orientations about the β-γ bond; in one orientation N_δ (or N3) of His 121 could be a hydrogen bond acceptor, and in the other orientation N_ϵ (or N1) can act as a hydrogen bond donor to neighboring residues such as Glu 75, Tyr 91, and/or Tyr 93.[9]

The direct observation of the H_δ protons of histidine residues has allowed heterogeneity to be detected under conditions where it would have been missed if only the H_ϵ protons had been studied. For example, our isotopic labeling revealed heterogeneity in addition to that caused by proline isomerism[1,2] and allowed direct observation of the H_δ resonance of His 121 that could not be located in studies recently reported by Markley's laboratory.[7] We expect that the ability to detect conformational heterogeneity in SNase via both the H_δ and H_ϵ protons will prove useful in our studies of the effect of active site mutations on the conformations of the mutant proteins.[5,6]

Acknowledgment. This research was supported by GM-34573 from the National Institutes of Health to P.H.B. and J.A.G. and by PCM-8314322 from the National Science Foundation to P. H.B.

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A Practical and Enantioselective Synthesis of Glycosphingolipids and Related Compounds. Total Synthesis of Globotriaosylceramide (Gb_3)

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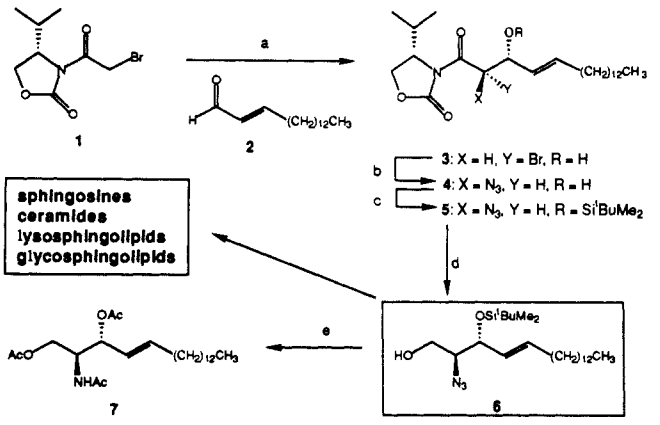
Glycosphingolipids are a class of naturally occurring bioactive compounds usually embedded in the membrane of all animal cells and in some plant cells.[1] The clinically important blood group antigens[2] and the immunologically relevant tumor-associated oligosaccharides[3] are examples of glycosphingolipids. The "intelligent" roles attributed to these biomolecules include mediation of cell-cell recognition and communication, growth regulation, and antibody interactions.[4] Due to their increasingly recognized importance in biomedical research, these molecules have attracted considerable attention from the isolation[5] and synthetic[6] points of view. Despite these efforts, however, these molecules remain relatively inaccessible, particularly in homogeneous form. In this communication, we report (1) a practical, short, and enantioselective route to glycosphingolipids which can also deliver enantiomerically pure sphingosine, ceramides, lysosphingolipids, and other related derivatives and (2) a total synthesis of globotriaosylceramide (Gb_3, **8**) and confirmation of its structure.

Scheme I[a]



[a] Reagents and conditions: (a) 1.2 equiv of $(nBu)_2BOTf$, 1.4 equiv of Et_3N, -78 °C, 30 min, then 20 °C for 2 h, added 0.75 equiv of **2** at 0 °C, 2 h, then H_2O_2/MeOH/ether, 0 °C, 1 h, 72%; (b) 2.0 equiv of NaN_3, DMSO, 25 °C, 12 h, 92%; (c) 1.5 equiv of t-$BuMe_2SiOTf$, 2.0 equiv of 2,6-lutidine, CH_2Cl_2, 0 °C, 2.5 h, 97%; (d) 3.0 equiv of $LiBH_4$, THF 0 °C, 3 h, 81%; (e) (i) 1.5 equiv of nBu_4NF, THF, 25 °C, 1 h, 90%, (ii) 10 equiv of $HS(CH_2)_3SH$, 10 equiv of Et_3N, MeOH, 25 °C, 24 h, (iii) 4.0 equiv of Ac_2O, 4.0 equiv of DMAP, CH_2Cl_2, 0 °C, 90%.

The strategy for the present synthesis of glycosphingolipids focuses on the asymmetric construction of the sphingosine equivalent **6** (Scheme I) following the principles advanced by Evans et al.[7] and Pridgen et al.[8] and its efficient and stereospecific coupling to carbohydrate fragments with the two-stage activation procedure for glycosidation recently reported from these laboratories[9] (Scheme II). The details for the synthesis of the sphingosine pregenitor **6** are shown in Scheme I. Thus, the oxazolidinone derivative **1** was converted to its boron enolate and condensed with the α,β-unsaturated aldehyde **2** to afford derivative **3**[10] in 72% yield.[11] Displacement of the bromide in **3** with NaN_3 led to the azide **4** in 92% yield with complete inversion of stere-

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‡ Visiting scientist from Kyowa Hakko Kogyo Co., Japan, 1987-1988.

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(10) All new compounds exhibited satisfactory spectral and analytical and/or exact mass data. Yields refer to spectroscopically and chromatographically homogeneous materials.

(11) In addition to compound **3**, a second product, presumed to be the other syn diastereoisomer of **3**, was obtained in ca. 5% yield.

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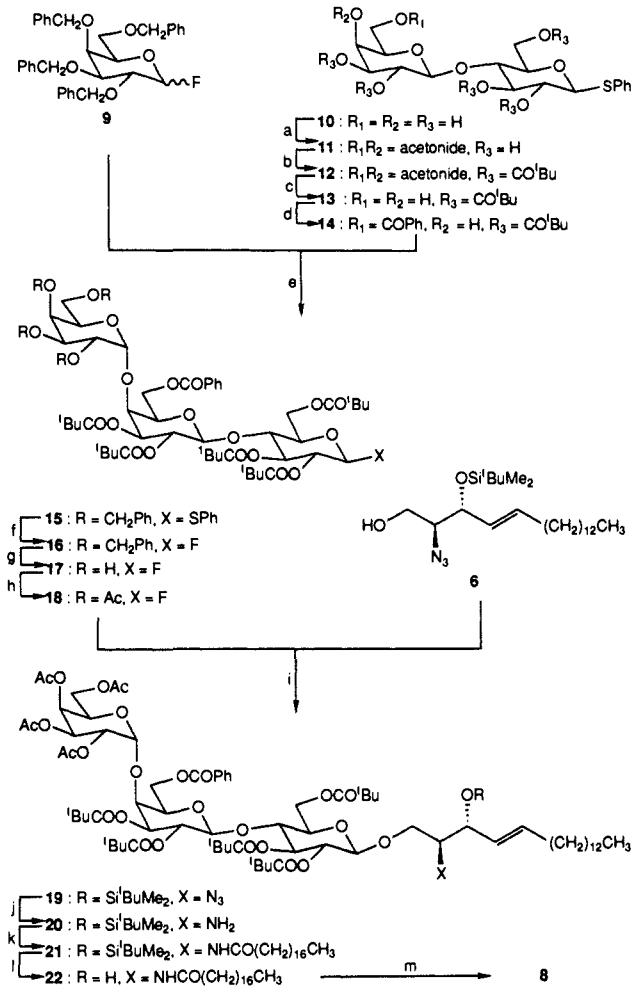
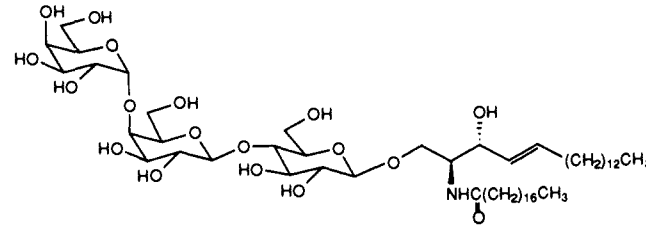
Scheme II[a]



[a]Synthesis of globotriaosylceramide (Gb_3, **8**). Reagents and conditions: (a) $Me_2C(OMe)_2$, TsOH catalyst, DMF, 25 °C, 2 h; (b) 8.0 equiv of ^{t}BuCOCl, DMAP catalyst, pyridine, 75 °C, 40 h, 60%; overall from **10**; (c) CF_3COOH, THF/H_2O; 2:1, 0 °C, 1.5 h, 95%; (d) 1.1 equiv of PhCOCN, 1.3 equiv of Et_3N, DMF, −20 to −10 °C, 0.5 h, 80%; (e) 2.0 equiv of **9**, 2.0 equiv of $AgClO_4$, 2.0 equiv of $SnCl_2$, 4 Å MS, Et_2O, 0 °C, 2 h, 60%; (f) 1.2 equiv of NBS, 10.0 equiv of HF·pyr, CH_2Cl_2 −20 to 0 °C, 89%; (g) H_2, $Pd(OH)_2$–C, EtOH, 25 °C, 24 h, 95%; (h) 5.0 equiv of Ac_2O, 5.0 equiv of pyridine, DMAP catalyst, CH_2Cl_2, 0–25 °C, 95%; (i) 4.7 equiv of **6**, 2.0 equiv of $AgClO_4$, 2.0 equiv of $SnCl_2$, 1.0 equiv of 2,6-lutidine, CH_2Cl_2, 0 °C, 12 h, 80%; (j) 2.0 equiv of Ph_3P, 10 equiv of H_2O, benzene, 45 °C, 6 h, 90%; (k) 1.2 equiv of octadecanoyl chloride, 1.5 equiv of Et_3N, DMAP catalyst CH_2Cl_2, 0 °C, 1 h, 97%; (l) 1.5 equiv of nBu_4NF, THF, 0–25 °C, 3 h, 95%; (m) 1.0 equiv of NaOMe, MeOH, 60 °C, 24, 90%.

ochemistry at the reaction center. Silylation of the hydroxy group in **4** then gave the silyl derivative **5** in 97% yield which was smoothly reduced with excess $LiBH_4$ in THF affording the requisite primary alcohol **6** (82% yield). The sphingosine equivalent **6** was converted to the known[12] triacetate **7** by (i) desilylation, (ii) azide reduction [$HS(CH_2)_3SH$, Et_3N,[13] leading to sphingosine], and (iii) acetylation (81% overall yield).

Besides proving to be an excellent precursor to optically active sphingosine and ceramide derivatives, compound **6**, with the azido group as a masked equivalent to a primary amine, served admirably as a coupling partner to form glycosphingolipid and lysosphingolipid precursors by glycosidation with suitable carbohydrate donors. Thus, galactosylceramide,[14] lactosylceramide,[15] and globotriaosylceramide (Gb_3, **8**)[16] were synthesized from **6** and



suitably protected glycosylfluorides. The chemistry involved in these syntheses is exemplified in Scheme II which outlines the construction of the biologically important[17] Gb_3 (**8**) in its naturally occurring form. The present synthesis utilizes the trisaccharide fluoride **18** and the sphingosine equivalent **6** as advanced intermediates (Scheme II). Lactosylphenylthioglycoside **10**[18] was selectively transformed to its terminal acetonide **11** and then fully esterified to the pentapivalate **12** in 60% overall yield. Removal of the acetonide group from **12** by acid hydrolysis (95%) followed by monobenzoylation led to the desired lactosyl derivative **14** (80%) via diol **13**. The benzylated galactosyl fluoride **9**[18] was then coupled with the dissaccharide **14** under the influence of $AgClO_4$–$SnCl_2$ to afford trisaccharide **15** in 60% yield.[18] As expected from the anomeric effect and the presence of a benzyl group at the 2-position of glycosyl fluoride **9**, the newly generated glycoside bond in **15** was exclusively of the α-stereochemistry as determined by 2D NMR experiments.[19] Having performed their function of stereospecific α-glycoside bond formation, the benzyl groups were then removed from the trisaccharide unit by sequential fluoride formation (**15** → **16**, 85%) and hydrogenolysis (**16** → **17**, 90%). The stability of glycosyl fluorides to hydrogenolysis conditions was crucial to the success of the present sequence and should considerably expand the utility of these intermediates in oligosaccharide synthesis. The free hydroxyl groups in **17** were then acetylated (**17** → **18**, 95%) in preparation for the final coupling reaction with the sphingosine equivalent **6**. The coupling of trisaccharide fluoride **18** with excess of **6** proceeded under the usual conditions ($AgClO_4$–$SnCl_2$)[18] to afford compound **19** in 80% yield and with complete stereocontrol of the new glycoside bond in the desired sense as expected from the β-directing ability of the pivalate group, strategically placed at the 2-position of the trisaccharide unit **18**.

The remaining steps of the synthesis involving (i) generation of an amino group from the azide (**19** → **20**, 90%), (ii) amide

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(18) Compound **9** was obtained from galactose pentaacetate in ca. 60% overall yield by (i) treatment with PhSH-$SnCl_4$, (ii) exposure to NaOMe-MeOH, (iii) benzylation with NaH-benzyl bromide, and (iv) fluoride formation with NBS-HF·pyr. Compound **10** was prepared from lactose octaacetate in ca. 70% overall yield by steps (i) and (ii) above. For more details of these and the coupling procedures, see: ref 9a. See, also: Mukaiyama, T.; Murai, Y.; Shoda, S. *Tetrahedron Lett.* **1981**, *22*, 431.

(19) Due to signal overlap, a 2D ^1H–^{13}C heterocorrelation experiment was carried out on compound **15** (500–125 MHz, $CDCl_3$). The three anomeric carbons were found at δ 86.1 (C-1), 100.1 (C-1′), and 100.4 (C-1″), whereas the anomeric protons resonated at δ 4.42 (d, J = 9.3 Hz, 1 H, H-1′), 4.61 (d, J = 9.8 Hz, 1 H, H-1), and 4.61 (d, J < 5.0 Hz, 1 H, H-1″). The latter coupling constant established the α-configuration of the newly formed glycoside bond in **15**. This structural assignment was confirmed by ^1H NMR spectroscopy at the stage of **8** which was, furthermore, identical with an authentic sample of natural Gb_3 (**8**).

formation with octadecanoyl chloride (**20** → **21**, 97%), (iii) desilylation (**21** → **22**, 95%), and (iv) pivalate removal (**22** → **8**, 90%) proceeded smoothly, leading to globotriaosylceramide (Gb_3, **8**) in excellent overall yield. Synthetic Gb_3 (**8**) was identical with an authentic sample of this compound by the usual criteria.[20]

The described total synthesis of Gb_3 (**8**) demonstrates the power of the developed strategy for the synthesis of complex glycosphingolipids, confirms the assigned structure[16] to Gb_3 as **8**, and renders this glycosphingolipid readily available in pure form for further biological investigations. Further extensions of this strategy to the synthesis of more complex glycosphingolipids from the globo-, ganglio-, and lactoseries are currently in progress.

Acknowledgment. We express our many thanks to Dr. Hans Lönn of Biocarb AB, S-223 70, Lund, Sweden for a sample of globotriaosylceramide (Gb_3, **8**). Our thanks are also due to Drs. George T. Furst and John Dykins of this department for their superb assistance and helpful comments regarding NMR and mass spectroscopy. This work was financially supported by the National Institutes of Health, Merck Sharp and Dohme, U.S.A., Nippon Zeon Co., and Kyowa Hakko Kogyo Co., Japan.

Supplementary Material Available: Schemes with reagents and conditions for the synthesis of galactosylceramide (gal-cer) and lactosylceramide (lac-cer) and a listing of R_f, mp*, $[\alpha]_D$, IR, ^1H NMR, and ^{13}C** NMR data for the compounds **6****, **7***, **9**, **14**, **15****, **18**, **19**, **21**, gal-cer, lac-cer, and Gb_3 (**8**)** (8 pages). Ordering information is given on any current masthead page.

(20) For previous syntheses of the trisaccharide fragment of Gb_3 (**8**), see: (a) Jacquinet, J.-C.; Sinay, P. *Carbohydr. Res.* **1985**, *143*, 143. (b) Garregg, P. G.; Hultberg, H. *Carbohydr. Res.* **1982**, *110*, 261. (c) Cox, D. D.; Metzner, E. K.; Reist, E. J. *Carbohydr. Res.* **1978**, *63*, 139. (d) Dahmen, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlstrom, A.-S. *Carbohydr. Res.* **1984**, *127*, 15. (e) Paulsen, H.; Bunsch, A. *Carbohydr. Res.* **1982**, *100*, 143. For previous synthesis of Gb_3, albeit in low overall yield, see: (a) Koike, K.; Sugimoto, M.; Sato, S.; Ito, Y.; Nakahara, Y.; Ogawa, T. *Carbohydr. Res.* **1987**, *163*, 189. (b) Shapiro, D.; Acher, A. *J. Chem. Phys. Lipids* **1978**, *22*, 197. To the best of our knowledge, this is the first reported comparison of synthetic and natural samples of Gb_3 thus providing an unambiguous proof of the structural identify of this glycosphingolipid.

ENDOR Detection of Diastereomers Formed by Inclusion of a Prochiral Spin Probe into β-Cyclodextrin

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Molecular receptors which are capable of recognizing chiral guests attract much attention as sophisticated models of enzymes which have the capability of binding with such substances.[1] Cyclodextrin is a natural product which can recognize chiral molecules by producing diastereomeric pairs upon inclusion of components of racemates,[2-6] and induced circular dichroism can be observed when an achiral guest molecule is included.[7,8] A combination of the induced chirality in the guest molecule and the chirality of cyclodextrin itself should result in the formation of a diastereomeric mixture. This report deals with the detection of such diastereomers by ENDOR spectroscopy.

It has been reported that the ESR spectra of diphenylmethyl *tert*-butyl nitroxide (aminoxyl) (**1**) in aqueous solutions of β-cyclodextrin show two kinds of inclusion complexes which are assigned to bimodal inclusion, i.e., "*tert*-butyl-in" or "phenyl-in".[9] Both complexes have similar β-hydrogen and nitrogen hyperfine splittings (hfs). Because of the small differences in hfs, ENDOR spectroscopy was applied to obtain more accurate values for the hfs constants. ENDOR spectra were obtained by choosing a relatively pure ESR line in which the line intensity from one species is dominant. When the external field is fixed on the line which was previously assigned to the "phenyl-in" inclusion complex,

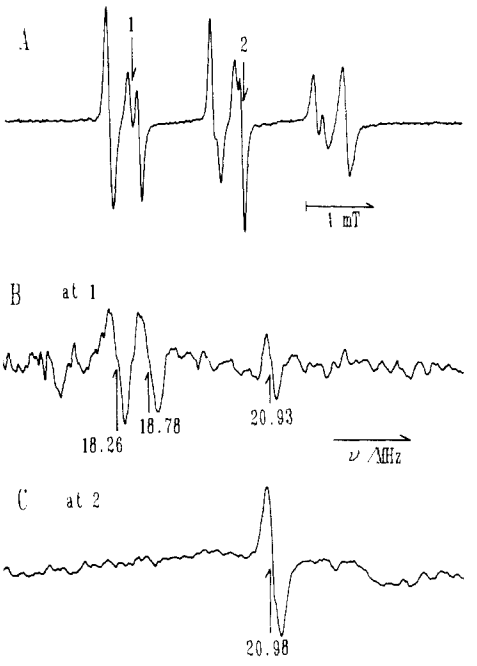
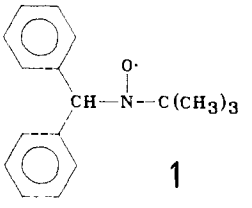


Figure 1. A: ESR spectrum of **1** in water in the presence of 1.0×10^{-2} M β-cyclodextrin at room temperature. Incident microwave power is 6 mW, and the modulation width is 0.0125 mT. B: Proton-ENDOR spectrum of **1** in water in the presence of 1.0×10^{-2} M β-cyclodextrin at 285 K. The external field is fixed at the position marked as **1** in Figure 1A. The incident microwave power is 100 mW, the rf power setting is 150 W, and the FM depth of rf is 100 kHz at the FM frequency of 12 kHz. The scan rate is 15 s over 10 MHz, and the signal is accumulated for 500 times. Free-proton frequency is 14.42 MHz. C: Proton-ENDOR spectrum of **1** in water in the presence of 1.0×10^{-2} M β-cyclodextrin at 285 K. The external field is fixed at the position marked as *2* in Figure 1A. The spectrometer settings are the same as Figure 1B, except the accumulation is 100 times. Free-proton frequency is 14.47 MHz.

Table I. Hyperfine Splitting Constants of β-Cyclodextrin Inclusion Complex of Nitroxide **1** in Water

	A_H,[a] mT	A_N,[b] mT
phenyl-in complex	0.311	1.565
	0.274	1.565
tert-butyl-in complex	0.465	1.541
1 in water	0.422[b]	1.590

[a] By ENDOR at 285 K, error is ±0.003 mT. [b] By ESR at room temperature, error is ±0.005 mT.



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