acidified to pH 3–5 with concentrated hydrochloric acid. The reaction mixture was diluted with 700 ml of water and extracted with three 200-ml portions of chloroform. The organic layer was washed with water until neutral and the product isolated by the standard procedure.[28] After trituration of the crude crystalline product with ether, there was obtained 20.3 g (68%) of the desired keto lactone as colorless prisms, mp 167–168°. An analytically pure sample was obtained by two additional recrystallizations from ethanol–acetone (4:1): mp 169–171°; ir ($CHCl_3$) 1720, 1770 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.98; H, 6.35.

If the annelation reaction was worked up before the basic hydrolysis step, the products consisted largely of the two ketol esters **16** and **17**. These isomers could easily be separated by column chromatography (Al_2O_3, neutral activity III). The isomer **17** was eluted with 1:1 ether–benzene as a colorless oil which crystallized on standing. Recrystallization from ether–hexane (4:1) afforded colorless prisms: mp 90–92°; ir ($CHCl_3$) 3300–3600 (OH) and 1720 cm^{-1}; ir (CCl_4) 0.016 *M*, 3600 cm^{-1}; nmr ($CDCl_3$) δ 1.29 and 4.87 (triplet and quartet for OCH_2CH_3), 1.27 (s, 3, methyl), 2.17 (broad, OH); mass spectrum (10 eV) *m/e* 302, 284, 257.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.47; H, 7.38.

The isomer **16** was eluted with 1:9 ethanol–ether as an oil which crystallized on standing. Recrystallization from ether–hexane afforded colorless prisms: mp 85.5–87.5°; ir ($CHCl_3$) 3300–3600 (OH) and 1720 cm^{-1}; ir (CCl_4) 0.015 *M* 3600, 3430 cm^{-1}; nmr ($CDCl_3$) δ 1.04 and 3.94 (triplet and quartet for OCH_2CH_3), 1.18 (s, 3, methyl), 2.58 (OH); mass spectrum (10 eV) 302, 284, 257.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.47; H, 7.24.

A discussion of the stereochemical assignments was included in the discussion.

Methyl 4,4a,9,10-Tetrahydro-2(3*H*)-phenanthrone-4a-acetate (19).—A slurry of 3.00 g (0.017 mol) of keto lactone **18** and 1.62 g of anhydrous potassium carbonate in 100 ml of acetone was heated at reflux under nitrogen for 0.5 hr. Methyl iodide, 2 ml, was added, and heating continued for 2 hr. An additional 2 ml of methyl iodide was then added followed by 2 hr of heating. The acetone was removed *in vacuo*, and 300 ml of benzene and 100 ml of water were added to the concentrate. The organic layer was separated and extracted once with 10% sodium thiosulfate solution and then with water until neutral. The standard work-up procedure[28] afforded a pale yellow crystalline substance. Trituration of this material with 1:1 pentane–ether afforded 2.89 g (94%) of crystalline keto ester **19**, mp 101–102°. Material of analytical purity was obtained by two additional crystallizations from acetone–hexane: mp 102–102.5°; ir ($CHCl_3$) 1723, 1660 (C=O's), 1625 cm^{-1} (C=C); nmr ($CHCl_3$) δ 3.52 (s, methoxyl), 6.04 (s, vinyl H).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.48; H, 6.63.

7,12-Dioxo-*N*-methylhasubanan (20).—The procedure followed in this experiment was essentially the same as that followed in the preparation of amide **11b**. To a dry, nitrogen-purged, 250-ml reaction vessel equipped with a Dry Ice condenser and addition funnel was added 150 ml of dry ether and 0.511 g (13.5 mmol) of pulverized lithium aluminum hydride. Anhydrous monomethylamine was distilled into the reaction vessel until all visible hydrogen evolution had ceased. The contents were allowed to stir for 1 hr, the Dry Ice condenser was replaced with a water-cooled condenser, and the solution heated at reflux for 0.5 hr and cooled to room temperature. The keto ester **19**, 1.0 g (3.4 mmol), in 100 ml of ether was added dropwise over a 3-min period and the reaction was allowed to stir at room temperature for 22 hr. Water, 150 ml, was added to the reaction and the contents were extracted with chloroform. The organic layer was washed with water until neutral and dried ($MgSO_4$). Removal of the solvent afforded 0.77 g of oil which was chromatographed on alumina (neutral activity III). Elution with 3:1 chloroform–ether afforded 0.654 g of crystalline lactam. On recrystallization from ethanol there was obtained 0.459 g (50%) of desired **20**: mp 146–147°; ir ($CHCl_3$) 1680, 1715 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.8 (s, NCH_3); mass spectrum (70 eV) *m/e* 269, 240, 226, 212.

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.84; H, 6.90.

Registry No.—**5**, 23657-79-6; **6**, 23953-64-2; **6** (HCl), 23953-65-3; **7**, 26156-79-6; **10**, 26210-99-1; **11a**, 26146-02-1; **11b**, 26146-03-2; **11c**, 26146-04-3; **12**, 23840-48-4; **16**, 26146-05-4; **17**, 26146-06-5; **18**, 26146-07-6; **19**, 26146-08-7; **20**, 26146-09-8.

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Synthesis of *trans*- and *cis*-Sphingosine[1]

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The Wittig reaction between the ylide **3** from tetradecyltriphenylphosphonium bromide (**2**) and 3-deoxy-3-ethoxycarbonylamino-1,2-*O*-isopropylidene-α-D-ribopentodialdo-1,4-furanose (**11**) yielded either 2,2-dimethyl-6-ethoxycarbonylamino-5-(1-*trans*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro[2,3-*d*]dioxolane (**13a**) or the cis isomer **13b** as the predominant product depending upon the reaction conditions. Subsequent deacetonation and degradative chain shortening gave *trans*-sphingosine (**17a**) and its triacetate **18a** or *cis*-sphingosine (**17b**) and its triacetate **18b**.

In a previous publication from these laboratories,[2a] a stereospecific synthesis of dihydrosphingosine was described. The condensation of 3-benzyloxycarbonylamino-3-deoxy-1,2-*O*-isopropylidene-α-D-ribopentodialdo-1,4-furanose (**9**) with the Wittig reagent (**3**) prepared from tetradecyltriphenylphosphonium bromide (**2**) was carried out to give an olefin **12** as a mixture of cis and trans isomers in which the cis isomer predominated. This olefin (**12a** and **b**) was transformed in four steps to dihydrosphingosine (2-amino-D-erythro-octadecane-1,3-diol). In order for the synthesis to be useful for the preparation of naturally occurring *trans*-sphingosine[2b] it was necessary to devise Wittig conditions which would result in the formation of trans olefin **12a** as the predominant product.

Among the variables that have been reported to affect the course of a Wittig reaction is the nature of the cation

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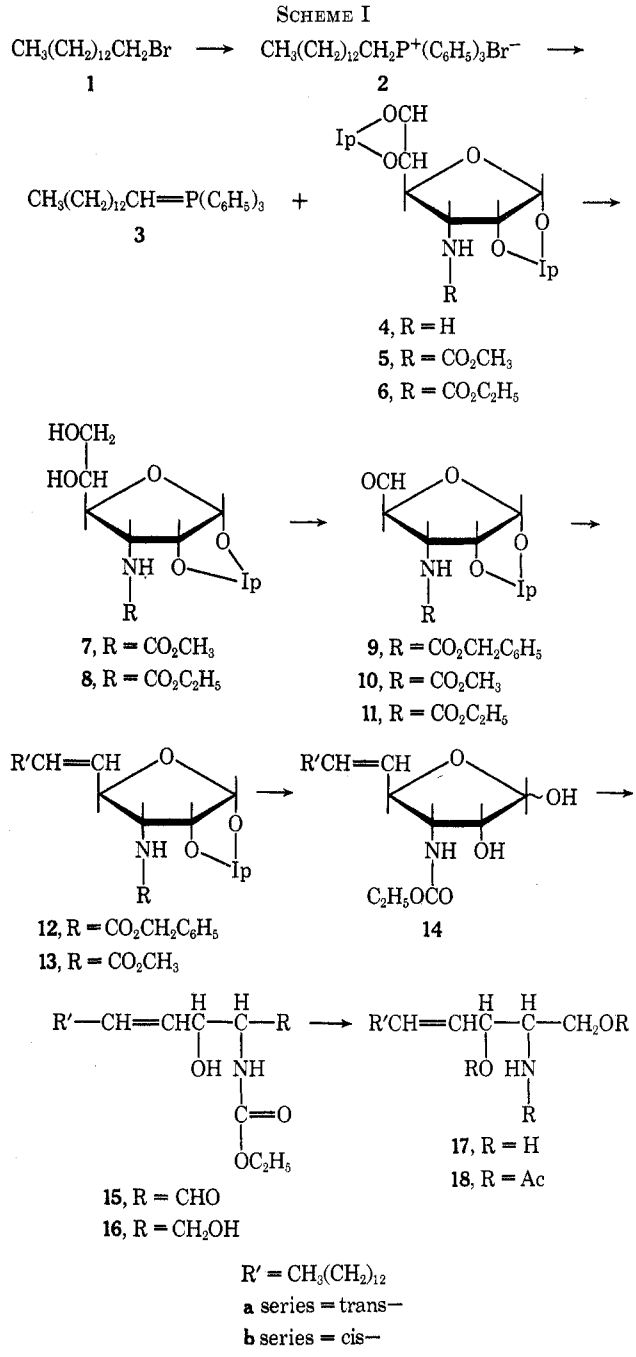
(1) This investigation was supported by the U. S. Public Health Service Research Grant NS 07776 from the National Institute of Neurological Diseases and Stroke.

(2) (a) E. J. Reist and P. H. Christie, *J. Org. Chem.*, **35**, 3521 (1970). (b) In this article, 2-amino-D-erythro-4-octadecene-1,3-diol is referred to as sphingosine.

from the base used to generate the ylide.[3] Thus the use of potassium *tert*-butoxide as the base in place of phenyllithium raised the yield of methylenecyclohexane from 48 to 91%. There are apparent effects on the course of the Wittig reaction by the halide anion which may be present. Lithium iodide was reported[4] to augment the yield of trans olefin in the case of nonstabilized ylides such as **3**. The presence of excess lithium salt is reported to favor trans products.[5] It is rationalized that the decomposition of the zwitterionic betaine to olefin is strongly hindered by lithium salts. This allows sufficient time for the establishment of the equilibrium between the *erythro*-betaine (which gives cis product) and the thermodynamically favored *threo*-betaine (which gives trans product).

A number of these variables were investigated as a means of promoting trans olefin. The substitution of a base other than phenyllithium was not encouraging. The use of a potassium *tert*-butoxide–*tert*-butyl alcohol complex suggested by Schlosser and Christmann[3] gave little product. The use of sodium *tert*-amylate[6] gave a relatively low yield of product. Changing the halogen ion from bromide to iodide showed no appreciable effect on the cis–trans ratio. The effect of extra lithium ions however was noteworthy. Determination[7] of the actual amount of phenyllithium in the 2 *M* phenyllithium solution that was used disclosed that the amount of phenyllithium present represented about one-third of the total base present. When the amount of phenyllithium solution was increased in order that 1 equiv of phenyllithium be added per mole of phosphonium bromide (**2**), the effect was dramatic. The visual effect was that the solution of Wittig reagent in benzene became a deep orange rather than the yellow color observed previously.[2a] The reaction with the sugar aldehyde (**9**) gave a product which showed much stronger absorption at 10.3 μ indicative of a trans olefin (**12a**); however the nmr spectrum indicated that there was not enough aromatic absorption to satisfy the requirements for a benzyloxycarbonyl group. Furthermore, the thin layer chromatograms indicated gross contamination by another product with similar mobility on silica gel which did not appear to be either cis or trans olefin (**12b** or **a**). In view of the apparent loss of some benzyloxy and since it would not be possible to utilize hydrogenolytic removal of the benzyloxycarbonyl group and still maintain the olefin, the benzyloxycarbonyl blocking group was replaced by the methoxycarbonyl blocking group to aid the nmr identification of product. Accordingly, 3-deoxy-1,2-*O*-isopropylidene-3-methoxycarbonylamino-α-D-ribopentodialdo-1,4-furanose (**10**) was prepared in three steps starting from 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**4**) and methyl chloroformate. The Wittig reaction of **3** with **10** using these same conditions gave a 60% yield of product which showed very little methoxyl absorption at τ 6.15 in the nmr and which analyzed for 2,2-dimethyl-6-ethoxycarbonylamino-5-(1-*trans*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro-

SCHEME I



[2,3-*d*]dioxolane (**13a**). The trans assignment was made on the basis of the strong absorption band at 10.3 μ in the infrared spectrum. The nmr spectrum showed a quartet at τ 5.90 which could be assigned to the methylene group of the ethoxyl. The accompanying triplet for the methyl group which should fall at τ 8.8 was masked by the absorption due to the long alkyl side chain. That the product was indeed the ethoxy derivative (**13a**) was proved by repeating the Wittig reaction using 3-deoxy-3-ethoxycarbonylamino-1,2-*O*-isopropylidene-α-D-ribopentodialdo-1,4-furanose (**11**). The same product (**13a**) was isolated as a crystalline solid which was homogeneous on thin layer chromatography and which again showed strong trans-disubstituted olefin absorption at 10.3 μ. The transesterification of alkoxycarbonylamino to give an ethoxycarbonylamino was surprising, however there is a precedent. Organolithium reagents have been reported to attack diethyl

(3) M. Schlosser and K. F. Christmann, *Angew. Chem. Int. Ed. Engl.*, **3**, 636 (1964).
(4) L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, **23**, 2709 (1967).
(5) M. Schlosser, *Angew Chem., Int. Ed. Engl.*, **7**, 650 (1968).
(6) J. M. Conia and J. C. Limasset, *Bull. Soc. Chim. Fr.*, 1936 (1967).
(7) R. G. Jones in *Org. React.*, **6**, 339 (1951).

ether to give lithium ethoxide and ethylene.[8] The lithium ethoxide should then be able to transesterify the alkoxycarbonylamine to the ethoxycarbonylamine, thus giving the observed product.

The dioxolane (**13a**) was converted to *N*-ethoxycarbonyl-*trans*-sphingosine (**16a**) by the sequence used successfully for the preparation of dihydrosphingosine.[2a] A number of different conditions were examined to effect the removal of the ethoxycarbonyl blocking group to give sphingosine (**17a**). The use of potassium hydroxide in ethanol, anhydrous hydrogen fluoride, or sulfuric acid were not successful and only traces of sphingosine resulted. Freshly prepared aqueous barium hydroxide was a satisfactory reagent[2a,9] however and sphingosine was obtained in 60% yield. Acetylation using acetic anhydride in pyridine gave a triacetate (**18a**) which was identical with the triacetate prepared from commercial sphingosine.

cis-Sphingosine (**17b**) was prepared using the earlier described[2a] Wittig conditions in which 1 mol of base (0.3 mol of phenyllithium) was used to generate the ylide (**3**) from phosphonium bromide. Addition of this yellow ylide (**3**) to the aldehydo sugar (**11**) gave a 16% yield of crystalline 2,2-dimethyl-6-ethoxycarbonylamino-5-(1-*cis*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro[2,3-*d*]dioxolane (**13b**). The cis assignment was made on the basis of the fact that trans absorption at at 10.3 μ was not present. The conversion of **13b** to *cis*-sphingosine (**17b**) and its triacetate (**18b**) were performed as described for the trans isomer.

An authentic sample of *cis*-sphingosine was not available for comparison purposes. The melting points of **17b** and the triacetate (**18b**) were compatible with those reported in the literature for *cis*-sphingosine and its triacetate and were significantly different from the melting points reported for any of the other isomers. These facts, coupled with the method of preparation leave little doubt that the product is indeed *cis*-sphingosine (Scheme I).

Experimental Section[10]

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-methoxycarbonylamino-α-D-allofuranose (**5**).—A solution of 4.2 g (16.2 mmol) of 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**4**) in 70 ml of dry pyridine was treated with 12 ml (157 mmol) of methyl chloroformate by the procedure described[2a] for the preparation of 3-benzoyloxycarbonylamino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose. The resulting oil was crystallized from 25 ml of cyclohexane to give 3.86 g (75%) of product, mp 79–84°. The analytical sample was recrystallized from cyclohexane and had mp 72–75°; $[\alpha]^{20}D$ +74° (*c* 0.50, chloroform); λ_{max}^{Nujol} 5.80 μ (carbonyl), 6.55 (amide II), 8.6 (*gem*-dimethyl).

Anal. Calcd for $C_{14}H_{23}NO_7$: C, 53.0; H, 7.31; N, 4.41. Found: C, 53.2; H, 7.45; N, 4.42.

3-Deoxy-3-ethoxycarbonylamino-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**).—A solution of 4.8 g (18.5 mmol) of 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**4**) in 80 ml of dry pyridine was treated with 15.6 ml (164 mmol) of ethyl chloroformate as described for the benzyloxycarbonyl analog[2a] to give 6 g of product as an oil. Chromatography of the crude oil on 120 g of silica gel using chloroform–ethyl acetate (4:1) as the developing solvent gave 4.19 g (68%) of product (**6**) as an oil: λ_{max}^{film} 5.85 μ (carbonyl), 6.60 (amide II), 8.6 (*gem*-dimethyl).

2,2-Dimethyl-6-ethoxycarbonylamino-5-(1-*trans*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro[2,3-*d*]dioxolane (**13a**). **A.**—From 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-methoxycarbonylamino-α-D-allofuranose (**5**). A solution of 1.0 g of **5** in 25 ml of 75% aqueous acetic acid was heated at 60° under nitrogen for 20 min then was cooled to 0° in an ice–salt bath. A solution of 5 *N* aqueous sodium hydroxide was added dropwise with stirring until neutrality was reached (pH ≈7.5). The mixture was extracted with four 50-ml portions of chloroform, and the chloroform extracts were combined, dried, and evaporated to dryness *in vacuo* to give 884 mg of 3-deoxy-1,2-*O*-isopropylidene-3-methoxycarbonylamino-α-D-allofuranose (**7**) as an oil. Thin layer chromatography showed 1 spot at R_f 0.20 in solvent A.

Treatment of the diol (**7**) (884 mg) in 14 ml of 50% aqueous methanol with sodium metaperiodate in the manner described for the benzyloxycarbonylamino derivative[2a] gave, after filtration and chloroform extraction, 702 mg of 3-deoxy-1,2-*O*-isopropylidene-3-methoxycarbonylamino-α-D-ribopentodialdo-1,4-furanose (**10**) as an oil. Thin layer chromatography in solvent A showed one spot at R_f 0.4: λ_{max}^{film} 3.0 μ (NH, OH), 5.85 (carbonyl).

To a stirred solution of 1.67 g (3.1 mmol) of tetradecyltriphenylphosphonium bromide (**2**) in 100 ml of dry benzene under nitrogen atmosphere was added 9.3 ml [3.25 mmol in ether–benzene (30:70)] of phenyllithium which contained 18.6 mmol of excess base and lithium ion. A bright orange color developed after 10 min and a solution of 700 mg (2.87 mmol) of aldehyde (**10**) in 10 ml of dry benzene was added. The Wittig reaction was carried out and the product was chromatographed by the procedure described for the benzyloxy analog.[2a] Evaporation of the solvent from the eluate of the silica gel column gave 748 mg (62% based on aldehyde **10**) of crystalline product. Thin layer chromatography in solvent B showed one main spot at R_f 0.52 with a minor component at R_f 0.45.

The nmr spectrum showed the complete absence of methoxyl band at τ 6.15. Instead the bands typical of ethoxyl, τ 5.90 (quartet) were present. Recrystallization from aqueous methanol gave the analytical sample: mp 45–48°; $[\alpha]^{22}D$ +9° (*c* 0.5, chloroform); λ_{max}^{Nujol} 5.80 μ (carbonyl), 6.60 (amide II), 8.60 (*gem*-dimethyl), 10.35 (trans-disubstituted olefin). Thin layer chromatography in solvent B showed on spot at R_f 0.52.

Anal. Calcd for $C_{25}H_{45}NO_5$: C, 68.3; H, 10.3; N, 3.19. Found: C, 68.7; H, 10.6; N, 3.23.

B. From 3-Deoxy-3-ethoxycarbonylamino-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**).—A solution of 2.9 g (8.75 mmol) of **6** in 65 ml of 75% aqueous acetic acid was deacetonated as described for the methoxycarbonyl analog (**5**) and the resulting 5,6-diol (**8**) was cleaved with sodium metaperiodate to give 2.12 g (90% overall) of 3-deoxy-3-ethoxycarbonylamino-1,2-*O*-isopropylidene-α-D-ribopentodialdo-1,4-furanose (**11**) as an oil.

Treatment of the Wittig reagent prepared from 4.72 g (8.75 mmol) of tetradecyltriphenylphosphonium bromide (**2**) and 31 ml of 0.3 *M* (9.7 mmol) phenyllithium which contained 63.6 mmol of excess lithium ion and base with the aldehyde (**11**) (8.2 mmol) as described for the methoxy analog (**10**) gave 2.0 g (55%) of crystalline product after evaporation of the benzene–ether eluent from the column.

Thin layer chromatography showed one spot at R_f 0.50 in solvent B: λ_{max}^{Nujol} 5.80 μ (carbonyl), 6.60 (amide II), 8.60 (*gem*-dimethyl), 10.35 (trans-disubstituted olefin). Chromatographically and spectroscopically (infrared and nmr) the product was identical with the recrystallized product obtained from 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-methoxycarbonylamino-α-D-allofuranose (**5**).

***N*-Ethoxycarbonyl-*trans*-sphingosine** (**16a**).—A solution of 1.9 g (4.3 mmol) of 2,2-dimethyl-6-ethoxycarbonylamino-5-(1-*trans*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro[2,3-*d*]dioxolane (**13a**) in 95 ml of 80% aqueous acetic acid was heated at reflux for 3 hr and then was evaporated to dryness *in vacuo* to give 1.64 g of 1,2-diol (**14a**) as a solid. Thin layer chromatography in solvent C showed one main spot at R_f 0.20 with minor

(8) (a) H. Gilman, A. H. Haubein, and H. Hartzfield, *J. Org. Chem.*, **19**, 1034 (1954); (b) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69** [5], 693 (1969).

(9) (a) E. Klenk, *Hoppe-Seyler's Z. Physiol. Chem.*, **153**, 74 (1926); (b) H. E. Carter, D. S. Galanos, and Y. Fujino, *Can. J. Biochem.*, **34**, 320 (1956).

(10) Melting points are corrected. Organic solutions were dried using anhydrous magnesium sulfate. Thin layer chromatograms were run on silica gel HF (E. Merck A. G. Darmstadt). Spots were detected using iodine vapor. Solvent systems used for developing the chromatograms were; A, ethyl acetate–chloroform (1:1); B, diethyl ether–benzene (1:9); C, diethyl ether–benzene (1:1); D, benzene–diethyl ether (1:9); E, chloroform–methanol–2 *N* aqueous ammonium hydroxide (40:10:1). The nmr spectra were run on the Varian T-60. The solvent used was deuteriochloroform with 1% tetramethylsilane as an internal standard unless otherwise indicated. The normality and total base content of a commercial sample of phenyl lithium in benzene–ether (70:30) were determined by the method described for the analysis of butyl lithium by R. G. Jones.

components at R_f 0.60 and 1.00: λ_{max}^{film} 5.90 μ (carbonyl), 6.50 (amide II), 10.30 (trans-disubstituted olefin).

A solution of the diol (1.64 g, 4.1 mmol) in 380 ml of methanol was treated with 1.05 g (4.9 mmol) of sodium metaperiodate under nitrogen in the manner described for the benzyloxy analog[2a] to yield 1.48 g of aldehyde (**15a**) as a brown oil: λ_{max}^{film} 5.85 μ (carbonyl), 6.60 (amide II), 10.30 (trans-disubstituted olefin).

Treatment of the aldehyde (**15a**) (1.48 g, 4 mmol) in 217 ml of methanol with 139 mg (3.7 mmol) of sodium borohydride in 16 ml of methanol by the procedure described for the benzyloxycarbonyl analog[2a] gave 1.23 g of crude product as an oil which partially crystallized. Thin layer chromatography in solvent D showed the major spot at R_f 0.50 with many trace contaminants.

The crude product was chromatographed on 100 g of silicic acid. The column was washed with 100 ml of dry benzene, and then the product was eluted with 1000 ml of 10% benzene in ether to yield 623 mg of material (19% overall yield based on **6**). Thin layer chromatography showed one spot at R_f 0.50 in solvent D: λ_{max}^{Nujol} 3.0 μ (OH, NH), 5.90 (carbonyl), 6.50 (amide II), 10.35 (trans-disubstituted olefin).

trans-**Sphingosine** (**17a**).—A solution of 100 mg (0.27 mmol of *N*-ethoxycarbonyl-*trans*-sphingosine (**16a**) in 1 ml of dioxane was treated with 1 ml of a solution of freshly prepared 10% aqueous barium hydroxide octahydrate under nitrogen. The reaction was heated at 105° for 16 hr then was cooled and diluted with 10 ml of water and treated with carbon dioxide to precipitate the excess barium ion. The mixture was extracted with several portions of chloroform. The chloroform layers were dried and evaporated to dryness *in vacuo* to give 50 mg of *trans*-sphingosine as a gummy pale brown solid: λ_{max}^{film} 6.30 μ (amine), 10.35 (trans-disubstituted olefin).

The crystals were triturated with cold ethyl acetate and filtered to give 30 mg of cream-colored solid, mp 80–84°. The analytical sample was recrystallized from ethyl acetate and had mp 80–84°.

Anal. Calcd for $C_{18}H_{37}NO_2 \cdot H_2O$: C, 68.1; H, 12.4; N, 4.41. Found: C, 68.4; H, 12.2; N, 4.20.

trans-Sphingosine triacetate (**18a**) was prepared using acetic anhydride in pyridine and recrystallized from acetone to give crystals, mp 99–101°, $[\alpha]^{24}D$ −13° (*c* 0.50, chloroform). The infrared spectrum was identical with that of a sample of sphingosine triacetate prepared from commercially available sphingosine and a mixture melting point between the two samples showed no melting point depression.

trans-Sphingosine is reported to have mp 82.5°, $[\alpha]^{22}D$ −3° (chloroform);[11] triacetate, mp 101–102°, $[\alpha]^{24}D$ −12° (chloroform).[12]

2,2-Dimethyl-6-ethoxycarbonylamino-5-(1-*cis*-pentadecenyl)-3a,5,6,6a-tetrahydro-D-ribofuro[2,3-*d*]dioxolane (**13b**).—The Wittig condensation was carried out starting with the ylide (**3**) prepared from 9.51 g (17.6 mmol) of tetradecyltriphenylphosphonium bromide (**2**) and 7.52 ml of "2.35 *M*" (17.7 mmol of total base, 2.6 mmol of phenyllithium) phenyllithium in 500 ml of dry benzene. After 10 min, a yellow color had developed and 4.23 g (16.3 mmol) of 3-deoxy-3-ethoxycarbonylamino-1,2-*O*-isopropylidene-α-D-ribopentodialdo-1,4-furanose (**11**) in 20 ml of dry benzene was added and the reaction was performed and worked up in the manner described for the benzyloxycarbonylamino analog.[2a] A total yield of 1.19 g (16% based on aldehyde **11**) of crystalline product was eluted from the silicic acid column using 10% ether in benzene. Recrystallization from aqueous methanol gave the analytical sample: mp 49–51°; $[\alpha]^{23}D$ −17° (*c* 0.50, chloroform); λ_{max}^{Nujol} 5.80 μ (carbonyl), 6.60 (amide II), 8.60 (*gem*-dimethyl). There was no absorption band at 10.3 μ. indicative of a trans-disubstituted olefin. Thin layer chromatography in solvent B showed one spot at R_f 0.48.

Anal. Calcd for $C_{25}H_{45}NO_5$: C, 68.3; H, 10.3; N, 3.19. Found: C, 68.4; H, 10.3; N, 3.14.

N-**Ethoxycarbonyl-*cis*-sphingosine** (**16b**).—The cis Wittig product (**13b**) (1.16 g, 2.65 mmol) was deacetonated with acetic acid, treated with sodium metaperiodate, and reduced with sodium borohydride by the same procedures used for the trans analogs to give 477 mg of product as a crystalline solid (47% overall yield). Recrystallization from hexane gave the analytical sample as a white powder: mp 55–56°; $[\alpha]^{20}D$ −11° (*c* 0.50, chloroform); λ_{max}^{Nujol} 2.95 μ (NH, OH), 5.95 (carbonyl), 6.50 (amide II). There was no trans olefin absorption at 10.3 μ. Thin layer chromatography in solvent D showed one spot at R_f 0.50.

Anal. Calcd for $C_{21}H_{41}NO_4$: C, 67.9; H, 11.1; N, 3.77. Found: C, 68.1; H, 11.3; N, 3.92.

cis-**Sphingosine** (**17b**).—A solution of 54 mg (0.145 mmol) of *N*-ethoxycarbonyl-*cis*-sphingosine (**16b**) in 2 ml of dioxane was treated with 2 ml of freshly prepared 10% aqueous barium hydroxide as described for the preparation of *trans*-sphingosine.

Evaporation of the chloroform layer gave 33.5 mg (77%) of white crystalline residue, mp 73–74°, $[\alpha]^{21}D$ −5° (*c* 0.50, chloroform).

Thin layer chromatography in solvent E showed one spot at R_f 0.50. *trans*-Sphingosine used for a reference had R_f 0.57.

Acetylation of *cis*-sphingosine using acetic anhydride in pyridine in the usual fashion gave the triacetate (**18b**), mp 86–87°. Recrystallization from acetone gave material with mp 90–91°. Thin layer chromatography in solvent A showed one spot at R_f 0.52. The triacetate of *trans*-sphingosine used for a reference had R_f 0.43.

Anal. Calcd for $C_{24}H_{43}NO_5$: C, 67.7; H, 10.2; N, 3.29. Found: C, 68.0; H, 10.2; N, 3.37.

The literature reports *cis*-sphingosine to have mp 72–73°[13] and its triacetate to have mp 83–84°.[13]

Registry No.—**5**, 26308-81-6; **6**, 26308-82-7; **10**, 26308-83-8; **13a**, 26308-84-9; **13b**, 26308-85-0; **14a**, 26308-86-1; **15a**, 26308-87-2; **16a**, 26308-88-3; **16b**, 26308-89-4; **17a**, 123-78-4; **17b**, 26308-91-8.

(11) E. Klenk and W. Diebold, *Hoppe-Seyler's Z. Physiol. Chem.*, **198**, 25 (1931).

(12) H. E. Carter, W. P. Norris, F. J. Glick, G. E. Phillips, and R. Harris, *J. Biol. Chem.*, **170**, 269 (1947).

(13) C. A. Grob and F. Gadient, *Experientia*, **12**, 334 (1956).