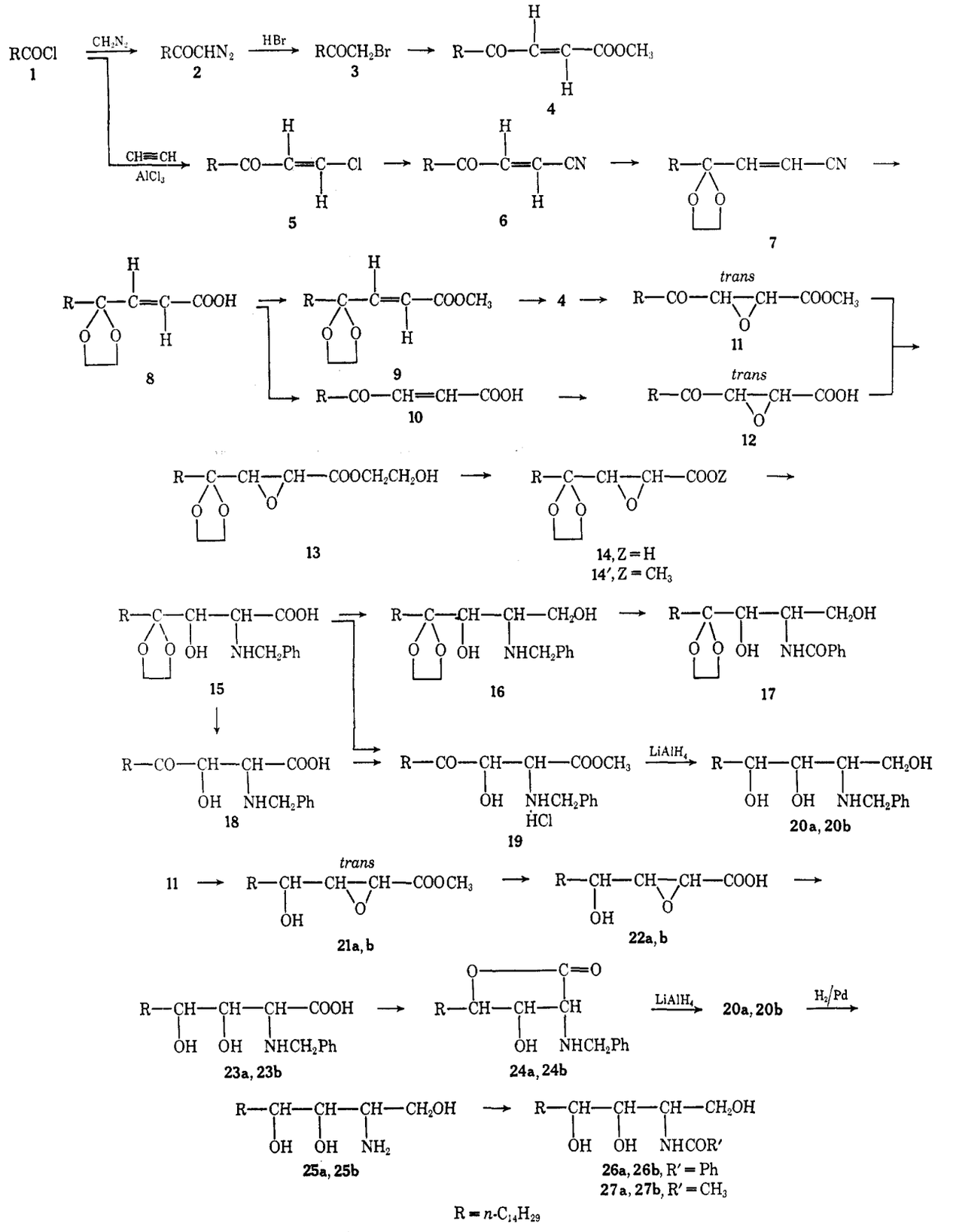

by the reaction of the acid chloride **1** with acetylene[8,9] *via trans*-β-chlorovinyl ketone (**5**) and *trans*-β-cyanovinyl ketone (**6**).[8] A direct saponification of the cyanide **6** was not successful. Ketalization of the carbonyl group of the cyanide **6** with ethylene glycol followed by saponification of the nitrile function yielded the ketal acid **8**, the methyl ester of which, on acidic hydrolysis, gave the *trans*-keto ester **4**. Epoxidation[10] of the *trans*-keto ester **4** or the keto acid (**10**) prepared from the ketal acid **8** by acidic hydrolysis afforded the keto epoxy ester (**11**) or the keto epoxy acid (**12**), respectively. On treatment of **12** with benzylamine, however, the de-

(8) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964).
(9) S. Wakayama, S. Itoh, and H. Suginome, *Nippon Kagaku Zasshi*, **76**, 94 (1955); *Chem. Abstr.*, **51**, 17727*g* (1957).
(10) E. C. Kornfeld, E. J. Fornefeld, G. B. Kline, M. J. Mann, D. E. Morrison, R. G. Jones, and R. B. Woodward, *J. Amer. Chem. Soc.*, **78**, 3087 (1956).

sired *dl-erythro*-2-benzylamino-3-hydroxy-4-oxooctadecanoic acid (**18**) was not obtained. Ketalization of the keto epoxy acid **12** or its methyl ester **11** with ethylene glycol yielded the ketal epoxy β-hydroxyethyl ester (**13**), which was saponified[11,12] to afford the ketal epoxy acid **14**. The nuclear magnetic resonance spectra of these compounds **11** and **14**, showed the absorptions of oxirane hydrogens as AB quartet patterns with a coupling constant of 2 Hz,[12,13] and the infrared spectrum of the ketal epoxy acid (**14**) exhibited the carbonyl doublet peaks at 1750 and 1726 cm^{-1}.[14] It was proved, therefore, that the configuration of the oxirane ring is *trans*.

Reaction of the ketal epoxy acid **14** or its sodium salt with benzylamine gave *dl-erythro*-2-benzylamino-3-hydroxy-4-ethylenedioxyoctadecanoic acid (**15**) in almost quantitative yield. In order to confirm that the benzylamino group was introduced selectively at the 2-carbon atom of the ketal *trans* glycidic acid **14**, the ketal benzylamino acid **15** was reduced with lithium aluminum hydride to furnish the ketal benzaylaminodiol (**16**), which was transformed into *dl-erythro*-2-benzamido-1,3-dihydroxy-4-ethylenedioxyoctadecane (**17**) by catalytic hydrogenolysis followed by benzoylation.[15] The N-benzoyl derivative **17** showed no oxidation on treatment with periodate,[16] so that the 1,2-diol structure was excluded. The ketal benzylamino acid **15** was converted into the ester hydrochloride **19**, and the purity of **19** was established by thin layer chromatography. The nmr spectrum was consistent with the assigned structure.

The carbonyl group of the keto epoxy ester **11** was selectively reduced with sodium borohydride[10] to afford a diastereoisomeric mixture of the hydroxy epoxy esters **21a** and **21b**, which was saponified to the sodium salts. The diastereoisomeric mixture of the sodium salts was treated with benzylamine to give a mixture of *dl-ribo*-2-benzylamino-3,4-dihydroxyoctadecanoic acid (**23a**) and the *dl-lyxo* isomer (**23b**). The separation of the diastereoisomers was performed by utilizing the insolubility of the *ribo* isomer **23a** in hot ethanol. The reduction of **12** by Meerwein–Ponndorf–Verley's method[17] instead of sodium borohydride gave a similar result. Lactonization of **23a** and **23b** was carried out individually, and the resulting lactones (**24a, 24b**) were reduced with lithium aluminum hydride to yield the respective benzylaminotriols (**20a, 20b**), which were debenzylated to *dl-ribo* aminotriol (**25a**) and its *dl-lyxo* isomer (**25b**) by catalytic hydrogenolysis. It was proved that, in the lactonization process, no epimerization occurred at the γ-carbon atom of the benzylamino acids **23a** and **23b**,[18] since the same benzylaminotriols **20a** and **20b** were obtained by reduction of the benzylamino acids **23a** and **23b** with lithium aluminum hydride. Reduction of the ester hydrochloride **19** with lithium aluminum hydride also gave a mixture of the benzylaminotriols **20a** and **20b**. On recrystallization of the *dl-ribo*-aminotriol **25a** from hot acetone, there was obtained the racemic acetone compound (**28a**)[15] as white plates, but the *dl-lyxo* isomer **25b** did not give the acetonide under the same reaction condition. The mass and infrared spectra of the N-benzoyl derivatives[15] were compared with those of natural N-benzoyl phytosphingosine[19] isolated from yeast, and it was proved that the prepared *dl-ribo*-aminotriol **25a** was racemic phytosphingosine.

Palameta and Zambeli[20] described a synthesis of 4-hydroxy-*trans*-2-octadecenoic acid (**29**) by allylic bromination of ethyl *trans*-2-octadecenoate followed by hydrolysis. The product was reported to exhibit two carbonyl absorption bands at 1750 and 1690 cm^{-1}, which led us to suspect that the product might be contaminated with 2-hydroxy-3-octadecenoic acid, an allylic rearrangement product. The hydroxy acid prepared in this laboratory from *trans*-2-octadecenoic acid, as well as from its methyl ester, by similar reaction sequences had melting point and double carbonyl absorption maxima as reported. In order to destroy any α-hydroxy acid present, the material was oxidized with lead tetraacetate.[21] The infrared spectrum of the purified acid **29** showed only a single carbonyl absorption at 1685 cm^{-1} and a *trans* double bond absorption at 980 cm^{-1}. The absorption maximum at 1755 cm^{-1} found in the crude product should therefore be attributed to α-hydroxy-β,γ-unsaturated acid. α-Hydroxypalmitic acid[22] prepared in this laboratory, for example, had a carbonyl stretching band at 1755 cm^{-1}. Alternatively, sodium borohydride reduction of the keto acid **10** and Grignard reaction of *n*-tetradecylmagnesium bromide with fumaraldehydic acid methyl ester followed by saponification gave the same hydroxy acid **29**. Attempted epoxidations of **29** to the hydroxy epoxy acids **22a** and **22b** in several ways were unsuccessful.

Experimental Section[23]

1-Bromo-2-hexadecanone (3).—A solution of 52.2 g (0.2 mol) of *n*-pentadecanoyl chloride (**1**)[24] in 100 ml of anhydrous ether was added dropwise at 0° to a stirred diazomethane solution (0.6 mol), and after stirring for an additional 3 hr at 0°, the mixture was kept overnight at room temperature. Recrystallization of the product from petroleum ether (bp 35–50°) gave 1-diazo-2-hexadecanone (**2**): ir (Nujol) 3090 (CH), 2120 (N_2), and 1620 cm^{-1} (C=O).

Dry hydrogen bromide gas was bubbled through the solution of the diazo ketone **2** in 300 ml of ether under reflux until the

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(23) Infrared spectra were measured on a Shimazu IR-27B spectrophotometer as Nujol mulls. Nmr spectra were determined as solutions in $CDCl_3$ with TMS as an internal standard on a Japan Electron Optics Laboratory C-60-H apparatus. Uv spectra were measured using a Hitachi recording spectrophotometer EPS-2. The purity of the compounds was established by thin layer chromatography using "Kieselgel G nach Stahl." Microelemental analyses were performed by Mrs. K. Huzimoto of this laboratory on a Yanagimoto Autoanalyzer CHN Corder MT-1. Table I lists the new compounds prepared in this experiment. All melting points are corrected.

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TABLE I
LIST OF NEW COMPOUNDS

Compd	Mp, °C	Formula	Analyses: Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2	61.5–62.5	$C_{16}H_{30}N_2O$	72.13	11.35		72.38	11.34	
3	61	$C_{16}H_{31}BrO$	60.18	9.79		60.39	9.81	
4	76–77	$C_{19}H_{34}O_3$	73.50	11.04		73.39	11.01	
5	51–52	$C_{17}H_{31}ClO$	71.16	10.90		71.43	10.69	
6	52.5–53	$C_{18}H_{31}NO$	77.92	11.26		77.88	11.51	
7	64.5–65.5	$C_{20}H_{35}NO_2$	74.71	10.97		74.59	10.83	
8	84–85	$C_{20}H_{36}O_4$	70.54	10.66		70.32	10.45	
9	39–40	$C_{21}H_{38}O_4$	71.14	10.80		70.91	10.92	
10	118	$C_{18}H_{32}O_3$	72.92	10.88		73.09	10.66	
11	80	$C_{19}H_{34}O_4$	69.90	10.50		69.99	10.64	
12	115	$C_{18}H_{32}O_4$	69.19	10.32		68.94	10.46	
13	69	$C_{22}H_{40}O_6$	65.97	10.07		66.01	10.36	
14	75–76	$C_{20}H_{36}O_5$	67.38	10.18		67.17	10.37	
14′	40–41	$C_{21}H_{38}O_5$	68.07	10.34		67.90	10.31	
15	169–170	$C_{27}H_{45}NO_5$	69.94	9.78	3.02	70.15	10.03	2.94
16	60–61	$C_{27}H_{47}NO_4$	72.12	10.54	3.12	72.15	10.65	3.19
17	93–94.5	$C_{27}H_{45}NO_5$	69.94	9.78	3.02	69.84	9.87	2.97
18	182 dec	$C_{25}H_{41}NO_4$	71.56	9.85	3.34	71.36	9.76	3.18
19	140 dec	$C_{26}H_{44}ClNO_4$	66.43	9.43	2.98	66.14	9.51	2.81
20a	76–78	$C_{25}H_{45}NO_3$	73.66	11.13	3.44	73.45	11.40	3.38
20b	78–79	$C_{25}H_{45}NO_3$	73.66	11.13	3.44	73.78	11.18	3.20
21a,b	66–67	$C_{19}H_{36}O_4$	69.47	11.05		69.34	11.23	
22a,b	88–96	$C_{18}H_{34}O_4$	68.75	10.90		68.63	11.07	
23b	185 dec	$C_{25}H_{43}NO_4$	71.22	10.28	3.32	71.29	10.35	3.28
24a	135–136	$C_{25}H_{41}NO_3$	74.40	10.24	3.47	74.39	10.29	3.33
24b	99–101	$C_{25}H_{41}NO_3$	74.40	10.24	3.47	74.18	10.04	3.41
25a	149–151	$C_{18}H_{39}NO_3$	68.09	12.38	4.41	67.87	12.33	4.21
25b	135–137	$C_{18}H_{39}NO_3$	68.09	12.38	4.41	68.05	12.34	4.44
26a	121–122	$C_{25}H_{43}NO_4$	71.22	10.28	3.32	71.13	10.48	3.25
26b	117–118	$C_{25}H_{43}NO_4$	71.22	10.28	3.32	71.10	10.50	3.54
27a	110–111	$C_{20}H_{41}NO_4$	66.81	11.49	3.90	66.70	11.52	3.88
27b	117–118	$C_{20}H_{41}NO_4$	66.81	11.49	3.90	66.51	11.36	3.71
28a	143–145	$C_{21}H_{43}NO_3$	70.53	12.12	3.92	70.53	12.18	4.08
29	76.5–77	$C_{18}H_{34}O_3$	72.43	11.48		72.17	11.53	
29′	64.5	$C_{18}H_{33}BrO_2$	59.83	9.20		59.96	9.18	

evolution of nitrogen ceased. From the ether solution, there was obtained 51.5 g (80% yield from **1**) of the α-bromo ketone **3**, as recrystallized from hexane; ir (Nujol) 1730 cm^{-1} (C=O).

Methyl 4-Oxo-*trans*-2-octadecenoate (4).—Into a boiling solution of 80.2 g (0.24 mol) of carbomethoxymethylenetriphenylphosphorane[25] in 500 ml of anhydrous benzene was added a solution of 38.3 g (0.12 mol) of the α-bromo ketone **3** in 300 ml of anhydrous benzene, and the mixture was heated under reflux for 3 hr. After 20 g (0.13 mol) of methyl bromoacetate was added, the heating was continued for an additional 2 hr.[7] The mixture was poured into ice-cooled dilute hydrochloric acid and the keto ester **4** was obtained in 82% yield as white plates, recrystallized from methanol: ir (Nujol) 3080 and 995 (*trans* CH=CH), 1740 (ester C=O), and 1665 cm^{-1} (C=O); R_f = 0.50 in ethyl acetate–chloroform (1:5).

The same compound **4** was obtained by acidic hydrolysis of the ketal ester **9** in 61% yield.

***trans*-β-Chlorovinyl *n*-Tetradecyl Ketone (5).**—The reaction of *n*-pentanedecanoyl chloride with acetylene was carried out according to the procedure of Benson and Pohland.[8] Recrystallization of the product from methanol gave the chloro ketone **5** in 72% yield: ir (Nujol) 1660 (C=O), 3090, 1597, and 948 cm^{-1} (*trans* CH=CH); uv λ_{max} (hexane) 228 mμ (ε 13,900).

***trans*-β-Cyanovinyl *n*-Tetradecyl Ketone (6).**—The keto nitrile **6** was prepared in 57% yield according to the procedure of Benson and Pohland,[8] except that the ammonium salt in toluene was directly used for the next reaction with potassium cyanide and the product **6** was recrystallized from methanol: ir (Nujol) 2230 (CN), 1705 (C=O), 3070, 1615, and 980 cm^{-1} (*trans* CH=CH); uv λ_{max} (hexane) 228 mμ (ε 14,700).

Semicarbazone: mp 151–152° (from ethanol). *Anal.* Calcd for $C_{19}H_{34}N_4O$: C, 68.22; H, 10.25. Found: C, 68.36; H, 10.48.

***trans*-β-Cyanovinyl *n*-Tetradecyl Ketone Ethylene Ketal (7).**—According to the ordinary method, ethylene ketal **7** was obtained from **6** in 85% yield as recrystallized from methanol: ir (Nujol) 2230 (CN), 3030, 1630, and 985 cm^{-1} (*trans* CH=CH).

4-Ethylenedioxy-*trans*-2-octadecenoic Acid (8).—A mixture of 7.0 g (0.0216 mol) of **7**, 4.8 g (0.0856 mol) of potassium hydroxide, and 1 ml of water in 65 ml of ethylene glycol was refluxed for 6 hr, and the ketal acid **8** was obtained in 88% yield as recrystallized from hexane: ir (Nujol) 1680 (acid C=O), 1640, and 980 cm^{-1} (*trans* CH=CH).

Methyl 4-Ethylenedioxy-*trans*-2-octadecenoate (9).—An ether or an acetone–methanol solution of the ketal acid **8** was treated with 1 mol equiv of diazomethane or methyl iodide,[26] respectively, to give **9** as white needles, recrystallized from methanol: ir (Nujol) 1725 (ester C=O), 1660, and 1000 cm^{-1} (*trans* CH=CH).

4-Oxo-*trans*-2-octadecenoic Acid (10).—Hydrolysis of **8** with *p*-toluenesulfonic acid in 50% aqueous ethanol furnished the keto acid **10** in 97% yield as recrystallized from ethyl acetate: ir (Nujol) 1685 (acid C=O), 1660 (C=O), 3050, 1625, and 1000 cm^{-1} (*trans* CH=CH); uv λ_{max} (ethanol) 222 mμ (ε 10,800). When the heating was continued for 6 hr, the yield was lowered to 41%.

Methyl *dl*-*trans*-2,3-Epoxy-4-oxooctadecanoate (11).—Epoxidation[10] was carried out in a modified condition. To a solution of 19.5 g (0.0628 mol) of **4** in 1.7 l. of acetone were added 80 ml of 30% aqueous hydrogen peroxide and 32 ml of 5% sodium carbonate solution, and the mixture was stirred for 36 hr at 45°,

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during which time, at 5-hr intervals, three 20-ml portions of 30% hydrogen peroxide were added. After removal of the solvent *in vacuo* and addition of 500 ml of dilute sulfuric acid, the product was extracted with ether–chloroform. The combined extracts were washed with water and treated with diazomethane solution in order to esterify any saponified product present. Evaporation of the solvent and recrystallization of the residue from hexane yielded 10.0 g (48.7%) of the keto epoxy ester **11**: ir (Nujol) 1765 (ester C=O), 1720 (C=O), 1230, and 885 cm^{-1} (epoxy); nmr ($CDCl_3$) δ 2.35 (m, 2), 3.50 (d, 1, J = 2 Hz), 3.60 (d, 1, J = 2 Hz), and 3.72 (s, 3); R_f = 0.45 in ethyl acetate–chloroform (1:5).

dl-trans-**2,3-Epoxy-4-oxooctadecanoic Acid (12).**—Epoxidation was carried out as above with a solution of 3.0 g (0.0101 mol) of **10** in 500 ml of methanol and 250 ml of acetone. Recrystallization of the product from ethyl acetate gave 1.3 g (41%) of **12**: ir (Nujol) 1720 (C=O, acid C=O), 1255, and 890 cm^{-1} (epoxy).

The same compound **12** was obtained in 90% yield by saponification of the keto epoxy ester **11** with an alcoholic solution of sodium hydroxide.

β-Hydroxyethyl *dl-trans*-**2,3-Epoxy-4-ethylenedioxyoctadecanoate (13).**—A mixture of 2.0 g (0.00613 mol) of the keto epoxy ester **11**, 50 ml of ethylene glycol, and 4.0 g (0.0232 mol) of *p*-toluenesulfonic acid in 200 ml of benzene was stirred under reflux for 24 hr using a water separator. After cooling, the solution was poured into a cold sodium bicarbonate solution, and the separated benzene solution was washed with water. Evaporation of the solvent and recrystallization from hexane gave 2.2 g (90%) of the ketal epoxy ester **13**: ir (Nujol) 3460 (OH), 1740 (ester C=O), 1260, and 905 cm^{-1} (epoxy).

Ketalization of the keto epoxy acid **12** under the similar reaction condition afforded the same compound in 94% yield.

dl-trans-**2,3-Epoxy-4-ethylenedioxyoctadecanoic Acid (14).**—Saponification of 2.2 g of **13** was carried out with alcoholic sodium hydroxide to give 2.0 g (96%) of the sodium salt of *trans* glycidic acid, from which 1.8 g (92% yield based on **13**) of the ketal epoxy acid **14** was obtained as recrystallized from hexane: ir (Nujol) 1750 and 1725 (*trans* glycidic acid), 1265 and 900 cm^{-1} (epoxy); nmr ($CDCl_3$) δ 3.25 (d, 1, J = 2 Hz), 3.40 (d, 1, J = 2 Hz), 3.95 (m, 4), and 10.10 (s, 1); R_f 0.51 in hexane–ether–acetic acid (80:20:25).

On treatment with diazomethane, **14** gave the methyl ester (**14'**) in 93% yield as recrystallized from methanol: ir (Nujol) 1750 (ester C=O), 1260, and 905 cm^{-1} (epoxy); R_f 0.50 in hexane–ether–acetic acid (80:20:30).

dl-erythro-**2-Benzylamino-3-hydroxy-4-ethylenedioxyoctadecanoic Acid (15).**—A mixture of 2.47 g (0.00693 mol) of **14** and 2.0 g (0.0187 mol) of benzylamine in 200 ml of water was stirred at room temperature for 1 hr and then heated under reflux for 3 hr. After cooling, the reaction mixture was acidified to pH 4 with dilute hydrochloric acid and the precipitate was collected, washed with water, and recrystallized from ethanol to yield 2.98 g (92.5%) of the ketal benzylamino acid **15**: ir (Nujol) 3330 (OH), 3000–2300 and 1260 (amino acid), 750, and 695 cm^{-1} (monosubstituted benzene); R_f 0.40 in chloroform–methanol–acetic acid (50:5:5).

On treatment with benzylamine, the sodium salt of *trans* glycidic acid, which was obtained from **13** by saponification, gave the same compound **15** in 88% yield.

dl-erythro-**2-Benzylamino-1,3-dihydroxy-4-ethylenedioxyoctadecane (16).**—A mixture of 1.50 g of **15** and 0.7 g of lithium aluminum hydride in 200 ml of anhydrous ether was refluxed for 6 hr. After excess lithium aluminum hydride was destroyed by water, the reaction mixture was made alkaline with 20% potassium hydroxide solution and extracted with ether, and there was obtained 1.10 g (75.6%) of the product **16**, as recrystallized from hexane: ir (Nujol) 3370 (OH, NH), 750, and 695 cm^{-1} (monosubstituted benzene).

dl-erythro-**2-Benzamido-1,3-dihydroxy-4-ethylenedioxyoctadecane (17).**—A solution of 1.0 g (0.00222 mol) of **16** in 200 ml of ethanol was stirred in an autoclave under hydrogen at 13 atm with 2.0 g of 5% palladium on carbon for 12 hr at 100°. Removal of the catalyst and evaporation of the solvent afforded 0.45 g (56%) of the ketal aminodiol: mp 78–80° (from hexane); ir (Nujol) 3500 (NH) and 3350–2700 cm^{-1} (hydroxy).

The ketal aminodiol was treated with benzoyl chloride according to the procedure of Carter and coworkers.[15] The product **17** was recrystallized from hexane: ir (Nujol) 3390 (OH), 3300, 1645, and 1550 cm^{-1} (amide). This N-benzoyl derivative **17** showed negative reaction with the periodate oxidation reagent.[16]

dl-erythro-**2-Benzylamino-3-hydroxy-4-oxooctadecanoic Acid (18).**—Hydrolysis was carried out by several ways, and it was found that the best condition was as follows. A mixture of 4.8 g (0.0104 mol) of **15**, 30 ml of concentrated hydrochloric acid, 300 ml of water, and 100 ml of acetic acid was refluxed until the clear solution turned cloudy. The solution was cooled, 500 ml of water was added, and the precipitate was filtered and washed with methanol to give 4.0 g (92%) of the product **18**, from which an analytical sample was obtained by recrystallization from dimethylformamide: ir (Nujol) 3200 (OH), 3050–2300 and 1620 (amino acid), 1720 (C=O), 750, and 690 cm^{-1} (monosubstituted benzene).

Methyl *dl-erythro*-**2-Benzylamino-3-hydroxy-4-oxooctadecanoate Hydrochloride (19).**—The keto benzylamino acid **18** was esterified by refluxing in methanol containing hydrogen chloride. Recrystallization of the product from acetonitrile afforded the ester hydrochloride **19** in 75% yield: ir (Nujol) 3300 (OH), 3000–2550 (>NH_2^+), 1760 (ester C=O), 1725 (C=O), 755, and 695 cm^{-1} (monosubstituted benzene); nmr ($CDCl_3$) δ 2.60 (CH_2CO), 3.65 ($COOCH_3$), 4.35 [$CH(N^+H_2CH_2Ph)$], and 4.85 (CHOH); R_f 0.64 in chloroform–ether–methanol (50:10:5).

The same compound **19** was prepared similarly from the ketal benzylamino acid **15** in 71% yield.

dl-ribo-**2-Benzylamino-3,4-dihydroxyoctadecanoic Acid (23a) and the** *lyxo* **Isomer (23b).**—To a solution of 6.55 g (0.02 mol) of **11** in 800 ml of methanol was added 0.38 g (0.01 mol) of sodium borohydride in 20 ml of water containing 2 drops of 1 *N* sodium hydroxide solution, and, after usual treatment, there was obtained a stereoisomeric mixture of the hydroxy epoxy esters (**21a,b**) in almost quantitative yield, as recrystallized from hexane: ir (Nujol) 3345 (OH), 1750 (ester C=O), 1260, and 900 cm^{-1} (epoxy).

The isomeric mixture of the hydroxy epoxy esters **21a** and **21b** was saponified with alcoholic sodium hydroxide solution in the usual way to give a stereoisomeric mixture of the sodium salt of hydroxy epoxy acids, from which the free acid mixture (**22a,b**) was obtained in almost quantitative yield, as recrystallized from hexane–chloroform: ir (Nujol) 3460 (OH), 1720 (acid C=O), 1260, and 895 cm^{-1} (epoxy).

A mixture of 4.0 g (0.0118 mol) of the sodium salts of hydroxy epoxy acids and 1.9 g (0.0175 mol) of benzylamine in 150 ml of water was stirred at room temperature for 1 hr and then heated under reflux for 3 hr. Recrystallization of the product from ethanol gave 1.0 g (20%) of the *dl-lyxo* isomer **23b**: ir (Nujol 3360 (hydroxy), 2800–2400 and 1615 (amino acid), 750, and 695 cm^{-1} (monosubstituted benzene).

The *dl-ribo* isomer **23a**, insoluble in hot ethanol, amounted to 1.3 g (26%): ir (Nujol) 3320 (hydroxy), 2650–2400, 1615 and 1580 (amino acid), 740, and 690 cm^{-1} (monosubstituted benzene).

When the same reaction was carried out with the isomeric mixture of hydroxy epoxy acids **22a** and **22b** and benzylamine, there were obtained the *lyxo* isomer **23b** and the *ribo* isomer **23a** in 21 and 22% yields, respectively.

The reduction product of 3.1 g (0.01 mol) of the keto epoxy acid **12** by Meerwein–Ponndorf–Verley's method was converted into the sodium salt and treated with benzylamine to afford 0.15 g (3.6% yield based on **12**) of the *lyxo* isomer **23b** and 0.40 g (9.5%) of the *ribo* isomer **23a**.

dl-ribo-**2-Benzylamino-3,4-dihydroxyoctadecanoic Acid Lactone (24a) and the** *dl-lyxo* **Isomer (24b).**—A mixture of 1.3 g (0.00308 mol) of the *ribo*-benzylamino acid **23a** and 0.6 g (0.0037 mol) of *p*-toluenesulfonic acid in 150 ml of benzene was heated under reflux for 10 hr using a water separator. After cooling, the reaction mixture was treated with 500 ml of ether, 50 ml of chloroform, and 200 ml of 10% sodium carbonate solution. From the separated organic layer, there was obtained 1.2 g (96%) of the *ribo* lactone **24a**, as recrystallized from ethyl acetate: ir (Nujol) 3295 (NH), 3050 (OH), 1775 (lactone C=O), 730, and 700 cm^{-1} (monosubstituted benzene).

The *lyxo* lactone **24b** was prepared similarly from the purified *lyxo* benzylamino acid **23b** in 70% yield, as recrystallized from hexane: ir (Nujol) 3280 (NH), 3180 (OH), 1770 (lactone C=O), 750, and 700 cm^{-1} (monosubstituted benzene).

dl-ribo-**2-Benzylamino-1,3,4-trihydroxyoctadecane (20a) and the** *dl-lyxo* **Isomer (20b). A. From the Racemic Lactones 24a and 24b.**—A mixture of 1.1 g (0.00273 mol) of the *dl-ribo* lactone **24a** and 0.5 g (0.0132 mol) of lithium aluminum hydride in 150 ml of anhydrous ether was refluxed for 5 hr under stirring. The reaction mixture was worked up in the usual way to furnish 0.85 g (76%) of the racemic *ribo*-benzylaminotriol **20a**, as recrystallized

from hexane: ir (Nujol) 3320 (NH), 3250–2700 (hydroxy), 750, and 700 cm^{-1} (monosubstituted benzene).

In a similar way, the racemic *lyxo* isomer **20b** was prepared from the *dl-lyxo* lactone **24b** in 82% yield as recrystallized from acetonitrile: ir (Nujol) 3350 (NH), 3275–2710 (hydroxy), 745, and 690 cm^{-1} (monosubstituted benzene).

B. From the Racemic Benzylamino Acids 23a and 23b.—A mixture of 0.50 g (0.00118 mol) of the *dl-ribo*-benzylamino acid **23a** and 0.23 g (0.006 mol) of lithium aluminum hydride in 50 ml of 1,2-dimethoxyethane was stirred under reflux for 6 hr, and there was obtained the same racemic *ribo*-benzylaminotriol **20a** in 83% yield. Similarly, the *dl-lyxo* isomer **20b** was prepared from the *dl-lyxo*-benzylamino acid **23b** in 73% yield.

C. From the Racemic Ester Hydrochloride 19.—To a suspension of 2.7 g (0.071 mol) of lithium aluminum hydride in 200 ml of anhydrous ether was added 7.6 g (0.0162 mol) of **19** under cooling with an ice bath, and the mixture was refluxed for 8 hr and worked up in the usual way to give 6.1 g (92%) of the reduction products. Recrystallization of the products from hexane–ethanol afforded 3.0 g (46%) of the racemic *ribo*-benzylaminotriol **20a**. The residue obtained from the mother liquor was recrystallized from acetonitrile to furnish the benzylaminotriol rich in the *dl-lyxo* isomer **20b**. The pure *dl-lyxo* compound **20b** was not obtained in this way.

D. From the Racemic *ribo* N-Benzoyl Derivative (26a).—A mixture of 0.145 g of the *dl-ribo* N-benzoyl derivative **26a** described below and 0.3 g of lithium aluminum hydride in 150 ml of anhydrous tetrahydrofuran was heated under reflux for 9 hr. The product **20a** was isolated in 70% yield by the method described above.

***dl-ribo*-2-Amino-1,3,4-trihydroxyoctadecane (25a) and the *dl-lyxo* Isomer (25b).**—A solution of 0.735 g (0.00185 mol) of the *dl-ribo*-benzylaminotriol **20a** in 80 ml of ethanol was stirred in an autoclave under hydrogen at 3 atm with 0.3 g of 5% palladium on carbon for 8 hr at 70°. Recrystallization of the product from acetonitrile–methanol gave 0.355 g (60.5%) of the racemic *ribo*-aminotriol **25a**: ir (Nujol) 3300 and 1580 (NH_2), 3300–2350, and 1075 cm^{-1} (hydroxy); R_f 0.38 in chloroform–methanol–2.8% ammonium hydroxide (35:10:1).

The racemic *ribo*-aminotriol **25a** was dissolved in boiling acetone and the plates formed on cooling were recrystallized from acetone to give the racemic acetone compound (**28a**): ir (Nujol) 3325 (NH), 3240, and 3110 cm^{-1} (hydroxy).

Debenzylation of the *dl-lyxo* isomer **20b** was carried out similarly to afford the racemic *lyxo*-aminotriol **25b** in 74% yield as recrystallized from hexane–ethanol: ir (Nujol) 3360 and 1615 (NH_2), 3220–2700, 1075, and 1000 cm^{-1} (hydroxy); R_f 0.45 in chloroform–methanol–2.8% ammonium hydroxide (35:10:1).

***dl-ribo*-2-Benzamido-1,3,4-trihydroxyoctadecane (26a) and the *dl-lyxo* Isomer (26b).**—The N-benzoyl derivatives were prepared according to the procedure of Carter and coworkers[15] from **25a** and **25b**, respectively. The racemic *ribo* isomer **26a** was recrystallized from hexane–ethyl acetate: ir (Nujol) 3320, 1615, and 1550 (amide), 3390, 3060, and 1060 cm^{-1} (hydroxy); the infrared spectrum measured as a solution in chloroform[19] was identical with that of natural N-benzoyl phytosphingosine; mass spectrum (70 eV)[19] *m/e* (rel intensity) 422 (0.2), 403 (0.2), 385 (0.4), 372 (0.11), 280 (0.8), 268 (0.4), 221 (0.4), 206 (0.12), 194 (22), 177 (13), 164 (38), 147 (43), 122 (30), 105 (100), and 77 (18); R_f 0.45 in chloroform–ethyl acetate–methanol (10:5:3).

The racemic *lyxo* isomer **26b** was recrystallized from acetonitrile: ir (Nujol) 3320, 1620, and 1535 (amide), 3400, 3130, 1070, 1035, and 1025 cm^{-1} (hydroxy); mass spectrum (70 eV)[19] *m/e* (rel intensity) 422 (0.3), 403 (0.2), 385 (0.3), 372 (0.5), 280 (0.7), 206 (0.9), 194 (10), 177 (18), 164 (35), 147 (49), 122 (42), 105 (100), and 77 (17); R_f 0.48 in chloroform–ethyl acetate–methanol (10:5:3).

A mixture of *ribo* and *lyxo* isomers melted at 105–110°.

***dl-ribo*-2-Acetamido-1,3,4-trihydroxyoctadecane (27a) and the *dl-lyxo* Isomer (27b).**—The N-acetyl derivatives were prepared using acetic anhydride and 1 *N* sodium hydroxide followed by saponification of any ester formed with saturated aqueous potassium hydroxide in methanol. The racemic *ribo* isomer **27a** was recrystallized from acetone to give white needles: ir (Nujol) 3300, 1650 and 1555 (amide), 3320–2700, and 1060 cm^{-1} (hydroxy); R_f 0.49 in chloroform–methanol–2.8% ammonium hydroxide (50:10:1).

The racemic *lyxo* isomer **27b** was recrystallized from acetonitrile: ir (Nujol) 3300, 1630 and 1540 (amide), 3340–3100, 1070, and 1040 cm^{-1} (hydroxy); R_f 0.52 in chloroform–methanol–2.8% ammonium hydroxide (50:10:1).

4-Bromo-*trans*-2-octadecenoic Acid (29').—A mixture of 14.1 g (0.05 mol) of *trans*-2-octadecenoic acid,[27] 8.9 g (0.05 mol) of N-bromosuccinimide, and 0.1 g of benzoyl peroxide in 200 ml of anhydrous carbon tetrachloride was refluxed for 30 min and the precipitated succinimide was filtered off. The filtrate was concentrated *in vacuo* and treated with 100 ml of water and 300 ml of ether. The ether solution gave 15.0 g (83%) of the bromo acid, as recrystallized from petroleum ether (bp 30–70°): ir (Nujol) 1695 (acid C=O), 1650, and 980 cm^{-1} (*trans* CH=CH).

4-Hydroxy-*trans*-2-octadecenoic Acid (29). A. From the Bromo Acid 29'.—A solution of 5.41 g (0.015 mol) of the bromo acid **29'** and 3.7 g (0.0375 mol) of potassium acetate in 50 ml of glacial acetic acid was heated under reflux for 10 hr and poured into 300 ml of water and 200 ml of ether. Removal of the solvent gave 3.2 g of an oily product, which was saponified with 10% aqueous sodium hydroxide. The crystals obtained were recrystallized from hexane to yield 1.90 g (43%) of a hydroxy acid mixture: mp 71–77°; ir (Nujol) 3420 (OH), 1755 and 1685 (acid C=O), 1640, 980, and 970 cm^{-1} (*trans* CH=CH). Elemental analysis gave the correct values for $C_{18}H_{34}O_3$.

A mixture of 1.90 g (0.00636 mol) of the hydroxy acid mixture and 2.7 g (0.0039 mol) of red lead oxide in 30 ml of glacial acetic acid was heated for 2 hr at 60°. After the excess of lead tetraacetate was destroyed with 5 ml of ethylene glycol, the reaction mixture was poured into 150 ml of water and the separated substances were extracted with ether. From the ether solution there was obtained 0.87 g (46%) of the purified hydroxy acid **29**, as recrystallized from hexane: ir (Nujol) 3420 (OH), 1685 (acid C=O), 1640, and 980 cm^{-1} (*trans* CH=CH).

B. From the Keto Acid 10.—To a warm solution of 0.60 g (0.00202 mol) of the keto acid **10** in 100 ml of ethanol was added 0.3 g of sodium borohydride in 10 ml of water containing a drop of 1 *N* sodium hydroxide. After the solution was refluxed for 1 hr, the solvent was removed *in vacuo* and the residue was treated with 20 ml of concentrated hydrochloric acid and 100 ml of ether. From the ether solution, 0.48 g (80%) of the hydroxy acid **29** was obtained.

C. By Grignard Reaction.—*n*-Tetradecylmagnesium bromide, prepared from 9.0 g (0.0325 mol) of *n*-tetradecyl bromide and 0.78 g (0.0325 g-atom) of magnesium in 120 ml of anhydrous ether, was added into a solution of 3.7 g (0.0325 mol) of fumaraldehydic acid methyl ester[28] in 100 ml of dry ether under cooling in a Dry Ice–methanol bath. The solution was gradually raised to room temperature in the course of 26 hr and then refluxed for 1.5 hr. Decomposition of the complex was performed with 200 ml of ammonium chloride solution. Evaporation of the solvent and addition of ethanol afforded crystals, from which 5.0 g (78%) of *n*-octacosane, mp 64–64.5° (lit. mp 60–61.5°,[29] 61–62°[30]), was obtained. The filtrate was concentrated and saponified in a usual way to give 1.0 g (10%) of the hydroxy acid **29**.

Registry No.—**2**, 21436-51-1; **3**, 21436-52-2; **4**, 21436-53-3; **5**, 21436-54-4; **6**, 21436-55-5; **7**, 21436-56-6; **8**, 21436-57-7; **9**, 21436-58-8; **10**, 21436-59-9; **11**, 21436-60-2; **12**, 21436-61-3; **13**, 21436-62-4; **14**, 21436-63-5; **14'**, 21436-64-6; **15**, 21436-65-7; **16**, 21436-18-0; **17**, 21436-19-1; **18**, 21436-20-4; **19**, 21436-21-5; **20a**, 21436-22-6; **20b**, 21436-23-7; **21a**, 21436-24-8; **22a**, 21436-06-6; **23b**, 21436-07-7; **24a**, 21436-08-8; **24b**, 21436-09-9; **25a**, 21436-10-2; **25b**, 21436-11-3; **26a**, 21494-26-8; **26b**, 21436-12-4; **27a**, 21436-13-5; **27b**, 21494-27-9; **28a**, 21436-14-6; **29**, 21436-15-7; **29'**, 21436-16-8.

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