(46%), and 2-nonyne (36%) by glpc analysis. These were separated by glpc and identified by infrared and nmr.

Partial Reduction of Phenylpropadiene.—Phenylpropadiene (1.16 g, 0.01 mol) was reduced with 0.23 g (0.01 g-atom) of sodium in 50 ml of liquid ammonia. The reaction product was stirred for 3 hr and worked up in the usual manner. The glpc analysis of the product (0.95 g) showed the presence of *n*-propylbenzene (17.2%), propenylbenzene (22.5%), 1-phenylpropyne (56.8%), and an unidentified product (3.5%). The first three components were separated by glpc and identified by nmr.

When the reaction in another lot was arrested and worked up after just 15 min, the product analysis showed 15.7% *n*-propylbenzene, 19.5% allylbenzene, and 64.8% 1-phenylpropyne.

Reduction of Phenylpropadiene with Equivalent Quantity of Sodium.—Phenylpropadiene (1.16 g, 0.01 mol) in dry ether was added into a solution of 0.46 g (0.02 g-atom) of sodium in 50 ml of liquid ammonia. The reaction mixture was stirred only for 15 min and worked up in the usual way. The product (0.92 g) analysis by glpc showed the presence of *n*-propylbenzene (21.9%), allylbenzene (15.3%), and 1-phenylpropyne (62.8%). These were separated and identified by nmr.

Registry No.—1,2-Octadiene, 1072-19-1; 1,2-nonadiene, 22433-33-6; 2,3-nonadiene, 22433-34-7; 4,5-nonadiene, 821-74-9; 3-ethyl-1,2-pentadiene, 2384-96-5; 2,4-dimethyl-2,3-pentadiene, 1000-87-9; phenylpropadiene, 2327-99-3; 3-phenyl-1,2-butadiene, 22433-39-2.

Acknowledgment.—The authors are indebted to Dr. Nityanand, Assistant Director, Central Drug Research Institute, Lucknow, India, for the nmr spectra.

Syntheses of All of the Racemic Diastereoisomers of Phytosphingosine

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Ethyl 2-acetamido-3-octadecynoate (**8**), derived from the 2,4-dinitrophenylhydrazone (**4**) of ethyl 2-oxo-3-octadecynoate (**1**) by reductive acetylation, was converted into *trans*- and *cis*-2-acetamido-1-acetoxy-3-octadecenes (**13** and **16**). Dihydroxylation in *trans* fashion of the *trans* compound **13** with performic acid followed by saponification afforded racemic N-acetyl phytosphingosine, the DL-*ribo* isomer **14**, together with the DL-*arabino* isomer **15**. From the *cis* compound **16** there was obtained in the same way the DL-*lyxo* isomer **17**, but the DL-*xylo* compound **18** was not obtained. *cis* dihydroxylation of **13** by silver iodoacetate furnished the DL-*xylo* isomer **18**.

In the previous paper,[1] a synthesis of racemic phytosphingosine and the *lyxo* isomer was described. The procedure was based on the stereospecific reaction of *trans*-glycidic acid with benzylamine to give 2,3-*erythro*-2-benzylamino-3-hydroxy acid.[2] The present paper deals with syntheses of all of the racemic diastereoisomers of phytosphingosine by stereospecific dihydroxylations[3] of 3-octadecene derivatives.

The stereochemical assignments of the products as compared with the natural and the diastereomeric compounds described in the previous paper[1] confirmed that all of the reactions proceeded with known stereochemistry.

The reaction of *n*-hexadecynylmagnesium bromide with diethyl oxalate[4] gave ethyl 2-oxo-3-octadecynoate (**1**) (identified by the semicarbazone **1'**) accompanied by a small amount of tetrakis(1-hexadecynyl)ethylene glycol (**2**), whose constitution was confirmed by oxidation with lead tetraacetate to afford bis(1-hexadecynyl) ketone (**3**) (identified by the 2,4-dinitrophenylhydrazone **3'**). On heating an alcoholic solution of the 2,4-dinitrophenylhydrazone (**4**) of the acetylenic keto ester **1** cyclization into the pyrazole derivative (**5**)[5] was observed. When **1** was treated with hydroxylamine hydrochloride, similar cyclization reaction occurred and the isoxazole derivative (**6**)[6] was formed. On the other hand, the treatment of **1** with hydroxylamine hydrochloride in the presence of sodium acetate furnished an addition–cyclization product (**7**).[7]

Reductive acetylation of the 2,4-dinitrophenylhydrazone **4** to the acetylenic amido ester **8** was carried out with zinc dust.[8] The ester group of **8** was selectively reduced with lithium aluminum hydride to give acetylenic amido alcohol **9**, which was partially hydrogenated to 2-acetamido-1-hydroxy-*trans*-3-octadecene (**10**) with sodium in liquid ammonia,[9] or to the *cis* isomer **12** with Lindlar's catalyst.[10] Alternatively, the same *cis* compound **12** was obtained from **8** by catalytic hydrogenation followed by reduction with lithium aluminum hydride or lithium borohydride.[11]

The *trans*-amido alcohol **10** was transformed into the O-acetate **13** and dihydroxylated in *trans* fashion with performic acid[12] followed by saponification to furnish racemic N-acetyl phytosphingosine (**14**) and the DL-*arabino* isomer **15**. The separation was carried out by fractional recrystallization. Excellent crystallizability of the DL-*arabino* compound **15** aided the isolation of both isomers. The compound **14** was identical

(1) K. Sisido, N. Hirowatari, and T. Isida, *J. Org. Chem.*, **34**, 3539 (1969).

(2) (a) Y. Liwschitz, Y. Rabinsohn, and D. Perera, *J. Chem. Soc.*, 1116 (1962); (b) K. Sisido, N. Hirowatari, and T. Isida, *J. Org. Chem.*, **29**, 2783 (1964).

(3) (a) D. Swern, G. N. Billen, T. W. Findley, and J. T. Scanlan, *J. Amer. Chem. Soc.*, **67**, 1786 (1945); (b) R. B. Woodward and F. V. Brutcher, Jr., *ibid.*, **80**, 209 (1958).

(4) I. I. Lapkin and Yu. S. Andreichikov, *Zh. Org. Khim.*, **1**, 480 (1965); *Chem. Abstr.*, **63**, 1692*h* (1965).

(5) (a) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946); (b) A. Vaitiekunas, R. E. Miller, and F. F. Nord, *J. Org. Chem.*, **16**, 1603 (1951); (c) K. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *ibid.*, **27**, 2663 (1962).

(6) (a) L. Claisen, *Ber.*, **44**, 1161 (1911); (b) A. Quilico, G. Gaudiano, and L. Merlini, *Tetrahedron*, **2**, 359 (1958).

(7) H. Reimlinger and J. J. M. Vandewalle, *Ann. Chem.*, **720**, 117 (1968).

(8) D. Shapiro, H. Segal, and H. M. Flowers, *J. Amer. Chem. Soc.*, **80**, 1194 (1958).

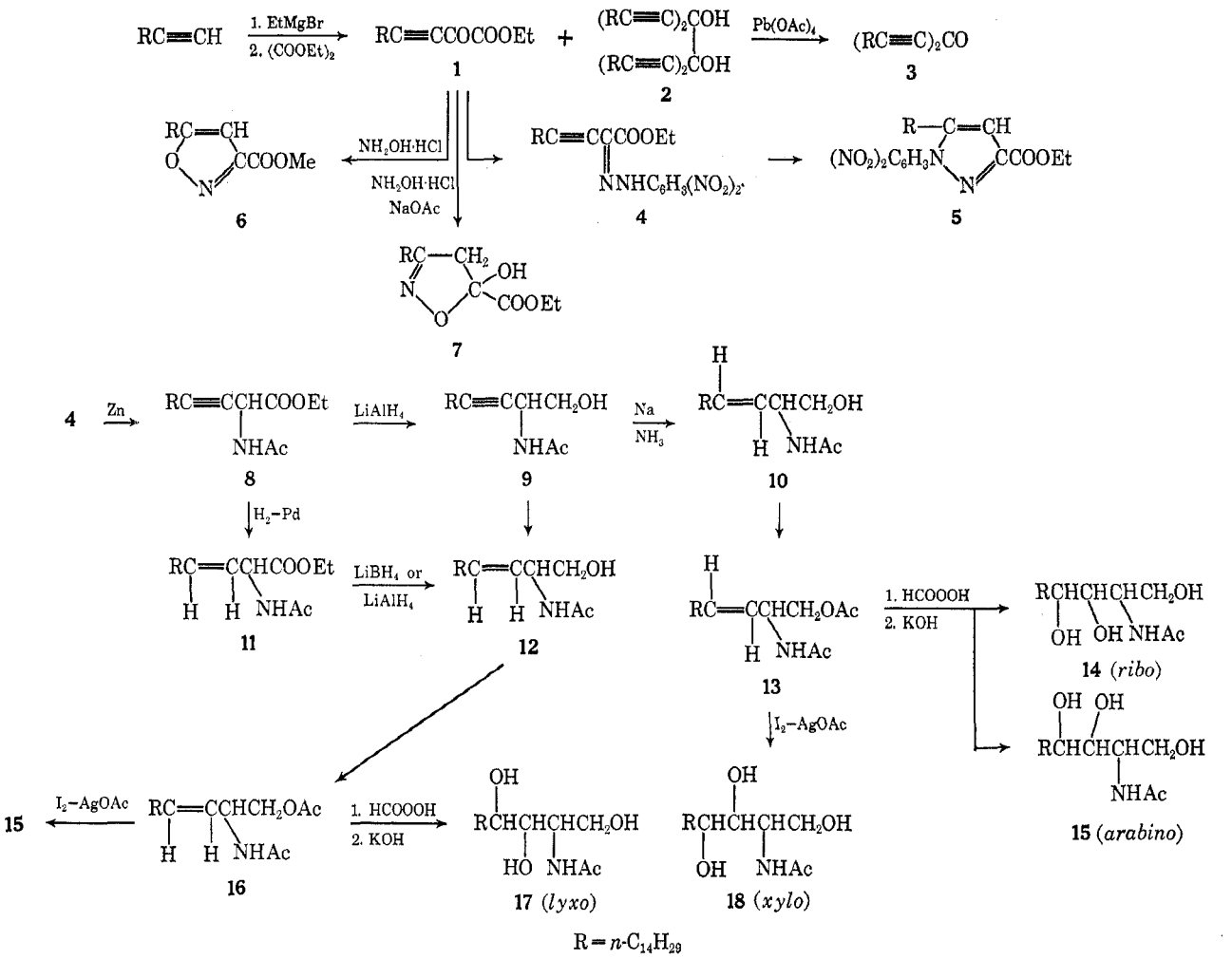
(9) (a) F. Sondheimer, *J. Chem. Soc.*, 877 (1950); (b) F. Asinger, B. Fell, and G. Steffan, *Chem. Ber.*, **97**, 1555 (1964).

(10) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(11) I. Sallay, F. Dutka, and G. Fodor, *ibid.*, **37**, 778 (1954).

(12) (a) See ref 3a; (b) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949); (c) L. F. Fieser and S. Rajagopalan, *ibid.*, **71**, 3938 (1949); (d) J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950); (e) O. Mancera, G. Rosenkranz, and C. Djerassi, *J. Org. Chem.*, **16**, 192 (1951); (f) W. J. Gensler and H. N. Schlein, *J. Amer. Chem. Soc.*, **77**, 4846 (1955).

SCHEME I



in all respects with racemic *ribo*-2-acetamido-1,3,4-trihydroxyoctadecane reported previously[1] and may readily be converted into racemic phytosphingosine.[13]

By similar *trans* dihydroxylation of 2-acetamido-1-acetoxy-*cis*-3-octadecene (**16**) with performic acid, there was obtained the DL-*lyxo* compound **17**; however, the DL-*xylo* isomer **18** was not obtained. By comparison of the spectroscopic data it was proved that the compound **17** was identical with racemic *lyxo*-2-acetamido-1,3,4-trihydroxyoctadecane reported previously.[1]

The failure of the isolation of the DL-*xylo* compound **18** might be accounted for by the preferential formation of the DL-*lyxo* isomer **17** due to the intramolecular asymmetric induction of the groups at the β carbon to the epoxidation point. The opening of the epoxide ring would occur at the δ-carbon position (not at the γ-carbon position) with Walden inversion,[14] owing to the steric effect of the groups at the β carbon. It is presumed that performic acid associates with the acetoxy group (the acetamido group is too short for further reaction), probably by hydrogen bonding with the carbonyl oxygen; as evidenced by the Dreiding model, the attack on the double bond would take place from the side opposite to the acetamido group in the conformation, which avoids the steric interaction between the tetradecyl group and the substituent at the β carbon, thus producing the DL-*lyxo* isomer **17**.

On the other hand, since in the *trans* compound **13** the steric interaction by the tetradecyl group would disappear, the epoxidation could occur irrespective of the conformation, so that there were obtained both DL-*ribo* **14** and DL-*arabino* **15** isomers. The detailed analyses of the products by gas chromatography as well as by thin layer chromatography failed, owing to low separability.

By *cis* dihydroxylation of **13** with silver iodoacetate according to Woodward's procedure[3b,15] there was isolated the DL-*xylo* compound **18**. The corresponding DL-*lyxo* isomer **17**, however, could not be obtained, presumably because of low separability. The infrared spectrum of the mother liquor concentrate showed that this consisted of the mixture. The infrared spectrum of **18** differed distinctly from those of the other three isomers. By the same procedure the DL-*arabino* compound **15** was obtained from **16**, but the DL-*ribo* isomer **14** was not isolated. This result would be consistent with the above reasoning.

Use of the free hydroxyl compounds **10** and **12** instead of **13** and **16** did not give satisfactory results.

(13) D. Shapiro, H. Segal, and H. M. Flowers, *J. Amer. Chem. Soc.*, **80**, 2170 (1958).

(14) D. Swern, *Org. Reactions*, **7**, 378 (1953).

(15) (a) D. Ginsburg, *J. Amer. Chem. Soc.*, **75**, 5746 (1953); (b) L. B. Barkley, M. W. Farrar, W. S. Knowles, H. Raffelson, and Q. E. Thompson, *ibid.*, **76**, 5014 (1954); (c) P. R. Jefferies and B. Milligan, *J. Chem. Soc.*, 2363 (1956); (d) F. D. Gunstone and L. J. Morris, *ibid.*, 487 (1957); (e) Md. E. Ali and L. N. Owen, *ibid.*, 1066 (1958).

TABLE I
LIST OF NEW COMPOUNDS

Compound	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1′	85–87	$C_{21}H_{37}N_3O_3$	66.45	9.83	11.07	66.19	9.88	11.15
2	62–63.5	$C_{66}H_{118}O_2$	84.00	12.60		83.92	12.78	
3′	59.5–60.5	$C_{39}H_{62}N_4O_4$	71.71	9.79		71.96	9.60	
4	87–90	$C_{26}H_{38}N_4O_6$	62.13	7.62	11.15	62.01	7.71	11.14
5	154–155	$C_{26}H_{38}N_4O_6$	62.13	7.62	11.15	62.38	7.81	10.91
6	72–73	$C_{19}H_{33}NO_3$	70.55	10.28	4.33	70.45	10.44	4.48
7	91.5–92.5	$C_{20}H_{37}NO_4$	67.57	10.49	3.94	67.68	10.65	4.14
8	81–82	$C_{22}H_{39}NO_3$	72.28	10.75	3.83	72.23	10.68	3.73
9	94–95	$C_{20}H_{37}NO_2$	74.25	11.53	4.33	73.98	11.36	4.22
10	81.5–82.5	$C_{20}H_{39}NO_2$	73.79	12.08	4.30	73.59	12.16	4.38
11	70–71	$C_{22}H_{41}NO_3$	71.88	11.24	3.81	71.66	11.12	3.81
12	69.5–70.5	$C_{20}H_{39}NO_2$	73.79	12.08	4.30	73.62	12.33	4.26
13	87.5–89	$C_{22}H_{41}NO_3$	71.88	11.24	3.81	72.00	11.31	3.98
15	138–139.5	$C_{20}H_{41}NO_4$	66.81	11.49	3.90	66.55	11.69	4.14
16	60–61.5	$C_{22}H_{41}NO_3$	71.88	11.24	3.81	71.64	11.36	3.71
18	107.5–109	$C_{20}H_{41}NO_4$	66.81	11.49	3.90	66.52	11.69	3.88
19	133	$C_{18}H_{39}NO_3$	68.09	12.38	4.41	67.86	12.65	4.39
20	101–103	$C_{18}H_{39}NO_3$	68.09	12.38	4.41	68.29	12.67	4.41

Attempted *cis* dihydroxylation with potassium permanganate[16] to yield 3,4-*erythro* compounds did not give the desired acetamidotriols.

Experimental Section[17]

Ethyl 2-Oxo-3-octadecynoate (1) and Tetrakis(1-hexadecynyl)-ethylene Glycol (2).—Using an inverse addition technique, *n*-hexadecynylmagnesium bromide, prepared from 11.1 g (0.05 mol) of 1-hexadecyne[18] and 0.055 mol of ethylmagnesium bromide in 200 ml of anhydrous ether, was added dropwise at −30° to a solution of 7.3 g (0.05 mol) of diethyl oxalate in 50 ml of dry ether. After stirring for 15 min at −30°, the reaction mixture was decomposed with a saturated ammonium chloride solution. After evaporation of the ether, the crystalline glycol **2** separated and was recrystallized from hexane in 6% yield: ir (Nujol) 3490 (OH), 2260 cm^{-1} (C≡C).

The mother liquor of **2** was concentrated and distilled under reduced pressure to give 6.6 g (41%) of **1**: bp 184–186° (2 mm); ir (neat) 2220 (C≡C), 1750 (ester C=O), 1690 cm^{-1} (C=O). Because of the lability of the compound **1** to heat, the elemental analyses did not give correct values for $C_{20}H_{34}O_3$.

Semicarbazone 1′ was recrystallized from hexane: ir (Nujol) 3425, 3340, 3240 and 1690 (=NNHCONH$_2$), 2220 (C≡C), 1740 (ester C=O), 1595 cm^{-1} (C=N).

The 2,4-dinitrophenylhydrazone[19] (4) of 1, was recrystallized from benzene–ethanol: ir (Nujol) 3270 and 3140 (NH), 2230 (C≡C), 1745 (ester C=O), 1620 and 1595 cm^{-1} (C=N).

When the Grignard reaction was carried out by a normal addition procedure, **1** and **2** were produced in 7.1 and 39% yields, respectively.

Bis(1-*n*-hexadecynyl) Ketone (3).—A mixture of 3.8 g (0.0022 mol) of **2**, 0.62 g of potassium carbonate, and 1.3 g (0.0022 mol) of lead tetraacetate in 50 ml of dry benzene was stirred for 3 hr at room temperature. The filtrate was concentrated and distilled under reduced pressure to furnish 1.3 g (62%) of **3**: bp 175–180° (1 mm); ir (neat) 2220 (C≡C), 1625 cm^{-1} (C=O).

The 2,4-dinitrophenylhydrazone (3′) was recrystallized from ethanol: ir (Nujol) 3280 and 3090 (NH), 2220 (C≡C), 1620, 1595 cm^{-1} (C=N).

1-(2,4-Dinitrophenyl)-3-ethoxycarbonyl-5-(1-tetradecyl)pyrazole (5).—When the 2,4-dinitrophenylhydrazone **4** was heated in boiling ethanol, the pyrazole derivative **5** was formed and was recrystallized from ethanol: ir (Nujol) 3080 (CH), 1735 (ester C=O), 1610 cm^{-1} (C=N).

3-Methoxycarbonyl-5-(1-tetradecyl)isoxazole (6) and 5-Ethoxycarbonyl-5-hydroxy-3-(1-tetradecyl)isoxazoline (7).—A mixture of 3.17 g (0.00984 mol) of **1** and 0.84 g (0.012 mol) of hydroxylamine hydrochloride in 100 ml of methanol was allowed to stand for 3 days at room temperature. Addition of water afforded precipitates, from which 1.8 g (57%) of the isoxazole derivative[20] **6** was obtained and was recrystallized from hexane: ir (Nujol) 3180 (CH), 1740 (ester C=O), 1605 cm^{-1} (C=N); nmr (CDCl$_3$), δ 2.78 (t, 2, J = 7 Hz), 3.96 (s, 3), 6.42 (s, 1).

When the same reaction was carried out in the presence of anhydrous sodium acetate, the addition product **7** was obtained in 40% yield and recrystallized from hexane: ir (Nujol) 3400 (OH), 1735 (ester C=O), 1625 cm^{-1} (C=N); nmr (CDCl$_3$), δ 1.35 (t, 3, J = 7 Hz), 2.35 (m, 2), 3.00 (d, 1, J = 18 Hz), 3.57 (d, 1, J = 18 Hz), 3.88 (s, 1), 4.32 (q, 2, J = 7 Hz).

Ethyl DL-2-Acetamido-3-octadecynoate (8).—To a suspension of 25 g (0.383 g-atom) of zinc powder in 60 ml of glacial acetic acid and 25 ml of acetic anhydride was added dropwise a solution of 4.00 g (0.00795 mol) of the hydrazone **4** in 100 ml of glacial acetic acid, with vigorous stirring. Filtration of the reaction mixture into ice–water yielded precipitates, from which 2.85 g (98%) of the acetylenic amido ester **8** was obtained and recrystallized from hexane: ir (Nujol) 3300, 1650, and 1535 (amide), 2250 (C≡C), 1760 cm^{-1} (ester C=O).

DL-2-Acetamido-1-hydroxy-3-octadecyne (9).—To a suspension of 0.32 g (0.0084 mol) of lithium aluminum hydride in 50 ml of dry ether was added dropwise[21] a solution of 2.2 g (0.006 mol) of **8** in 100 ml of dry ether at −15°, and the mixture was stirred for 5 hr. The reaction mixture was worked up in the usual way to give 1.5 g (78%) of the product **9**, which was recrystallized from ethyl acetate: ir (Nujol) 3290, 1630 and 1575 (amide), 3160, 3080, 1080, and 1055 cm^{-1} (hydroxy).

DL-2-Acetamido-1-hydroxy-*trans*-3-octadecene (10).—A solution of 2.1 g (0.0065 mol) of **9** in 30 ml of anhydrous tetrahydrofuran was added dropwise to a stirred solution of 3 g (0.13 g-atom) of sodium in 150 ml of liquid ammonia. The mixture was stirred for 3 hr and worked up in the usual way to furnish 1.6 g (76%) of **10**, recrystallized from hexane–ethyl acetate: ir (Nujol) 3270, 1635 and 1585 (amide), 3200, 3120, and 1075 (hydroxy), 965 cm^{-1} (*trans* CH=CH).

Ethyl DL-2-Acetamido-*cis*-3-octadecenoate (11).—A mixture of 2.0 g (0.00548 mol) of **8** and 0.25 g of Lindlar's catalyst in 100

(16) (a) R. P. Linstead, L. N. Owen, and R. F. Webb, *J. Chem. Soc.*, 1225 (1953); (b) P. D. Bartlett and A. Bavley, *J. Amer. Chem. Soc.*, **60**, 2416 (1938).

(17) Ir spectra were measured on Shimazu IR-27B spectrophotometer. Nmr spectra were determined as solutions in CDCl$_3$ with TMS as an internal standard on Japan Electron Optics Laboratory JEOL C-60-H apparatus. 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. In Table I are listed the new compounds prepared in this experiment. All melting points were corrected.

(18) E. F. Jenny and J. Druey, *Helv. Chim. Acta*, **42**, 401 (1959).

(19) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 219.

(20) Under the acidic conditions, transesterification occurred.

(21) When the addition was carried out as fast as possible at −50°, a large amount of unidentifiable oily materials were formed. The yield depended on the rate of addition and the reaction temperature.

ml of ethyl acetate was hydrogenated at room temperature under hydrogen at atmospheric pressure until the calculated amount of hydrogen (135 ml) was absorbed. In a usual treatment 1.9 g (94%) of **11** was obtained, and recrystallized from hexane: ir (Nujol) 3300, 1650 and 1555 (amide), 3060 and 810 (*cis* CH=CH), 1755 cm^{-1} (ester C=O).

DL-**2-Acetamido-1-hydroxy-*cis*-3-octadecene (12). A. By Reduction of 11 with Lithium Aluminum Hydride.**—To a suspension of 0.273 g (0.007 mol) of lithium aluminum hydride in 20 ml of dry ether was added dropwise a solution of 1.84 g (0.005 mol) of **11** in 100 ml of dry ether at −10° and the mixture was stirred for 5 hr. Upon working up in the usual way there was obtained 1.37 g (84%) of **12**, recrystallized from hexane: ir (Nujol) 3300, 1640 and 1585 (amide), 3240, 3120, 1080, and 1045 cm^{-1} (hydroxy).

B. By Reduction of 11 with Lithium Borohydride.—Selective reduction of **11** to **12** was carried out according to the procedure used by Sallay and coworkers[11] and the product **12** was obtained in 68% yield.

C. By Partial Hydrogenation of 9.—The *cis*-amido alcohol **12** was also prepared in 74% yield by partial hydrogenation of **9** using Lindlar's catalyst.

DL-**2-Acetamido-1-acetoxy-*trans*-3-octadecene (13).**—To a solution of 6.2 g (0.019 mol) of **10** in 100 ml of pyridine was added 30 ml (0.294 mol) of acetic anhydride and the mixture was allowed to stand for 24 hr. There was obtained 4.8 g (69%) of the acetoxy compound **13**, recrystallized from ethyl acetate: ir (Nujol) 3300, 1645, and 1570 (amide), 3090, 1675, and 980 (*trans* CH=CH), 1725 cm^{-1} (ester C=O); R_f 0.40 in chloroform–ethyl acetate–methanol (5:3:1).

DL-**2-Acetamido-1-acetoxy-*cis*-3-octadecene (16).**—In a way similar to that described above the *cis* isomer **16** was prepared in 85% yield and recrystallized from methanol: ir (Nujol) 3320, 1660, 1650, and 1550 (amide), 3120 (*cis* CH=CH), 1740 cm^{-1} (ester C=O); R_f 0.87 in chloroform–ethyl acetate–methanol (5:3:1).

DL-*ribo*-**2-Acetamido-1,3,4-trihydroxyoctadecane (14) and the** DL-*arabino* **Isomer 15.**—A mixture of 3.043 g (0.00828 mol) of **13** and 2 ml of 30% hydrogen peroxide in 50 ml of formic acid was stirred for 24 hr at 40°, during which time, at 7-hr intervals, two 2-ml portions of 30% hydrogen peroxide were added. The reaction mixture was poured into ice–water and the resulting dihydroxylated products were extracted with ether. The combined ether extracts were washed successively with sodium bisulfite, sodium bicarbonate, and water. After drying over sodium sulfate the solvent was removed, and the residue was dissolved in 150 ml of methanol and treated with a saturated aqueous potassium hydroxide solution for 24 hr at room temperature. After removal of the solvent *in vacuo* water was added and the precipitates formed were extracted with ether–chloroform. From this solution there was obtained 2.644 g (88.9%) of a mixture of diastereoisomers, which were recrystallized from ethanol–ethyl acetate–hexane to give 0.563 g (18.9%) of the *arabino* isomer **15**: ir (Nujol) 3440, 1605 and 1585 (amide), 3330, 3240, 3100, and 1060 cm^{-1} (hydroxy); R_f 0.48 in chloroform–methanol–2.8% ammonium hydroxide (50:10:1).

The residue obtained from the mother liquor was recrystallized from acetone to furnish 0.441 g (14.9%) of the *ribo* isomer **14**, identical in all respects with racemic N-acetyl phytosphingosine reported previously.[1]

DL-*lyxo*-**2-Acetamido-1,3,4-trihydroxyoctadecane (17).**—By similar *trans* dihydroxylation of **16** with performic acid followed by saponification as described above, there was isolated in 63% yield the racemic N-acetylaminotriol **17**, identical in all respects with the racemic *lyxo* compound reported previously.[1]

From the mother liquor the DL-*xylo* isomer **18** could not be isolated.

DL-*xylo*-**2-Acetamido-1,3,4-trihydroxyoctadecane (18) and the** DL-*arabino* **Isomer 15.**—To a vigorously stirred mixture of 3.68 g (0.01 mol) of **13** and 3.7 g (0.022 mol) of silver acetate in 65 ml of glacial acetic acid was added at room temperature 2.6 g (0.0102 mol) of finely powdered iodine, in small portions. After stirring for 30 min, 10 ml of aqueous acetic acid (containing 0.20 g of water) was added and the reaction mixture was heated at 90–95° for 6 hr with vigorous stirring. After the usual work-up,[3b] there was obtained 0.54 g (15%) of the racemic *xylo* compound **18**, recrystallized from acetone: ir (Nujol) 3300, 1635, and 1540 (amide), 3200 and 1065 cm^{-1} (hydroxy); R_f 0.40 in chloroform–methanol–2.8% ammonium hydroxide (50:10:1).

The DL-*lyxo* compound **17** could not be isolated.

When **16** was treated similarly, the *arabino* isomer **15** was obtained in 29% yield. The *ribo* compound **14** was not obtained.

DL-*arabino*-**2-Amino-1,3,4-trihydroxyoctadecane (19) and the** DL-*xylo* **Isomer 20.**—A solution of 0.32 g of **15** and 1.5 g of potassium hydroxide in 100 ml of 90% methanol was heated under reflux for 6 hr.[13] After removal of the solvent *in vacuo*, water was added, and the precipitate formed was recrystallized from acetonitrile–ethanol to give 0.22 g (78%) of **19**: ir (Nujol) 3370, 1595, and 1575 (amino), 3350–2770 and 1040 cm^{-1} (hydroxy); R_f 0.42 in chloroform–methanol–2.8% ammonium hydroxide (35:10:1).

Similarly, the *xylo* compound **20** was obtained from **18** in 73% yield and was recrystallized from hexane–ethanol: ir (Nujol) 3330 and 1600 (amino), 3300–2740 and 1100–970 cm^{-1} (hydroxy); R_f 0.51 in chloroform–methanol–2.8% ammonium hydroxide (35:10:1).

Registry No.—**1**, 22566-56-9; **1′**, 22577-01-1; **2**, 22566-57-0; **3**, 22566-58-1; **3′**, 22566-59-2; **4**, 22566-60-5; **5**, 22594-00-9; **6**, 22566-24-1; **7**, 22566-25-2; **8**, 22565-70-4; **9**, 22565-71-5; **10**, 22565-72-6; **11**, 22577-02-2; **12**, 22565-73-7; **13**, 22565-76-0; **15**, 22565-77-1; **16**, 22565-78-2; **18**, 22565-79-3; **19**, 22565-80-6; **20**, 22565-81-7.