particular interest although it is lengthy due to the protection, deprotection and activation steps required to elongate the oligosaccharide chain. The use of glycosyltransferases, which achieve regio- and stereospecific reactions, is an attractive alternative.

We describe the chemo-enzymatic synthesis of an analogue of the ganglioside GM_3[1]. A glycolipid acceptor has been chemically prepared and glycosylated using commercially available glycosyltransferases.

The results show that, despite its hydrophobicity, a glycolipid can be recognised by the glycosyltransferases in an aqueous medium.

[1] B. Guilbert, T. H. Khan, S. L. Flitsch, *J. Chem. Soc. Chem. Commun.*, 1992, 1526.

S17.9
Enzyme-Aided Synthesis and NMR-Studies of *O*-Linked Type Oligosaccharides in Reducing Form

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Starting from disaccharide Galβ1-3GalNAc (Sigma), the core 2 type O-linked oligosaccharides up to the pentasaccharide GlcNAcβ1-3Galβ1-4GlcNAcβ1-6(Galβ1-3)GalNAc have been synthesised in reducing form by enzyme-aided *in vitro* biosynthesis. The ^{1}H NMR resonances of all the saccharides in D_2O have been totally assigned by the use of DQFCOSY and TOCSY techniques. The assignment of ^{13}C resonances was carried out by DEPT and HMQC spectra, which also made it possible to conform the assignments of the H6 resonances of every monosaccharide unit.

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S17.10
Synthesis of Glycosyl-*Threo*-Sphingosines via Schiff Base-Protected Amino Acids

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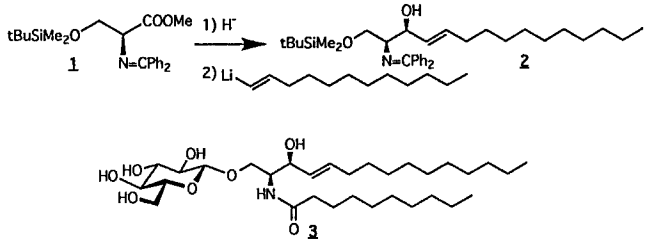

The use of serine Schiff base esters such as ***1*** permits the construction of *threo*-sphingosines in good chemical yield with excellent stereocontrol. Complexation of the bidentate Schiff base esters with $iBu_3Al \cdot iBu_2AlH$, followed by the addition of a Li or Mg carbanion provided high yields of *threo*-amino alcohols ***2*** without the intermediacy of labile α-amino aldehydes.(1) Subsequent 3-OH protection and 1-OH deprotection provided sphingosine derivatives which were glycosylated. Elaboration to the *threo*-glycosphingolipids ***3*** is described. (2)

(1) R. Polt, M. Peterson and L. DeYoung, *J. Org. Chem.*, **57**, 5469 – 5480 (1992).
(2) M. Peterson and R. Polt, *J. Org. Chem.* submitted.

S17.11
Functional Fluorescent Labeling of Carbohydrates and its Application to Lipopolysaccharide

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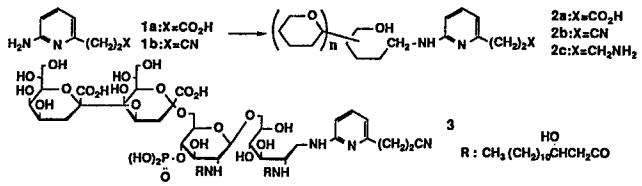
Recently, much attention has been paid for utilization of neoglycoconjugates to elucidate the biological functions of sugar chains. In the present study, we described the novel methodology for the preparation of neoglycoconjugates from fluorescent labeled sugars. Since 2-aminopyridine proved to be very versatile for fluorescent labeling, we synthesized functional fluorescence-labeling reagents **1a** and **1b** which possess linker moieties for binding to matrices such as proteins and polymers. Reductive amination of sugar chains with **1a** and **1b** gave the labeled sugars **2a** and **2b**, which were readily purified by reversed phase HPLC. The labeled sugar **2a** could be coupled with the ε-amino group of a Lys derivative to give a neoglycoprotein model. Some neoglycoconjugates were also prepared from **2b** via amine **2c**.



This method was then applied to immunological study of R-type lipopolysaccharide (LPS). After selective cleavage of the 1-phosphoryl group of Re-LPS in the presence of the acid-sensitive ketosidic linkages of Kdo, all *O*-acyl moieties were removed to facilitate purification of the product. The acyl moieties proved to have no significant influence to the immunogenic properties of LPS. Functional fluorescent labeling of the resultant 1-dephospho derivative with **1b** gave labeled product **3** which was readily purified by reversed phase HPLC. Biological analyses of **3** are now being investigated.