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NEW SURFACE ACTIVE COMPOUNDS CONTAINING SUGAR MOIETIES

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ÖZET

ŞEKER KISIMLARI İÇEREN YENİ YÜZEY AKTİF MADDELER

SARIKAHYA, Hasan

Doktora Tezi, Kimya Bölümü
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Yüzey aktif maddelerin baş grubu olarak kullanılabilmeye uygun karbohidrat türevleri sentezlendi. Bu hidrofilik guruplar, şeker molekülünün ve hidrofobik yan zincirlerin boyutu ve tabiatına bağlı olarak, su içinde çözünürlük ve/veya dispersiyon sağlarlar. Çeşitli zincir uzunluğuna sahip hidrofobik gurupların, hidrofil gurup ile bir araya gelmesi, ya alkil halojenürler ile doğrudan eterifikasyon ile, örneğin allil, butil ve oktil klorürle ya da epiklorohidrin ile eterleştirilmiş üründeki epoksi halkasının çeşitli uzun zincirli alkoller ve aminlerle açılması ile gerçekleşmektedir. Bir diğer yaklaşım ise serbest hidroksil gurubu içeren korunmuş şekerin ketona yükseltgenip alkil mağnezyum bromür reaksiyonu ile meydana gelen alkil zincirine sahip üründür. Ayrıca bazı çifte bağ içeren enofuranoz türevlerinin siloksan oligomerleri ile reaksiyonu da denendi.

Şeker kısımları ile graftlanmış olan polimetilsiloksan bazlı, non-iyonik ve polimerik yüzey aktif madde üretilmesi amaçlandı. Platin katalizör varlığında hidrosililleme reaksiyonu ile polimetilhidrojensiloksan ile reaksiyona girebilecek bazı enofuranoz türevleri olarak bileşikler **6, 8,**

9, 28, sentezlendi. Hidrosililleme koşulları hakkında tecrübe kazanmak için öncelikle çift bağlı uç gruba sahip bazı bileşiklerle (örneğin, polietilenglikol 500 allil eter ve allil alkol (bileşik **29**) ile reaksiyonlar yapıldı. Reaksiyon FTIR spekturumundaki Si-H absopsiyonuna ait 2166 cm^{-1} (Erdik, E 1998) deki keskin pikin azalması ile kolaylıkla izlenebilmektedir. . Böylece, bileşik **9** ile siloksan oligomeri arasındaki reaksiyon bu yöntem ile takip edilerek bileşik **30** oluşturuldu.

İkinci olarak, aşağıda açıklandığı gibi, şeker kısmı ve alkil grubu arasında uzatıcı gruba (3-*O*-2'-hidroksipropil) sahip non-iyonik yüzey aktif maddeler sentezlendi. Glukozun epoksi türevi olan bileşik **10**, epiklorohidrin ile D-glukozun reaksiyonu ile elde edilmiştir ve epoksi halkasının, uzun zincirli alkoller ile açılmasıyla, muhtemel yüzey aktif özellik gösteren yeni bileşikler sentezlenmiştir. Epoksi halkası hem asidik hemde bazik ortamda açılabilir. Ancak asidik ortama yeterince dayanıklı olmayan koruyucu guruplara sahip bileşik **10** söz konusu olunca halka açılma reaksiyonu bazik şartlarda yapılmak zorundadır. Böylece sırasıyla butil, oktil, dodesil, hegzadesil ve siklohegzil alkoller, halka açılmasında kullanılarak sırasıyla **11, 13, 15, 17,** ve **21** nolu bileşikler sentezlendi. Üç farklı baz katalizör, metalik sodium, toz potasyum hidroksit ve baryum oksit kullanılarak, bileşik **10** un oktil alkol ile olan reaksiyonu ile elde edilen bileşik **13** ün verimleri sırasıyla 88, 55, 27 % olmuştur. Bu nedenle metalik sodyum diğer reaksiyonlar için katalizör olarak seçilmiştir. Tüm korunmuş furanoz türevleri sulu hidroflorik asit ile hidrolizlenerek sırasıyla **12, 14, 16, 18, 20, 22** nolu bileşikler sentezlenmiştir. Koruyucu guruplar ayrıldıktan sonra (hidroliz sonrası), beklenileceği gibi, furanoz halkasının daha kararlı piranoz türevine dönüştüğü gözlemlenmiştir. Bu bilgi ^{13}C NMR verileri ile desteklenmiştir. (bak. **4.2)**

Ek olarak, pH a bağımlı amino grubu içeren katyonik yüzey aktif maddeler, epoksi halkasının ikincil amin ile açılmasıyla , bileşik **19**; birincil amin ile açılmasıyla bileşik **27** sentezlenmiştir.

Anahtar Kelimeler: Yüzey aktif maddeler, Bio yüzey aktif maddeler, Şeker bazlı yüzey aktif maddeler.

ABSTRACT

NEW SURFACE ACTIVE COMPOUNDS CONTAINING SUGAR MOIETIES

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PhD. in Chemistry
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Some carbohydrate derivatives were prepared which are suitable for use as hydrophilic head groups for some surface-active agents. Hydrophilic sugar moieties can provide solubility and/or dispersion in water, depending on the size and the nature of the sugar and non-sugar parts. Hydrophobic groups with various chain lengths were introduced onto these carbohydrate based compounds. Hydrophobic groups were introduced by the reaction of free hydroxyl groups on the protected sugar, either by direct etherification with the use of alkyl halides, such as allyl, butyl and octyl bromides or after introducing reactive epoxide groups, using direct etherification with epichlorohydrin and subsequent opening of the epoxide rings with several long chain alcohols and amines. A different approach was also used, where a free hydroxyl group was oxidized to a keto group and the resulting keto group was further reacted with allylmagnesium halide to provide a hydrophobic allyl side chain. Allyl groups, were introduced to the protected sugar derivatives which were further used for bonding these molecules to some siloxane oligomers through double bond addition.

We aimed to produce a non-ionic and polymeric surfactant with a polymethylsilicon backbone which is grafted with a glucose moiety. Some enofuranose derivatives **6, 8, 9, 28**, were synthesised which were thought

to be suitable for reactions with polymethylhydrogensiloxane, by a hydrosilylation reaction in the presence of a platinum catalyst. Hydrosilylation reaction was first carried out with terminal double bond containing compounds (e.g. polyethyleneglycol-500 allyl ether and allyl alcohol) **29** in order to get some experience on the reaction conditions. We have found out that these reactions could be monitored easily by observing the decrease of the characteristic sharp peak of the Si-H absorbsion at 2166 cm^{-1} on the FTIR spectra. (Erdik, E 1998). Thus the formation of the product **30** from the siloxane oligomer and the compound **9** was monitored by this method.

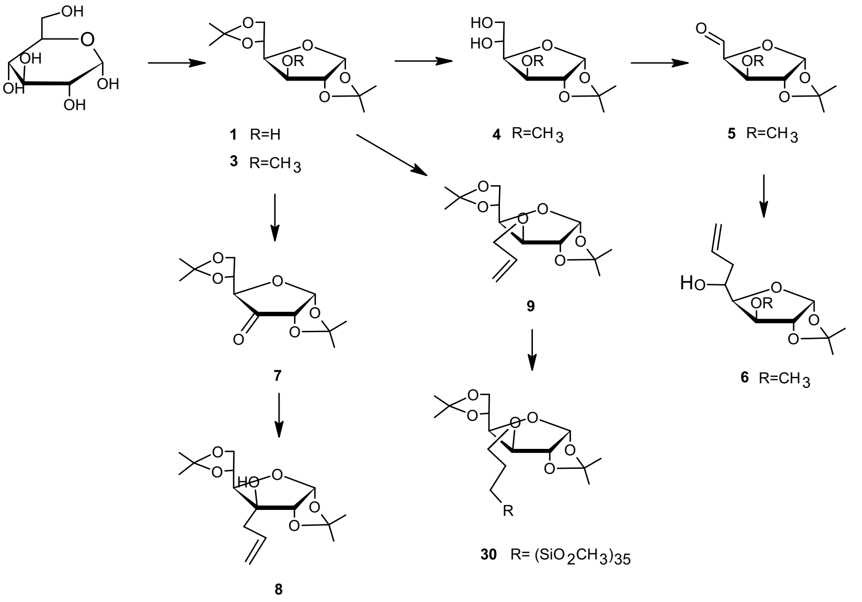
Secondly, a number of non-ionic surfactants, which have spacer group (3-*O*-2'-hydroxypropyl) between glucose moiety and alkyl chain, were produced as follows. An epoxy derivative of D-glucose (**10)** was prepared by the reaction of epichlorohydrin with diacetone-α-D-glucofuranose and the epoxide ring of the resulting molecules were opened with long chain alcohols to produce novel compounds. Removal of the isopropylidene groups of these compounds would be expected to yield free sugar derivatives with probable surfactant properties. Epoxy rings could be opened under both acidic and basic media. However, in case of the compound **10** epoxy ring opening reactions with alcohols, having different chain lengths, had to be performed with a base catalyst since the protecting groups were not sufficiently stable under acidic conditions. Thus the compounds **11, 13, 15, 17,** and **21** were obtained using butyl, octyl, dodecyl, hexadecyl, cyclohexyl alcohols respectively. Three base catalysts, metallic sodium, powdered potassium hydroxide and barium oxide were used in the reaction of octanol to provide the compound **13** with yields of 88, 55, 27 % respectively. Therefore metallic sodium, which gave the

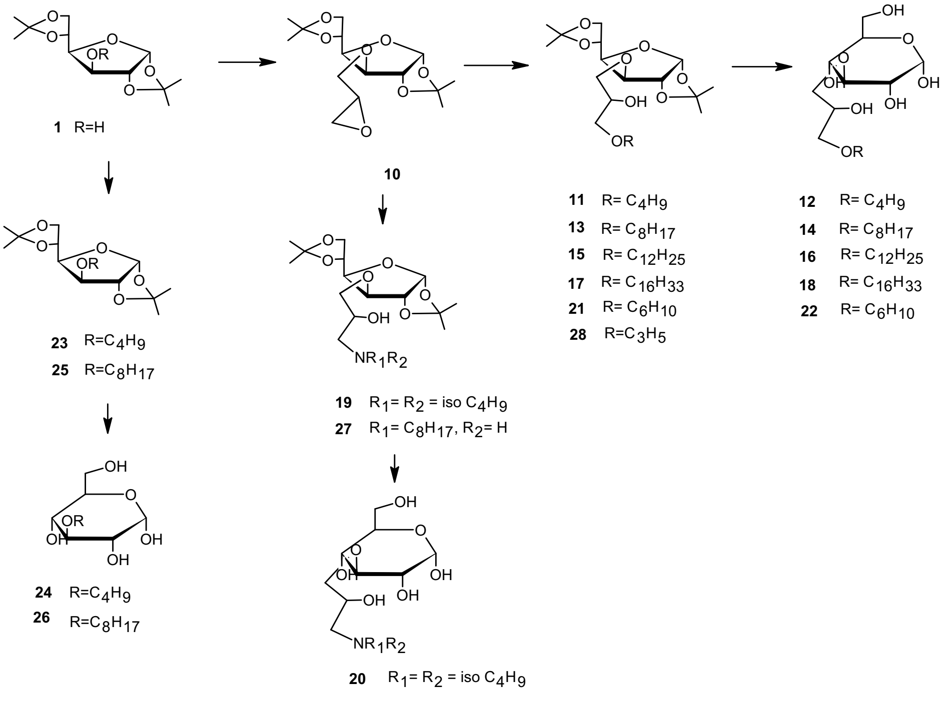
highest yield, was chosen as a catalyst for the other reactions. All the protected furanose derivatives were hydrolyzed with aqueous hydrofluoric acid to afford the compounds **12, 14, 16, 18, 20** and **22.** After the removal of the protecting groups (after hydrolysis), the conversion of the furanose rings to much more stable pyranose forms were observed as expected and this was supported by the ^{13}C NMR data.(see **4.2**)

In addition, pH dependant, cationic surfactants that contains amine groups, were synthesized by opening of the epoxide rings with a secondary amine (compound **19**) and also with a primary amine (compound **27**).

Keywords: Surfactants, Biosurfactants, Surface active agents, Sugar based surface active agent.

GRAPHICAL ABSTRACT





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ABBREVIATIONS

Abbreviation	**Explanation**
2,2-DMP	2,2-Dimethoxypropane
APG	Alkylpolyglycoside
b.p.	Boiling point
CMC	Critic micelle concentration
DCCI	Dicyclohexylcarbodiimide
DME	Ethylene glycol dimethyl ether
DMF	*N,N*-Dimethylformamide
DMSO	Dimethylsulfoxide
EtOAc	Ethyl Acetate
FTIR	Fourier Transform Infrared Spectroscopy
h.	Hours
HLB	Hydrophil Lipophil Balance
LC-MS	Liquid Chromatography-Mass Spectrometry
m.p.	Melting point
MeOH	Methanol
Min.	Minute
NMR	Nuclear Magnetic Resonance Spectroscopy
PMHS	Polymethylhydrogensiloxane
r.t.	Room temperature
t.l.c	Thin layer chromatograph
THF	Tetrahydrofuran
Tol	Toluene
TBAB	Tetrabutylamonium bromide

1. INTRODUCTION

1.1. Surfactants

Surfactants have very important roles in our everyday life. They find applications in almost every chemical industry, such as detergents, paints, dyestuffs, paper coatings, inks, plastics and fibers, personal care, cosmetics, agrochemicals, pharmaceuticals and food processing, etc. In addition, they play a vital role in the oil industry, e.g. in enhanced and tertiary oil recovery, oil slick dispersion for environmental protection, among others. It is important to choose the right molecule for a specific application, so it is essential to understand the basic phenomena involved in any application. (Tadros, T.F., 2005)

Surface active agents that are usually referred to as surfactants are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or a fluorocarbon chain containing 4–18 carbon atoms, which are attached to a polar or ionic portion (hydrophilic). A number of variations are possible in the types of the headgroup and tail group of surfactants. (Nagarajan, R., 2003) The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole-dipole or ion–dipole interactions. This strong interaction with the water molecules renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. The balance between hydrophobic and hydrophilic parts of the molecule that is called HLB gives these systems their special properties, e.g. accumulation at various interfaces and association in solution that is called as micelles. (Holmberg, K., 2003)

Basically, a first classification of surfactants based on the nature of the hydrophilic group is commonly used. According to, this classification, a surfactant can be either ionic, non-ionic and special. (Os Van, N.M., 1993.)

1.1.1. Ionic Surfactans

This group is classified as ionic charge on the surfactant molecule. Therefore, an ionic structure can be anionic, cationic or amphoteric.

1.1.1.1. Anionic Surfactants

These are the most widely used class of surfactants in industrial applications due to their relatively low cost of their manufacture and they are used in practically every type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. Linear chains are preferred since they are more effective and more biologically degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. Sodium dodecyl sulphate (**1**), sodium dodecylbenzene sulphonate (**2**), sodium stearate (soap) **(3)** are some of the most widely consumed anionic surfactants as shown in **Figure 1.1** (Linfield, W.M., 1967.)

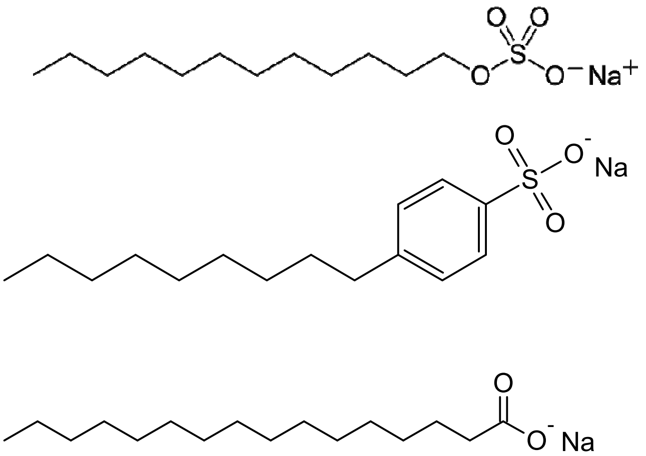

Figure1.1. Structures of Some Significant Anionic Surfactants

1.1.1.2. Cationic Surfactants

The most common cationic surfactants are the quaternary ammonium compounds (Jungerman, E., 1970) A common class of cationics is the alkyl trimethyl ammonium chloride, where R contains 8–18

C atoms, e.g. cetyl trimethyl ammonium chloride (**4**). A widely used cationic surfactant is alkyl dimethyl benzyl ammonium chloride (**5**) (sometimes referred to as benzalkonium chloride and widely used as a bactericide) Imidazolines can also form quaternaries, the most common product being the ditallow derivative quaternized with dimethyl sulphate (**6**). The most common cationic surfactants are mentioned above, as shown in **Figure 1.2** (Rubingh, N., 1991)

The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, e.g. anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents for plastics, other antistatic agents and fabric softeners, hair conditioners, anticaking agent for fertilizers and as bactericides.

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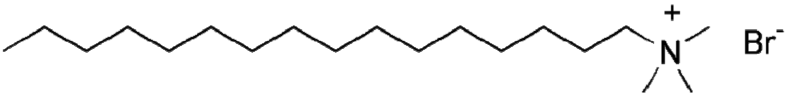

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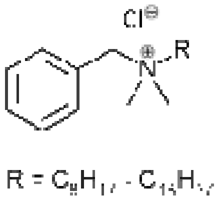

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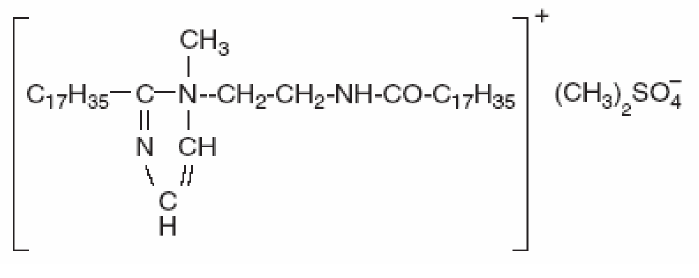

$$\left[C_{17}H_{35}-\underset{\underset{\underset{H}{C}}{N}}{\overset{}{C}}-\overset{CH_3}{\underset{CH}{N}}-CH_2-CH_2-NH-CO-C_{17}H_{35} \right]^{+} (CH_3)_2SO_4^{-}$$

Figure1.2. Structures of Some Significant Cationic Surfactants

1.1.1.3. Amphoteric Surfactants

These are surfactants containing both cationic and anionic groups. The most common amphoterics are the N-alkyl betaines. An example of betaine surfactant is coco amido propyl dimethyl betaine (**7**) (see **Figure 1.3)**. The main characteristic of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic one. Amphoteric surfactants have excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other personal care products (cosmetics). (Buestein, B.R., 1982)

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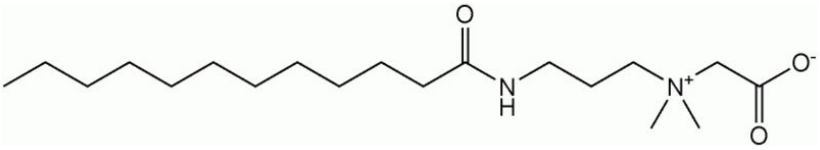

Figure1.3. Structure of a Amphoteric Surfactants

1.1.2. Non-ionic Surfactants

An important group of non-ionics include those where the hydrophile comprises a chain of ethoxy groups and is known as the ethoxylates. Varying the number of ethoxy groups in the chain adjusts the amount of hydrophilic character in the final products. This class is consist of several sub-groups; alcohol ethoxylates (**8**), alkyl phenol ethoxylates (**9**), fatty acid ethoxylates, alkanolamide ethoxylates, fatty amine ethoxylates and ethylene oxide–propylene oxide copolymers (**10**). These are shown in **Figure 1.4** below.

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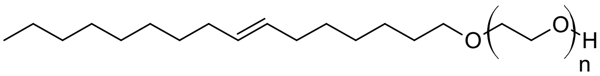

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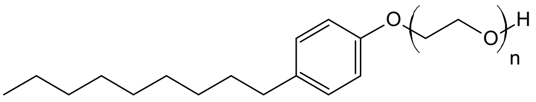

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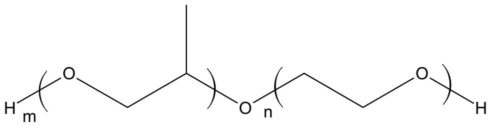

Figure1.4. Structures of Some Significant Ethoxylated Non-Ionic Surfactants

The other group of nonionics is composed of multihydroxy groups such as glycerol (and polyglycerol) esters, sorbitan esters (**11**), glucosides (and polyglucosides) (**12**) and sucrose esters (**13**). (Schick, M.J., 1987) (Schonfeldt, N., 1970) These examples (see **Figure 1.5)** are also known as carbohydrate containing surfactants, beside they are nonionic.

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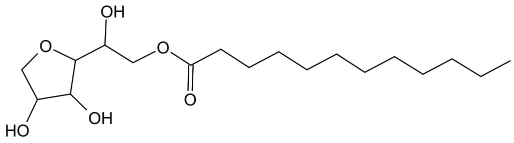

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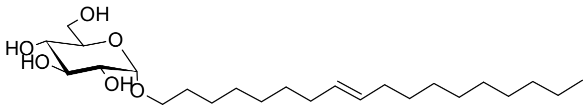

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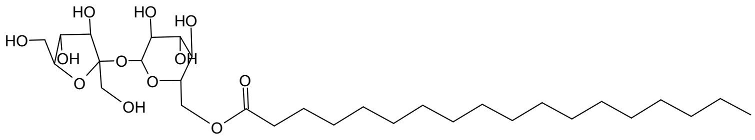

Figure1.5. Structures of Some Significant Non-Ionic Surfactants with Carbohydrate Moieties.

1.1.3. Special Surfactants

These surfactants are quite different from the conventional ones, because they have certain unique properties such as lower surface tension, distinctive oil and water solubility and high wetting characteristics, etc. These classified mainly three groups are fluorocarbon, silicon and polymeric surfactants.

Fluorocarbon and silicon surfactants can reduce the surface tension of water to below 20 mN m^{-1}. On the other hand, the most surfactants, which are shown above, are only able to decease the surface tension of water in the region of 25-27 mN m^{-1}. These are sometimes referred to as superwetters as they cause enhanced wetting and spreading of their aqueous solution. However, they are much more expensive than formal surfactants and are only applied for specific applications whereby the low surface tension is a desirable property. (Kissa, E., 2001)

Fluorocarbon surfactants have been prepared with various structures, consisting of perfluoroalkyl chains and anionic, cationic, amphoteric and poly(ethylene oxide) polar groups. These surfactants have good thermal and chemical stability and they are excellent wetting agents for low energy surfaces. An example of fluorocarbon surfactant is shown in **Figure 1.6.**

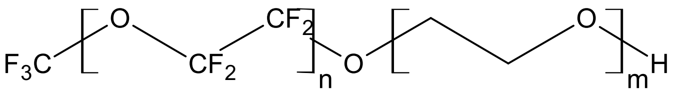

Figure1.6. Structure of a Fluorocarbon Surfactant

Silicone surfactants, sometimes referred to as organosilicones, are those with a poly(dimethyl siloxane) backbone. They are prepared by incorporation of a water soluble or hydrophilic group into a siloxane backbone. The most common hydrophilic groups are EO/PO and the structures produced are rather complex and most manufacturers of silicone surfactants do not reveal the exact structure. An example of the organosilicone is polyoxyethylene polymethyl siloxane (**15**). The mechanism by which these molecules lower the surface tension of water to low values is far from well understood. The surfactants are widely applied as spreading agents on many hydrophobic surfaces. (Hill, R.M., 1999)

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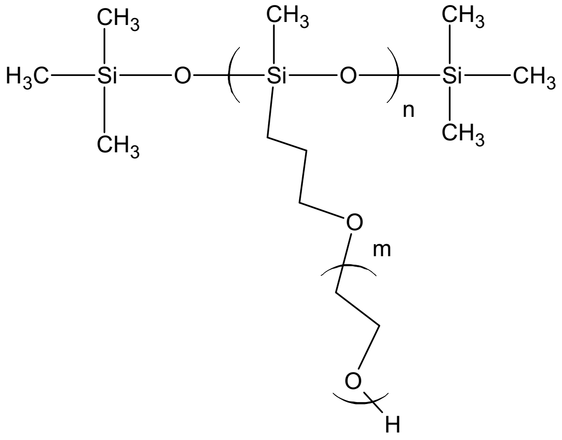

Figure1.7. Structure of a Silicon Surfactant

Polymeric surfactants has recently been an interested area due to wide range of applications and unique properties for dispersions, suspensions and emulsions. Silicone surfactants may also be considered as polymerics. However, the recent development of specialty polymeric surfactants of the graft type is also known as comb-like polymers. These have enabled one to obtain specific applications in dispersions. An example is the graft copolymer of a poly(methyl methacrylate) backbone with several PEO side chains (**16**), which has excellent dispersing and stabilizing properties for concentrated dispersions of hydrophobic particles in water.

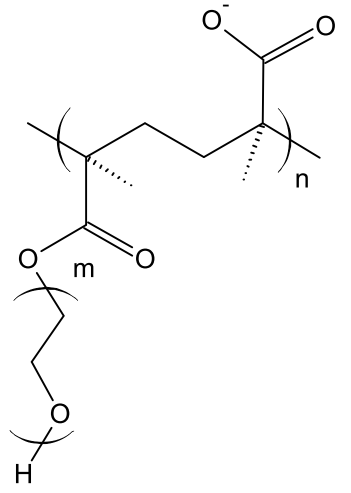

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Figure1.8. Structure of a Polymeric Surfactant

1.2. Characteristic Features of Surfactants

Surface-active agents are most commonly organic molecules that, when dissolved in a solvent at low concentration, have the ability to adsorb at interfaces, thereby altering significantly the physical properties of those interfaces. The term “interface” is commonly employed here to describe the boundary in liquid/liquid, solid/liquid and gas/liquid systems, although in the latter case the term “surface” can also be used. This adsorption behaviour can be attributed to the solvent nature and to a chemical structure for surfactants that combine both a polar and a non-polar group into a single molecule that structure is also mentioned as amphiphilic. To accommodate for their dual nature, their lyophobic moiety keeps away from strong solvent interactions while the lyophilic part remains in solution. Since water is the most common solvent, and is the liquid of most academic and industrial interest, amphiphiles will be described with regard to their “hydrophilic” and “hydrophobic” moieties, or “head” and “tail” respectively. (Tanford, C., 1978)

Adsorption is associated with significant energetic changes since the free energy of a surfactant molecule located at the interface is lower than that of a molecule solubilised in either bulk phase. Accumulation of amphiphiles at the interface is therefore a spontaneous process and results in a decrease of the surface tension. However, such a definition applies to many substances medium or long chain alcohols are also surface active (e.g., n-hexanol, dodecanol) but these are not considered as surfactants. True surfactants are distinguished by an ability to form oriented monolayers at the interface (air/water or oil/water) and, most importantly, self-assembly structures (micelles). A typical surfactant has a large lipophile (hydrophobe) which restricts its aqueous solubility and creates limited concentration. Beyond this concentration the molecules associate to form colloidal aggregates known as micelles. This concentration is the critical micelle concentration (CMC). Different surfactants have different CMC values. They also stand out from the more general class of surface-active agents owing to emulsification, dispersion, wetting, foaming or detergency properties. (Tanford, C., 1978) (Hargreaves, T., 2003)

Just for nonionic surfactants are used a scale from 0 to 20 depicting the Hydrophilic/Lipophilic Balance (HLB) of a surfactant. According to this scale, surfactants with low HLB value have tendency to be soluble more in oil whereas high HLB value surfactants soluble more in water. This value is calculated by Griffin method. (Griffin, W.C., 1954)

1.3. Raw Materials for the Production of Surfactants

Surfactants were originally made from renewable resources, whereas today the major part is of petrochemical origin. Still, renewables have not entirely lost their importance as surfactants are now manufactured from both kinds of feedstocks. Most biobased surfactants are made from vegetable oils and are therefore also referred to as oleochemical surfactants. The surfactant industry currently uses roughly equal amounts of ”natural” oleochemicals and ”synthetic” petrochemicals. The coexistence of biobased and petrochemical surfactants leads to the question of whether the increased use of renewable feedstocks could contribute to the conservation of petro chemical resources, such as crude oil and natural gas. (Patel, 2004)

Beside Vegetable oils, fats are also important constituents of human and animal foodstuffs, certain grades are industrially used and together with carbohydrates and proteins, are important renewable resources compared to fossil and mineral raw materials, whose occurrence is finite. Rapidly consuming of them has created serious risks for environment. In concepts for new products, the price, performance, and product safety criteria are equally important and have a correspondingly high importance right at the start of product development. To ensure a high degree of product safety for consumers and the environment, renewable resources have often been shown to have advantages when compared with petrochemical raw materials and can therefore be regarded as being the ideal raw material basis (Hill, K., 2000). Results from oleochemistry show that the use of vegetable fats and oils allows the development of competitive, powerful products, which are both consumer-friendly and environment-friendly. Recently developed products, which fit this requirement profile, are the anionic surfactants cocomonoglyceride sulfate and the nonionic sugar surfactant “alkyl polyglycoside”. These products are used especially as mild surfactants in cosmetic formulations (Davis, B., 1987).

1.4. Carbohydrate Base Surfactants

Carbohydrates are found among the most unique natural products. They consist of aldehydes or ketones with many hydroxyl groups added. These abundant functionality have created wide range of chemical modifications. Modified carbohydrates are able to use many different applications for instance, paper, construction chemicals, sweeteners, surfactans and so on.

1.4.1. Applications of Carbohydrate Base Surfactants

Two Canadian scientists studied nonionic alkylpolyglycoside (APG) solutions, containing β-cyclodextrin (β-CD) with a view to characterize the inclusion complexes formed and to determine if the sugar entities of the host and guest molecules played a significant role in the process. The APGs investigated were four glucopyranosides (octyl G8, decyl G10, dodecyl G12, tetradecyl G14) and two maltosides (decyl M10, dodecyl M12). Critical micelle concentration (CMC) and surface tension were obtained in the surfactant–β-CD systems, which in all cases increased with increasing β-CD concentration. (Reinsborough, V.C., 2004)

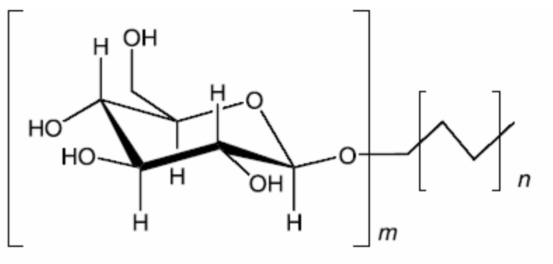


Figure1.9 Alkylpolyglycoside (APG), where *m* = 1 (glucopyranoside) or 2 (maltoside) and *n* = 6–12.

In 2001, nonionic, anionic, and amphoteric Sucrose-based surfactants have been synthesized by both chemical and enzymatich paths with special focus on methods for the regioselective synthesis of these surfactants. These are compatible with skin. They elicit little or no irritation, suggesting applications in cosmetics including skin preparations, hair treatments, eyelash products, cosmetic oil gels, and deodorant formulations. They have also been used as plasticizers and as antistatic agents in plastics. Di-n-butyltin oxide was used as the regioselective catalyst. A single product, 6-O-acyl sucrose was obtain. (see **Figure1.9**)

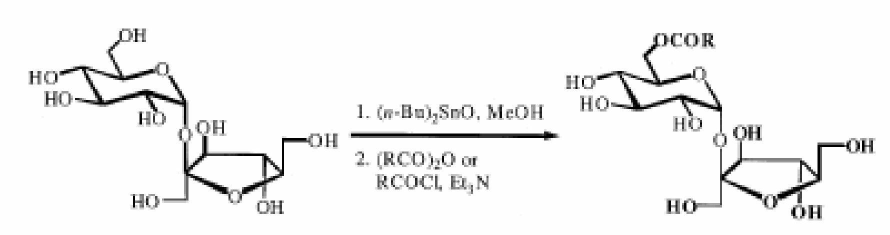


Figure1.10 Synthesis of Nonionic Sucrose Ester Surfactants R= Lauroyl, Myristoyl, Palmitoyl, Stearoyl

Sulfation of 6-O-acyl-sucrose in pyridine in the presence of excess Pyr.SO_3 complex afforded the 6-O-acyl-4’-sulfo-sucrose and 6-O-acyl-1’-sulfo-sucrose in 70 and 10 % yields, respectively. (see **Figure 1.10**)

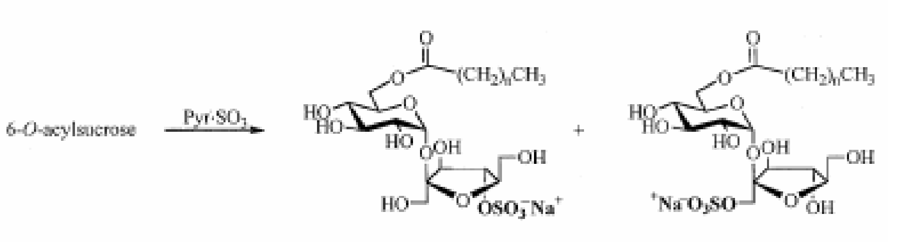


Figure1.11 Anionic Form of Corresponding Sucrose Ester Surfactant n=12,14,16,18

The sulfation of sucrose involves the use of sucrose cyclic sulfate intermediate. This intermediate is readily obtained in a two-step procedure involving the reaction of sucrose with thionyl chloride followed by the catalytic oxidation of the cyclic sulfite. The resulting sucrose cyclic sulfate can be opened up using *O*-nucleophiles (palmitic, stearic, and eicosanoic acids) and *N*-nucleophiles (hexadecylamine and octadecylamine). On heating sucrose cyclic sulfate in DMF containing a slight excess (1.2 eq) of fatty acid and potassium bicarbonate, the 6-*O*-acyl-4-sulfatesucrose is obtained regiospecifically in 75% yield. Reaction of sucrose cyclic sulfate with a slight excess of hexadecylamine or octadecylamine in DMF led to the corresponding amphoteric 6-deoxy-6-hexadecylammonio-4-sulfate-sucrose and 6-deoxy-6-octadecylammonio-4-sulfate-sucrose in 76 and 60% yields, respectively. (Polat and Linhardt, 2001) **(Figure 1.11)**

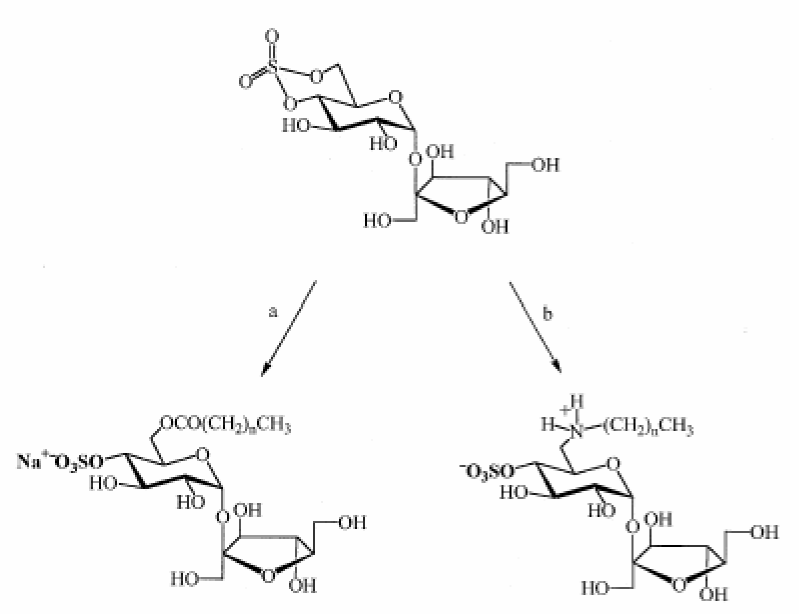
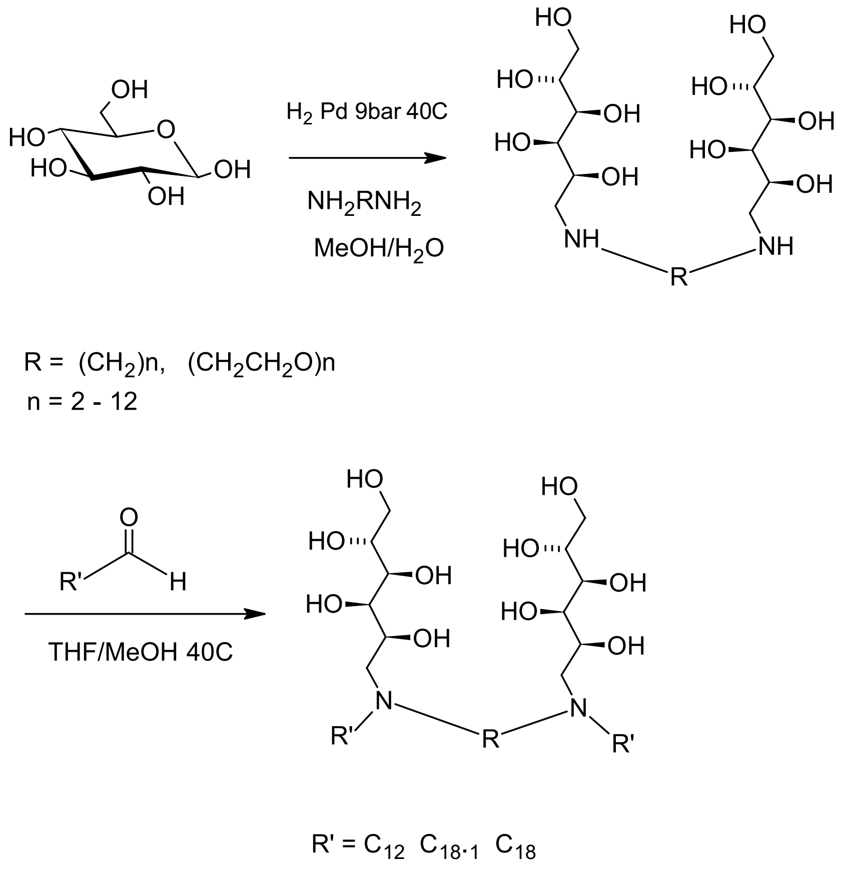


Figure1.12 Anionic and Amphoteric Forms of The Corresponding Sucrose Ester Surfactant n=12,14,16,18

Wagenaar and Engberts studied the reduced sugar based surfactants. Gemini surfactants possess two amphiphilic groups connected to each other by a spacer, bound to the headgroups. Gemini surfactants were synthesized with different carbohydrate headgroups including glucitol, mannitol, galactitol, lactitol, melibitol, arabinitol, erithritol. Hydrocarbone tails and spacers were oleic and stearic acids. (see **Figure 1.12**) (Wagenaar and Engberts, 20007)



R = $(CH_2)n$, $(CH_2CH_2O)n$
n = 2 - 12

R' = C_{12} $C_{18\cdot1}$ C_{18}

Figure1.13 Nonionic Reduced Sugar Based Gemini Surfactants

Some Swedish researchers synthesized a new surfactant head group, bis-α-D-glucopyranoside amine, and then they coupled it with a tail group. (see **Figure 1.13**) (Andersson, N.K., 2006)

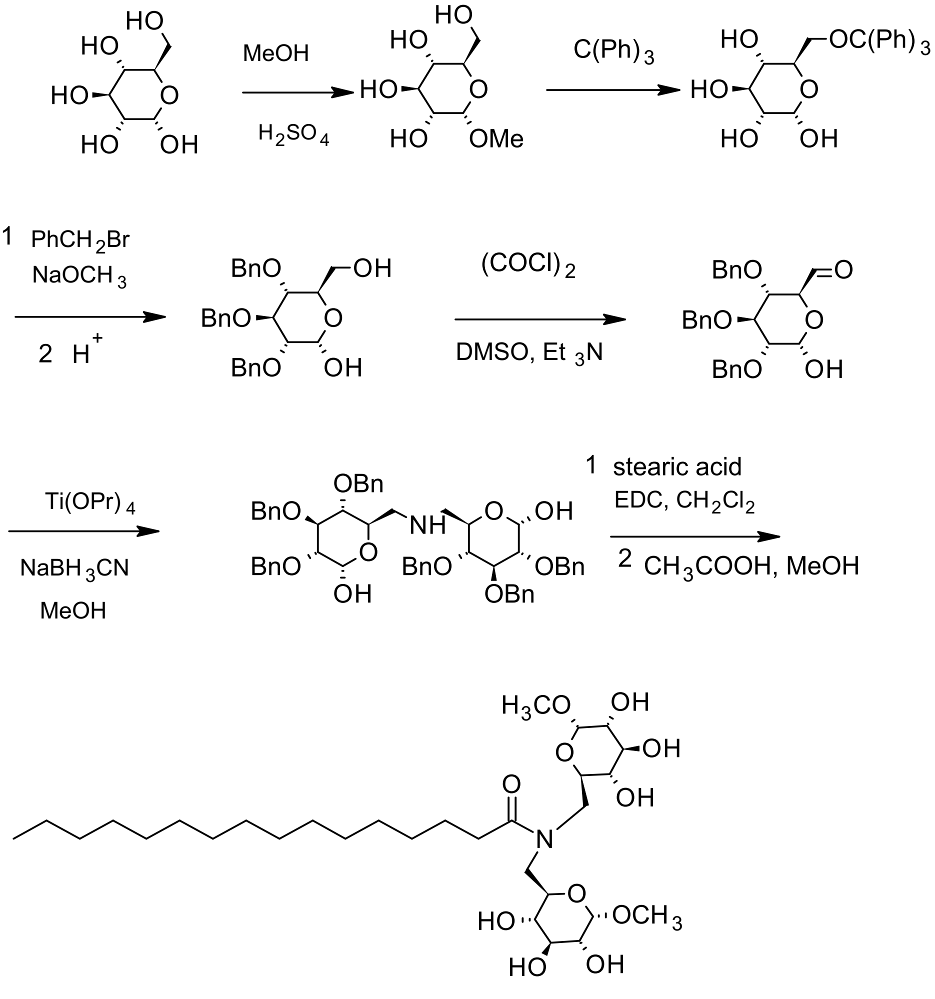
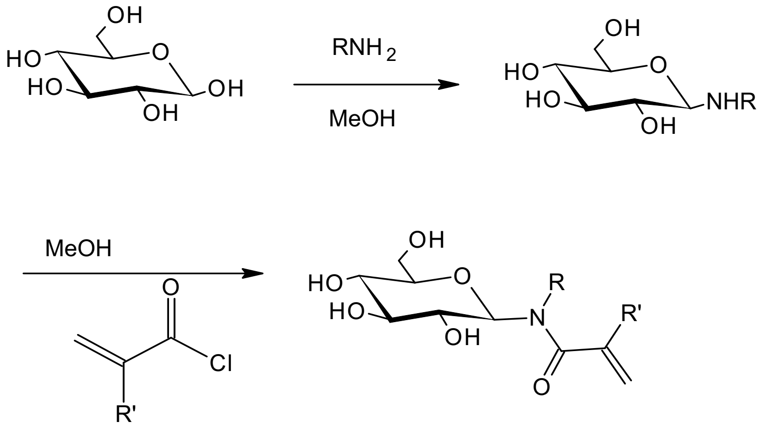


Figure1.14 Structure of stearyl-bis(1-O-methyl-α-D-glucopyranoside) amide

C. Larpent and co-workers synthesized new reactive surfactants that were easily prepared in two steps from glucose without protection. (Retailleau, L., 1998) (see **Figure 1.14**) Due to the acryl amine functional group, product is able to polymerize readily. Thus, polymeric or oligomeric surfactants can be obtained.



R' = H or Me

R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{18}H_{37}$

Figure1.15 A New Reactive Sugar Surfactant

In another article, a series of nonionic saccharide surfactants with an amine group linking hydrophilic saccaharide segment to hydrophobic alkyl segment were synthesized and their surface active properties were determined. They examined the effects of hydrophobic and hydrophilic chain lengths on the surface active properties. They used hexyl, octyl, decyl, dodecyl, and octadecyl for alkyl segments and glucose, maltose, and dextran for saccharide segments. (Zhang, T. and Marchant, R.E., 1996)

Scientists from France synthesized compounds starting from D-gluconolactone. Three different functional groups were used to link the sugar moiety and the hydrophobic part. The physico-chemical properties for the use as adjuvant for pesticidal formulations of one of these compounds were evaluated and compared. (Abert, M., 2002)

M.P. Savelli and co-workers studied 1-Z-R-D,L-xylitol compounds. They determined the main amphiphilic properties (Z = ester, ether and tioether) as a function of alkyl chain length (R = C_nH_{2n+1} n= 4-17) (see **Figure 1.15**) (Savelli, M.P., 1999)

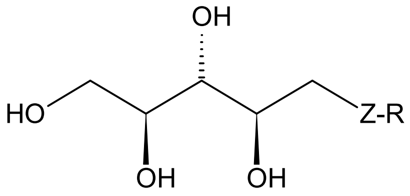


Figure1.16 1-Z-R-D,L-xylitol Compounds

Related to Liquid Crystals, an homologous series of 6-O-n-alkyl-α-D-galactopyranoses were prepared by alkylation of 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose using appropriate *w*-bromoalkanes and KOH to produce the intermediate 6-O-n-alkyl-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoses, followed by deprotection using trifluoro acetic acid. (see **Figure 1.16**) (Bault, P.,1997)

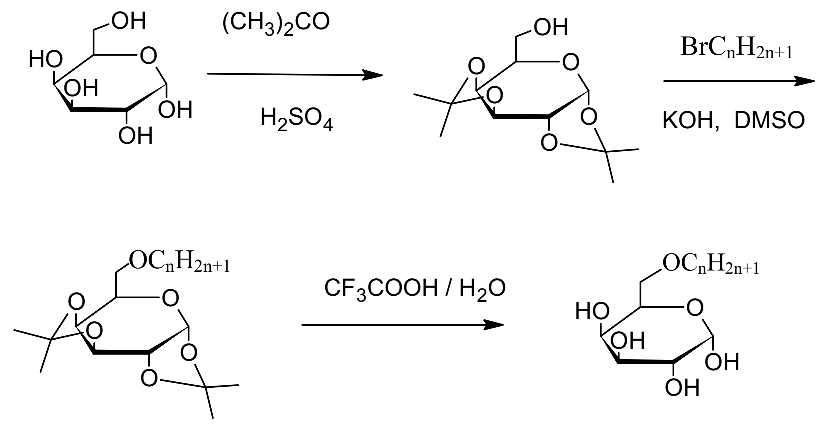


Figure1.17 Synthesis of 6-O-n-alkyl-α-D-galactopyranoses

Bazito and El Seoud employed 2-amino-D-glucose, which is found naturally on the shells of some crustaceous sea animals, as a starting material to synthesize sugar based anionic surfactants. (see **Figure 1.17**) (Bazito, R.C.,2001)

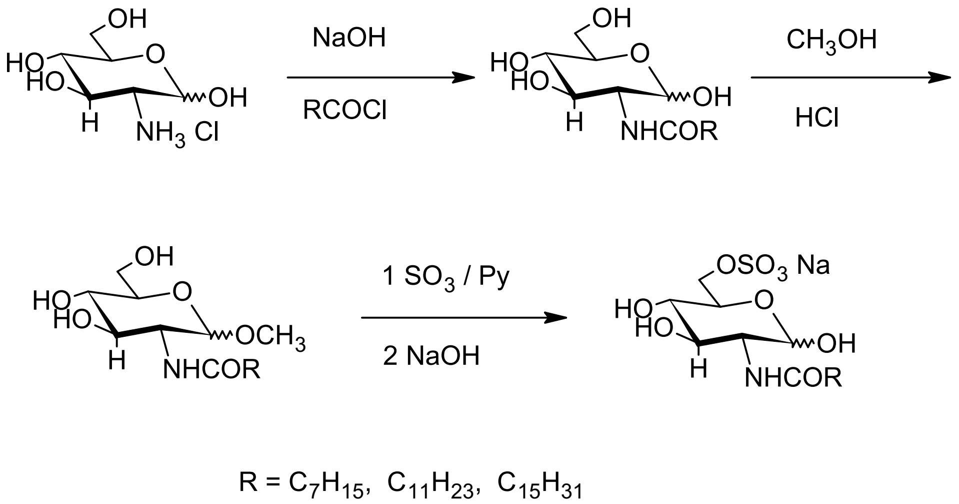


Figure1.18 Synthesis of 2-acylamido-2-deoxy-6-O-sulfo-D-glucopyranose

Some researchers from Sweden synthesized the alkylaminoamide sugar surfactants. They aimed to obtain lowest toxicity and highest biodegradation rates. They studied the physical and chemical properties of the product. Adsorptions and surface tensions were measured. (Oskarsson, H., 2007) **(Figure 1.18)**

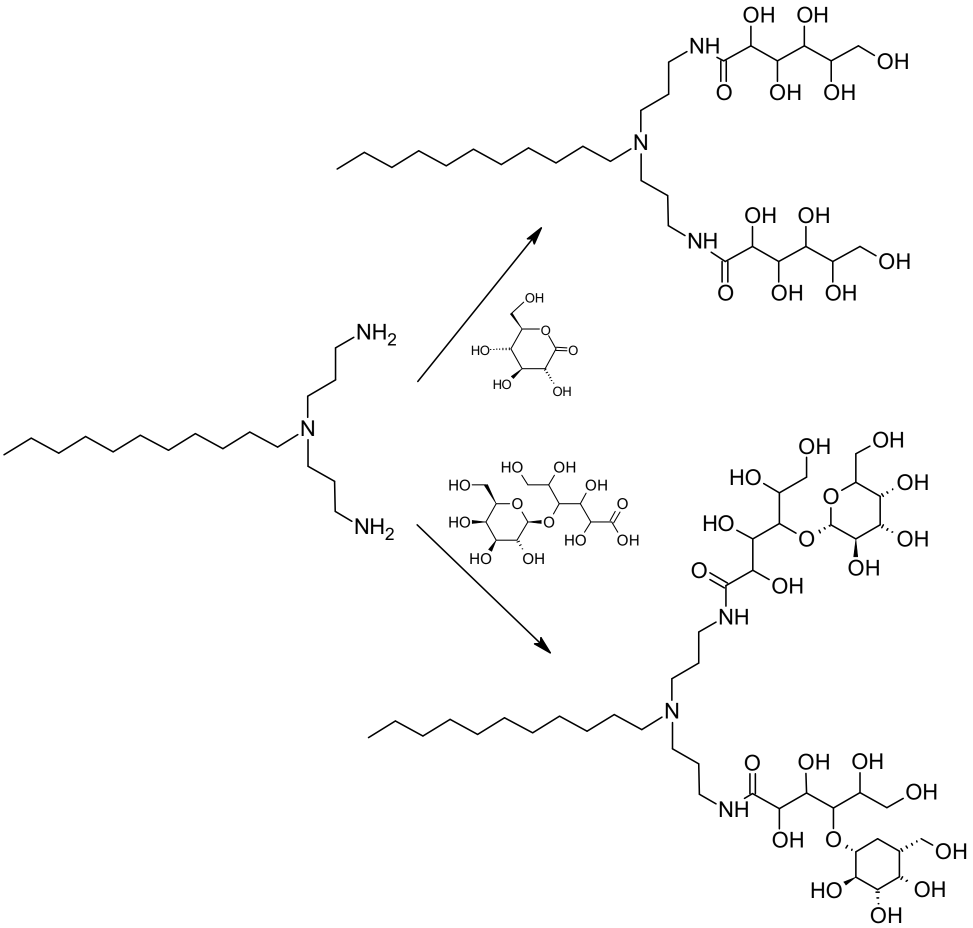


Figure1.19 Alkylaminoamide Sugar Surfactans

In another article, the air/water interfacial activity and self-assembly of the mono-dodecyl esters of glucose, sucrose, raffinose and stachyose have been investigated. These four non-ionic surfactants provide a series where the hydrocarbone chain length is invariant while the surfactant head group sequentially increases in size. (Söderberg, I., 1995)

Some Japanese scientists studied the heterogemini surfactants which included a sugar moiety. A heterogemini surfactant comprising two hydrocarbon chains and two different hydrophilic groups such as a quaternary ammonium cation and gluconamide. *N*,*N*-dimethyl-*N*-[2-(*N'*-alkyl-*N*'-gluconamide)ethyl]-1-alkylammonium bromides (hydrocarbon alkyl chain lengths of 8, 10, 12, and 14) were synthesized by reacting *N*,*N*-dimethylethylenediamine with an alkyl bromide, followed by a reaction with 1,5-D(+)-gluconolactone. (see **Figure 1.19**) (Nyuta, K., 2006)

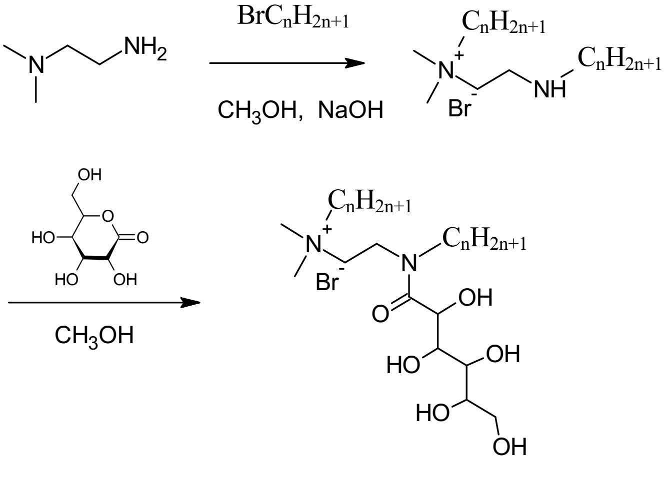


Figure1.20 *N*,*N*-dimethyl-*N*-[2-(*N'*-alkyl-*N*'-gluconamide)ethyl]-1-alkylammonium bromides

Similar molecules were synthesized by a scientist from Poland. Both used same spacer and sugar in their molecules. The report describes the synthesis of newly designed nonionic gemini compounds comprising two reduced sugar head groups, two alkyl tails and 1,1' ethylenebisurea entity as the spacer linking two amphiphilic glucose derived moieties. (see **Figure 1.20**) (Laska, U., 2006)

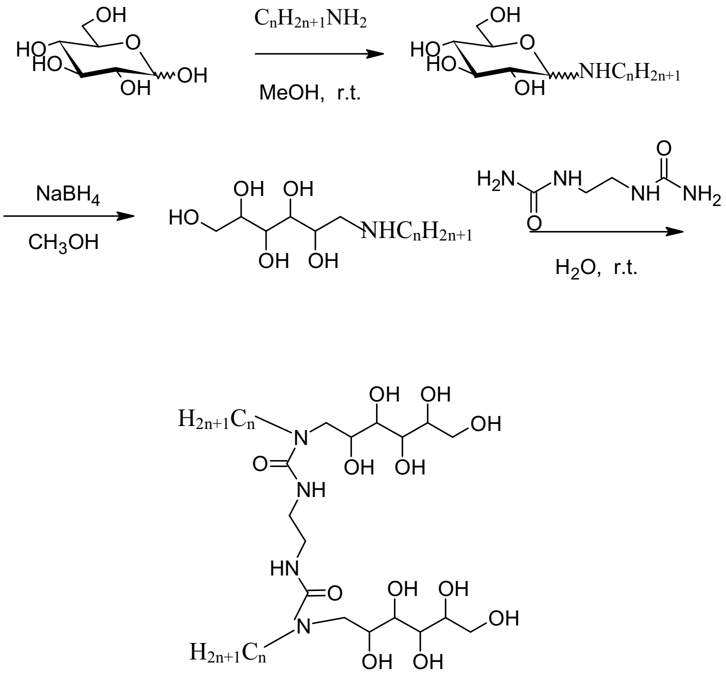


Figure 1.21 Synthetic Route of N,N'-bis[(3-alkyl-3-deoxy-D-glucitol)ureido]ethylenediamines

L. Choplin and his colleagues worked with trehalose, which is one of the most abundant natural disaccharide. They used enzymatic path for the synthesis of surfactants of a sugar. CMC, surface tension and reological properties were investigated for each of the product. (Choplin, L., 2006) **(Figure 1.21)**

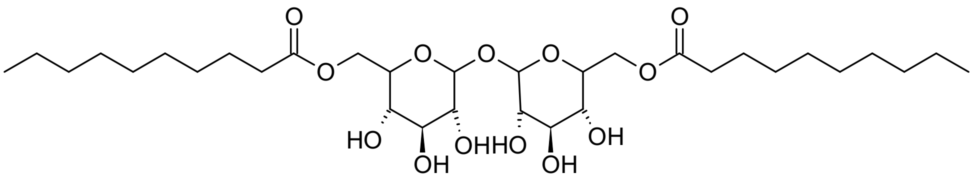


Figure 1.22 Structure of trehalose didecanoate

L-H. Lin and K-M.Chen from Taiwan, designed some cleavable-modified silicon surfactants. A series of cleavable water-soluble silicon surfactants were prepared by the reaction of a hydroxyl-terminated polyester and an organopolysiloxane. Cleavable surfactants can decompose into water insoluble moiety of a silanol and to a water soluble product under acidic conditions, whereas these compounds are stable under neutral or alkaline conditions. Cleavable surfactants are surfactants that may degrade into non-surface active species or into new surface-active compounds with different properties by chemical means. (Lin, L-H., 2006) **(Figure 1.22)**

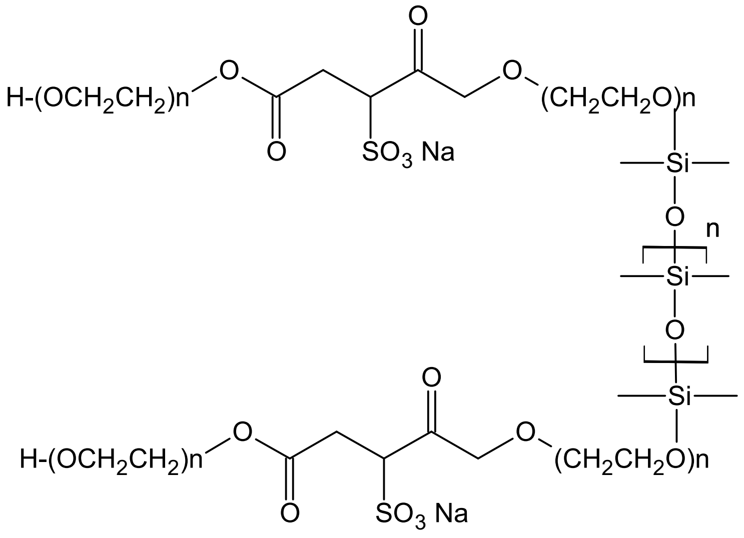


Figure 1.23 Cleaveble of Modified Silicone Surfactant.

The number of studies on the carbohydrate-modified siloxanes increase day by day. The idea is to combine the extraordinary surface activity and wetting properties of siloxanes with the biodegradability of carbohydrates. Some years ago, alkyl polyglycosides were first synthesized and now they are common surfactants for different applications. Binding of siloxanes and carbohydrates can be achieved by means of glycosyl bonds (Si-C) with or without a spacer. The patent that is published by Wacker Chemie GmbH describes the hydrosilylation with 1-allyl glycildly ether -6-maleate-D-glucose and 2-hydrogen-tri(methylsiloxane) which gives a white solid with a good solubility in water.(see **Figure 1.23**) (Sejpka, J., 1994)

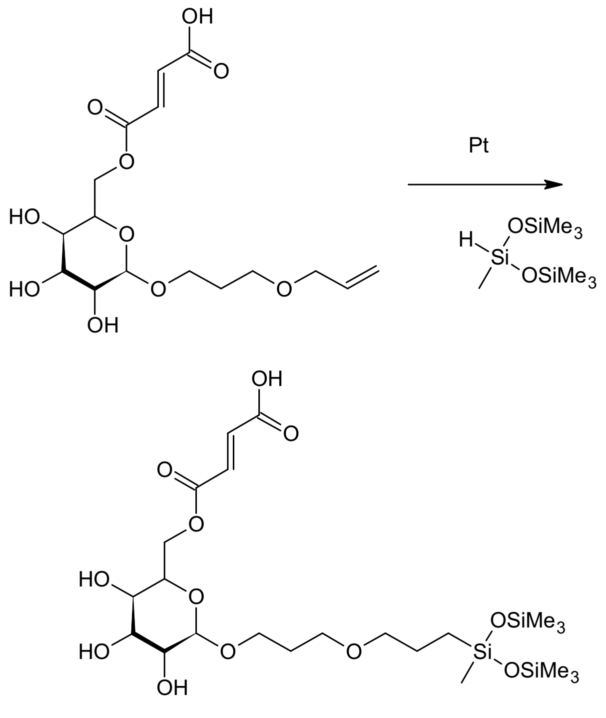


Figure 1.24 An Example Carbohydrate-Modified Siloxane

2. MATERIALS AND METHODS

2.1. General Techniques

- Silica gel (Merck 5554) was used for thin layer chromatography (TLC). The spots of TLC were developed by spraying 5 % aqueous sulphuric acid and by heating the plates above 120 ºC for about 3 minutes.

- Starting compounds and reagents were obtained from Merck, Carlo Erba and Aldrich; and solvents such as acetone, hexane, methanol, dichloromethane etc. were obtained from industrial grade solvents which were further purified by distillation.

- Solvents were dried with molecular sieve (type 4 ^{o}A). Anhydrous sodium sulphate was used for drying organic solvent extracts. All solvents were evaporated under reduced pressure using rotary evaporator.

- Light petroleum refers to a fraction of b.p. 40-60 ^{o}C.

- Anhydrous ether and THF were used as the solvent for Grignard reactions and they were dried by refluxing in the presence of sodium turnings.

- IR spectra were obtained by Perkin Elmer Spectrum 100 FTIR Spectrometer.

- ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Varian AS 400 instrument.

- Melting points were recorded on a Gallenkamp electrotermal melting point apparatus.

- Elemental analysis were carried out on a LECO CHNS-932 at İnönü University.

- Optical rotation measurements were carried out on a Schmidt-Haensch Polartronic E polarimeter.

2.2.1. Synthesis of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1) and 1,2-*O*-isopropylidene- α-D-glucofuranose (2)

Anhydrous D-glucose which was dried at 80 ^{0}C for 24 h (50g, 0,2778mol) was dissolved in dry acetone (dried with MS 4^{o}A) (1000mL). The mixture was cooled in crashed ice (5 ^{0}C). Concentrated sulphuric acid (40 mL, 96 %, 0,721mol) was added, as slowly as possible (in 10mL portions at 10-15 min intervals) . At the end of the addition, reaction temperature was allowed to rise to ambient temperature. The reaction was continued for 5 hours. Before adding sodium hydroxide solution (61,2g, 1,53mol in 240 mL water), both solution and the reaction mixture were cooled in ice-salt mixture to below 5 ^{0}C. After the neutralization was mostly completed with sodium hydroxide, pH of the mixture was carefully adjusted between 8-9 with the addition of sodium bicarbonate. The solution was kept overnight and then filtered. There were two products. The product mixture was extracted with hot hexane (5x100 mL), then crystallized from cooled (below 0 ^{0}C) hexane solution to afford white crystals. It was filtered and dried (29,7 g, 40% m.p. 111 ^{0}C, $[\alpha]^{16}_D$ -19,4 (*c* 0.97, CH_2Cl_2). IR (cm^{-1}) υ^{KBr} 3430 O-H, 2985, 2941, 2872 C-H, 1382, 1222 $C(CH_3)_2$. The residue was extracted with hot ethyl acetate (5x100 mL) then crystallized from ethyl acetate to give white crystals, at below 0 ^{0}C. It was filtered and dried (12,3 g, 19 % m.p. 159 ^{0}C, $[\alpha]^{16}_D$ -14 (*c* 0.92, H_2O).

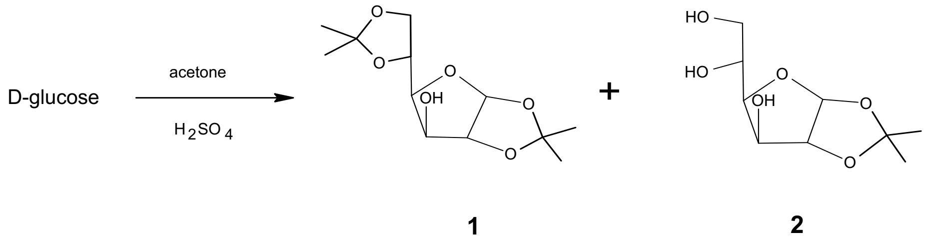
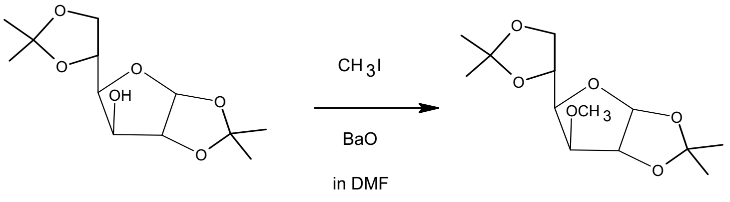


Figure 2. 1. Synthesis of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) and 1,2-*O*-isopropylidene- α-D-glucofuranose (**2**)

2.2.2. Synthesis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl- α-D-glucofuranose (3)

A solution of compound **1** (12 g, 46,15 mmol) in DMF (100 mL) was stirred with BaO (12 g, 78,27 mmol) and MeI (12 mL, 0,192 mol) at room temperature for 24 hours. The reaction flask was covered to keep the mixture in dark. At the end of the reaction, the solution was filtered and poured into crashed ice-water mixture. The mixture was extracted with dichloromethane (3 x 100 mL), decolorized with dilute sodium thiosulphate solution and washed with water. The dichloromethane solution was dried with anhydrous sodium sulphate, filtered and evaporated to give the compound **3** (11,12g, yield 88 %).

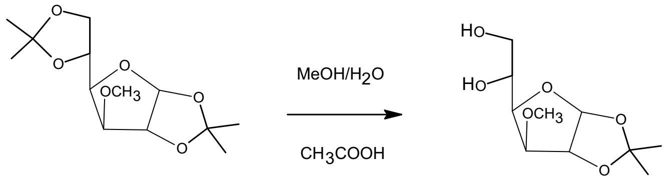


1 **3**

Figure 2.2 Synthesis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl- α-D-glucofuranose **(3)**

2.2.3. Synthesis of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-glucofuranose (4)

A solution of compound **3** (10 g, 36,4 mmol) in methanol-water (150 mL - 50 mL) mixture was stirred with acetic acid (10 mL) for about 48 hours until TLC indicated the complete hydrolysis of the compound. Then, the solution was neutralized with aqueous sodium bicarbonate. The solvents were removed and the residue was extracted with ethyl acetate and crystallized from the same solution to give the product **4** (7,15 g, yield 83,8 %) .



3

4

Figure 2.3 Synthesis of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-glucofuranose **(4)**

2.2.4. Synthesis of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-*xylo*-dialdo-furanose (5)

Sodium metaperiodate (8,5 g, 39,73 mmol) was dissolved in water (50 mL) and added to the solution of the compound **4** (6,25 g, 26,68 mmol) in methanol (100 mL). The mixture was stirred at ambient temperature. The reaction was monitored with TLC. Only a single spot was observed after 5 hours. The pH of the solution was adjusted between 8-9 with sodium bicarbonate and the solution was filtered. The filtrate was concentrated using rotary evaporator. Water phase was extracted with dichloromethane (3 x 50 mL) and dried with sodium sulphate and filtered. Finally, the solvent was evaporated to give a viscous liquid. FTIR spectra, of the compound showed that it is a mixture of the free aldehyde and the hydrated forms of **5** (4,73 g, yield 87,6 %) IR (cm^{-1}) υ^{KBr} 3461 O-H, 2988, 2939 C-H, 1735 C=O, 1375, 1214 $C(CH_3)_2$, 1080, C-O-C.

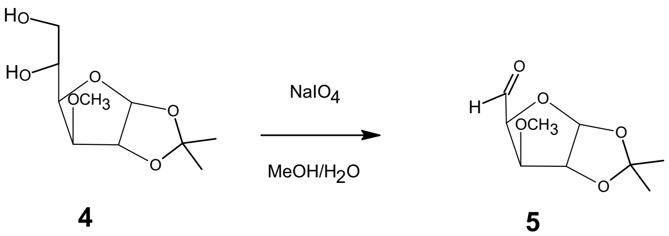


Figure 2.4. Synthesis of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-xylo-dialdo-furanose **(5)**

2.2.5. Preparation of allyl bromide

To a stirred HBr solution (48%, 250 g, 169 mL) was added H_2SO_4 (96 %, 40,5 mL) slowly and allyl alcohol (58 g, 1 mol). The mixture was heated. The another part H_2SO_4 (96 %, 40,5 mL) was added from the dropping funnel drop by drop. Simultaneously, allyl bromide condensed within 40 min. Crude allyl bromide was washed with sodium carbonate solution (5%) and further with water and dried over $CaCl_2$. It was distilled for purification (b.p.68-71 ^{0}C) (Vogel, A.I., 1956).

2.2.6. Preparation of allylmagnesium bromide

The apparatus and reagents were thoroughly dried. Dry magnesium turnings and sodium-dried ether were placed in a flask. The stirrer was started and the solution of allylbromide in sodium-dried ether was added at such a rate that the mixture refluxed gently. After the addition of the bromide solution, the stirring was continued for 30 minutes. All proses was carried out under dry N_2.

2.2.7. Grignard Reaction of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-*xylo*-dialdofuranose with allylmagnesium bromide.

A solution of compound **5** (4,03 g, 19,93 mmol) in sodium-dried ether was stirred with excess allylmagnesium bromide for 3 hours. The reaction was monitored by TLC. The reaction mixture was cooled to 0 °C and quenched by the addition of saturated aqueous ammonium chloride. TLC indicated multiple spots. The syrupy residue was purified on a silica gel column, eluting with hexane - EtOAc (10:1) to give the title product **(6)**. (0,3225g, 6,6%).

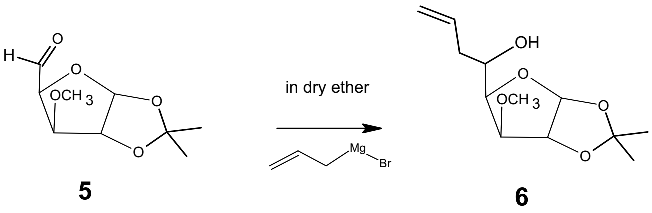


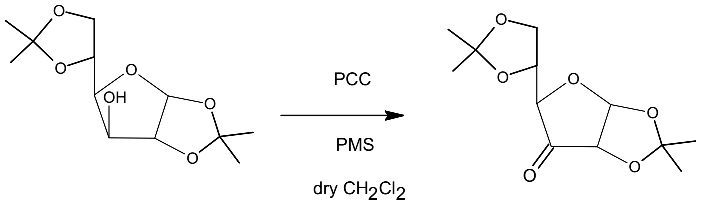
Figure 2.5. Grignard Reaction of 1,2-*O*-isopropylidene-3-*O*-methyl- α-D-xylo-dialdofuranose **(6)**

2.2.8. Preparation of Pyridinium Chlorochromate (PCC)

To a solution of HCl (6M, 184 mL, 1,1mol) was added CrO_3 (100 g, 1mol) rapidly with stirring. After 5 min. the homogeneous solution was cooled to 0 °C and pyridine (79 g, 1 mol) was carefully added over 10 min. Recooling to 0 °C gave a yellow-orange solid which was collected on a sintered glass funnel and dried for 1 h under reduced pressure (yield 180,8 g, 84%, m.p. 205 °C). The solid is not appreciably hygroscopic and can be stored for extended periods at room temperature without change. (Corey, Suggs, 1975).

2.2.9. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (7)

To a solution of compound **(1)** (10 g, 38.46 mmol) in dry-dichloromethane (200 mL) were added PCC (20 g) and powdered molecular sieve (PMS) which was activated at 350 °C for 24 h. The mixture was stirred at ambient temperature for 24 h. A single product was observed at TLC and ether was added. This mixture was applied on a silica column which was eluted with ether. Fractions were combined and extracted with aqueous saturated sodium hydrogen carbonate and dried using anhydrous sodium sulphate. A dried ethereal solution was filtered and evaporated under reduced pressure to give a thick syrup **7** (9.5 g, yield 95.9 %). m.p. 104-106, $[\alpha]^{16}_{D}$ -14 (*c* 0.92, CH_2Cl_2) IR (cm^{-1}) υ^{film}_{max} 2983, 2945, 2873 C-H, 3423 HO-C, 1080 C-O-C.



1 **7**

Figure 2.6. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**7**)

2.2.10. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-hydroxy-3-C-(2-propenyl)-α-D-gluco/allo- furanose (8)

To a stirred solution of allylmagnesium bromide in sodium-dried ether at 0 °C was added dropwise a solution of the compound **7** (0,1 g, 0,38 mmol) in dried ether. After the completion of the addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was cooled to 0 °C and quenched by adding saturated aqueous ammonium chloride solution. The reaction mixture was purified by column chromatography, using ether-petroleum ether (1-4) to give white crystals of **8**. Only one of the two possible isomers (*gluco* or *allo*) was obtained (54 mg. 47 %).

Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 59.32; H, 7.99.

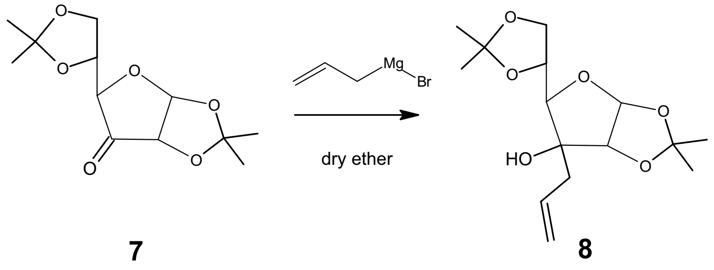


Figure 2.7. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-hydroxy-3-C-(2-propenyl)-α-D-gluco/allo- furanose **(8)**

2.2.11. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2'-propene-1'-yl)- α-D-glucofuranose (9)

NaH (%60, 0,7g, 17,4 mmol) was suspended in dry THF (5 mL) under N_2 at 0°C. A solution of the compound **1** (3 g, 11,6 mmol) in THF (30 mL) was added dropwise using a dropping funnel and the mixture was stirred for 30 min at r.t. Allyl bromide (2,2 mL, 24 mmol) was added slowly at 0 °C. Then, the mixture was heated under reflux for 6 h. After the end of this period, saturated NH_4Cl was added very slowly at 0 °C and the solution was extracted with CH_2Cl_2 (3x50 mL), dried over anhydrous

Na_2SO_4 and filtered. The filtrate was concentrated to give a yellow syrup. The crude syrupy product was purified by column chromatography to give the allyl derivative **9** of the corresponding sugar as a yellow syrup (3,548 g, yield 96%) $[\alpha]^{18}_{D}$ -30,2 (*c* 0.9, CH_2Cl_2). IR (cm^{-1}) υ^{film}_{max} 2983, 2945, 2873 C-H, 3080 =C-H, 1647 C=C, 1076 C=CH_2 (Shing, T.K.M., 2002)

Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 60.04; H, 8.07.

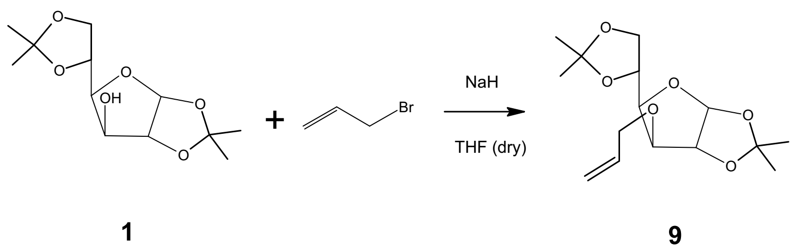


Figure 2.8. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2'-propene-1'-yl)- α-D-glucofuranose **(9)**

2.2.12. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2',3'-epoxypropan-1'-yl)- α-D-glucofuranose (10)

Epichlorohydrine (50 mL, 640 mmol) was stirred with aq NaOH (50%, 100 mL) and tetrabutyl ammonium bromide (5 g, 15,5 mmol) for 30 min. The compound **1** (20g, 76,92 mmol) was added slowly at approx. 5 °C and under stirring and the reaction continiued at same temp. for 3 h, followed by additional 12 h. at r.t. The reaction mixture was poured over crushed ice and extracted with EtOAc (4x100 mL), the organic layer was washed with aq. NH_4Cl (10%, 2x 25 mL) followed by water (2 x 50mL) and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrup. The crude syrupy product was purified by column chromatography using Hexane - CH_2Cl_2 (1:1) as the eluent to yield epoxy derivative of the corresponding sugar as an almost colorless syrup (**10**) (21,63 g, yield 89%) $[\alpha]^{19}_D$ -26 (*c* 1, CH_2Cl_2) IR (cm^{-1}) υ^{film}_{max} 2988, 2936, C-H, 1373, 1254 $C(CH_3)_2$, 1080, C-O-C. (Khan, A.R., 2001).

Anal. Calcd for $C_{15}H_{24}O_7$: C, 56.95; H, 7.64. Found: C, 56.83; H, 7.61.

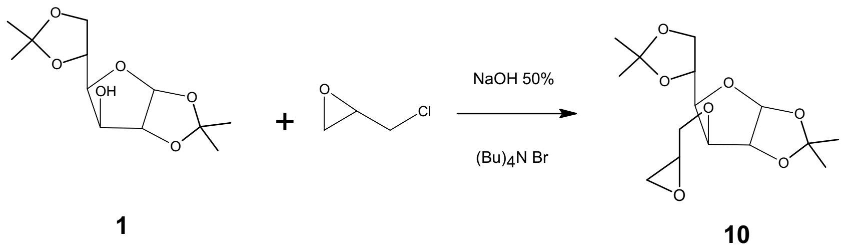


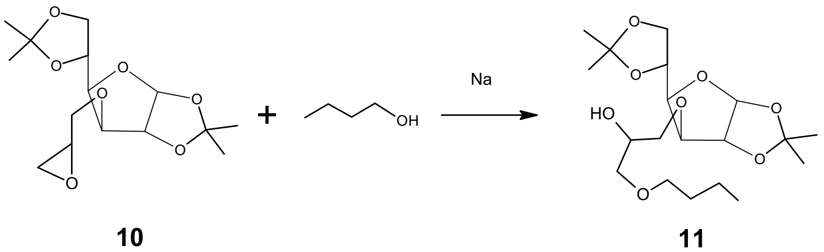
Figure 2.9. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[2',3'-epoxypropan-1'-yl)- α-D-glucofuranose **(10)**

2.2.13. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' -butyloxy-2'-hydroxy)propyl]-α-D-glucofuranose (11)

Na (0,1096 g, 4,76 mmol) was dissolved under reflux in excess dry n-butanol (4 mL) under N_2. A solution of the compound **10** (0,444 g, 1,405 mmol) in n-butanol (6 mL) was added dropwise using a dropping funnel while the mixture was stirred at 5 °C. Then, the mixture was heated under reflux under N_2 for 24 h. After the end of this period, water was added very slowly at 0 °C and the mixture was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrup. The crude syrup was purified by column chromatography using Hexane - CH_2Cl_2 (1:1) as the eluent to yield compound **11** as an odorless syrup (0,511g, yield 93 %).$[\alpha]^{18}_D$ -14.3

(*c* 0,15, CH_2Cl_2) IR (cm^{-1}) υ^{film}_{max} 3470 O-H, 2987, 2959, 2935, 2873 C-H, 1373, 1216 $C(CH_3)_2$, 1082, C-O-C.

Anal. Calcd for $C_{19}H_{34}O_8$: C, 58.44; H, 8.77. Found: C, 58.61; H, 8.80.



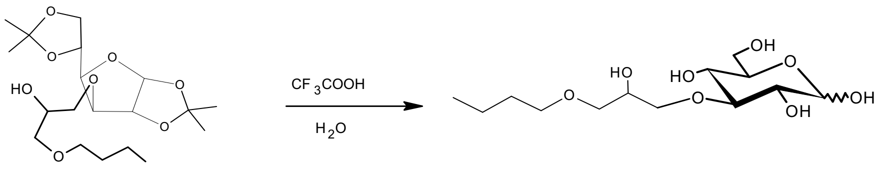
10 **11**

Figure 2.10. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' -butyloxy-2'-hydroxy)propyl]-α-D-glucofuranose **(11)**

2.2.14. Synthesis of 3-*O*-[(2'-Hydroxy-3'-butyloxy)propyl]- α,β-D-glucopyranose (12)

To a stirred solution of compound **11** (0,25 g, 0,64 mmol), in water (6 mL) was added conc. CF_3COOH (2 mL) at r.t. The mixture was stirred for 5 h. at r.t. After the end of this period, the solution was concentrated under reduced pressure. The crude syrup was purified by column chromatography with CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative as a pale yellow viscous syrup **12** (0,185 g, 93%). $[\alpha]^{18}_D$ +27.2 (*c* 0,1, MeOH).

Anal. Calcd for $C_{13}H_{26}O_8$: C, 50.31; H, 8.44. Found: C, 51.46; H, 8.73.



11 **12**

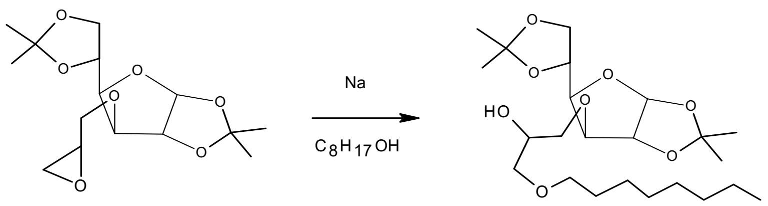
Figure 2.11. Synthesis of 3-*O*-[(2'-Hydroxy-3'-butyloxy)propyl]- α,β-D-glucopyranose **(12)**

2.2.15. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(-2'-hydroxy-3' -octyloxy) propyl]-α-D-glucofuranose (13)

2.2.15.1. Method 1

Na (0,218 g, 9,47 mmol) was dissolved under reflux in excess dry n-octanol (6 mL) under N_2. A solution of the compound **10** (0,92 g, 2,91 mmol) in n-octanol (6 mL) was added dropwise while the mixture was stirred at 5 ^{o}C. Then, the mixture was heated under N_2 for 24 h at 100 ^{o}C. After the end of this period, water was added very slowly at 0^{o}C and the solution was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrup. The crude syrup was purified by column chromatography using Hexane - CH_2Cl_2 (1:1) as the eluent to yield compound **13** as an colourless odorless syrup. (%88). $[\alpha]^{18}_{D}$ -20.4 (*c* 1,12, CH_2Cl_2). IR (cm^{-1}) υ^{film}_{max} 3533 O-H; 2987, 2936, C-H; 1373, 1216 $C(CH_3)_2$, 1082, C-O-C.

Anal. Calcd for $C_{23}H_{42}O_8$: C, 61.85; H, 9.47. Found: C, 61.87; H, 9.48.



10 **13**

Figure 2.12. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(-2’-hydroxy-3’ -octyloxy) propyl]-α-D-glucofuranose **(13)**

2.2.15.2. Method 2

To a stirred solution of the compound **10** (3 g , 9,49 mmol), and dry octanol (3,7 g, 28,5 mmol) in toluene-DMSO (1:1) was added powdered KOH (4 g, 71,28 mmol). After 84 h at 50 °C, the mixture was filtered and the filtrate was neutralized with saturated NH_4Cl. The above procedure was used, to obtain the pure compound **13** (%55).

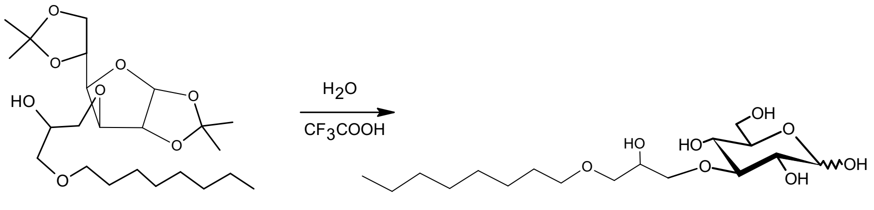
2.2.15.3. Method 3

BaO (1 g,) was suspended in dry octanol (10 mL) under N_2 at r.t. To the suspension was added the compound **10** (0,57 g, 1,8 mmol). The mixture was heated under N_2 at 75 °C for 72 h, the above procedure was used, to obtain the pure compound **13** (%27).

2.2.16. Synthesis of 3-*O*-[(2’-hydroxy- 3’-octyloxy)propyl]-α,β-D-glucopyranose (14)

To a stirred solution of the compound **13** (0,7 g , 1,56 mmol), in water (6mL) was added conc. CF_3COOH (2mL) at r.t. The mixture was stirred for 5 h. at r.t. The reaction was monitored by TLC. After the end of this time, the solution was concentrated under reduced pressure. The crude syrupy product was purified by column chromatography using CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative as a pale yellow wax (0,55 g, 92%) **14**. $[\alpha]^{18}_D$ +28.7 (*c* 0,81, MeOH).

Anal. Calcd for $C_{17}H_{34}O_8$: C, 55.719; H, 9.35. Found: C, 55.66; H, 9.32.

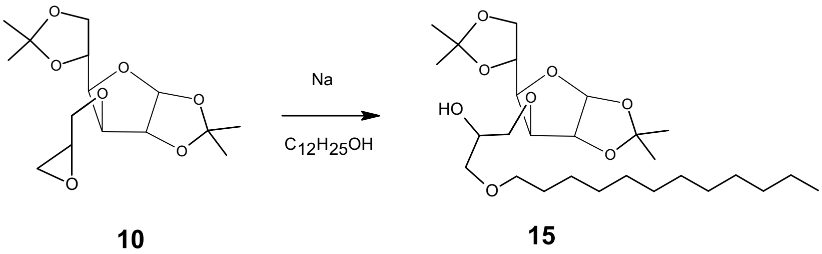


13 **14**

Figure2.13. Synthesis of3-*O*-[(2’-hydroxy-3’--octyloxy)propyl]-α,β-D-glucopyranose **(14)**

2.2.17. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2’-hydroxy-3’ -dodecyloxy)propyl]-α-D-glucofuranose (15)

Na (0,24 g, 10,4 mmol) was dissolved in dodecanol (8g, 42,9 mmol) under N_2 at 140 °C. Then, the mixture was cooled to r.t. The compound **10** (2,0358 g, 6,43 mmol) was added dropwise while the mixture was stirred at 5 °C. The mixture was heated at 120 °C under N_2 for 24 h. After the end of this period, small amount of water was added very slowly at r.t. and the mixture was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give viscous liquid. The liquid was dissolved in methanol and cooled to precipitate excess dodecanol and filtered. The filtrate was purified by column chromatography using Hexane - CH_2Cl_2 (1:1) as the eluent to yield the compound **15** as a yellow viscous syrup (2,9g, %89). $[\alpha]^{18}_{D}$ -33,8 (*c* 0.91, CH_2Cl_2).



10 **15**

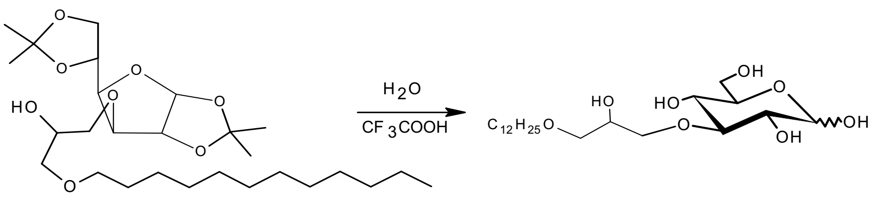
Figure 2.14. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy-3' -dodecyloxy)propyl]-α-D-glucofuranose **(15)**

2.2.18. Synthesis of 3-*O*-[(2'-hydroxy-3'-dodecyloxy)propyl]-α,β-D-glucopyranose (16)

NMR studies of the compound **15** showed that it still contained some unreacted dodecanol. It was not possible to remove the unreacted dodecanol completely, therefore the crude product was used directly for the hydrolysis step as described below.

To a stirred solution of the compound **15** (2,532 g , 5,043 mmol), in water (10 mL) and methanol (3 mL) was added conc. CF_3COOH (5 mL) at r.t. The mixture was stirred for 24 h. at r.t. After the end of this period, the water layer was extracted with hexane. The remaining water phase was concentrated to give a syrup. The crude syrupy product was purified by column chromatography using CH_2Cl_2-MeOH (4:1) as the eluent to yield a syrupy product **16**. (0,965g, 45%) $[\alpha]^{18}_{D}$ +35,0 (*c* 0.73, MeOH).

Anal. Calcd for $C_{21}H_{42}O_8$: C, 59.69; H, 10,018. Found: C, 61.48; H, 10.36.

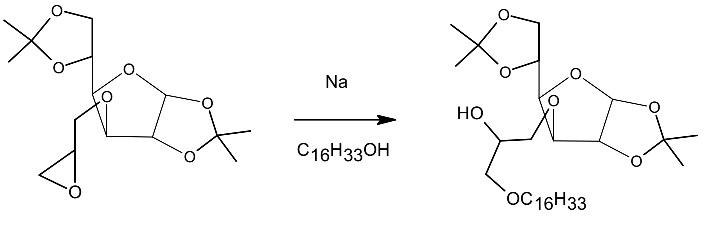


15 **16**

Figure2.15. Synthesisof3-*O*-[(2'-hydroxy-3'-dodecyloxy)propyl]-α,β-D-glucopyranose **(16**

2.2.19. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy- 3' -hexadecyloxy)propyl]-α-D-glucofuranose (17)

Na (0,2368 g, 10,3 mmol) was dissolved in hexadecanol (6,51g, 24,06 mmol) under N_2 at 140 °C for 2h. Then, the mixture was cooled to 60 °C. The compound **10** (2,0864 g, 6,59 mmol) was added. The mixture was heated again at 120 °C under N_2 for 24 h. After the end of this period, small amount of water was added very slowly at about 60°C and the mixture was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50 mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated. The concentrated solution was cooled to precipitate some waxy unreacted alcohol. This was filtered and the filtrate was evaporated completely. The residue was dissolved in methanol and cooled to precipitate some more excess hexadecanol and filtered. The filtrate was purified by column chromatography using Hexane - CH_2Cl_2 (1:1) as the eluent to yield compound **17** as a wax (3,7 g, %96).

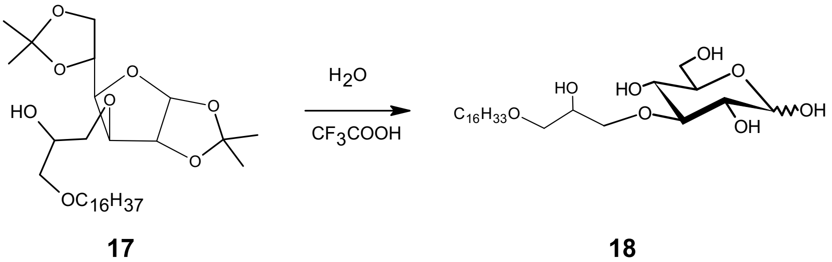


10 **17**

Figure 2.16. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy- 3' -hexadecyloxy)propyl]-α-D-glucofuranose **(17)**

2.2.20. Synthesis of 3-*O*-[(2'-hydroxy-3'-hexadecyloxy)-α,β-D-glucopyranose (18)

To a stirred solution of the compound **17** (3,55 g , 6,35 mmol), in water (10 mL) and methanol (3 mL) was added cocnc. CF_3COOH (5 mL) at r.t. The mixture was stirred for 48 h. at 40 °C. After the end of this period, the water layer was extracted with hexane. The remaining water phase was concentrated to give a syrup. The crude waxy product was purified by column chromatography using CH_2Cl_2-MeOH (4:1) as the eluent to yield a wax **18**. (0.85g., 28%)



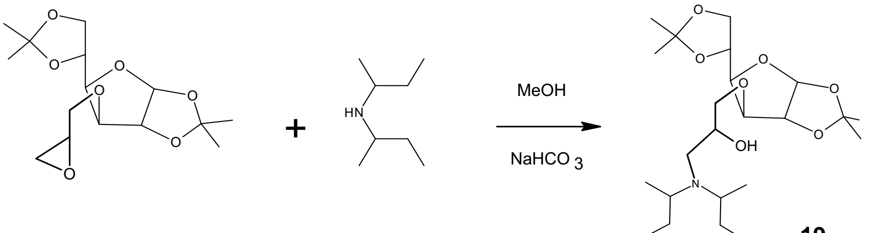
17 **18**

Figure 2.17. Synthesis of 3-*O*-[(2'-hydroxy-3'-hexadecyloxy)-α,β-D-glucopyranose **(18)**

2.2.21. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' –N,N-diisobutylamino-2'-hydroxy)propyl]-α-D-glucofuranose (19)

To a stirred solution of the compound **10** (2,56 g , 8,09 mmol), in methanol (20 mL) was added diisobutylamine (1,05 g, 8,12 mmol) and sodium hydrogencarbonate (0,2 g) at r.t. The mixture was stirred under reflux for 7 h. During the reaction, the colour of the solution darkened. The solution was diluted with ethyl acetate, washed with water (2x 50 mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrup. The crude syrup was purified by column chromatography using Hexane - Acetone (1:1) as the eluent to yield a dark yellow syrup **19** (2,75g, %84). $[\alpha]^{17}_{D}$ -29.7 (*c* 0.8, CH_2Cl_2).

Anal. Calcd for $C_{23}H_{43}NO_7$: C, 61.99; H, 9.72. Found: C, 60.75; H, 9.54.



10 **19**

Figure 2.18. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' –N,N-diisobutylamino-2'-hydroxy)propyl]-α-D-glucofuranose **(19)**

2.2.22. Synthesis of 3-*O*-[(3'-N,N- diisobutylamino-2'-hydroxy)propyl]-α,β-D-glucopyranose (20)

To a stirred solution of compound **19** (2,3 g , 5,16 mmol), in water (10 mL) was added conc.CF_3COOH (3 mL) at r.t. The mixture was stirred for 3 days at 50 ^{o}C. After the end of this period, the solution was concentrated under reduced pressure. The crude syrup was purified by column chromatography using CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative as triflouroacetate as the counter ion of the corresponding compound as a reddish syrup **20**. $[\alpha]^{17}_D$ +45.8 (*c* 0.22, MeOH).

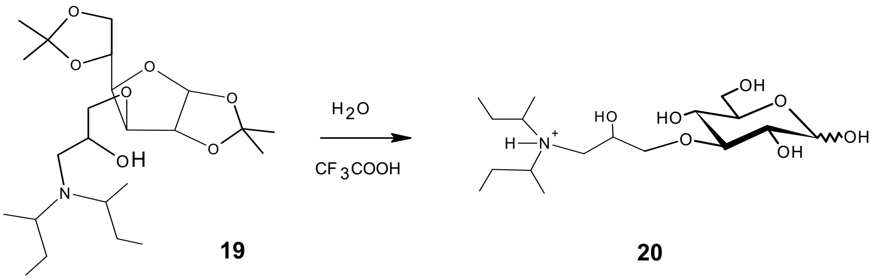


Figure 2.19. Synthesis of 3-*O*-[(3'-N,N- diisobutylamino-2'-hydroxy)propyl]-α,β-D-glucopyranose **(20)**

2.2.23. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy-3' -cyclohexyloxy)propyl]-α-D-glucofuranose (21)

Na (0,188 g, 8,17 mmol) was dissolved in cyclohexanol (6,22 g, 62,2 mmol) and toluene (10 mL) under N_2 at 140 °C. Then, the mixture was cooled to r.t. The compound **10** (2,08 g, 6,57 mmol) was added while the mixture was stirred at r.t. The mixture was heated under reflux and N_2 for 15 h. After the end of this period, water was added very slowly at r.t. and the mixture was extracted with ethyl acetate, washed with water (2x 50 mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrup. The filtrate was purified by column chromatography using CH_2Cl_2 - methanol (9:1) as the eluent to yield the compound **21** as a slightly yellow syrup (2,36 g, %86). $[\alpha]^{18}_D$ -11,2 (*c* 1,0 CH_2Cl_2).

Anal. Calcd for $C_{21}H36O_8$: C, 60.55; H, 8.71. Found: C, 60.24; H, 8.64.

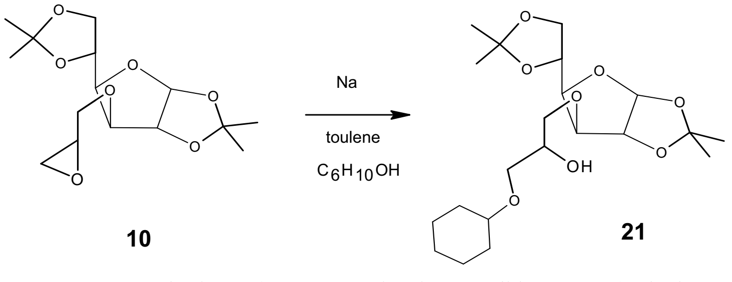


Figure 2.20. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2’-hydroxy-3’-cyclohexyloxy)propyl]-α-D-glucofuranose **(21)**

2.2.24. Synthesis of 3-*O*-[2’-hydroxy-3’-cyclohexyloxy)propyl]-α,β-D-glucopyranose (22)

To a stirred solution of the compound **21** (2,19 g , 5,26 mmol), in water (10 mL) was added conc. CF_3COOH (1 mL) at r.t. The mixture was stirred for 7 h. at r.t. After the end of this period, the solution was concentrated under reduced pressure. The crude syrup was purified by column chromatography, eluting with CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative of the corresponding sugar derivative as a slightly yellow syrup **22.** (1.502g, 85%) $[\alpha]^{17}_D$ +19.5 (*c* 0.9, MeOH).

Anal. Calcd for $C_{15}H_{28}O_8$: C, 53.55; H, 8.39. Found: C, 54.21; H, 8.30.

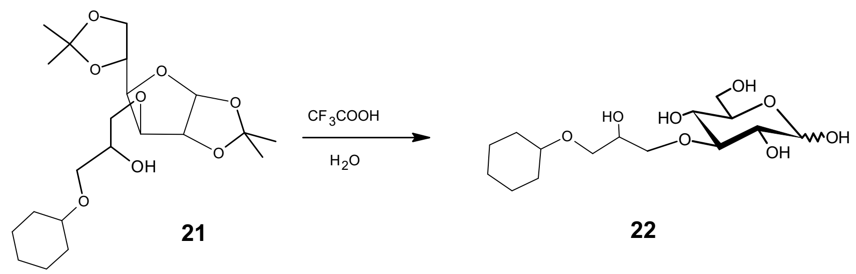
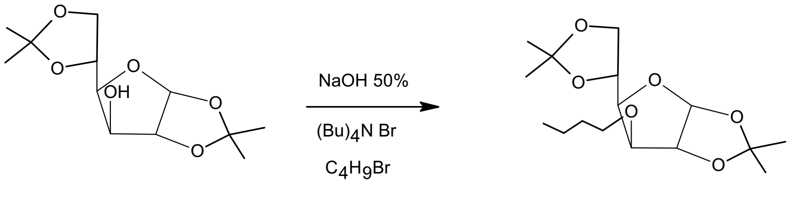


Figure 2.21. Synthesis of 3-*O*-[2'-hydroxy-3'-cyclohexyloxy)propyl]-α,β-D-glucopyranose **(22)**

2.2.25. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-butyl-α-D-glucofuranose (23)

n-Butylbromide (10 g, 72,98 mmol) was stirred with aq NaOH (50%, 20 g) and tetrabutyl ammonium bromide (0,5 g, 1,55 mmol) for 30 min. The compound **1** (2g, 7,69 mmol) was added slowly at approx. 5 ^{o}C under stirring and the reaction continiued at the same temp. for 30 min. followed by additional 15 h. at r.t. The reaction mixture was poured over crushed ice and extracted with EtOAc (4x100 mL), the organic layer was washed with aq. NH_4Cl (10%, 1x 25 mL) followed by water (2x 50mL) and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a liquid. The crude liquid was purified by column chromatography using CH_2Cl_2 - methanol (9:1) as the eluent to yield 3-O-n-butyl derivative of the corresponding sugar derivative as a colorless liquid (2,25 g %92). **23** (Shinji, Y., 1995) $[\alpha]^{16}_{D}$ -21.2 (*c* 0.5, CH_2Cl_2).

Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.73; H, 8.92. Found: C, 60.51; H, 8.88.



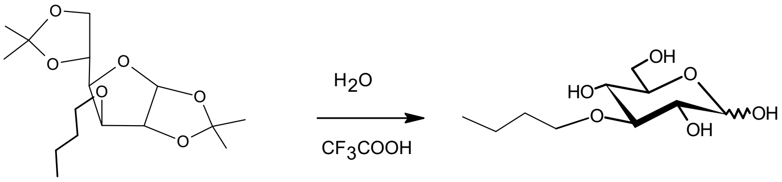
1 **23**

Figure 2.22. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-butyl-α-D-glucofuranose **(23)**

2.2.26. Synthesis of 3-*O*-butyl- α,β-D-glucopyranose (24)

To a stirred solution of compound **23** (2,137 g, 6,75 mmol), in water (10 mL) was added conc. CF_3COOH (1 mL) at r.t. The mixture was stirred for 12 h. at r.t. After the end of this period, the solution was concentrated under reduced pressure to give a liquid. The crude creamy product was purified by column chromatography eluting with CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative of the corresponding sugar as a white paste **24**.(1.5097g., 94%) $[\alpha]^{18}_D$ +28.4 (*c* 0.42, MeOH).

Anal. Calcd for $C_{10}H_{20}O_6$: C, 50.83; H, 8.53. Found: C, 50.62; H, 8.44.

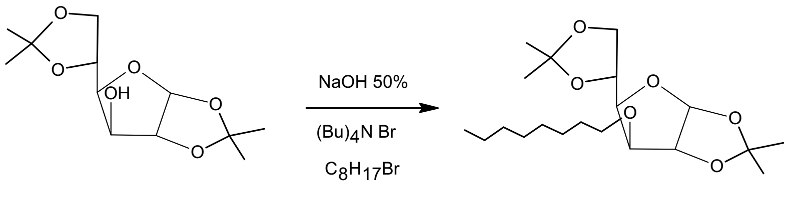


23 **24**

Figure 2.23. Synthesis of 3-*O*-butyl- α,β-D-glucopyranose **(24)**

2.2.27. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (25)

n-Octylbromide (11,9 g, 61,6 mmol) was stirred with aq NaOH (50%, 20 g) and tetrabutyl ammonium bromide (0,5 g, 1,55 mmol) for 30 min. The compound **1** (2g, 7,69 mmol) was added slowly at approx. 5 ^{o}C and under stirring and the reaction continiued at same temp. for 30 min, followed by additional 15 h. at r.t. The reaction mixture was poured over crushed ice and extracted with EtOAc (4x100 mL), the organic layer was washed with aq. NH_4Cl (10%, 1x 25 mL) and then with water (2x 50mL) and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a liquid **25**. (2,7934g, 97,5%).

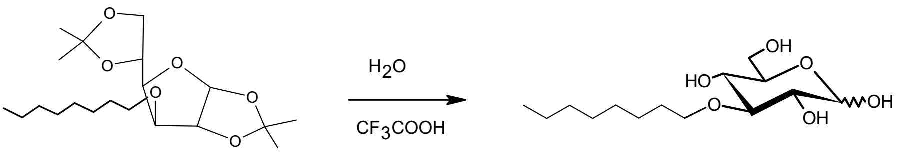


1 **25**

Figure 2.24. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose **(25)**

2.2.28. Synthesis of 3-*O*-octyl- α,β-D-glucopyranose (26)

To a stirred solution of compound **25** (2,5369 gr, 6,81 mmol), in water (10 mL) was added conc. CF_3COOH (1 mL) at r.t. The mixture was stirred for 12 h. at r.t. After the end of this period, the solution was concentrated under reduced pressure to give a crude creamy product which was purified by column chromatography eluting with CH_2Cl_2 – Methanol 4:1 to give the pyranose derivative of the corresponding sugar as white paste **26**.

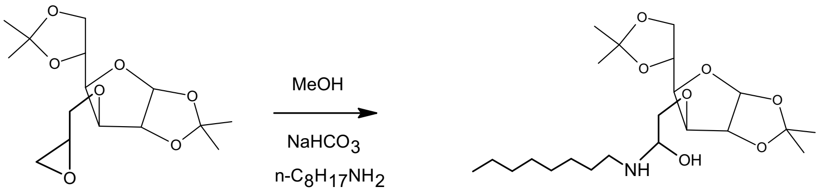


25 **26**

Figure 2.25. Synthesis of 3-*O*-octyl- α,β-D-glucopyranose **(26)**

2.2.29. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy-3' -N-octylamino)propyl]-α-D-glucofuranose (27)

A solution of compound **10** (2,02 g, 6,39 mmol) in n-octyl amine was stirred for 24 h. at 80 °C. The reaction was monitored by TLC. After the end of this period, the solution was concentrated under reduced pressure. TLC indicated a single spot. The product was purified by column chromatography eluting with CH_2Cl_2 – Methanol 4:1 to give the compound **27** (2,82 g, 98 %).



10 **27**

Figure 2.26. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy-3' -N-octylamino)propyl]-α-D-glucofuranose **(27)**

2.2.30. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' -allyloxy-2'-hydroxy)propyl]-α-D-glucofuranose (28)

Na (0,25 g, 1,08 mmol) was dissolved readily in excess dry allyl alcohol (9 mL). The compound **10** (1,11 g, 3,512 mmol) was added while the mixture was being stirred at r.t. Then, the mixture was heated at 70 ^{o}C for 24 h. After the end of this period, water was added very slowly at 0^{o}C and the solution was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give syrup. The crude syrup was purified by column chromatography using Hexane - Acetone (1:1) as the eluent to yield a yellow syrup (**28)** (1,12 g, 85,2 %). $[\alpha]^{17}_{D}$ -19.2 (*c* 0.43, CH_2Cl_2).

Anal. Calcd for $C_{18}H_{30}O_8$: C, 57.74; H, 8.07. Found: C, 58.01; H, 8.12.

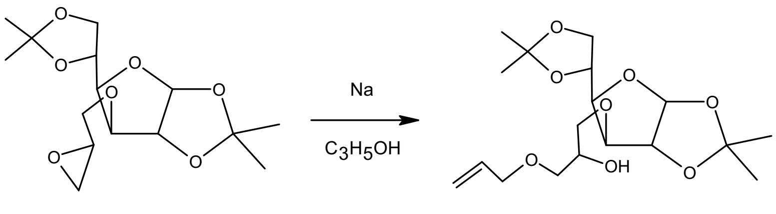


Figure 2.27. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' -allyloxy-2'-hydroxy)propyl]-α-D-glucofuranose **(28)**

2.2.31. Synthesis of Polymethyl-(3-hydroxypropyl)siloxane (29)

To a stirred solution of PMHS (5,12 g, 2,26 mmol) and 30 equivalents of allyl alcohol (3,81 gr, 65,68 mmol) in dry toluene (12mL) was added H_2PtCl_6 (1,4 mL) as a solution in isopropylalcohol (0,2%) under N_2 at r.t. The mixture was heated at 100 ^{o}C. The viscosity increased markedly during the reaction. After 2 h., a gel formed. Solvent and other volatile material were evaporated under reduce pressure at 100 °C for 24 h. Then, the gel turned to a glassy matrix. This material did not dissolve in any organic solvent, hence it was difficult to identify. On the other hand, FTIR spectra of both PMHS and the product showed that the reaction took place.

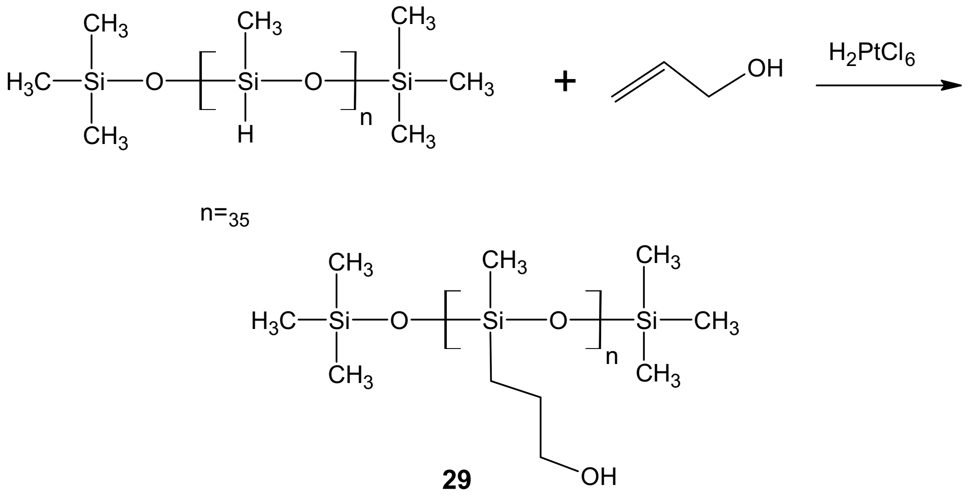


Figure 2.28. Synthesis of Polymethyl-(3-hydroxypropyl)siloxane **(29)**

2.2.32. Synthesis of Polymethylglucosiloxane (30)

To a stirred solution of PMHS (0,11 g, 0,0485 mmol) and 35 equivalents of the compound **9** (0,47 g, 1,56 mmol) in dry toluene (25mL) was added H_2PtCl_6 (0,5 mL) as a solution in isopropylalcohol (0,2%) under N_2 at r.t. The mixture was heated at 100 °C. The viscosity increased during the reaction. After 24 h, NaOH solution was added to stop reaction. The solution was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x 50mL) dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give very viscous syrup. The IR spectrum indicated the disappearance of the Si-H bond absorbance at (2164 cm^{-1}) which is indicative of the reaction however ^{1}H NMR indicated the presence of some unreacted sugar derivative **9** .

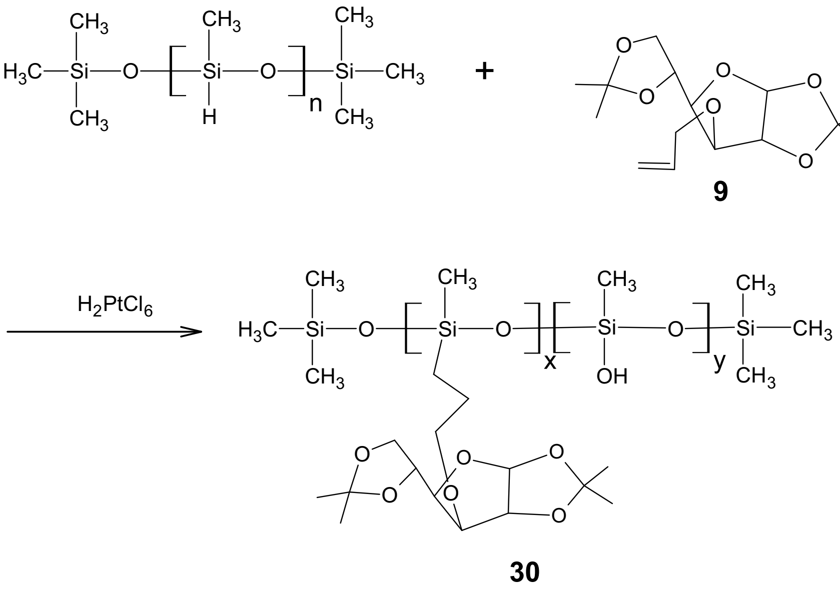


Figure 2.29. Synthesis of Polymethylglucosiloxane **(30)**

3. SPECTROSCOPIC DATA

3.1. 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (1)

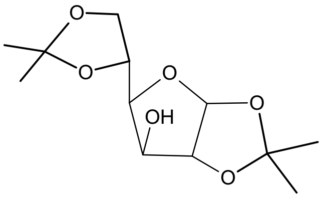
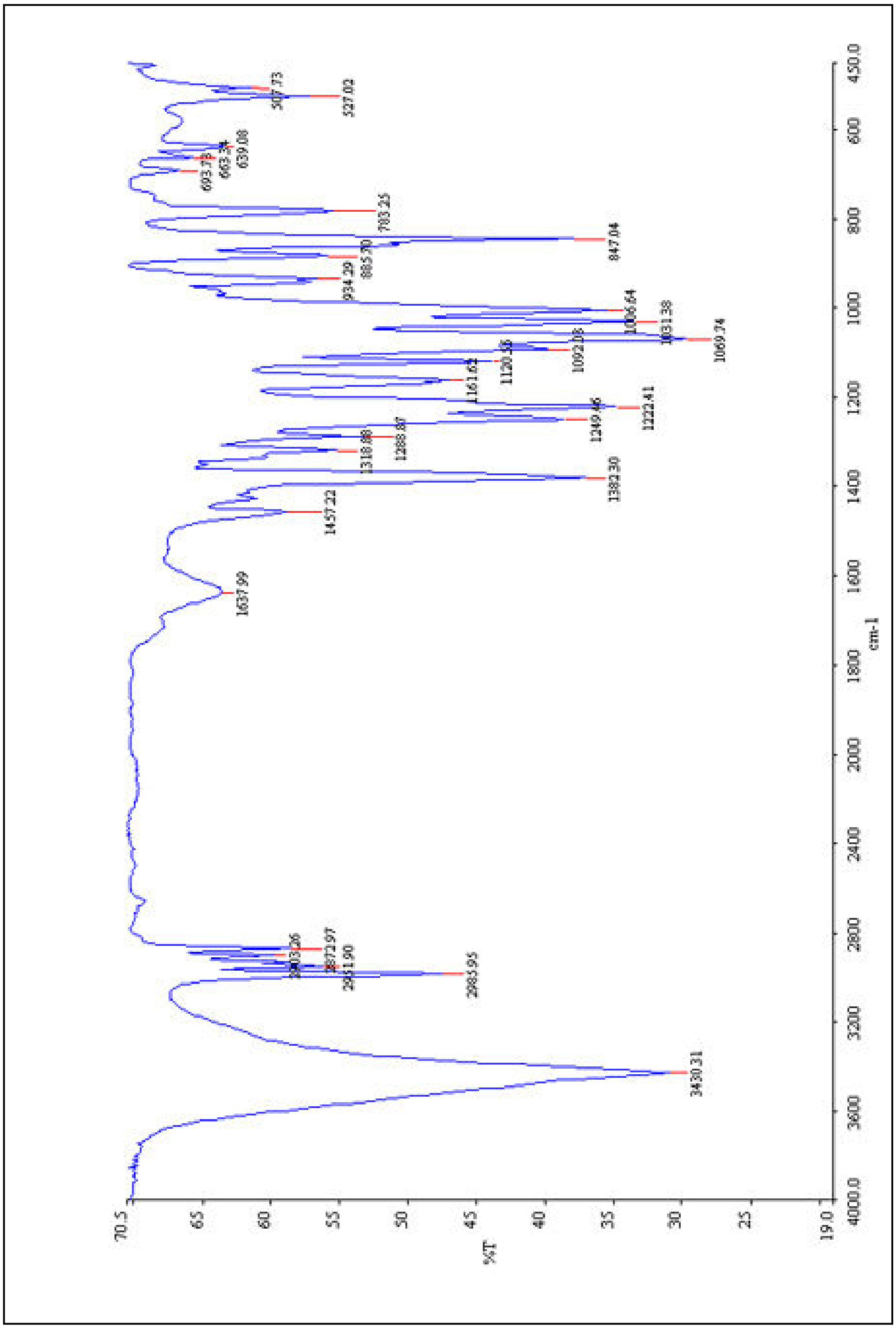


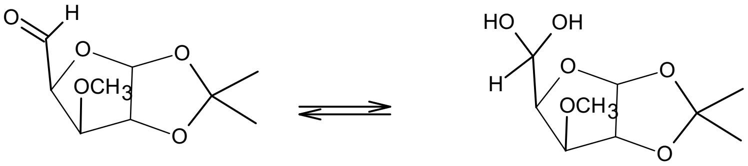
Table 3.1 FTIR data (cm^{-1}) of the compound **1**

Functional Groups	**cm^{-1}**
-O-H	3430
C-H	2985, 2951, 2872
$C(CH_3)_2$	1382, 1222
C-O-C	1069

Figure 3.1 FTIR spectrum of the compound **1**



3.2. 1,2-*O*-isopropylidene-3-*O*-methyl-D-xylo-dialdo-furanose (5)

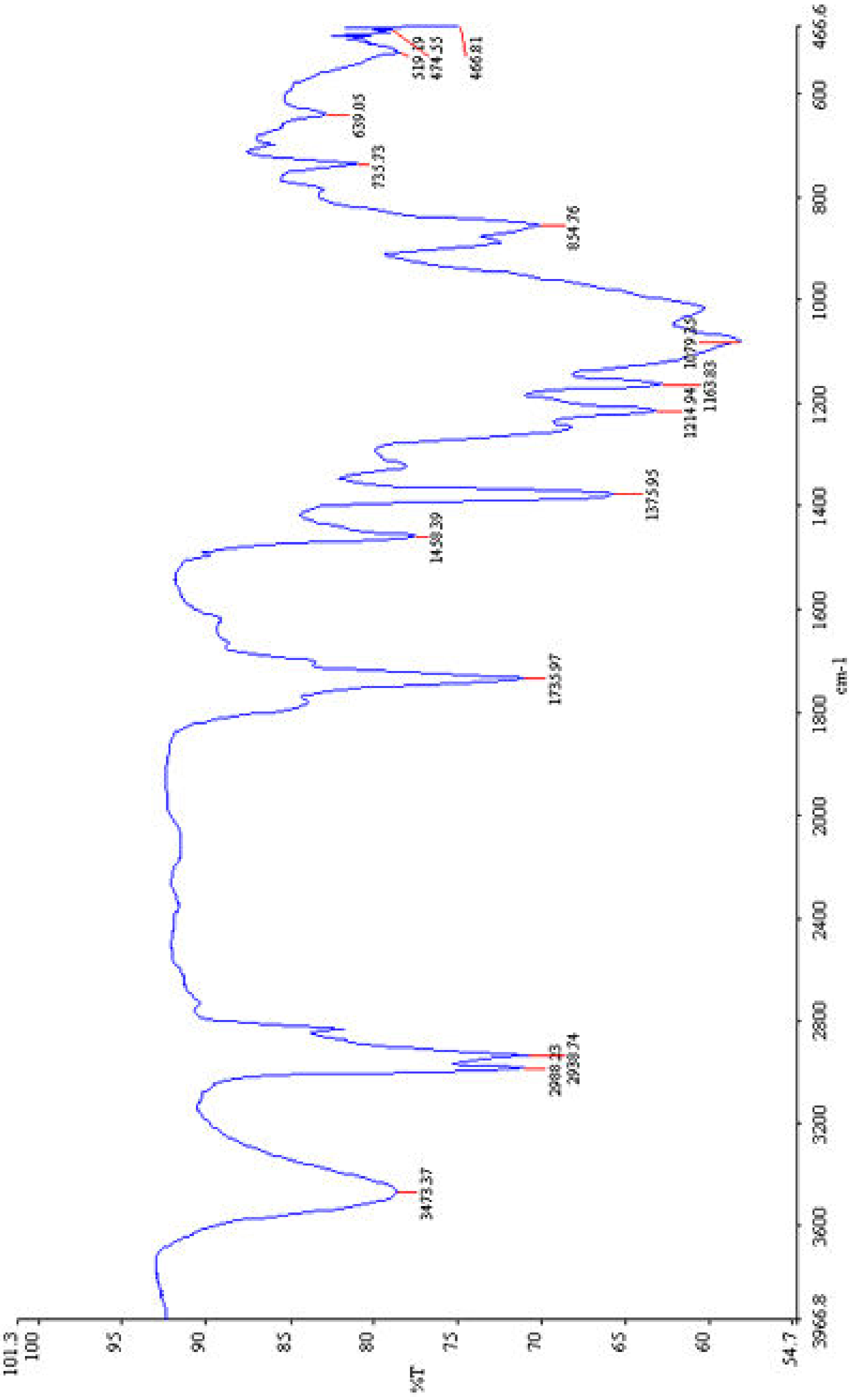


This compound is converted into its hydrate form on standing. The FTIR spectrum (**Figure 3.2**) shows that both forms of the compound **5** are present as a mixture. The hydrate form cannot be easily converted to the free aldehydic form. We think, Grignard reaction with the compound **5** did not give a single product due to the presence of the hydrate form since these reactions are extremely sensitive to even a trace of water. Further purification was not sufficient to give a pure product of **6.**

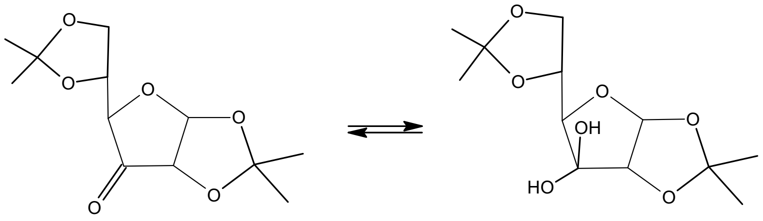
Table 3.2 FTIR data (cm^{-1}) of the compound **5**

Functional Groups	**cm^{-1}**
-O-H	3461
C-H	2988, 2939
C=O	1735
$C(CH_3)_2$	1375, 1214
C-O-C	1080

Figure 3.2 FTIR spectrum of the compound **5**



3.3 1,2:5,6-Di-*O*-isopropylidene-α-D-ribo-hexofuranos-3-ulose (7)



This compound is converted into its hydrate form on standing. The FTIR spectrum of the keto form is shown in **Figure 3.3,** and the hydrate form is shown in **Figure 3.4**. Hydrate form of this compound (unlike the aldehyde **5**) can easily be converted into its keto form by azeotroping with toluene.

Table 3.3 FTIR data (cm^{-1}) of the compound **7**

Functional Groups	**Keton form (cm^{-1})**	**Hydrate form (cm^{-1})**
-O-H	-	3423
C-H	2938, 2900	2988, 2939
C=O	1738	-
$C(CH_3)_2$	1330, 1254	1375, 1214
C-O-C	1085	1080

Figure 3.3 FTIR spectrum of the compound **7** (keton form)

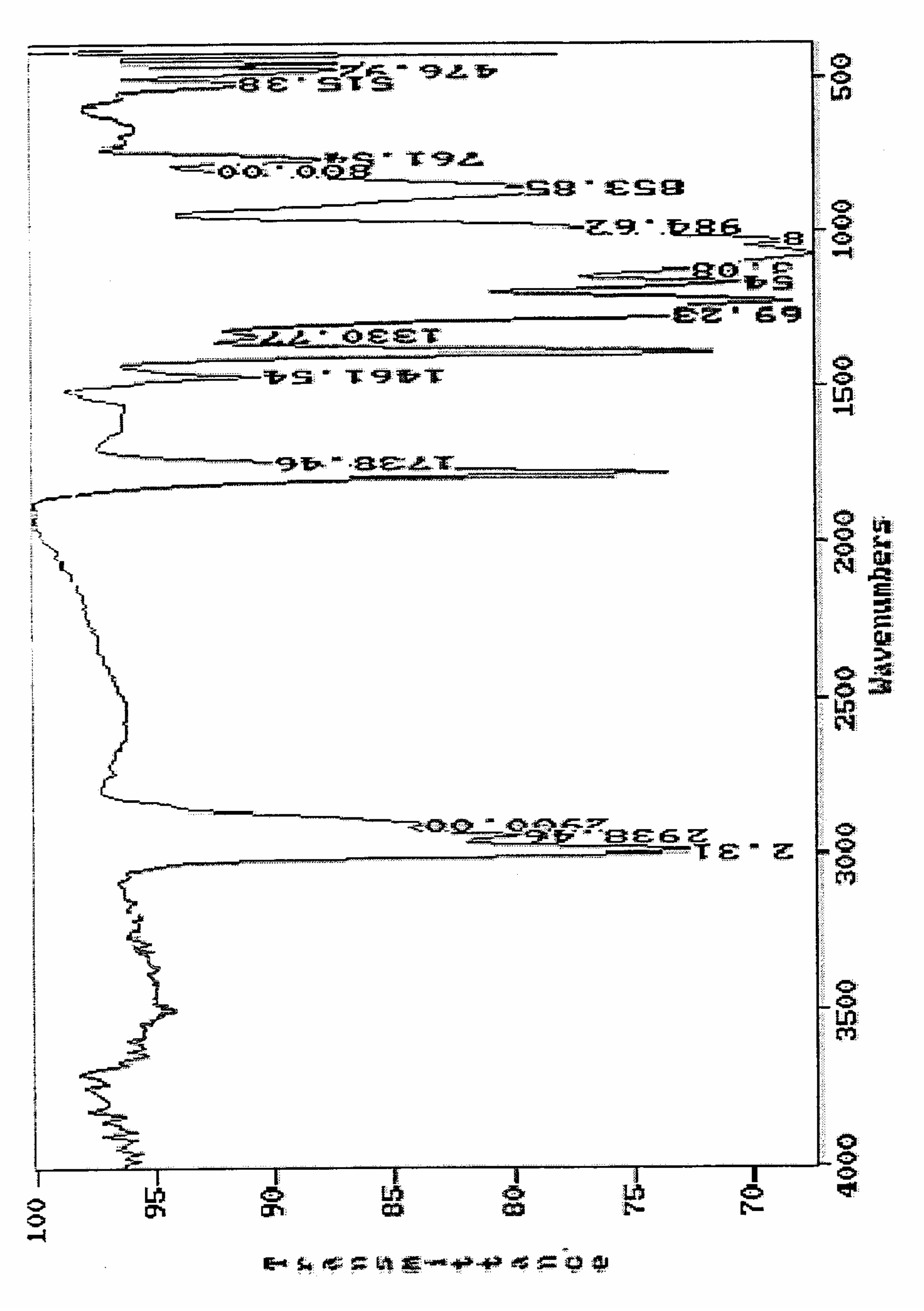
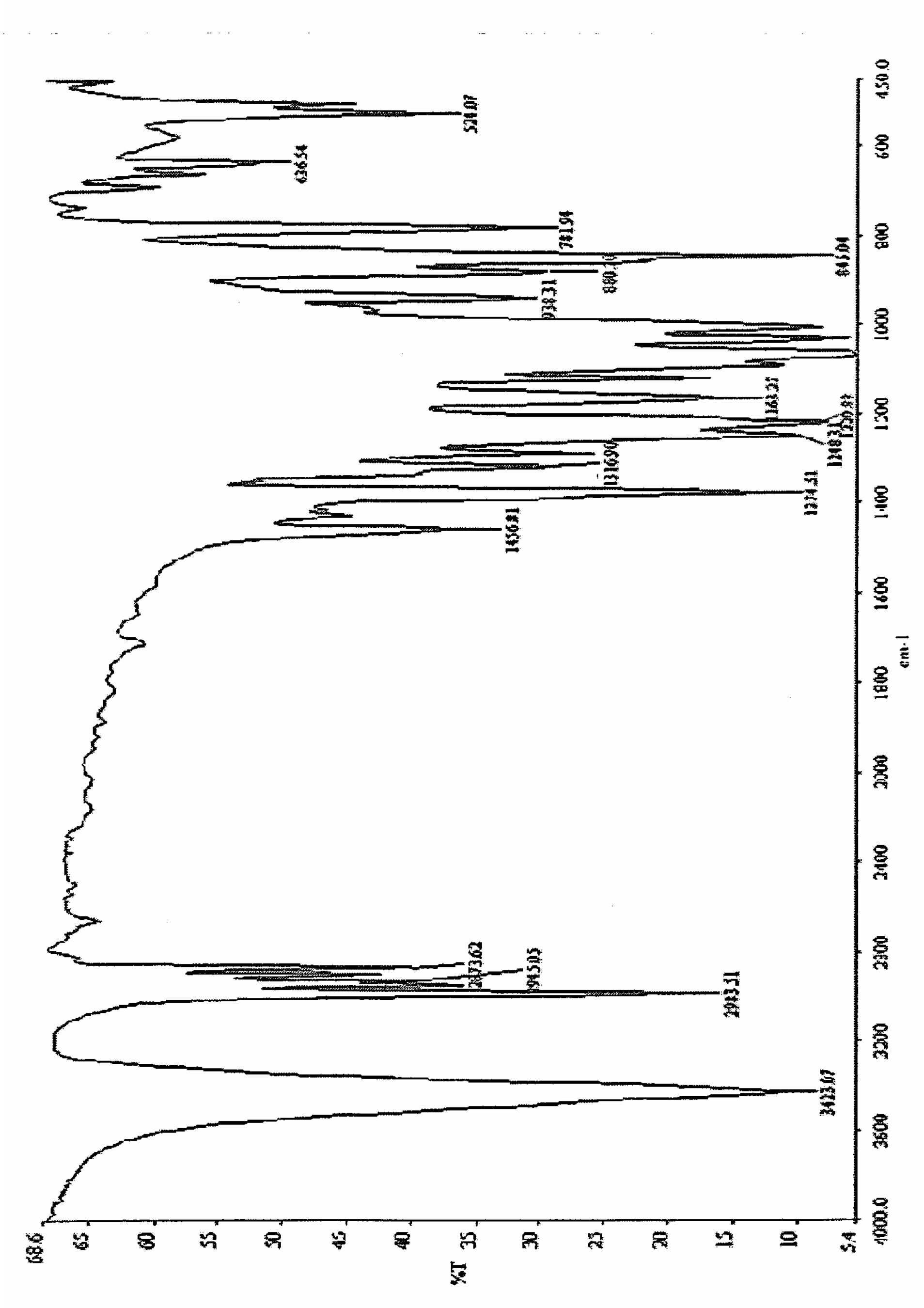
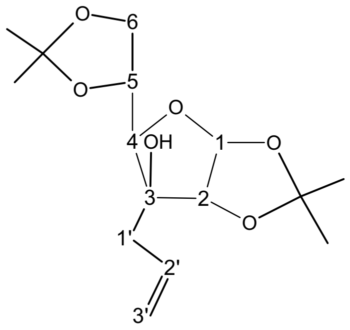


Figure 3.4 FTIR spectrum of the compound **7** (hydrate form)



3.4. 3-*C*-Allyl-3-hydroxy-1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (8)



Both gluco and allo forms were observed. (see **2.2.10**). Major isomer (most probably the gluco isomer) was isolated by column chromatography.

Table 3.4 ^{1}H NMR spectral data of the compound **8**

Position of atoms	**^{1}H NMR (δ)**	**H and *J* couplings (Hz)**
H-2'	5.81 m	1 H
H-1	5.68 d	1 H, $J_{1,2}=3.9$
H-3'	5.00 m	1 H, $J_{2',3'}$(trans)=16,
H-3'	4.95 m	1 H, $J_{2',3'}$(cis) =12
H-2	4.34 d	1 H, $J_{1,2}=3.9$
H-5, H6a	4.07-4.15 m	2 H
H-6b	3.91 m	1 H
H-4	3.78 d	1 H, $J_{4,5}$=8.2
H-1'	2.09 m	2 H
Me	1.58 s	3 H
Me	1.44 s	3 H
Me	1.36 s	3H
Me	1.35 s	3H

Figure 3.5 ^{1}H NMR spectrum of the compound **8** (low field part)

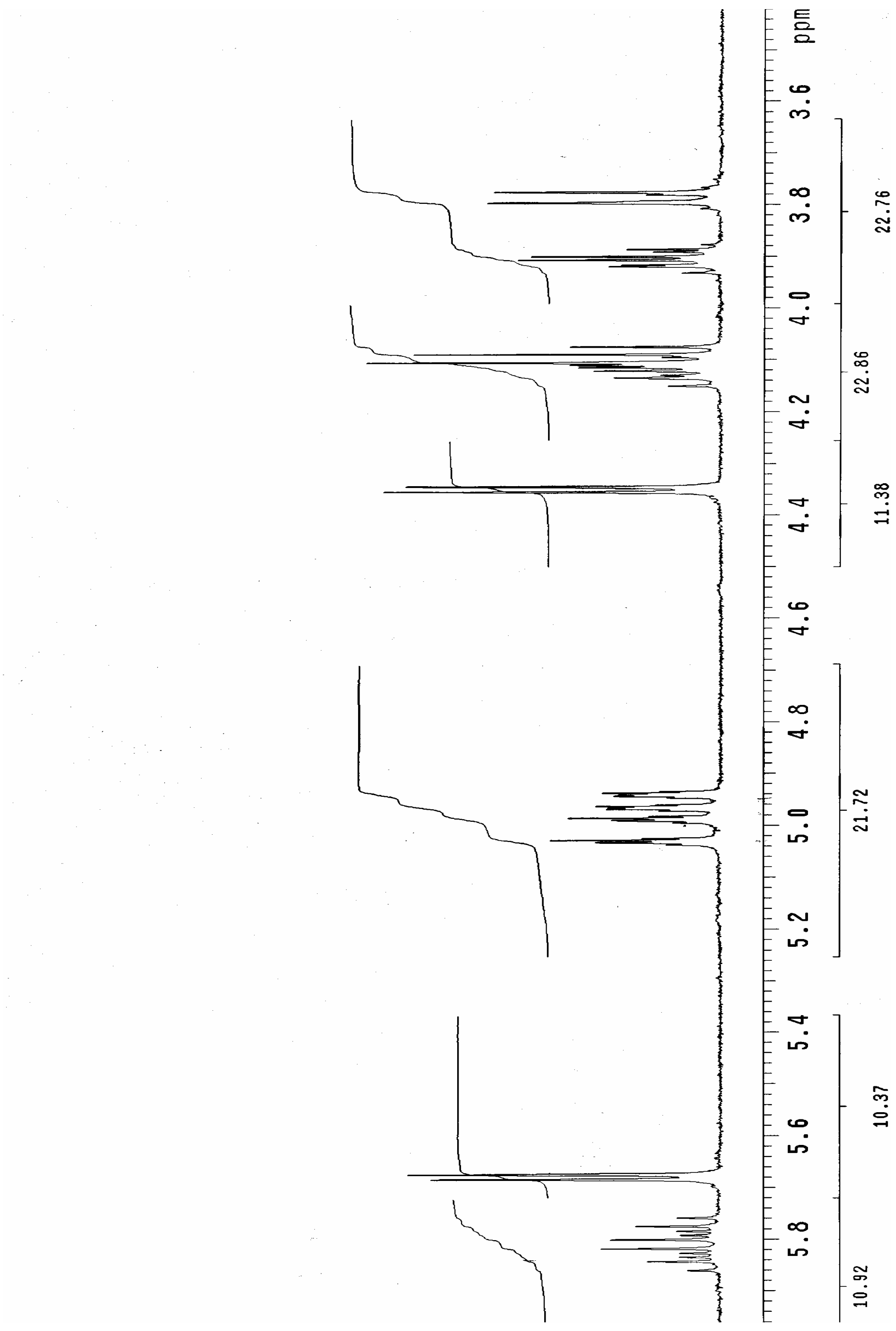
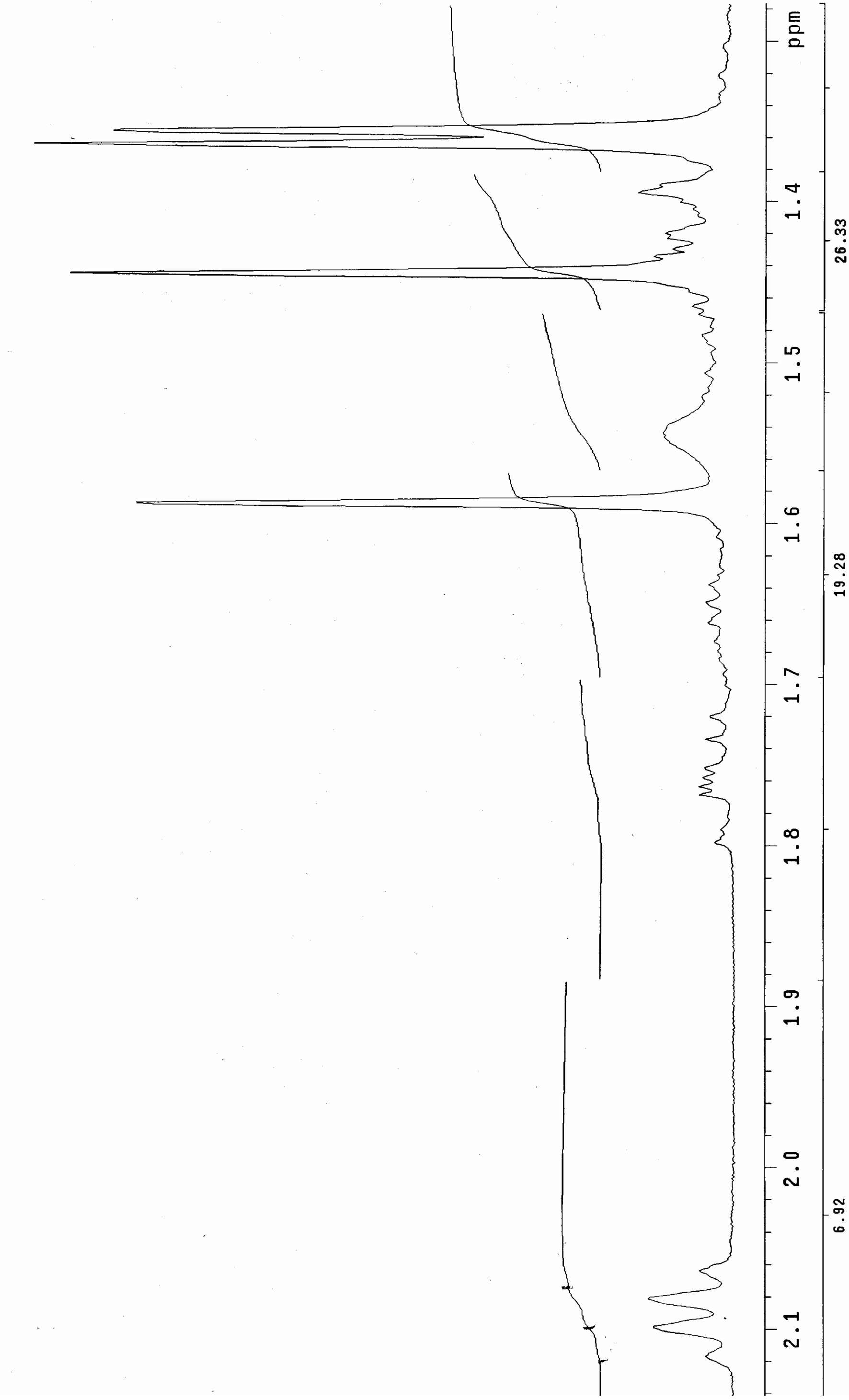


Figure 3.6 ^{1}H NMR spectrum of the compound **8** (high field part)



3.5 1,2:5,6-Di-O-isopropylidene-3-O-(2-propene-1-yl)-α-D-glucofuranose (9)

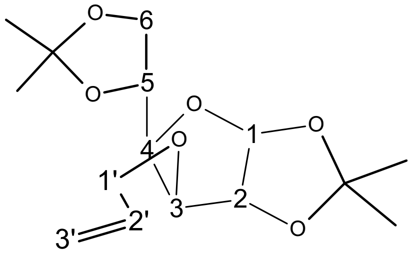


Table 3.5 FTIR data (cm^{-1}) of the compound **9**

Functional Groups	**cm^{-1}**
=C-H	3080
C-H	2987, 2934
C=C	1647
$C(CH_3)_2$	1375, 1214
C-O-C	1076

Table 3.6 ^{1}H NMR spectral data of the compound **9**

Position of atoms	**^{1}H NMR (δ)**	**H and *J* couplings (Hz)**
H-1	5.87 d	1 H $J_{1,2}=3.6$
H-2’	5.88 m	1 H
H-3’	5.29 m	1 H, $J_{2',3'}$(trans)$=16.0$
H-3’	5.18 m	1H, $J_{2',3'}$(cis)$=12.0$
H-2	4.53 d	1H,
H-5	4.30 dt	1H
H-4, H-6a, H-1’	4.20-4.05 m	4H
H-6b	3.98 dd	1H, $J_{5,\&b}= 6.0$
H-3	3.93 d	1H, $J_{1,2}=3.2$
Me	1.48 s	3 H
Me	1.41 s	3 H
Me	1.34 s	3H
Me	1.30 s	3H

Figure 3.7. FTIR spectrum of the compound **9**

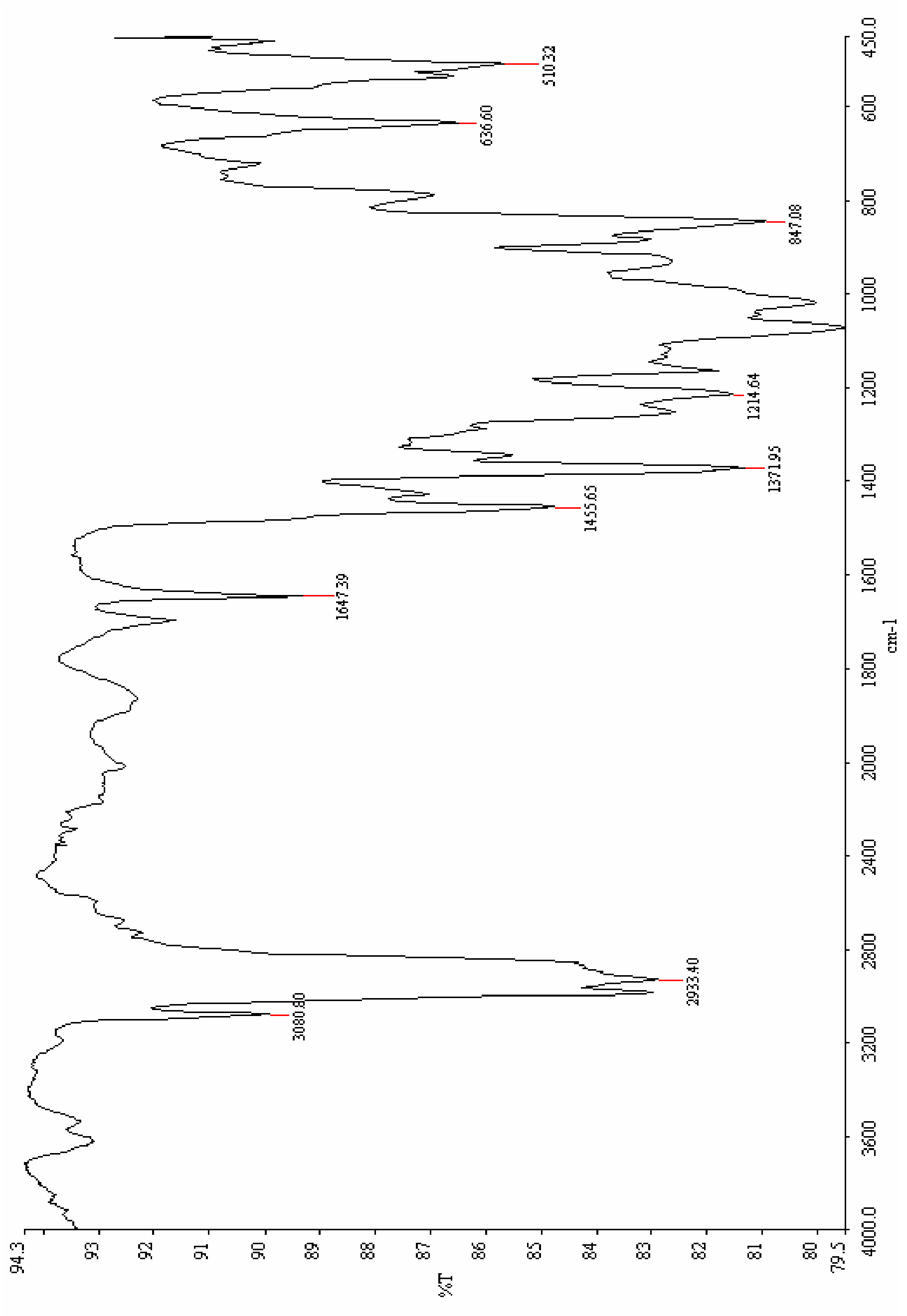


Figure 3.8 ^{1}H NMR spectrum of the compound **9** (low field part)

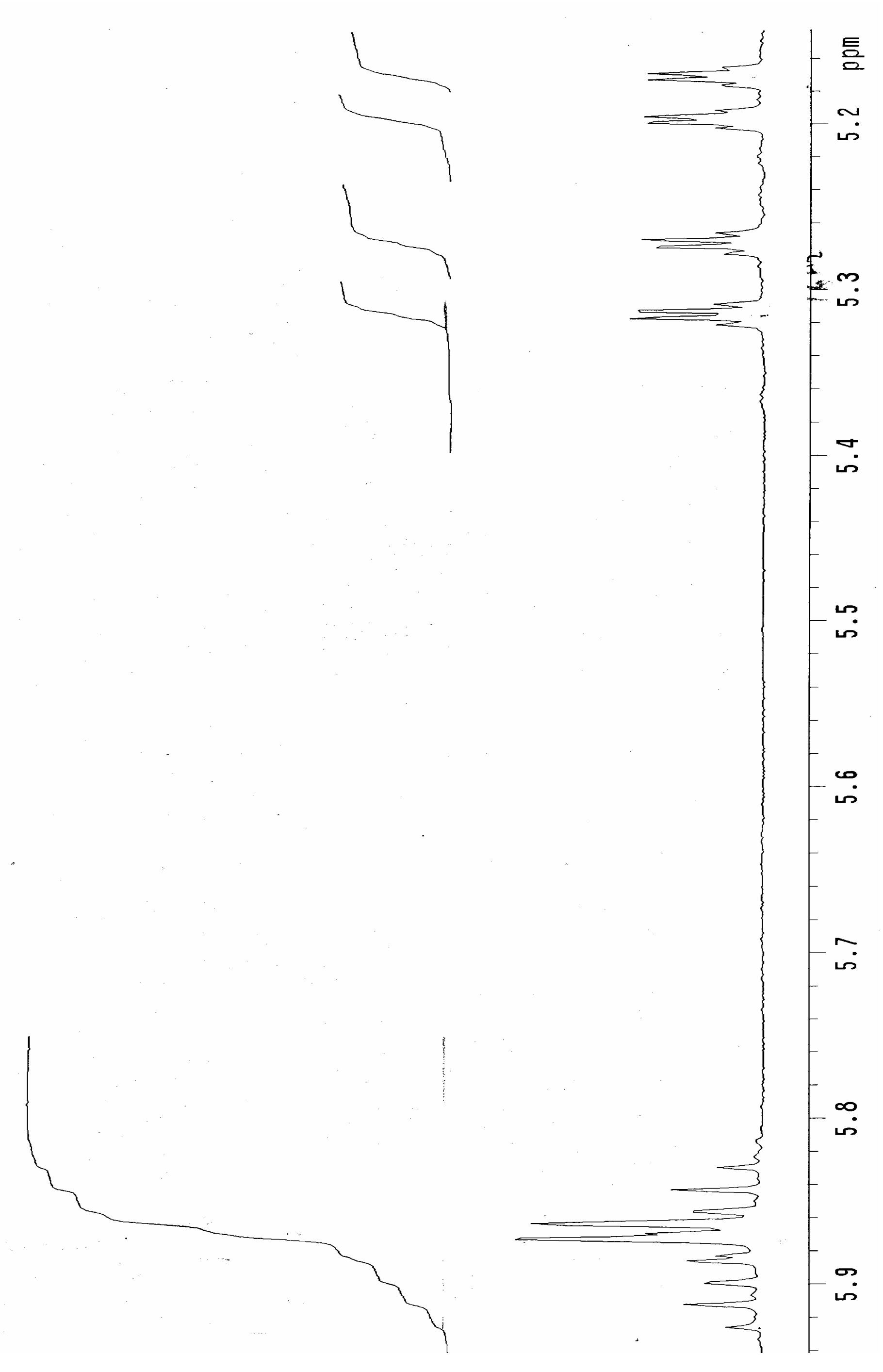


Figure 3.9 ^{1}H NMR spectrum of the compound **9** (centre field part)

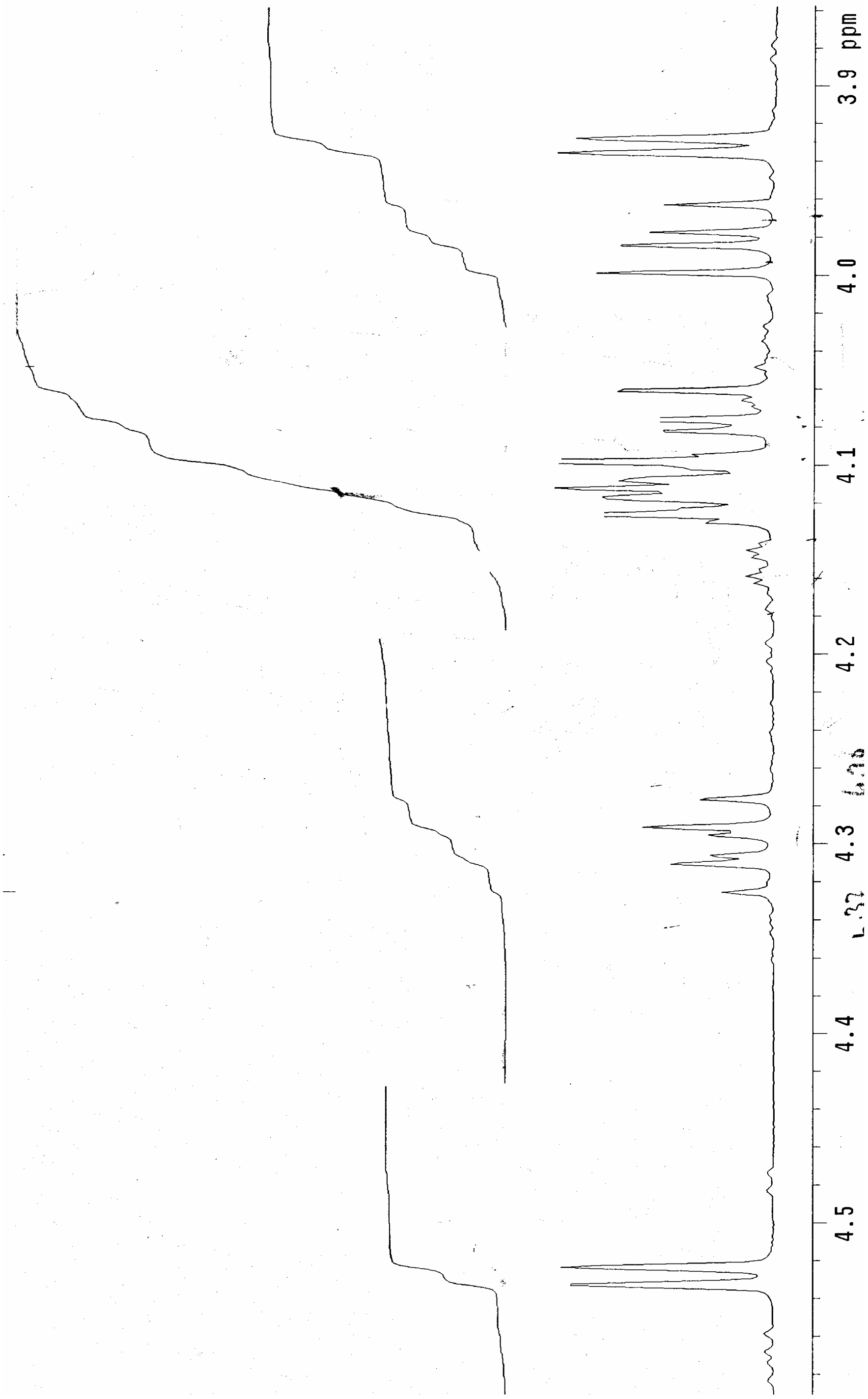
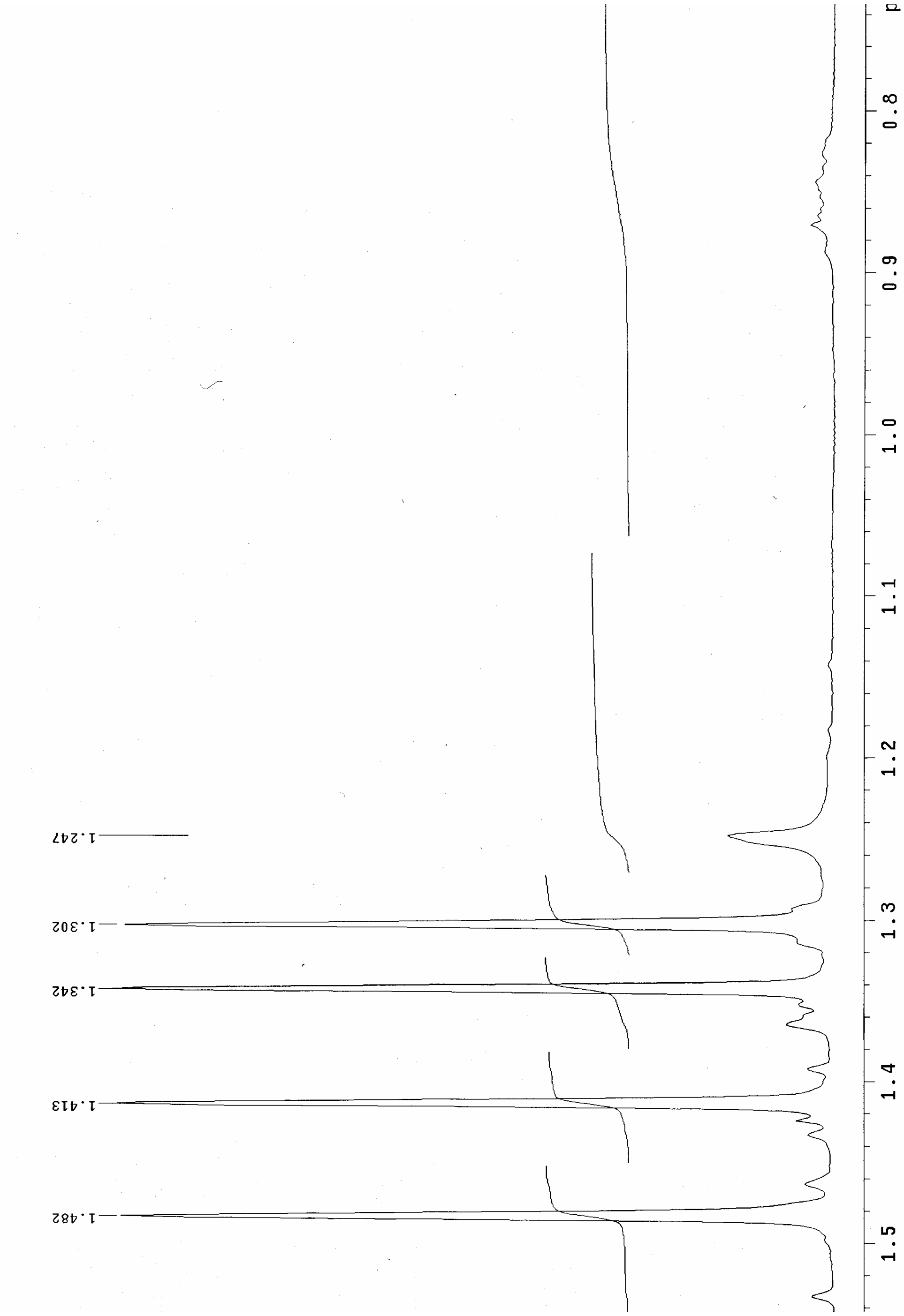


Figure 3.10 ^{1}H NMR spectrum of the compound **9** (high field part)



3.6. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[2(R/S)-3-epoxypropan-1-yl)- α-D-glucofuranose (10)

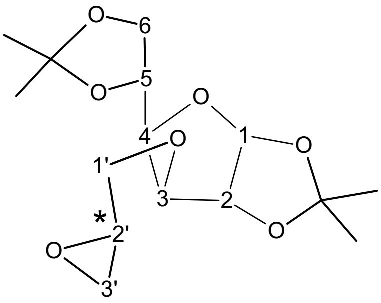
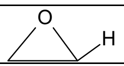


Table 3.7. FTIR data (cm^{-1}) of the compound **10**

Functional Groups	**cm^{-1}**
	3056
C-H	2988, 2936
$C(CH_3)_2$	1373
C-O-C	1080

Due to the use of rasemic epichlorohydrine, the title compound exist as a mixture of two diastereoisomers (new chiral carbon at C-2') in equal amounts. There are two H-1 doublets at δ 5.86 and 5.84 and two H-2 doublets at δ 4.56 and 4.52. Coupling constants between H-1 and H-2 are 3.6 Hz and typical for an α-D-furanose derivative. Coupling constant between H-2 and H-3 is 0 Hz which is again typical for an α-D-furanose derivative. H-5 signal of the stereoisomers coincidentally overlapped, giving a complex multiplet at δ 4.28. Epoxy group signals (H-3') are resolved giving two dd signals at δ 2.59 and 2.58 for each of the diastereoisomers, with a geminal coupling 4.8 Hz, and H-2’ signals are also resolved giving two triplets at δ 2.79 and 2.76. The coupling constants $J_{2',3'}$ = 2.8 and 4.8 Hz. Isopropylidene methyl groups resonate at δ 1.47, 1.40, 1.32, 1.29.

Figure 3.11. . FTIR spectrum of the compound **10**

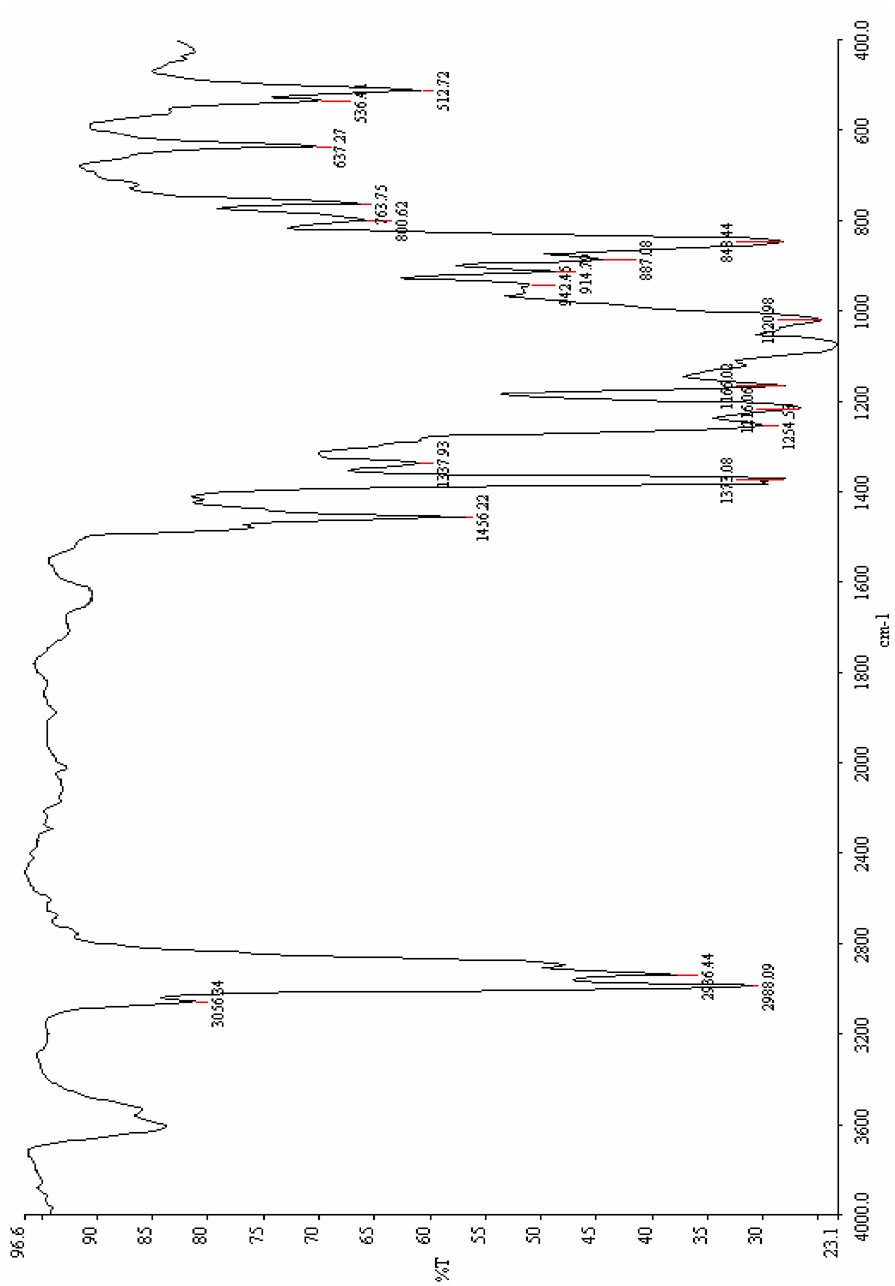


Figure 3.12 ^{1}H NMR spectrum of the compound **10** (low field part)

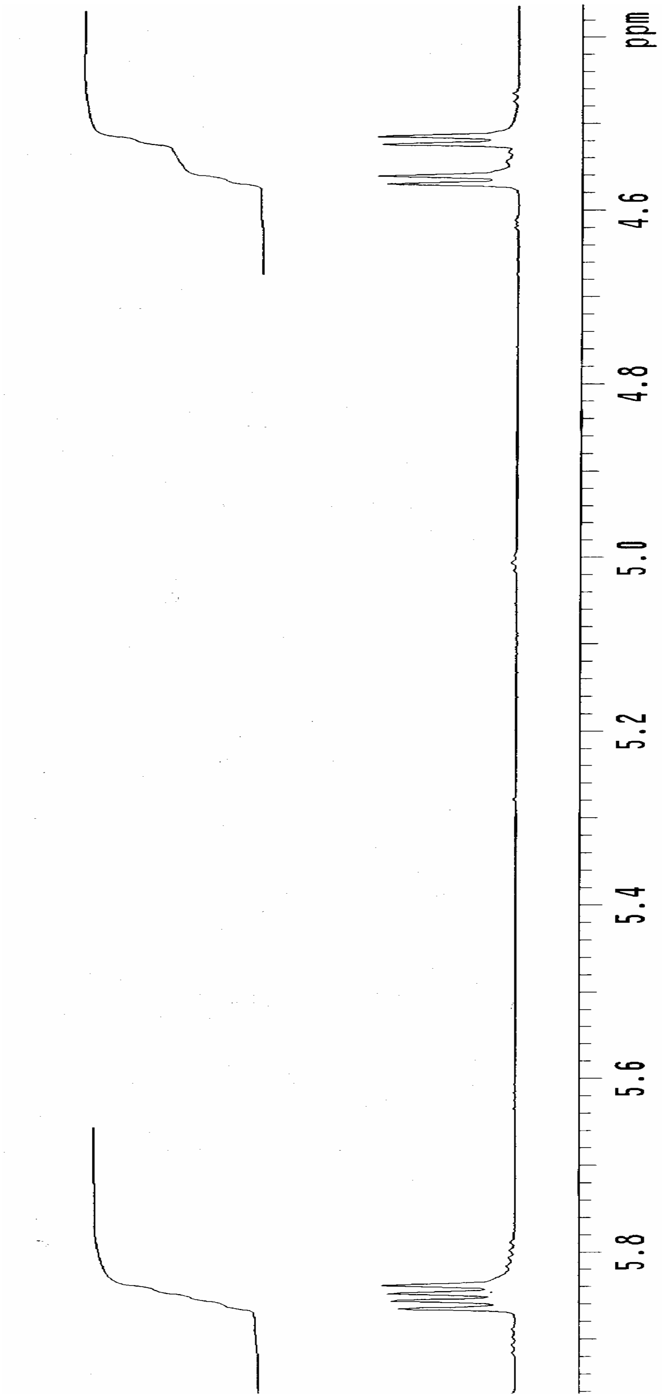


Figure 3.13 ^{1}H NMR spectrum of the compound **10** (centre field partI)

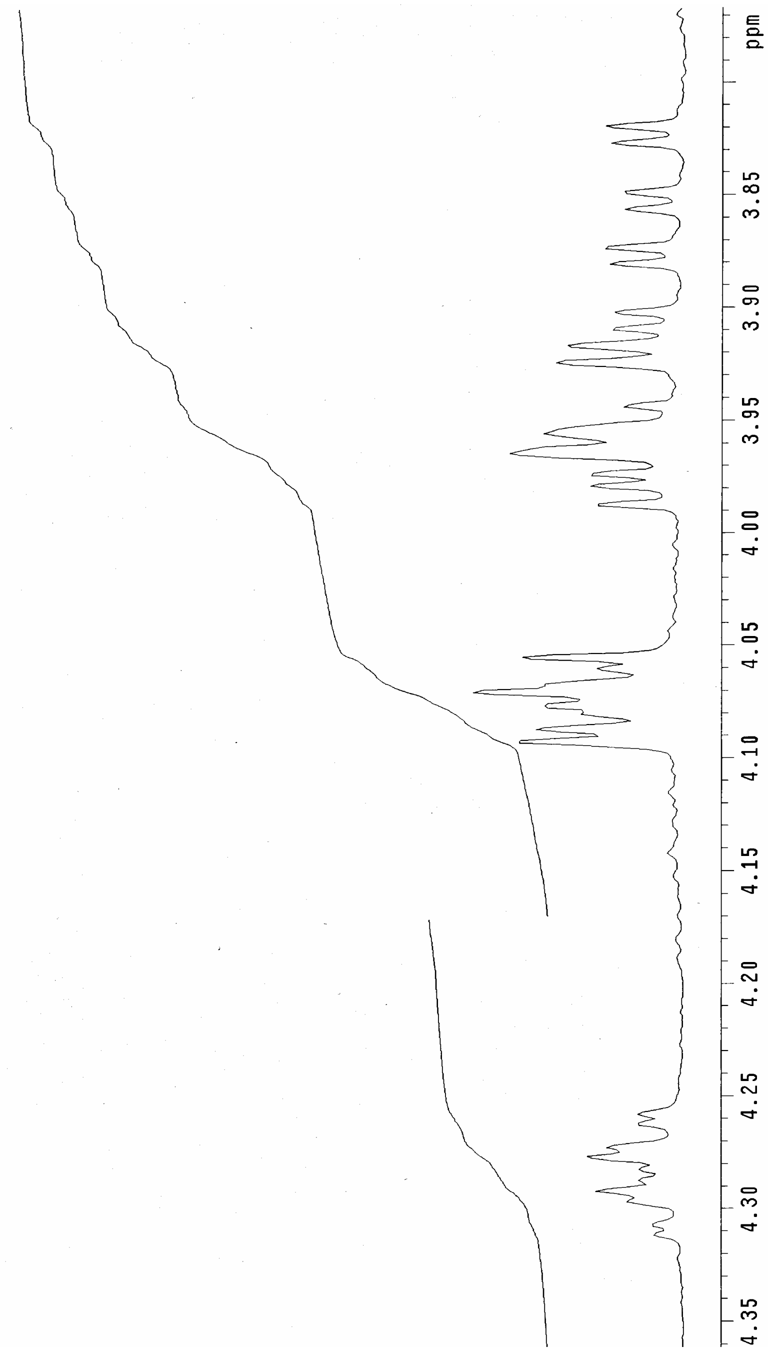


Figure 3.14 ^{1}H NMR spectrum of the compound **10** (centre field partII)

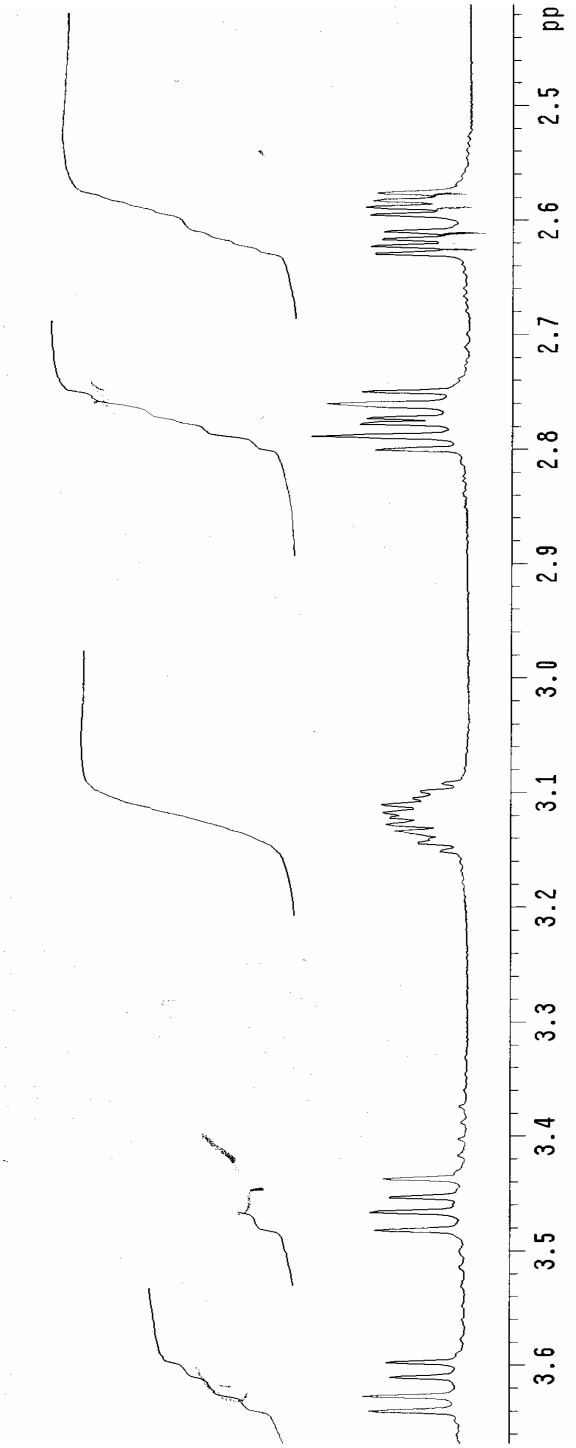
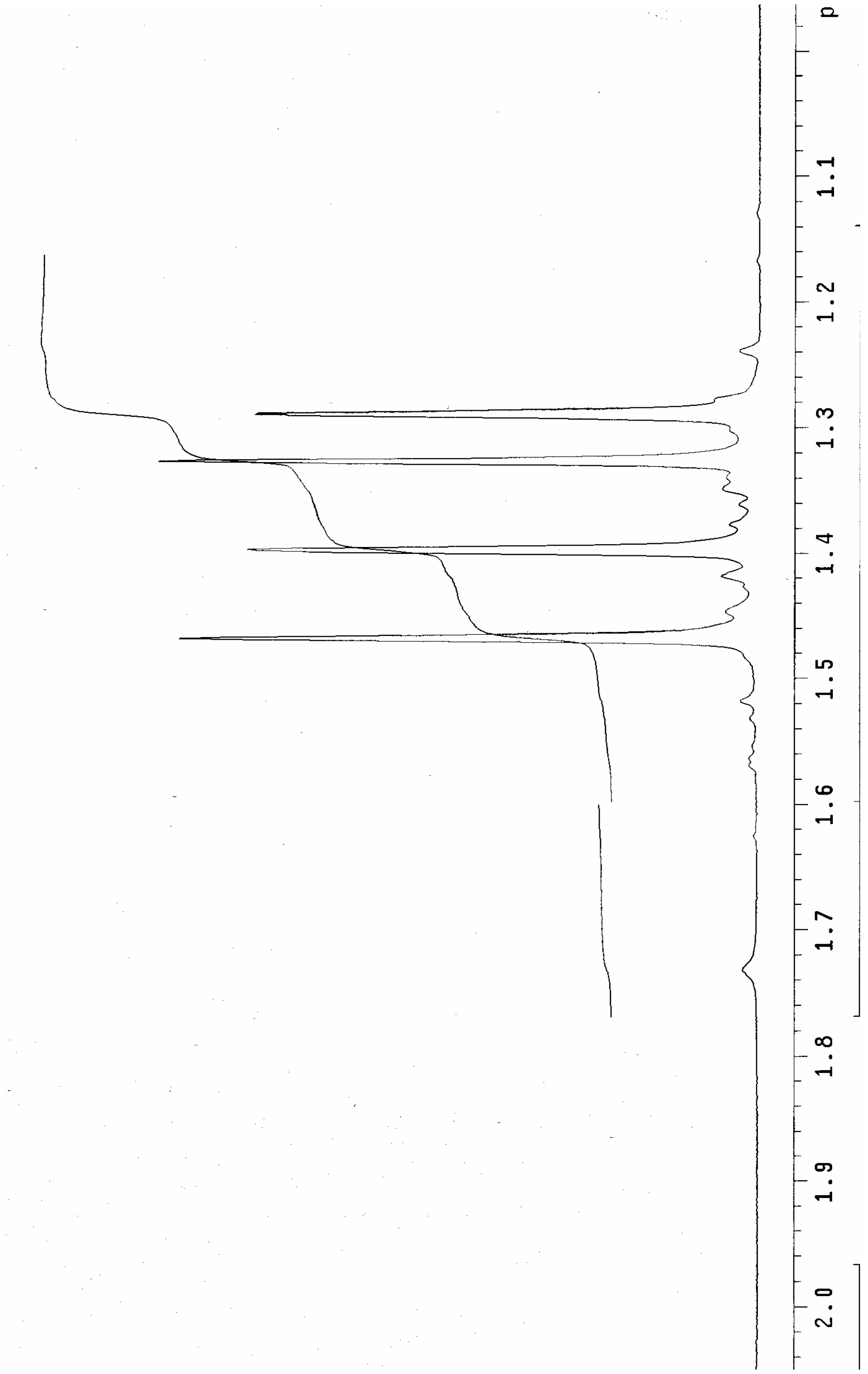


Figure 3.15 ^{1}H NMR spectrum of the compound **10** (high field part)



3.7. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3’ -butyloxy-2’-hydroxy)propyl]-α-D-glucofuranose (11)

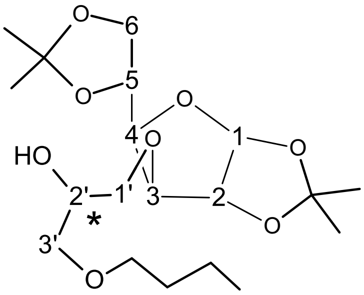


Table 3.8. FTIR data (cm^{-1}) of the compound **11**

Functional Groups	**cm^{-1}**
O-H	3470
C-H	2987, 2959, 2935, 2873
$C(CH_3)_2$	1375, 1214
C-O-C	1076

The spectrum is very similar to the octyl analogue. It is a mixture of the diastereoisomers in a 50:50 ratio. But in this case a small amount of the structural isomer exist. This is probably due to the smaller size of the butanol which unlike octanol, makes it possible to attack the other carbon of the epoxide ring. H-1 signals resonate at δ 5.90 (the minor structural isomer) and 5.88 and 5.87. H-2 signal is not resolved for the stereoisomers and resonates at δ 4.53. Coupling between H-1 and H-2 is typically 3.6 Hz. H-5 proton also is not resolved and appears at δ 4.33 as a typical ddd signal (8 lines). Signals of the four CH_2 protons of the butyl side chain overlaps with the isopropylidene methyl signals. Integration of all these signals give a total of 16 protons (12 isopropylidene methyl protons and 4 CH_2 protons). OCH_2 group of the butyl side chain resonates at lower field. Methyl end group of the butyl side chain appears as a triplet (3H) at δ 0.90.

Figure 3.16. . FTIR spectrum of the compound **11**

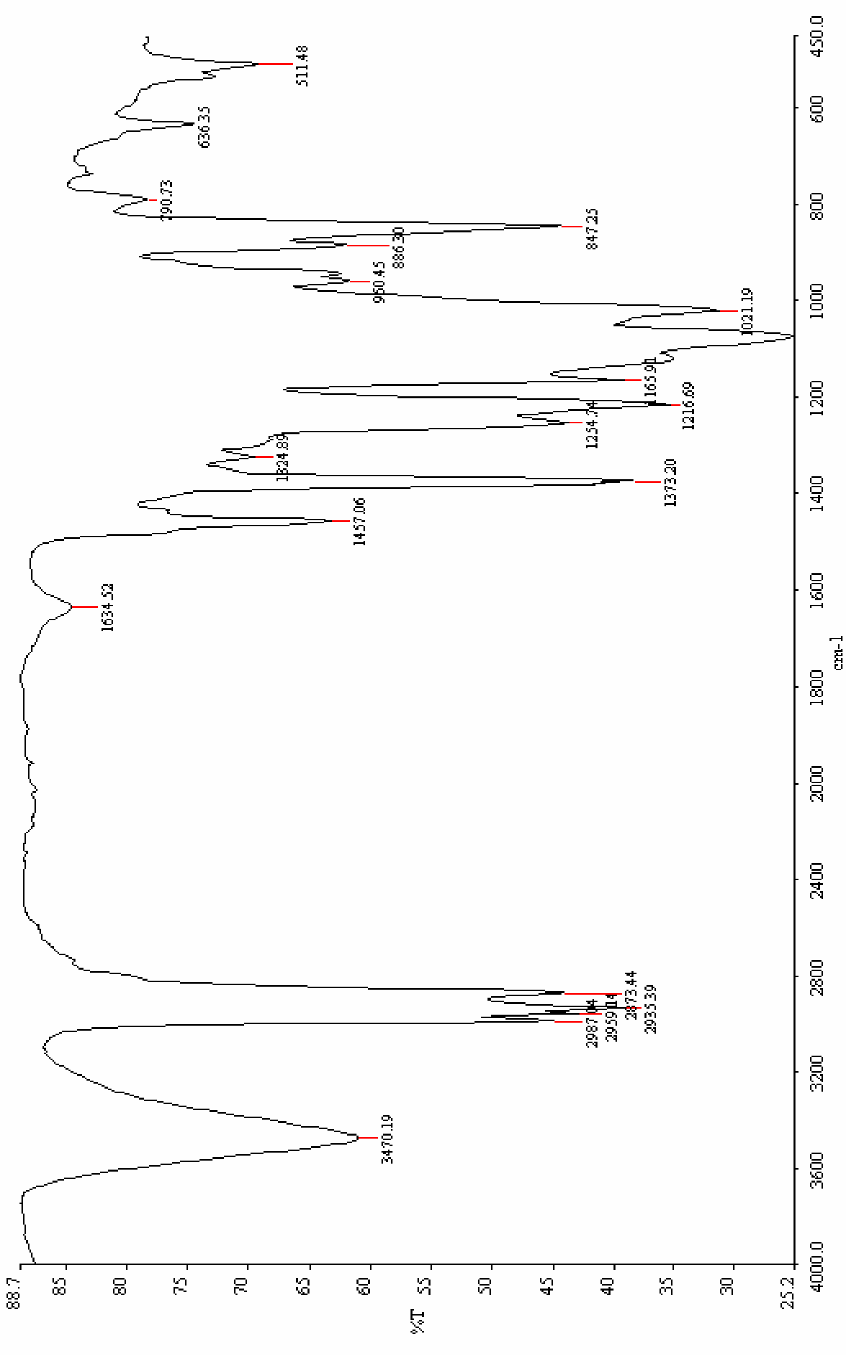


Figure 3.17 ^{1}H NMR spectrum of the compound **11** (low field part)

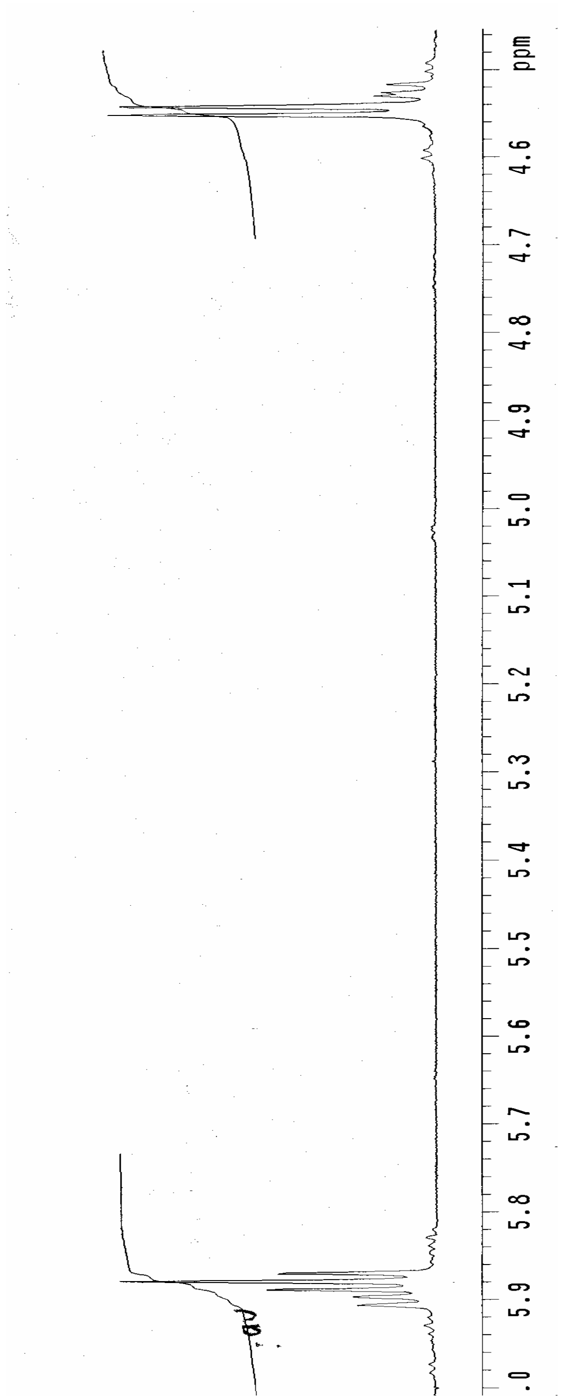


Figure 3.18^{1}H NMR spectrum of the compound **11** (centre field part)

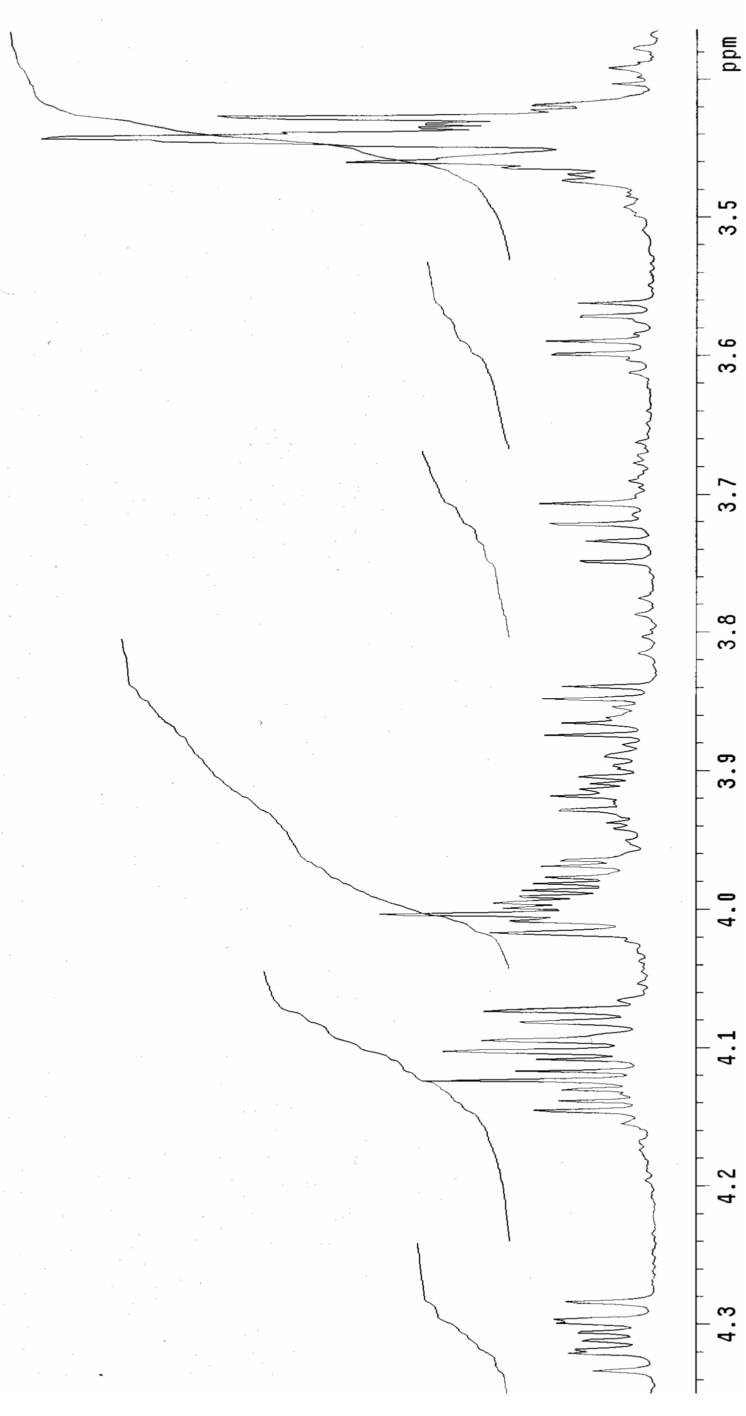
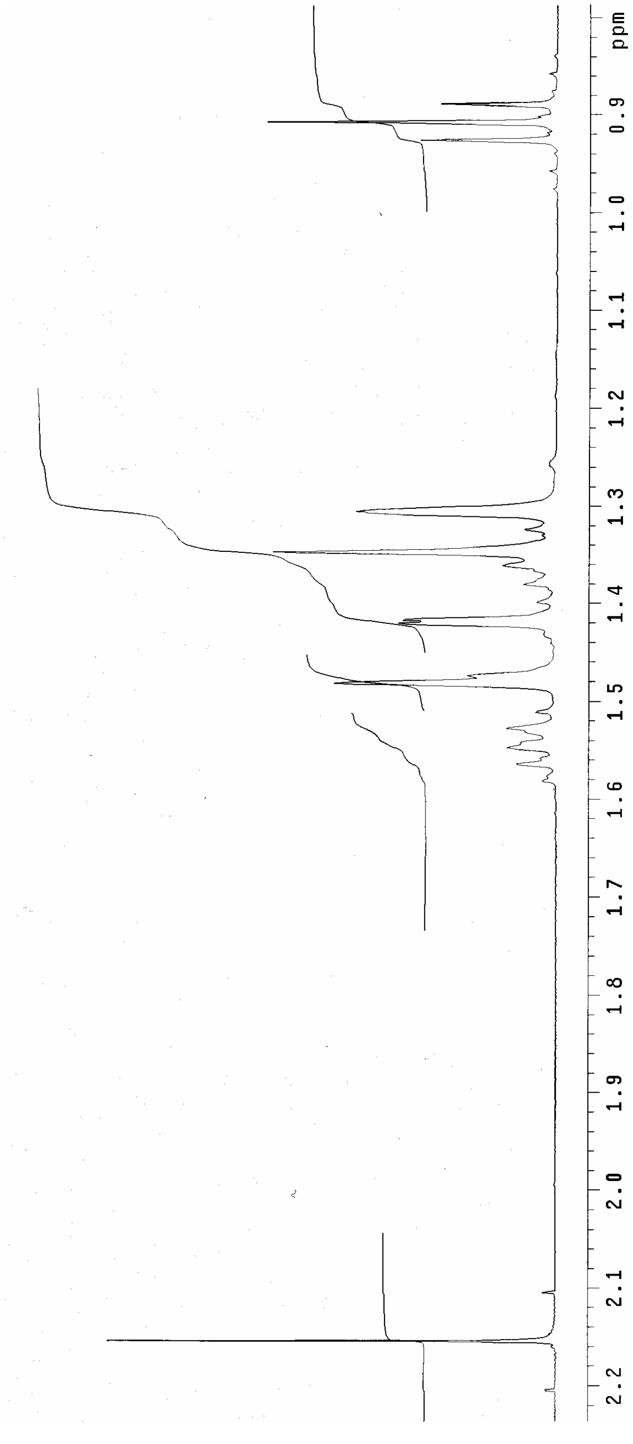
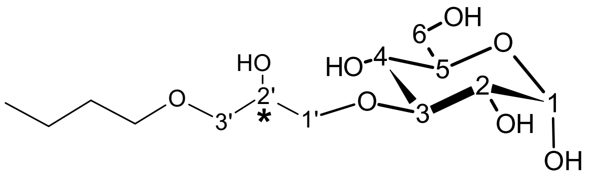


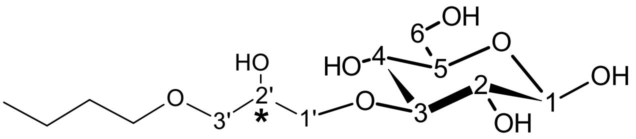
Figure 3.19 ^{1}H NMR spectrum of the compound **11** (high field part)



3.8. 3-*O*-[(2’-Hydroxy-3’-butyloxy)propyl]-α,β-D-glucopyranose (12)



α



β

Table 3.9. FTIR data (cm^{-1}) of the compound **12**

Functional Groups	**cm^{-1}**
O-H	3366
C-H	2934, 2874
C-O-C	1080

Figure 3.20. . FTIR spectrum of the compound **12**

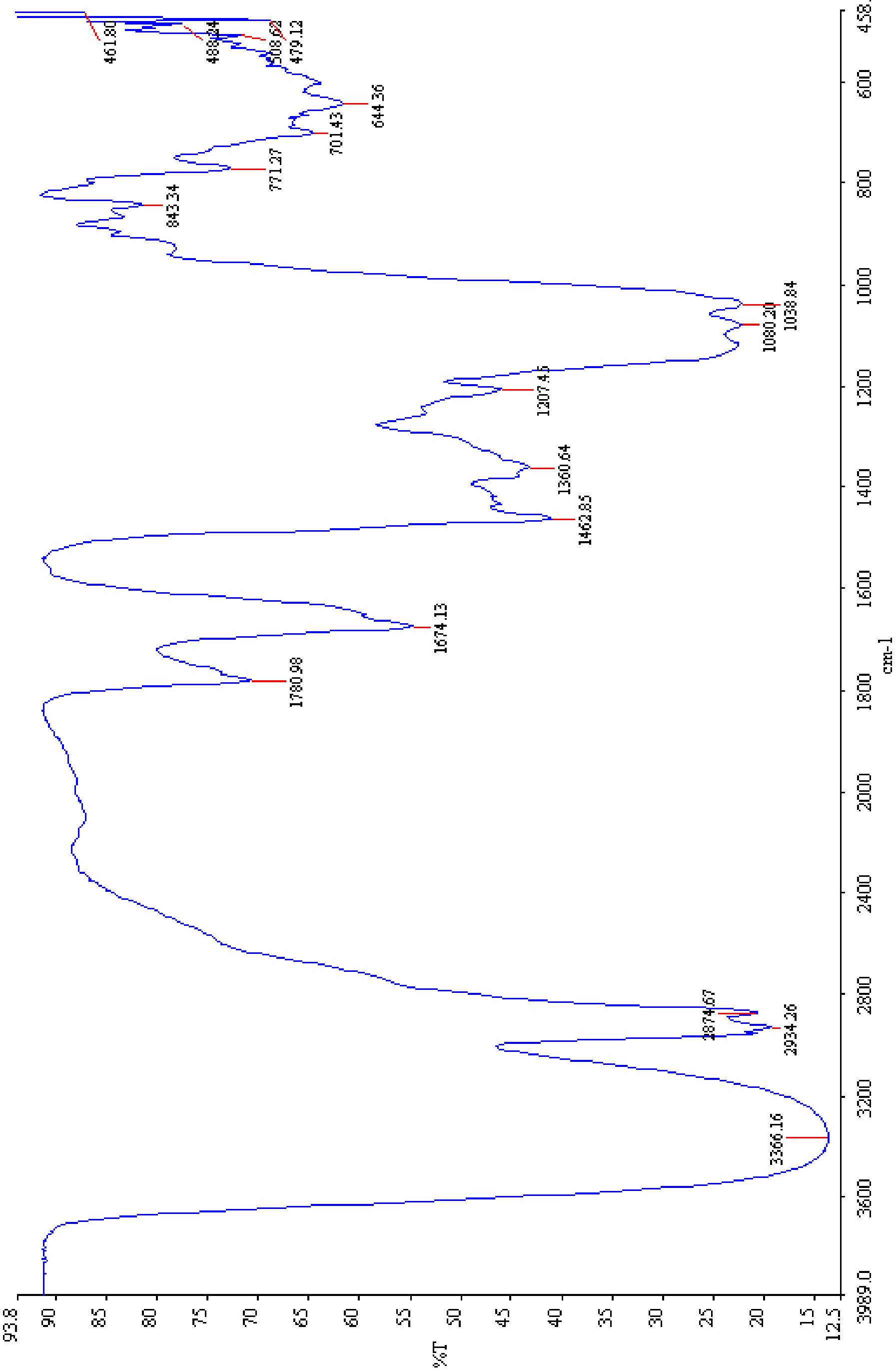
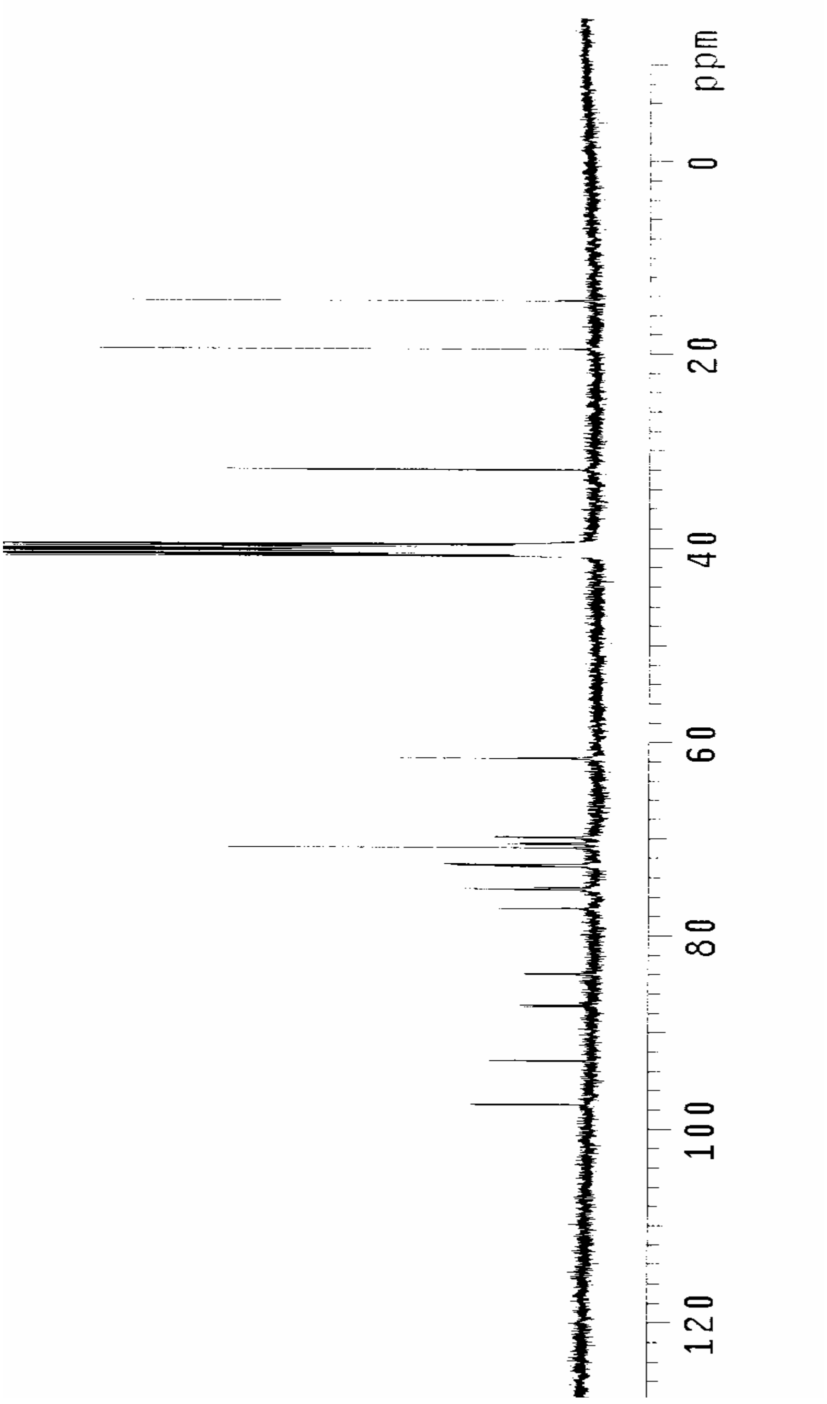
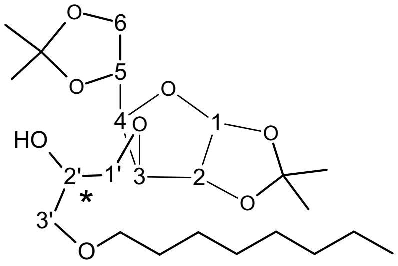


Figure 3.21 ^{13}C NMR spectrum of the compound **12**



3.9. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(-2'-hydroxy-3'-octyloxy) propyl] -α-D-glucofuranose (13)



This compound has a new chiral centre at C-2' position and hence it is a mixture of diastereoisomers. Characteristic H-1 signal at δ 5.85 indicates that the diastereoisomers are present roughly in equal amounts (two overlapping doublets). H-2 signal is also a characteristic doublet at δ 4.52. Only one H-2 doublet was observed (coincidentally overlapped). H-5 signal (ddd) is also detectable at δ 4.29. Rest of the spectrum is too complicated for analysis. The high field part of the spectrum indicates the presence of four isopropylidene methyl grups indicating that the protecting groups are intact on the molecule. A high field (δ 0.85) triplet for three protons is due to the methyl group of the octyl side chain. Signals of the six CH_2 protons of the octyl side chain overlaps with the isopropylidene methyl signals. Integration of all these signals give a total of 24 protons (12 isopropylidene methyl protons and 12 CH_2 protons). OCH_2 group of the octyl side chain resonates at lower field.

Figure 3.22 ^{1}H NMR spectrum of the compound **13** (low field part)

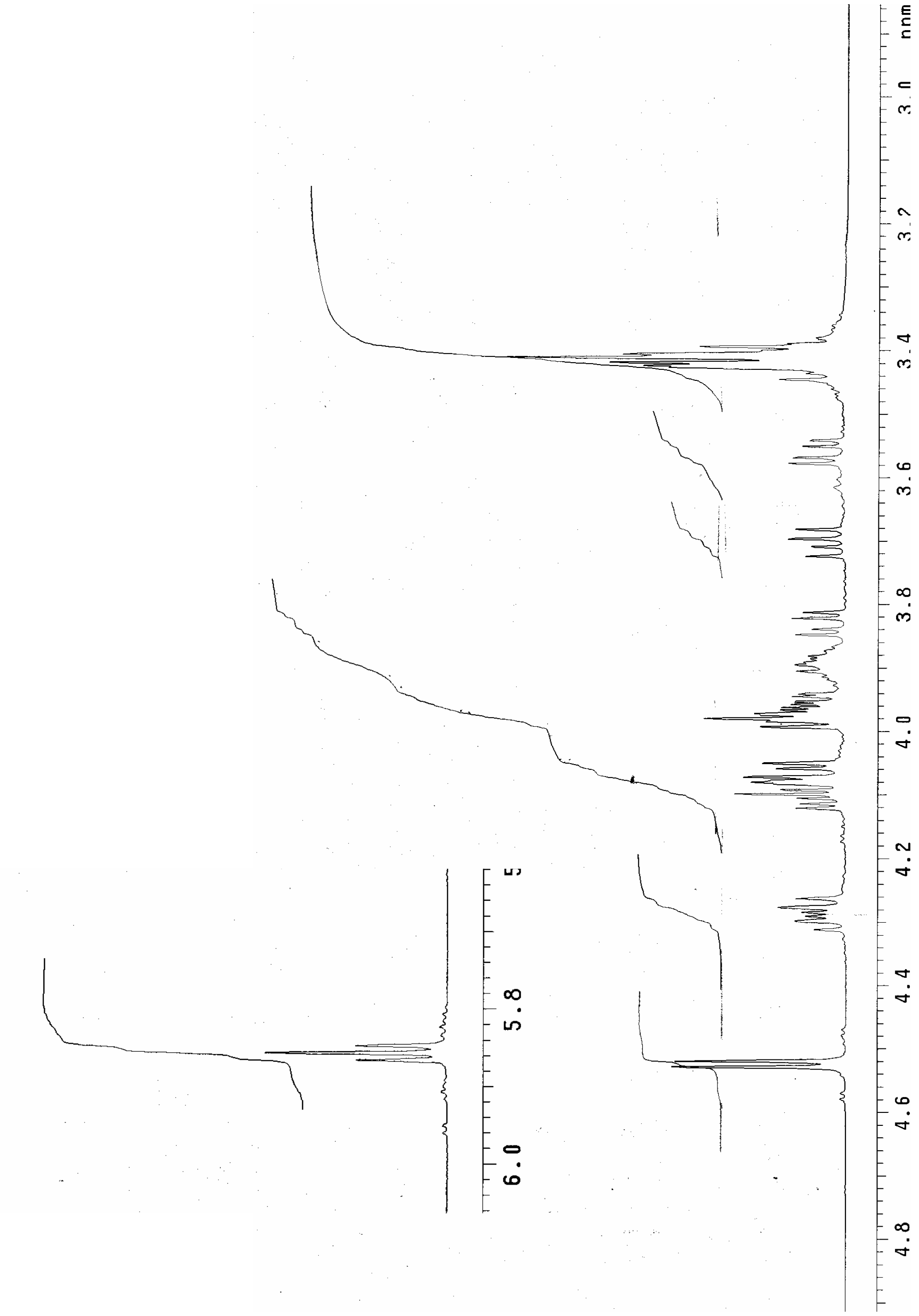
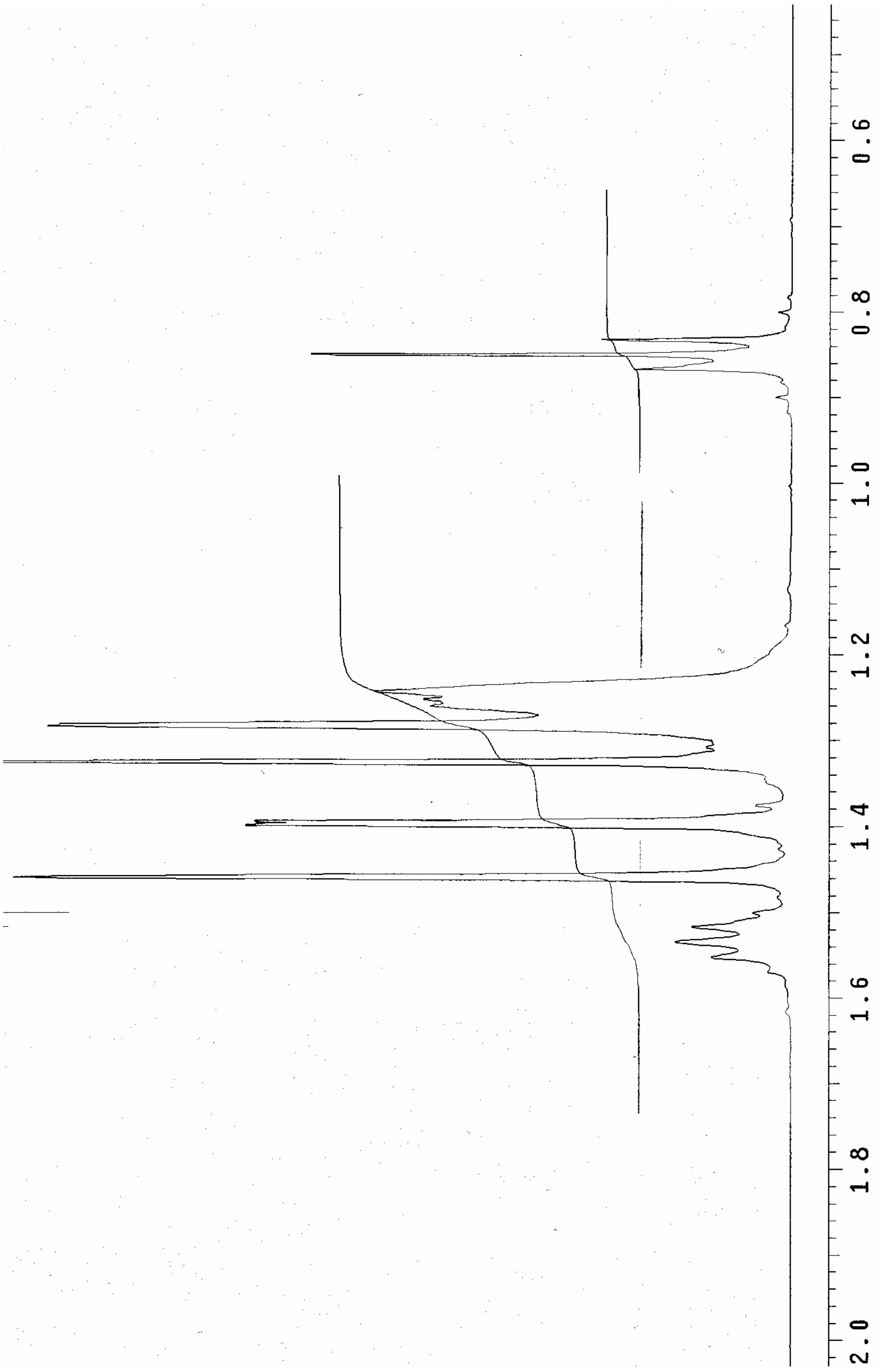
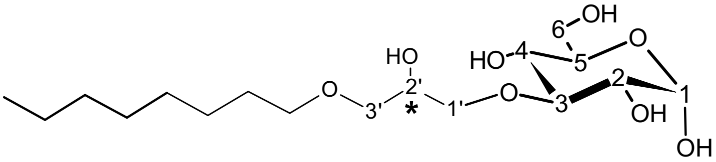


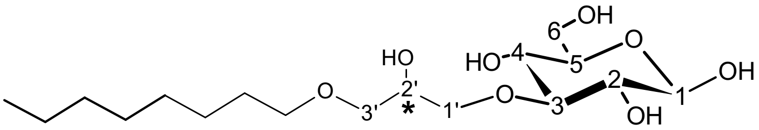
Figure 3.23 ^{1}H NMR spectrum of the compound **13** (high field part)



3.10. 3-*O*-[(2’-hydroxy- 3’-octyloxy)propyl]-α,β-D-glucopyranose (14)



α



β

Table 3.10. FTIR data (cm^{-1}) of the compound **14**

Functional Groups	**cm^{-1}**
O-H	3368
C-H	2926, 2856
C-O-C	1078

Figure 3.24. . FTIR spectrum of the compound **14**

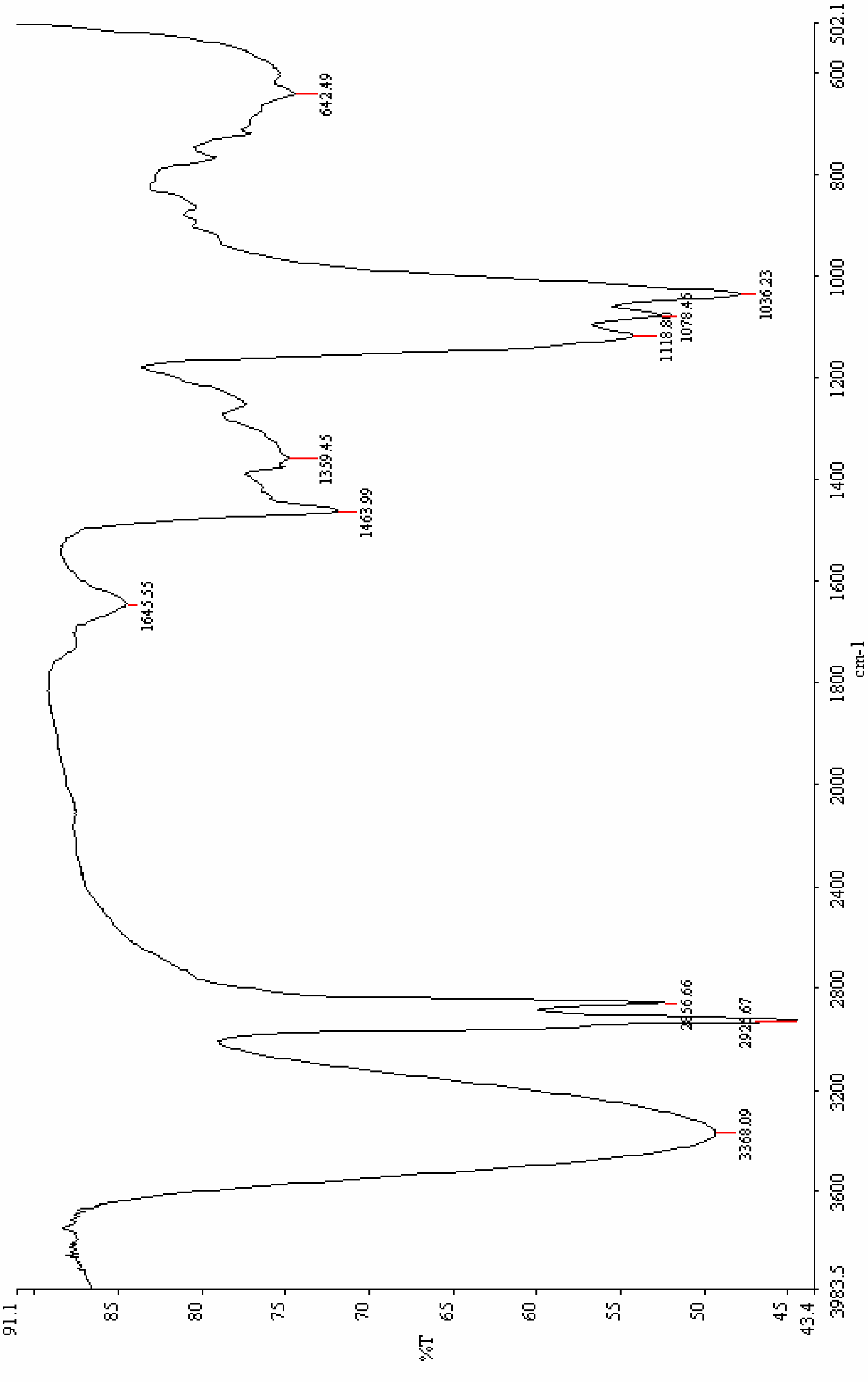
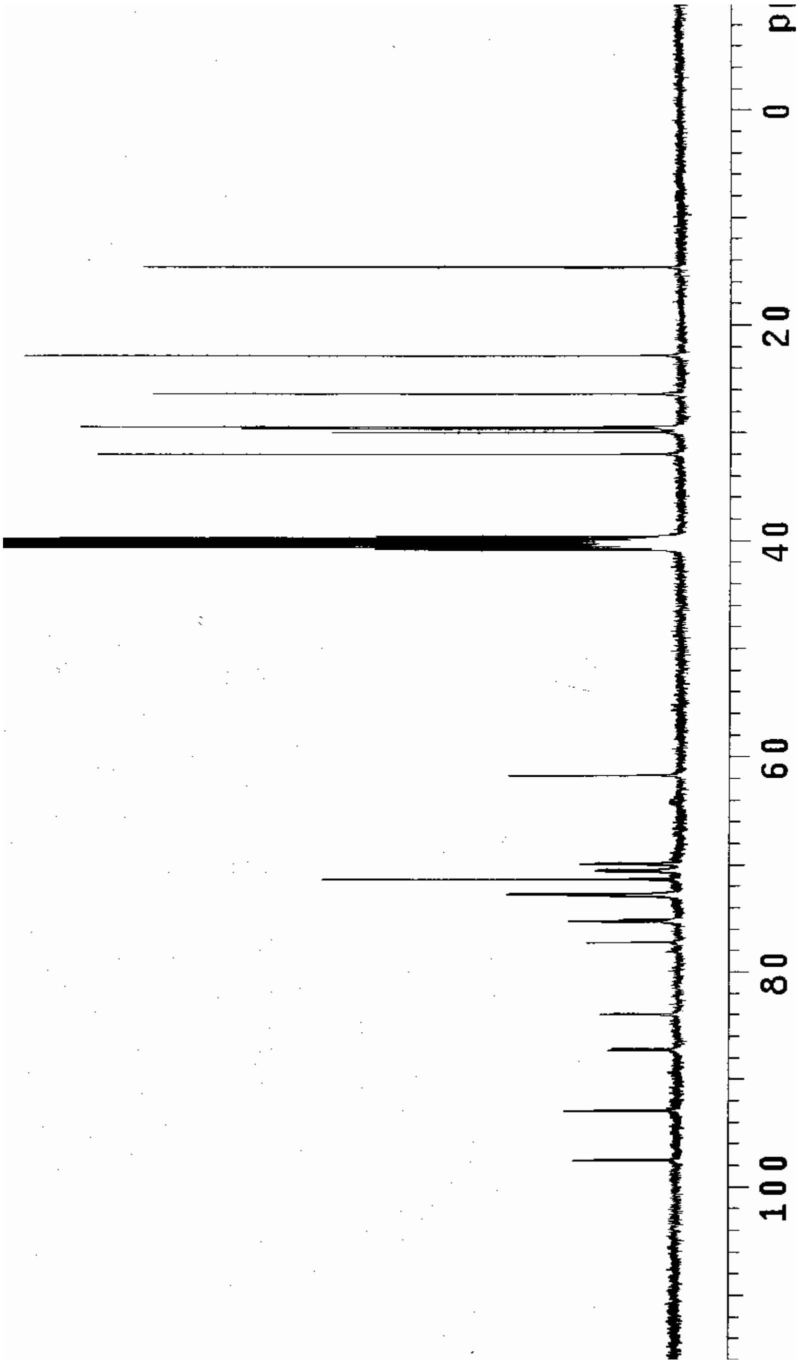
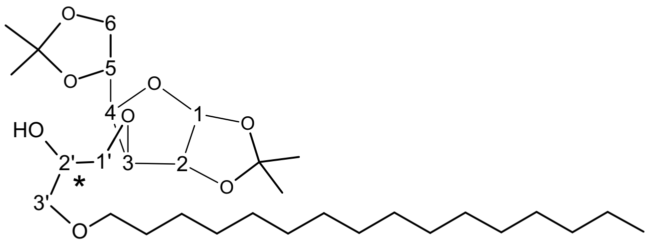


Figure 3.25 ^{13}C NMR spectrum of the compound **14**



3.11. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy- 3' - hexadecyloxy)propyl]-α-D-glucofuranose (17)



General appearance of the ^{1}H NMR spectrum is very similar to the butyl and octyl analogues. Characteristic H-1 signals at δ 5.88 and 5.87 indicate that the diastereoisomers are present roughly in equal amounts (two overlapping doublets). H-2 signal is also a characteristic doublet at δ 4.54. Only one H-2 doublet was observed (coincidentally overlapped). Integration of the high field side of the spectrum indicates 40 protons for 14xCH_2 groups and 4x isopropylidene methyl groups and a 3 proton triplet at δ 0.85 for the terminal methyl group of the hexadecyl chain.

Figure 3.26 ^{1}H NMR spectrum of the compound **17** (low field part)

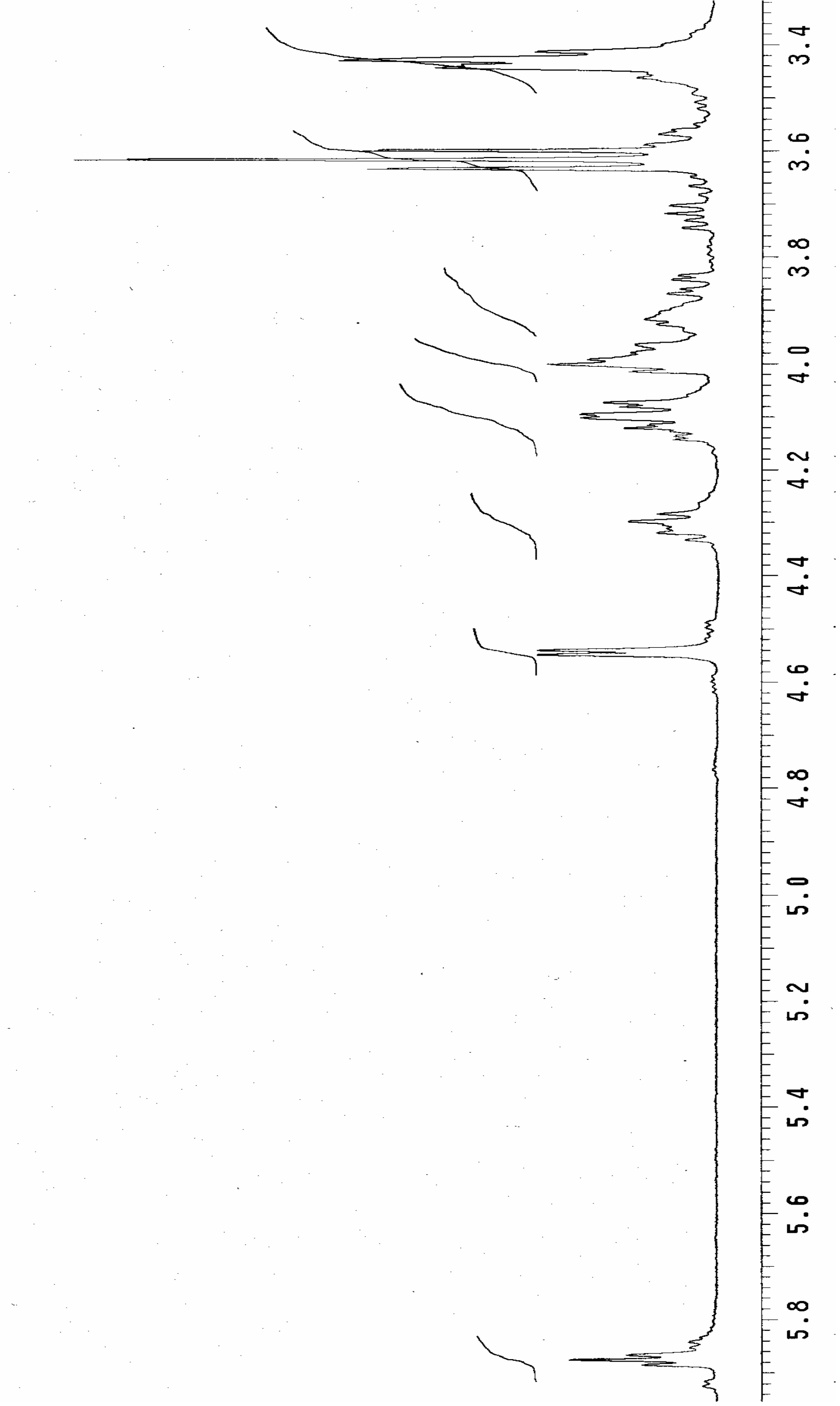
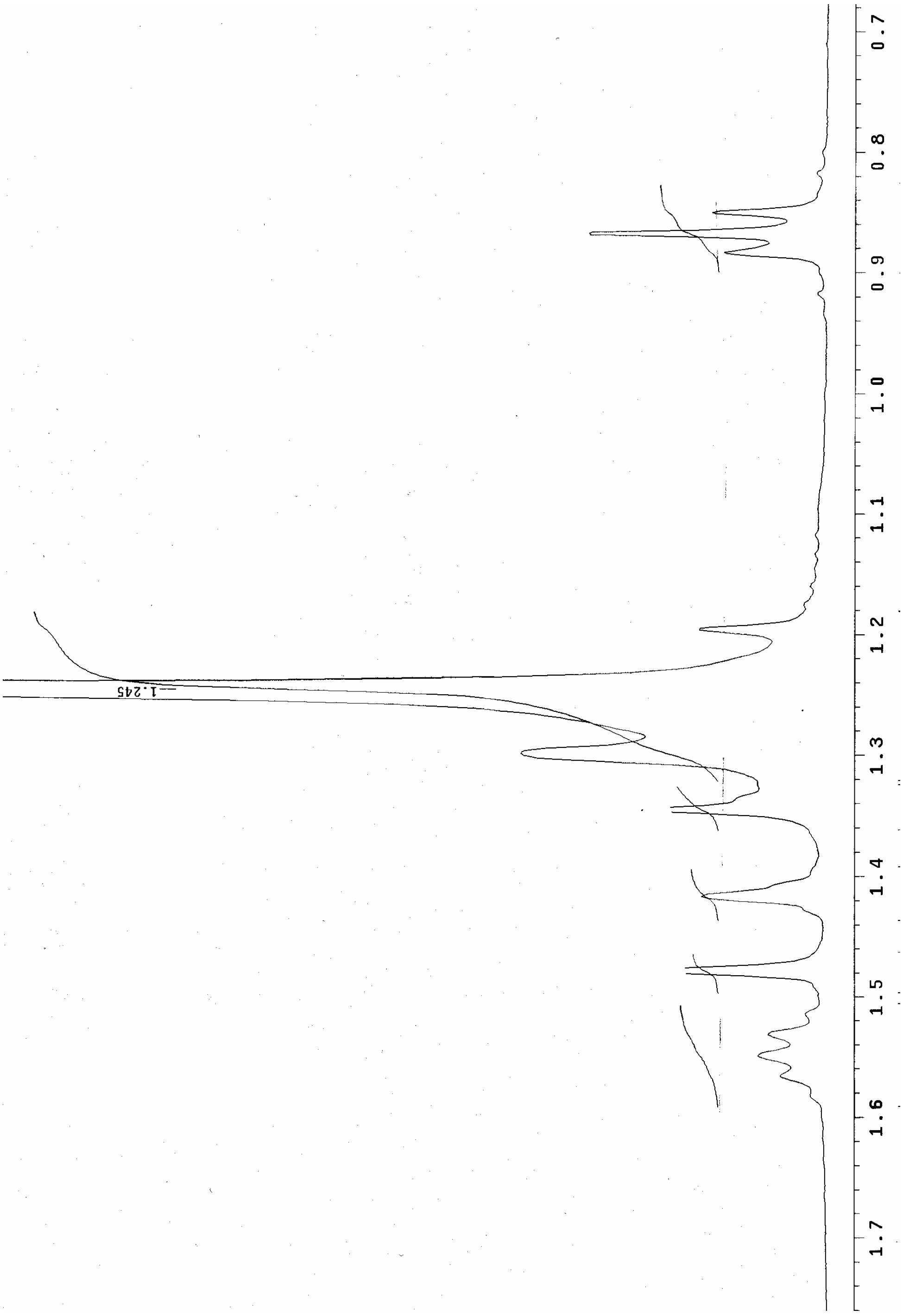
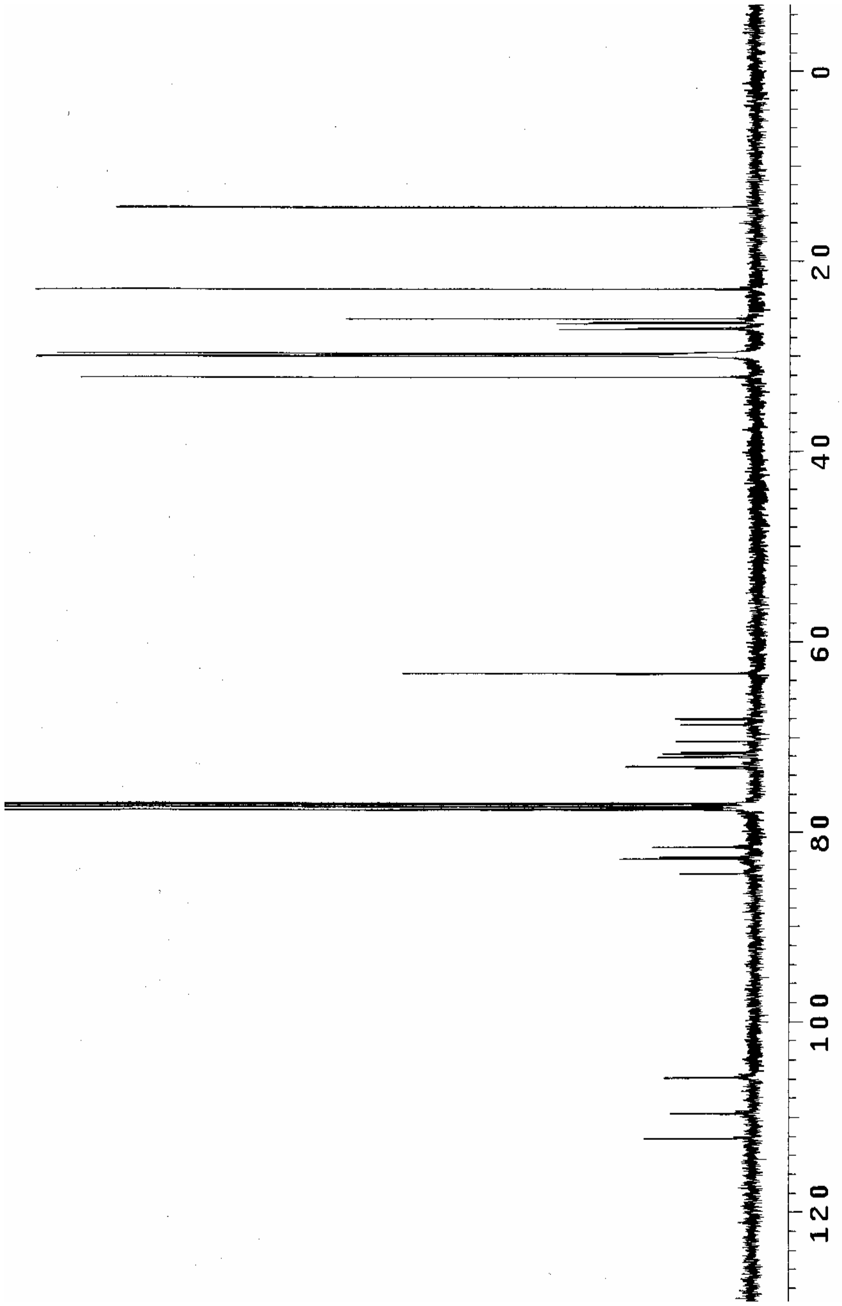


Figure 3.27^{1}H NMR spectrum of the compound **17** (high field part)

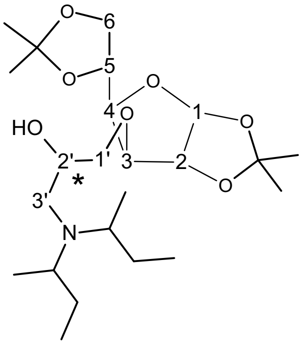


3.12. 3-*O*-[(2'-hydroxy-3'-hexadecyloxy)-α,β-D-glucopyranose (18)

Figure 3.28 ^{13}C NMR spectrum of the compound **18**



3.13. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3' –N,N-diisobutylamino-2'-hydroxy)propyl]-α-D-glucofuranose (19)



Characteristic low field signal (δ 5.88) of H-1 anomeric proton can be easily identified as with the other furanose derivatives. Coupling constant between H-1 and H-2 is 3.6 Hz which is typical for α-D-furanose derivatives. H-2 proton signal is not a doublet, but it is a doublet of doublet (dd) in this case, indicating that coupling constant between H-2 and H-3 is not zero (the coupling constant between H-2 and H-3 is 2.0 Hz) and the dihedral angle between H-2 and H-3 is not 90°. This is possible due to a different substituent on C-3 which could alter the geometry of the furanose ring, changing the usual twist conformation. The high field part of the spectrum indicates the presence of four isopropylidene methyl groups indicating that the protecting groups are intact on the molecule. Methyl group signals due to the methyl groups of the isobutyls are overlapped but their integration indicate their presence.

Figure 3.29 ^{1}H NMR spectrum of the compound **19** (low field part)

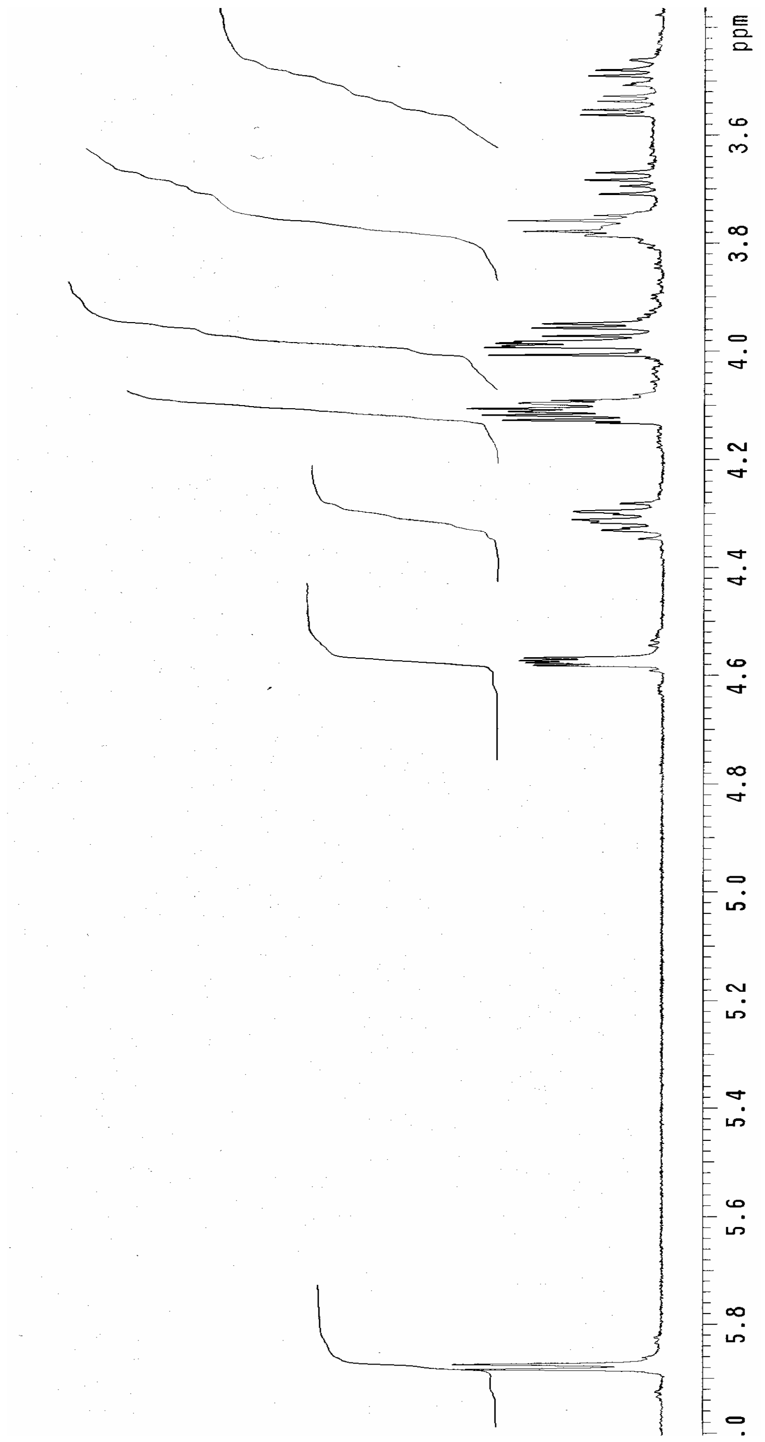
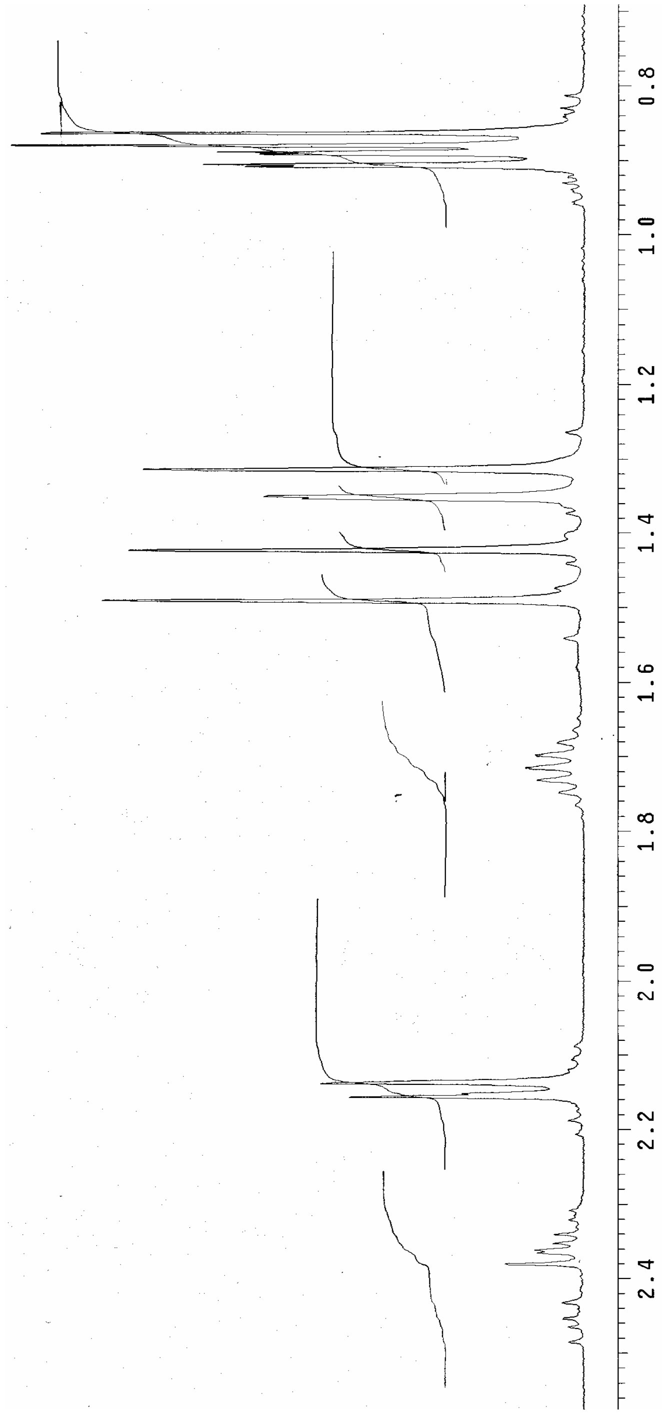
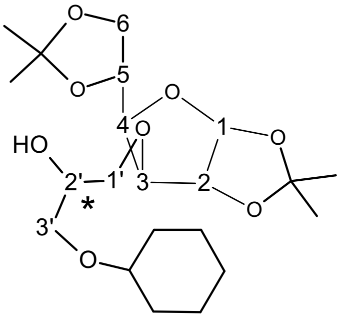


Figure 3.30 ^{1}H NMR spectrum of the compound **19** (high field part)



3.14. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2'-hydroxy-3'-cyclohexyloxy) propyl]-α-D-glucofuranose (21)



This compound has a new chiral centre at C-2' position and hence it is a mixture of diastereoisomers. Characteristic H-1 signal at δ 5.86 indicates that the diastereoisomers are present roughly in equal amounts (two overlapping doublets). H-2 signal is also a characteristic doublet at δ 4.55. Only one H-2 doublet was observed (coincidentally overlapped). Rest of the spectrum is too complicated for analysis. The high field part of the spectrum indicates the presence of four isopropylidene methyl grups indicating that the protecting groups are intact on the molecule.

Figure 3.31 ^{1}H NMR spectrum of the compound **21** (low field part)

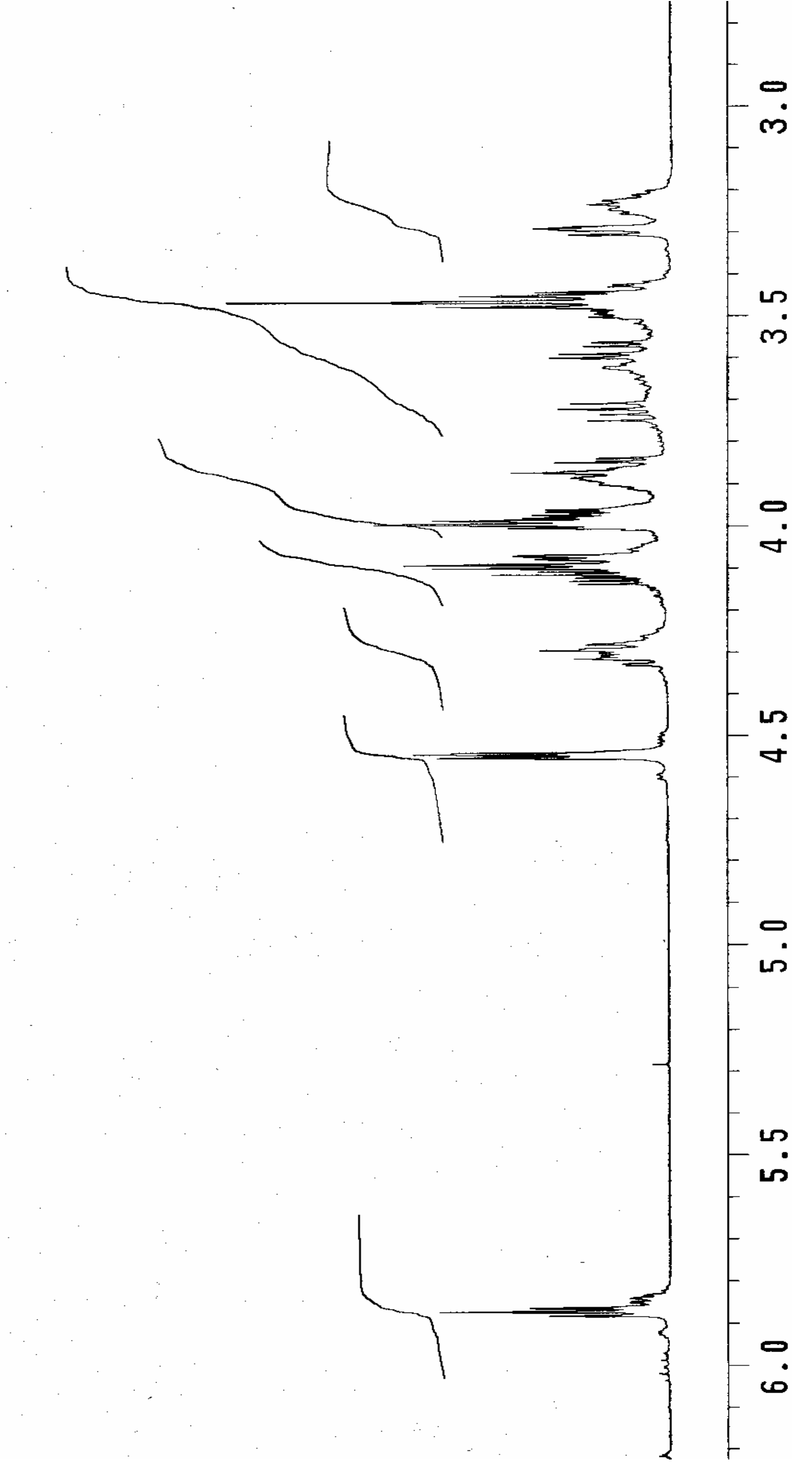
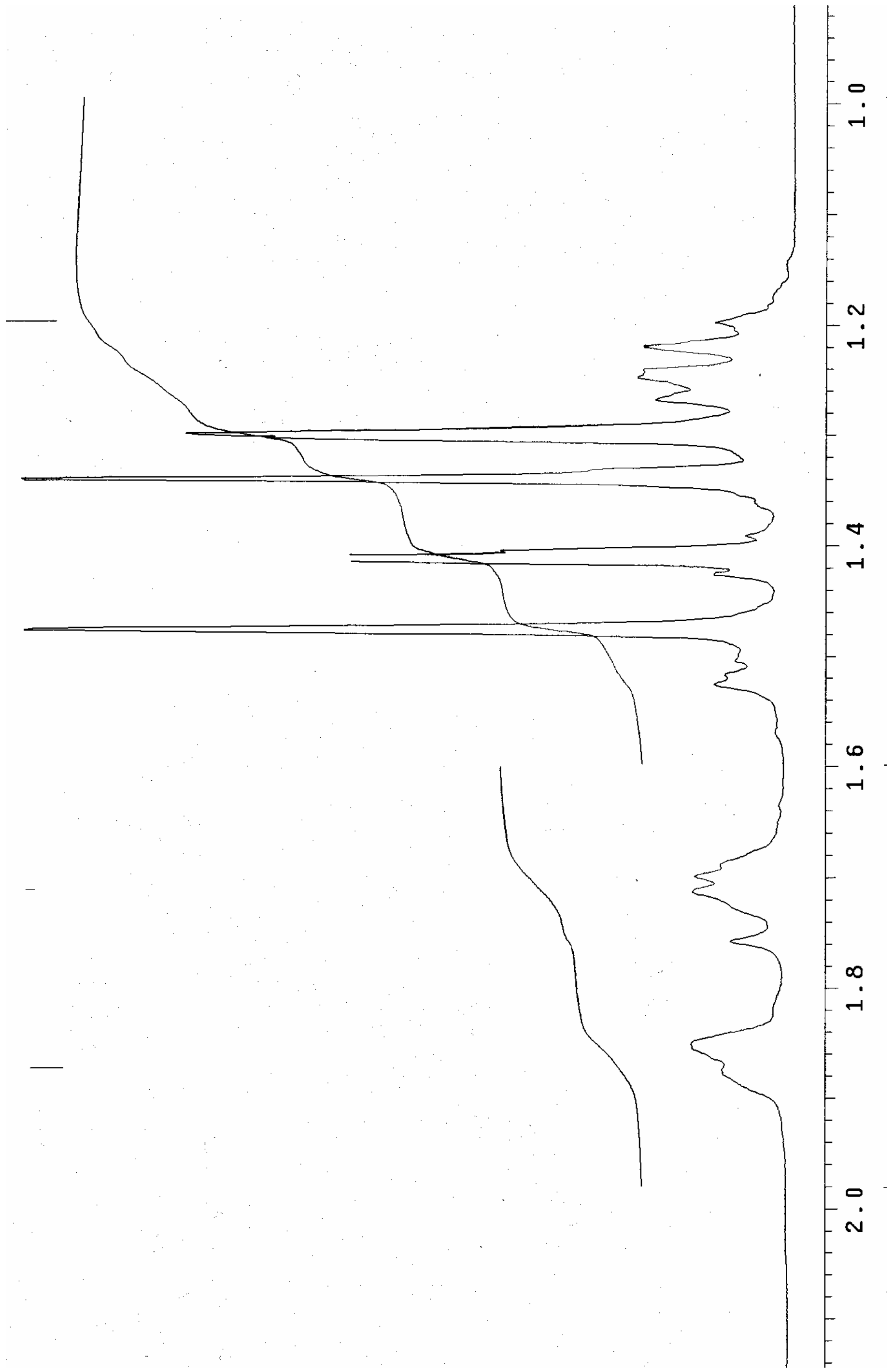


Figure 3.32 ^{1}H NMR spectrum of the compound **21** (high field part)



3.15. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-butyl-α-D-glucofuranose (23)

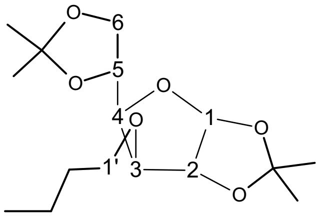


Table 3.11 ^{1}H NMR spectral data of the compound **23**

Position of atoms	^{1}H NMR (δ)	H and *J* couplings (Hz)
H-1	5.86 d	1 H $J_{1,2}=3.6$
H-2	4.51 d	1 H, $J_{1,2}=3.6$
H-5	4.29 dt	1 H
H-4	4.11 dd	1H, $J_{4,5}=8.0$
H-6a	4.06 dd	1H, $J_{6a,6b,5}=8.8$, $J_{5,6a}=6.4$
H-6b	3.76 dd	1H, $J_{5,6a}=6.4$
H-3	3.84 d	1H, $J_{3,4}=3.2$
H-1’	3.59 m	1H
H-1’	3.50 m	1H
2xCH_2	1.63-1.3 m	4H
Me	1.48 s	3 H
Me	1.41 s	3 H
Me	1.34 s	3H
Me	1.30 s	3H
Me	0.9 t	3H

Figure 3.33 ^{1}H NMR spectrum of the compound **23**

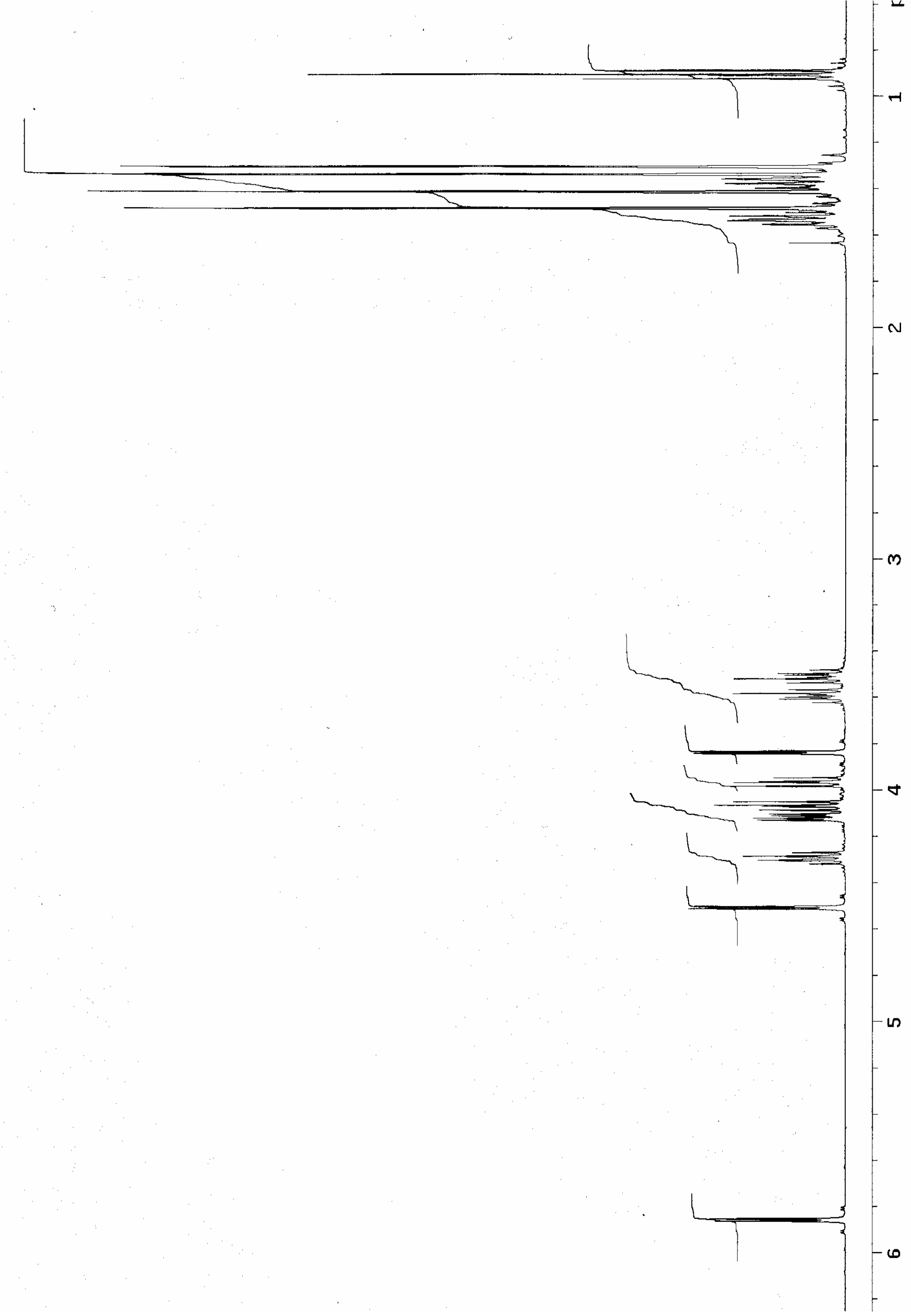
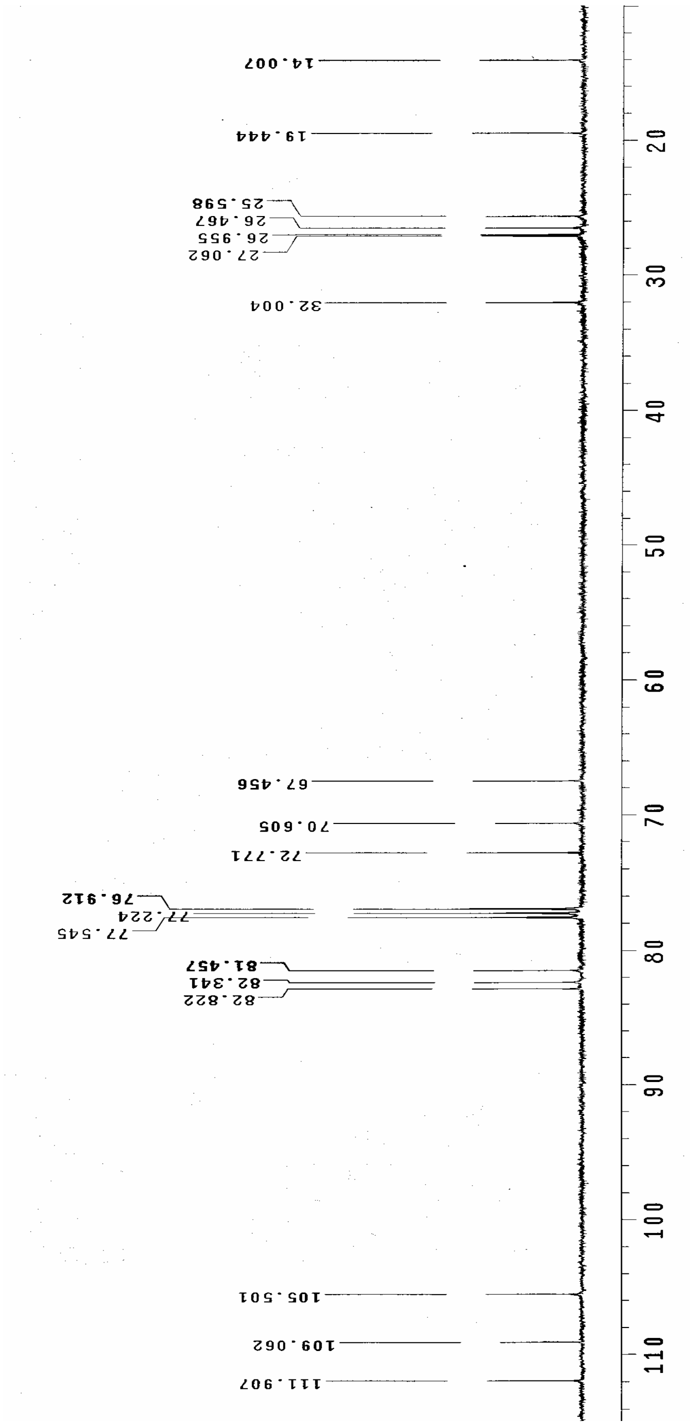
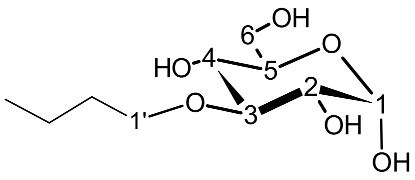


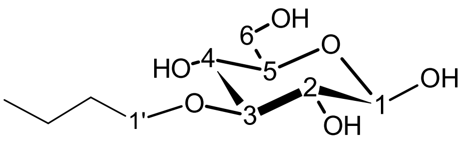
Figure 3.34 ^{13}C NMR spectrum of the compound **23**



3.16 3-*O*-butyl- α,β-D-glucopyranose (24)

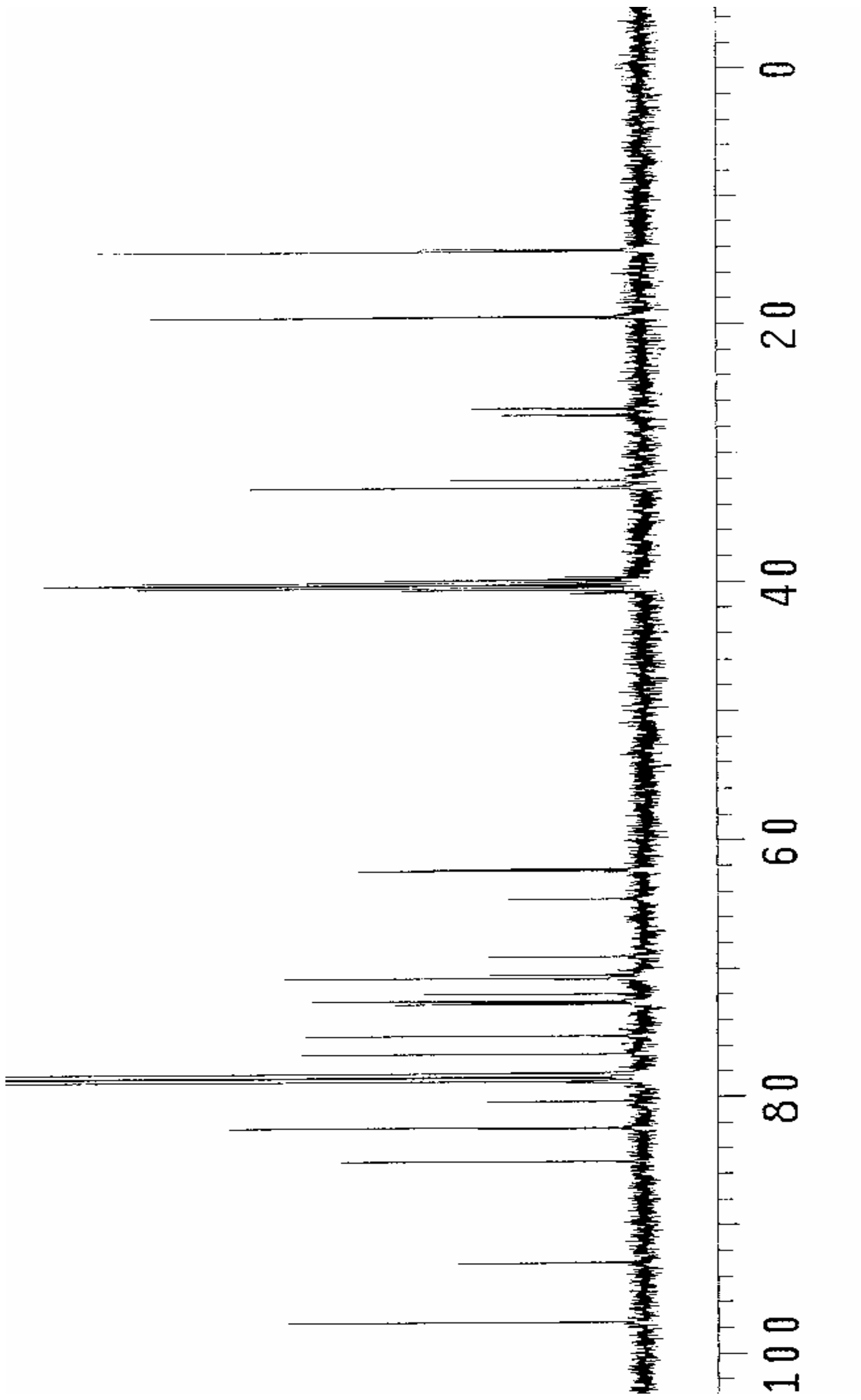


α



β

Figure 3.35 ^{13}C NMR spectrum of the compound **24**



3.17. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (25)

Table 3.12 ^{1}H NMR spectral data of the compound **25**

Position of atoms	**^{1}H NMR (δ)**	**H and *J* couplings (Hz)**
H-1	5.85 d	1 H $J_{1,2}=3.6$
H-2	4.50 d	1 H, $J_{1,2}=3.6$
H-5	4.28 dt	1 H
H-4	4.10 dd	1H, $J_{4,5}=8.0$
H-6a	4.05 dd	1H, $J_{6a,6b,5}=8.6$, $J_{5,6a}=6.0$
H-6b	4.00 dd	1H, $J_{5,6a}=6.0$
H-3	3.83 d	1H, $J_{3,4}=3.2$
H-1’	3.58 m	1H
H-1’	3.48 m	1H
6xCH_2	155-1.20 m	12H
Me	1.48 s	3 H
Me	1.41 s	3 H
Me	1.34 s	3H
Me	1.30 s	3H
Me	0.86 t	3H

Figure 3.36 ^{1}H NMR spectrum of the compound **25**

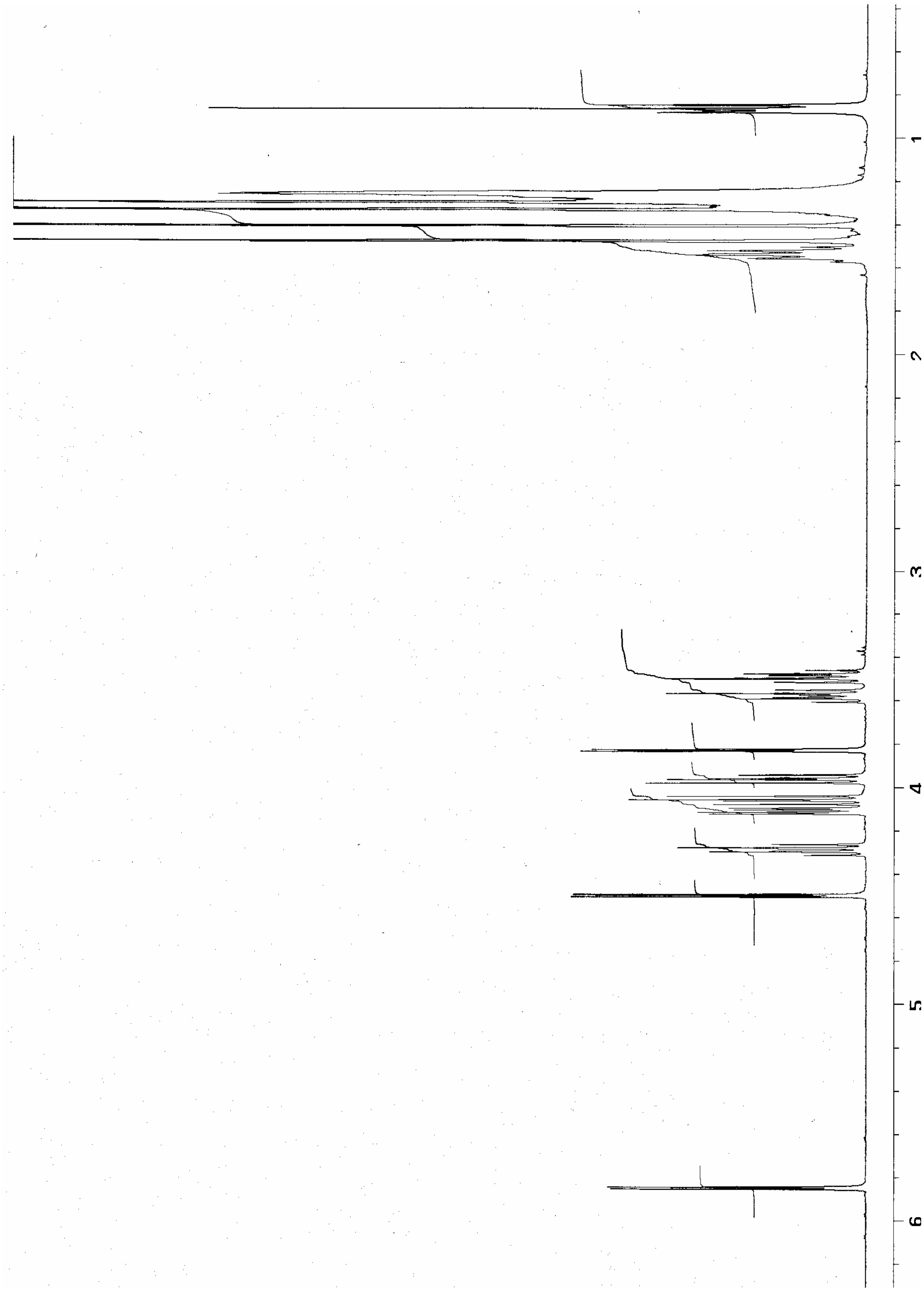
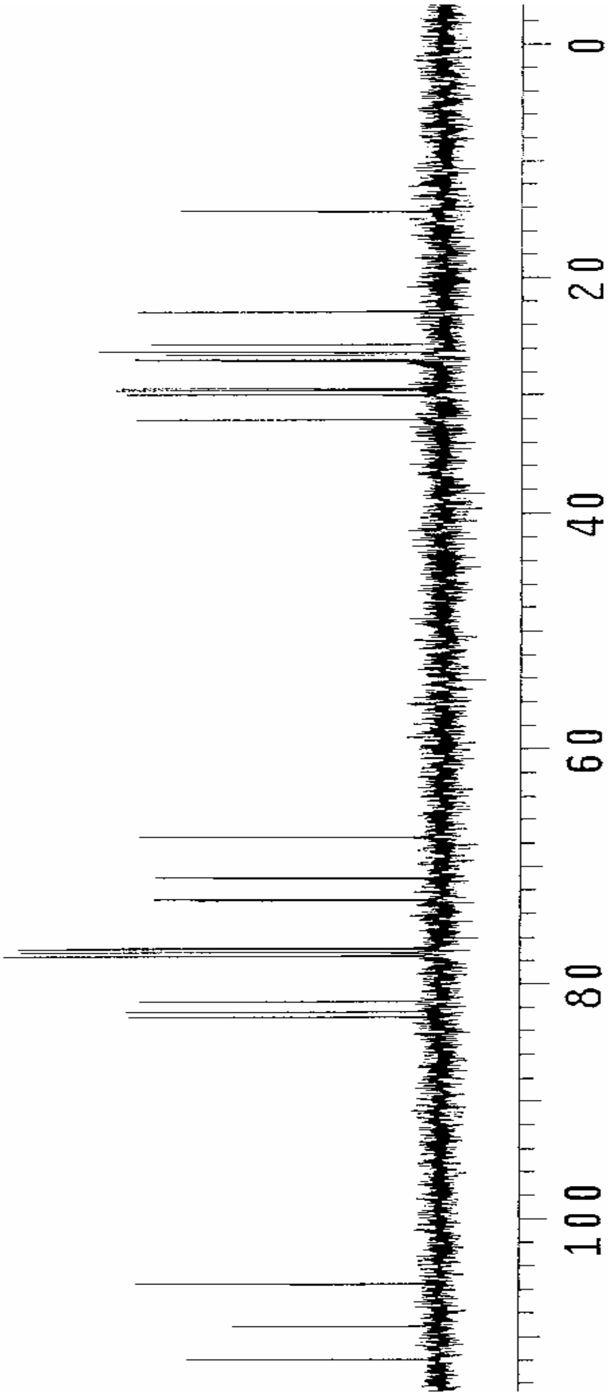
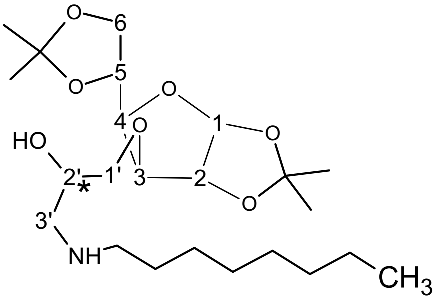


Figure 3.37 ^{13}C NMR spectrum of the compound **25**



3.18. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(2’-hydroxy-3’ -N-octylamino)propyl]-α-D-glucofuranose (27)



This compound has a new chiral centre at C-2’ position and hence it is a mixture of diastereoisomers. Characteristic H-1 signals at δ 5.86 and 5.85 indicate that the diastereoisomers are present roughly in equal amounts (two overlapping doublets). H-2 signal is not a single doublet in this case (not overlapped) as observed with the other amino derivative. The high field part of the spectrum indicates the presence of four isopropylidene methyl grups indicating that the protecting groups are intact on the molecule. A high field (δ 0.85) triplet for three protons is due to the methyl group of the octyl side chain. Integration indicates the existance of correct number of CH_2 protons.

Figure 3.38 ^{1}H NMR spectrum of the compound **27** (low field part)

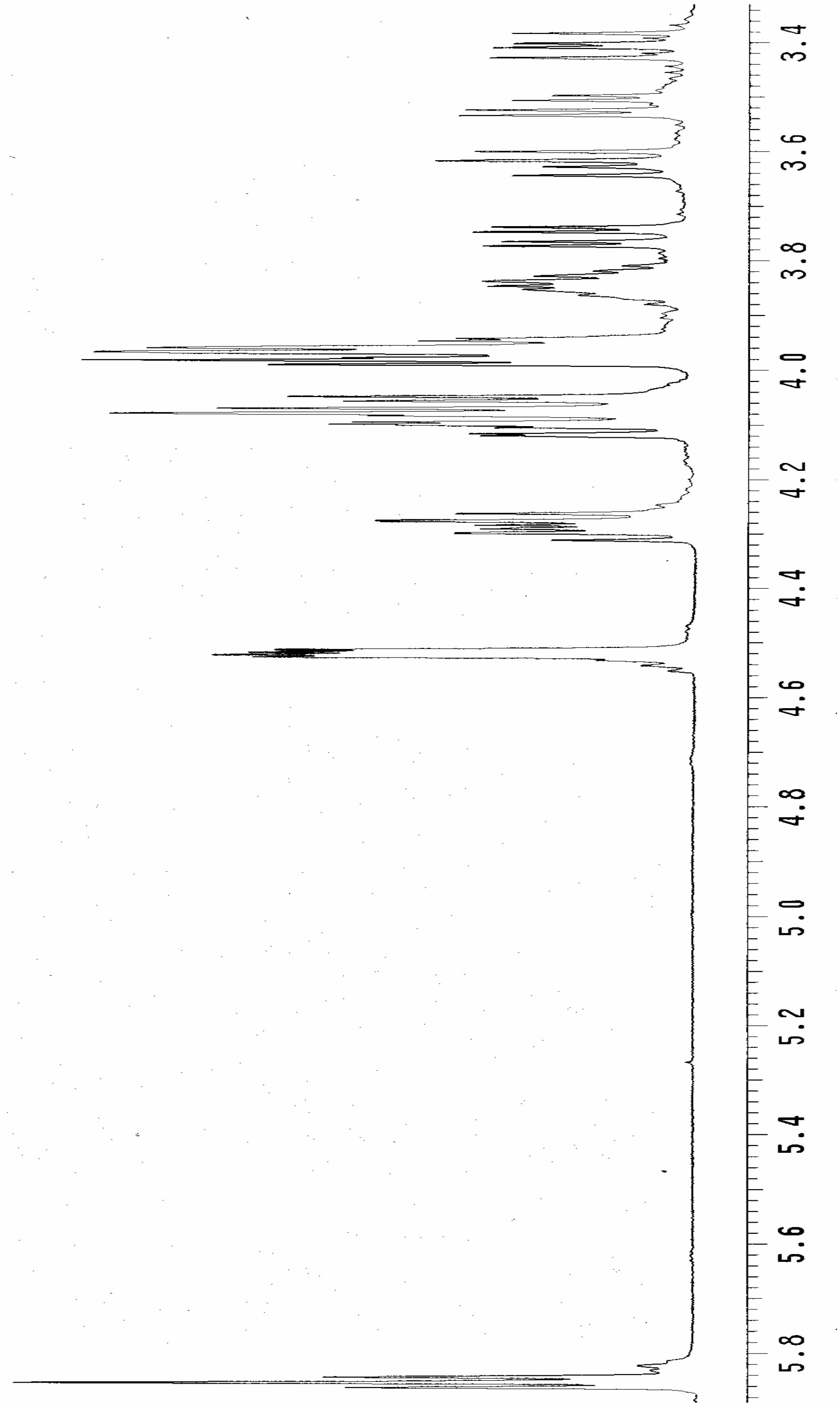


Figure 3.39 ^{1}H NMR spectrum of the compound **27** (high field part)

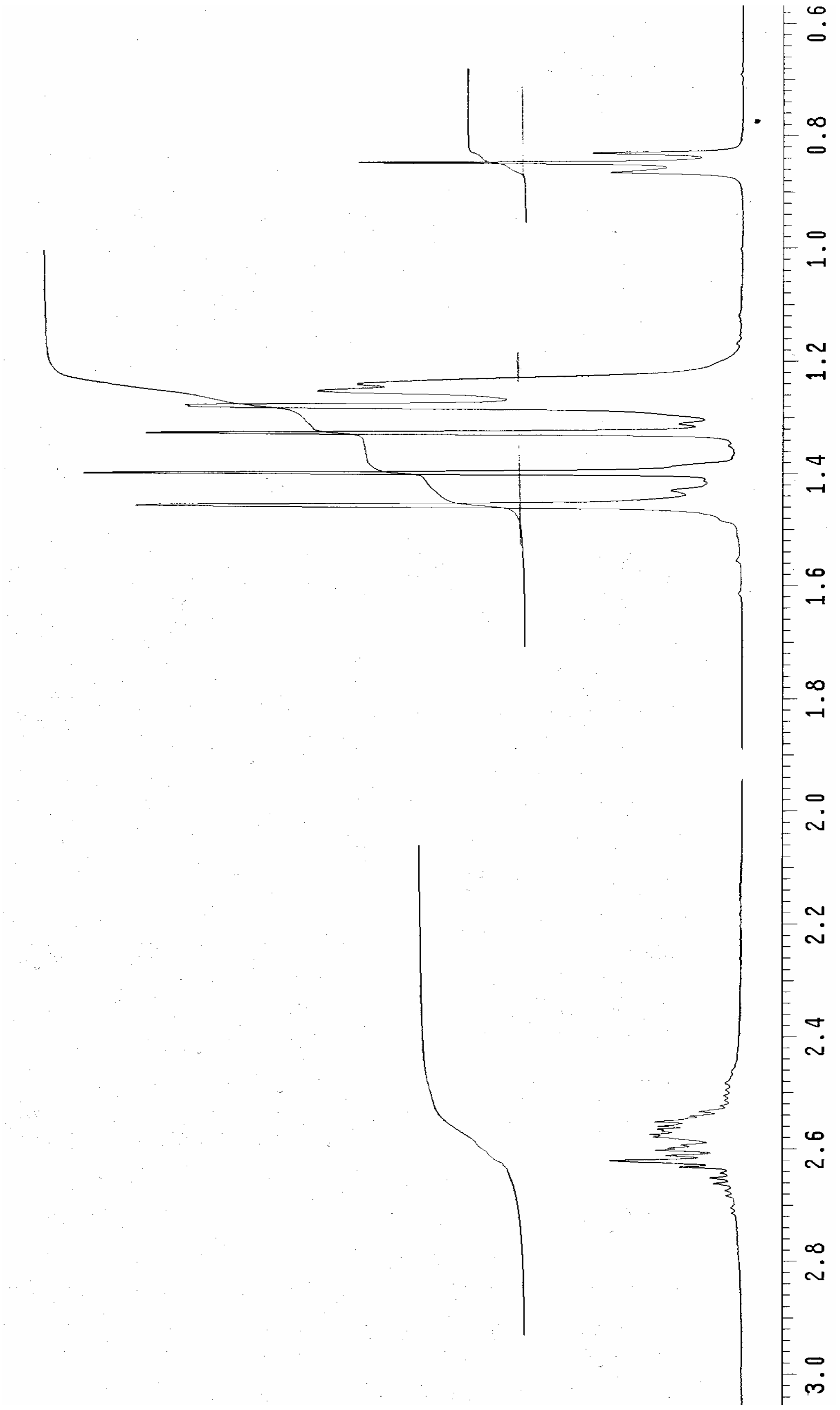
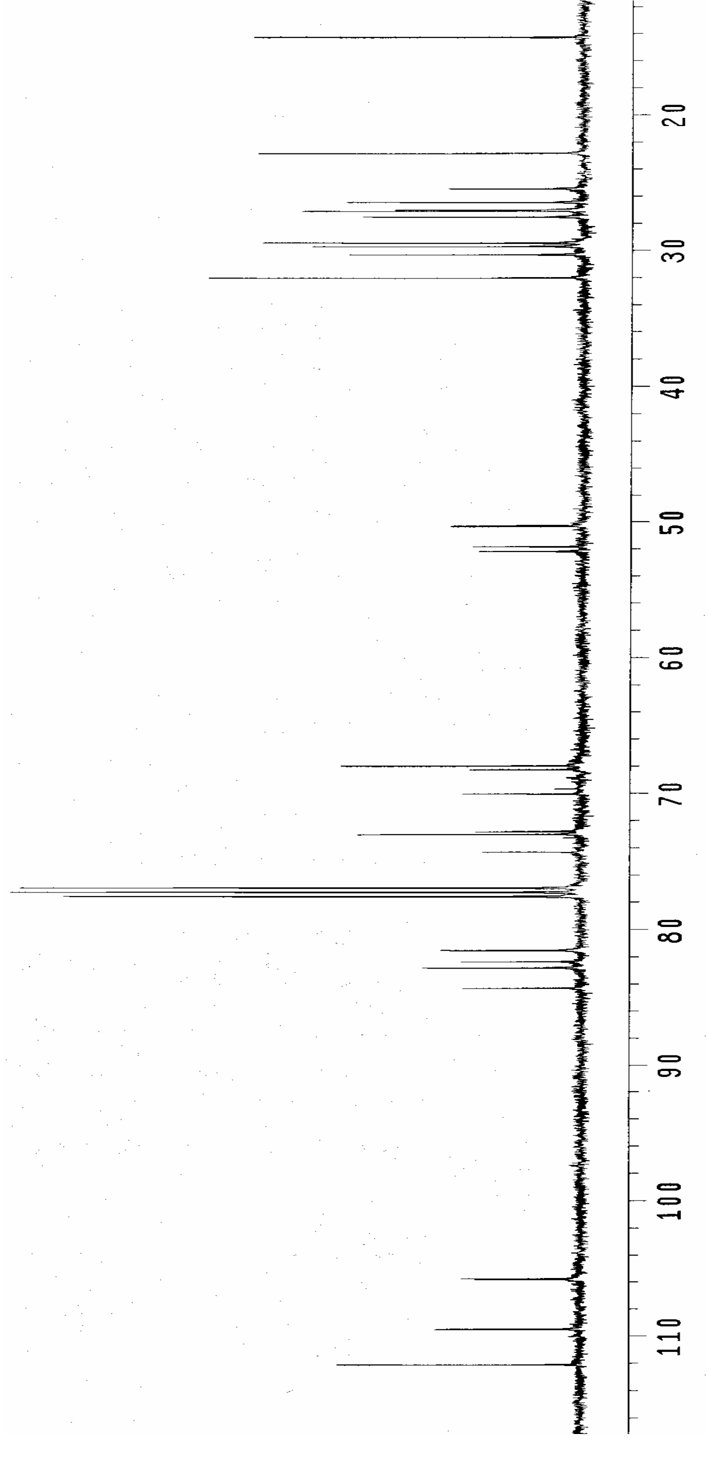
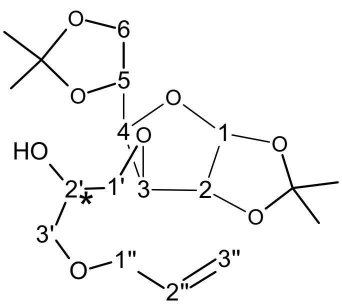


Figure 3.40 ^{13}C NMR spectrum of the compound **27**



3.19. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(3’-allyloxy-2’-hydroxy) propyl]-α-D-glucofuranose (28)



^{1}H NMR spectrum of the compound **28** is very complicated for a complete analysis, as expected due to the presence of diastereoisomers but it provides sufficient information about the structure. Low field peaks of the allylic duoble bond proton overlaps with the H-1 doublet but H-2 doublet is a single doublet at δ 4.52 with a coupling constant value of 3.6 Hz, between H-1 and H-2. This value is typical for furanose rings. Allylic CH_2 proton signals are also present at δ 5.25, 5.21, 5.16, 5.13. Presence of four isopropylidene methyl groups indicate that the protecting group is intact on the molecule.

^{13}C NMR spectrum of the same compound is also too complicated but precence of allylic double bond carbon signals at 117.68 and 117.60 ppm and at 111.95 ppm and isopropylidene acetal carbons and C-1 anomeric carbon signals at 109. 50, 109.46, 105.63, 105.55 ppm are characteristic for the structure.

Figure 3.41 ^{1}H NMR spectrum of the compound **28** (low field part)

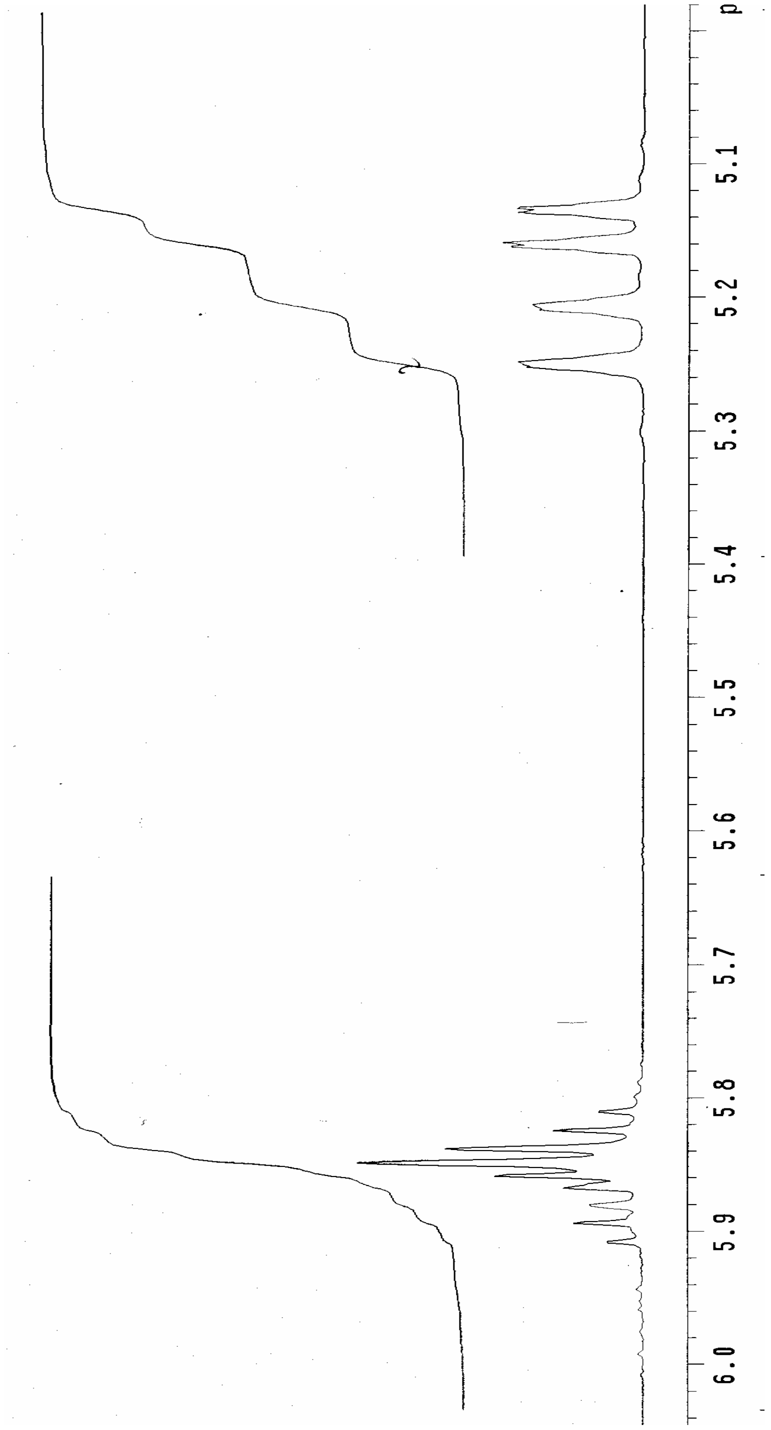
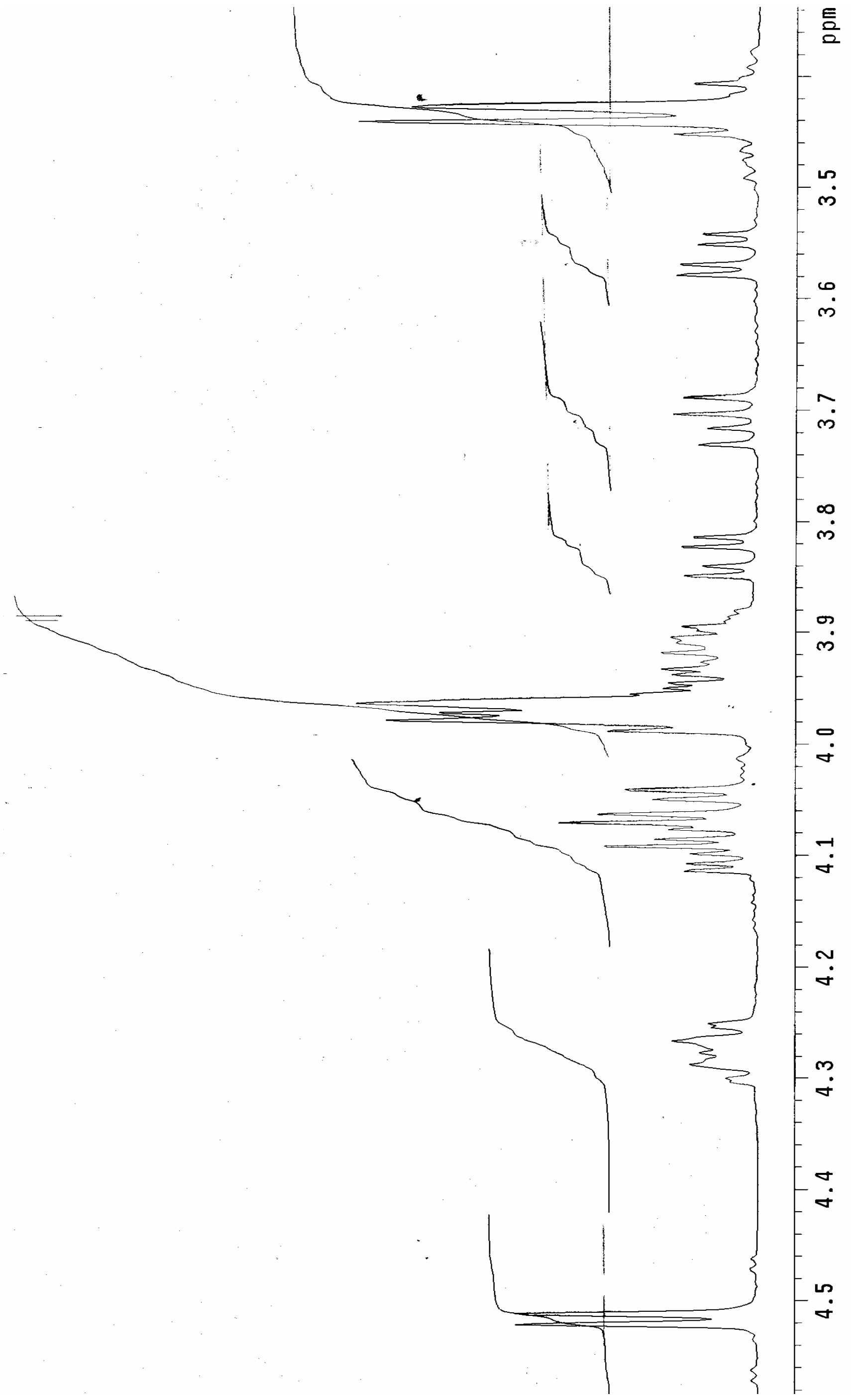


Figure 3.42 ^{1}H NMR spectrum of the compound **28** (high field part)



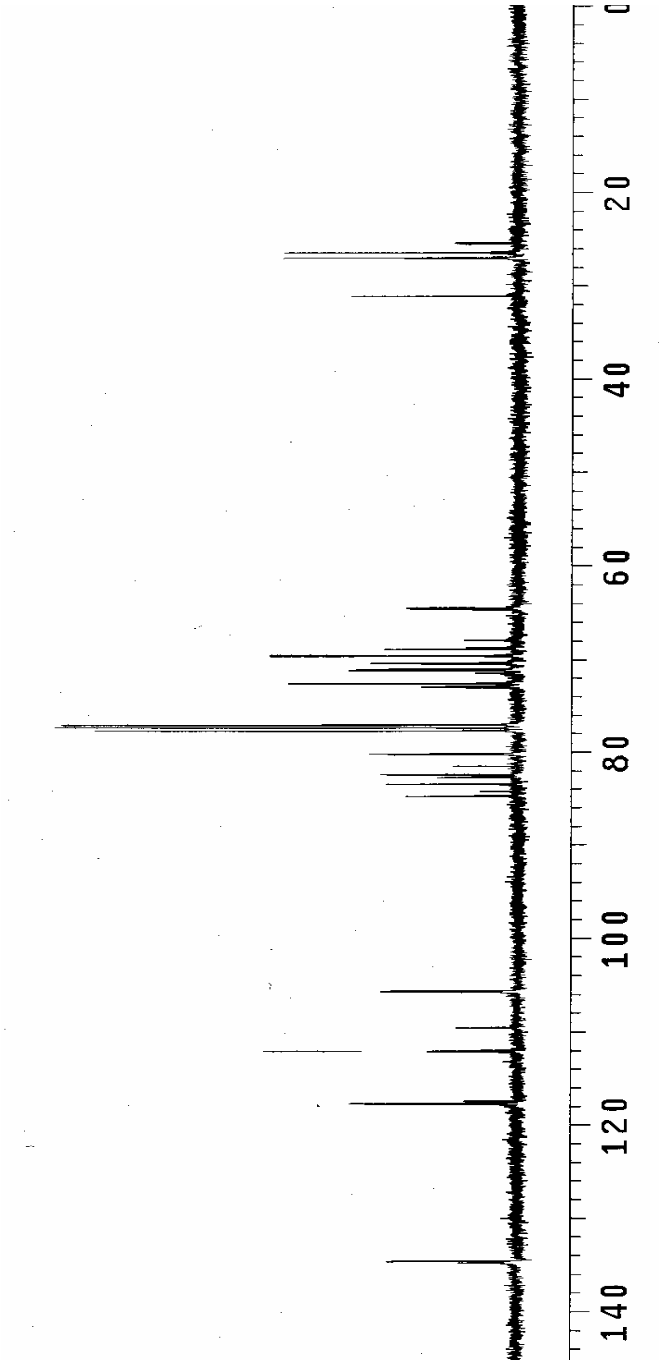
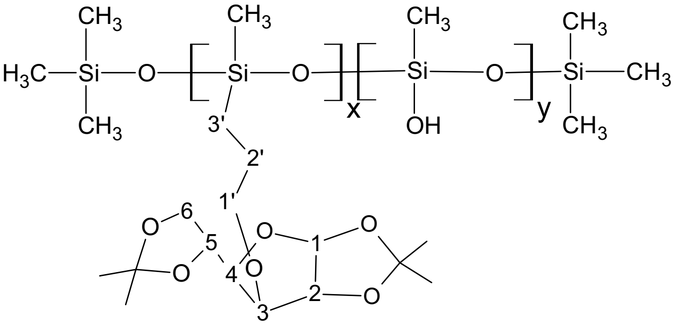


Figure 3.43 ^{13}C NMR spectrum of the compound **28**

3.20. Synthesis of Polymethylglucosiloxane (30)



As discussed previously, the reaction of the compound **9** with polymethylhydrogensiloxane oligomer (see **2.2.32**) was monitored by IR spectroscopy and it was clearly shown that the reaction proceeds as expected. We now discuss the ^{1}H NMR data of the product in order to obtain information about its structure and purity.

Polymethylhydrogensiloxane is an oligomer which was obtained from Merck. The manufacturers claim that it has an avarage of 35 siloxane groups between two trimethylsilyl terminal groups. According to the manufacturers claim, the siloxane oligomer containes a total of 41 methyl groups and 35 Si-H bonds. Thus it contains a total of 123 methyl protons and 35 Si-H protons. The ratio of these protons: 123/35 = 3.5. ^{1}H NMR spectrum of the siloxane oligomer (**Figure 3.48.**) indicates Si-Me group signals (singlets) at δ 0-0.2 (two small peaks for the terminal methyl groups and a big one for the siloxane (-O-Si(CH_3)O-) methyl groups and also a Si-H singlet at δ 4.72. On the spectrum, the ratio of the integral curves (integration of the total Me group signals / Si-H bond protons) is

12/3 = 4. This indicates that the oligomer containes less than 35, actually about 30 siloxane groups.

Reaction of oligomer with the compound **9** was carried out with a large excess of the compound **9** since we did not know how many sugar groups would be bonded to the oligomer. During the chromatographic purification, unreacted compound **9** eluted from the column first and the reaction product eluted rather late. This implies that the reaction product did not contain appreciable amount of unreacted **9**, but it might contain some unreacted oligomer and small amount of the compound **9**. Since the product has a very complicated structure, its ^{1}H NMR spectra are also complicated. However, it is possible to obtain some important information related to the structure. Thus, ^{1}H NMR spectrum of the reaction product (**Figure 3.49.)** indicates the absence of the Si-H bond singlet. This is due to the hydrolysis of the remaining Si-H bonds at the end of the reaction,with sodium hydroxide solution, which were converted to hydroxyl groups. Low field part of the spectrum (between δ 6.2 and 3.2) containes no Si-Me signals and H-2' methylene proton signals (C-CH_2-C group on the grafted side chain). The remaining low field signals will be due to the sugar protons (except the isopropylidene methyls) and also Si-CH_2 (H-3') and the 3-*O*-CH_2- (H-1') group on the sugar. H-1 and H-2 characteristic signals of the furanose ring are easily detectable at δ 5.86 and 4.53 (resolution is not good since the structure is polymeric). When we accept the integration of these protons as one proton each, we find a total of 11 protons. The grafted side chain (only one) indeed contains 11 protons, excluding the C-CH_2-C group on the grafted side chain which appear at the high field. It is important to mention that the spectrum contains only a trace of the double bond signals of the compound **9.** These results are indicative that the sugar moity is actually bonded to the siloxane back-bone. Now the question, of how many sugar groups were bonded to the parent siloxane oligomer, remains. We can roughly calculate the number of the grafted sugar groups from the ratio of the integration curves. The high field part of the spectrum contains more methyl groups and some methylene groups now, since isopropylidene methyl protons and C-CH_2-C group protons were also added to the total Si-Me protons. On the spectrum, the largest Si-Me signal is found at δ 0.09 this must be due to the (-O-Si(CH_3)O-) methyl group protons. The high field shift is probably due to the sterical effects of the sugar side chains. If we accept that there are 30 (-O-Si(CH_3)O-) groups on the siloxane back-bone, this sums up to 90 protons. Integral of these protons is 2.5 cm. Integral of the low field part of the spectrum is measured as 5.4 cm. If 2.5 cm is equal to 90 protons, 5.4 cm will be equal to 194 protons. If we divide this number with the number of the low field protons in one sugar unit we find the number of ~18. This calculation with an approximation indicates that very roughly about 17-18 sugar units are bound to the back-bone polymer. This means almost half of the siloxane groups were grafted.

Figure 3.44. . FTIR spectrum of pure PMHS

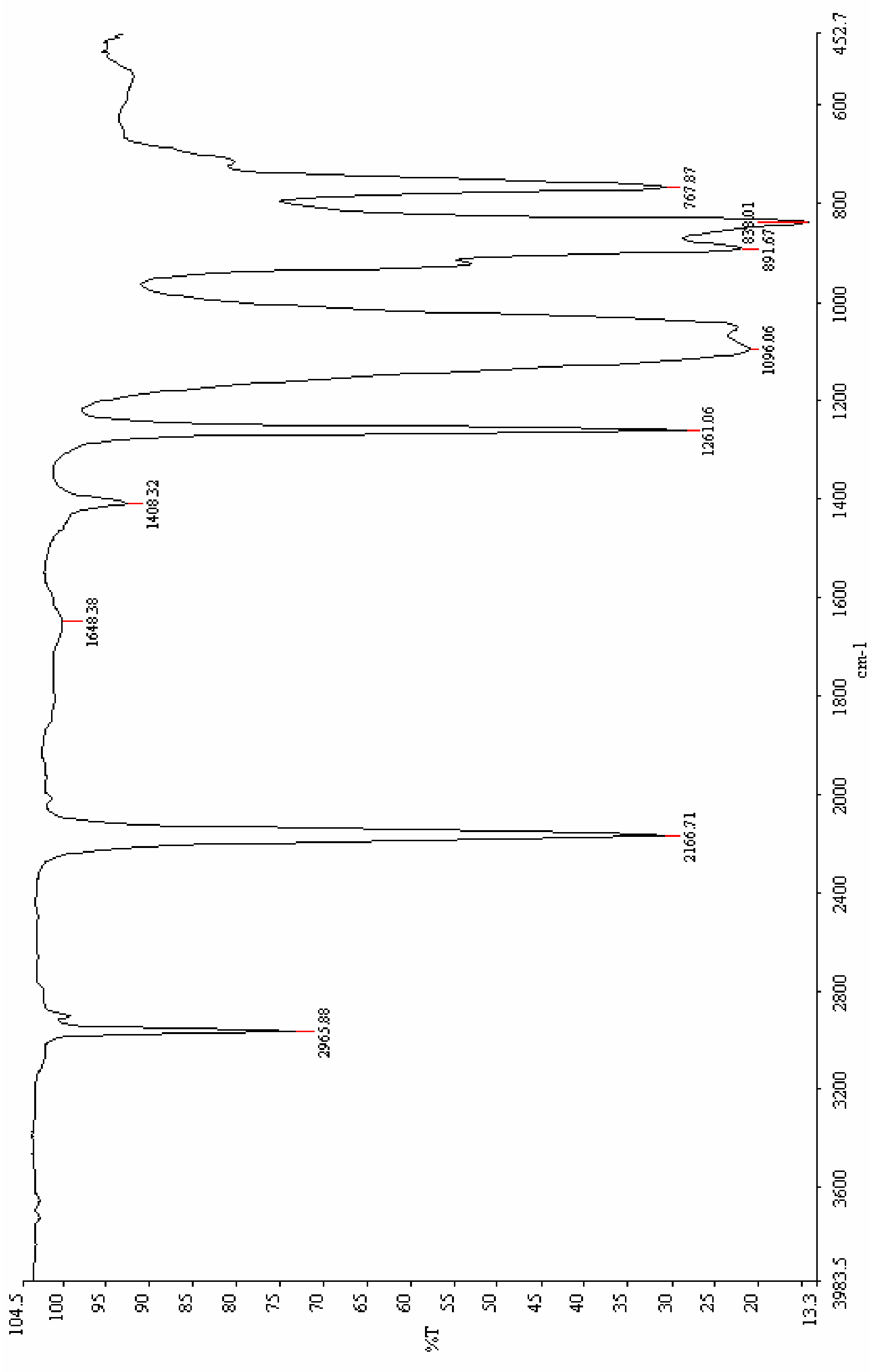


Figure 3.45 . FTIR spectrum of initial state of the reaction 2.2.32

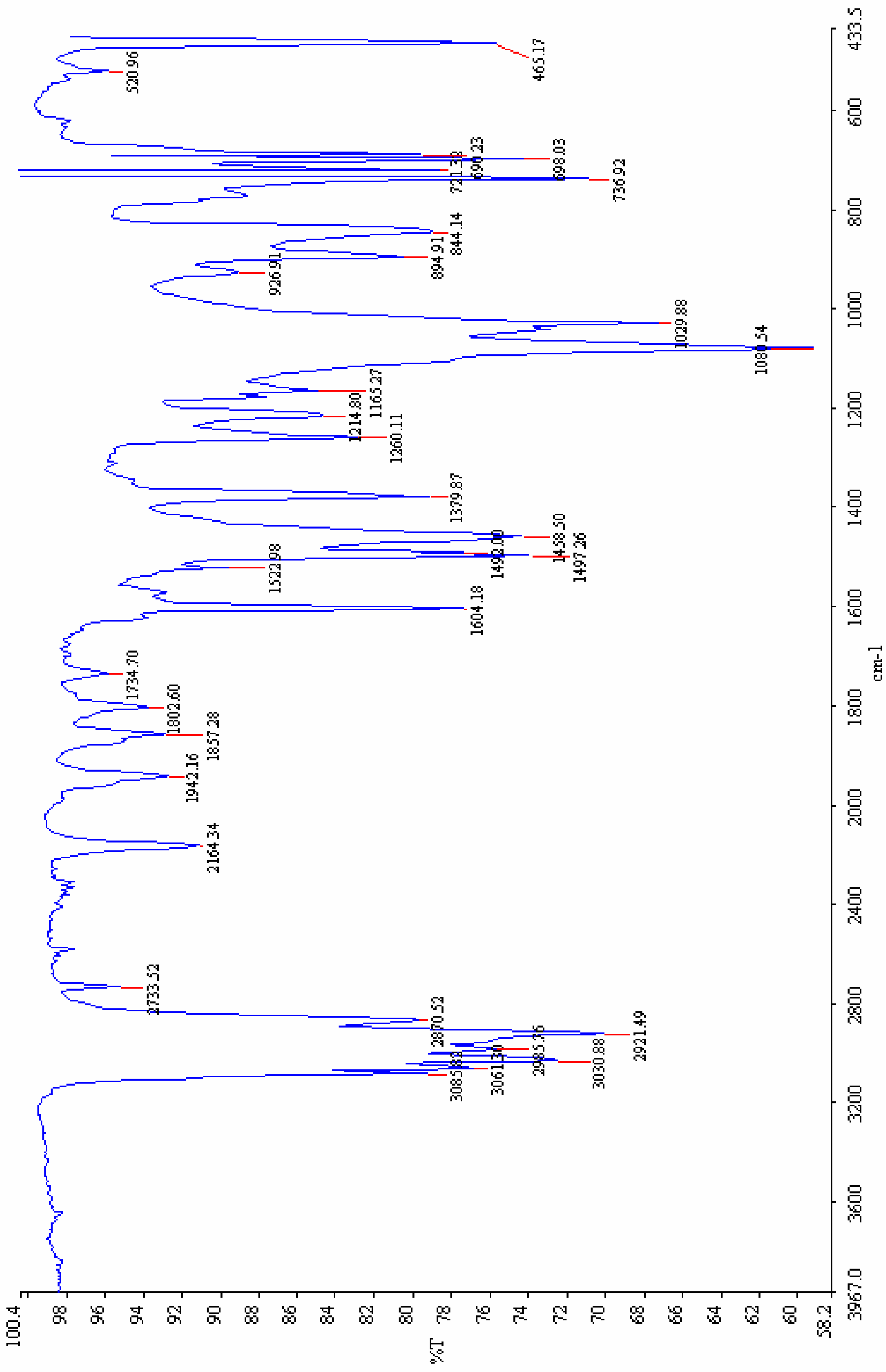


Figure 3.46. . FTIR spectrum of the end of the reaction 2.2.32

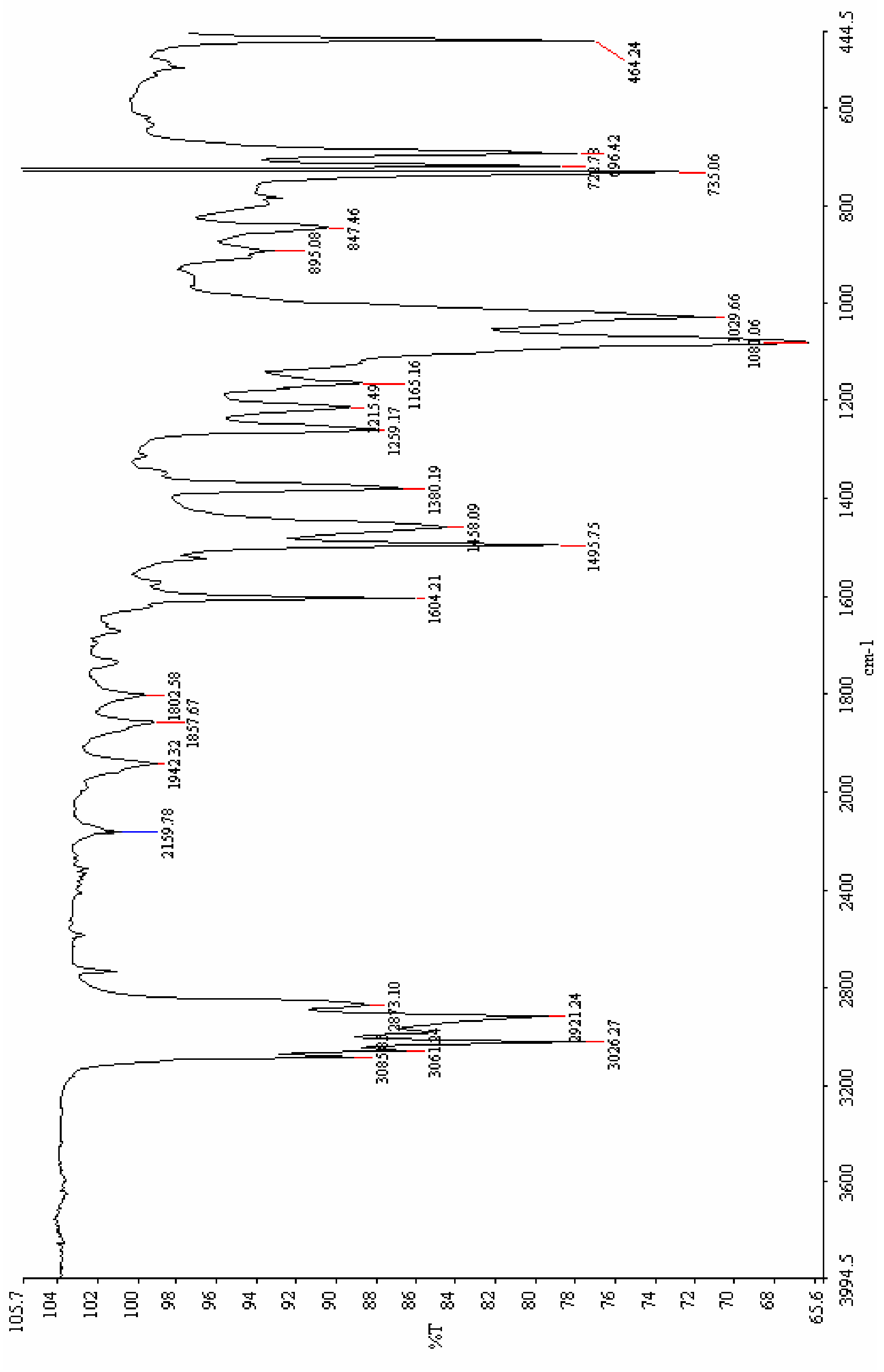


Figure 3.47. . FTIR spectrum of the compound 30

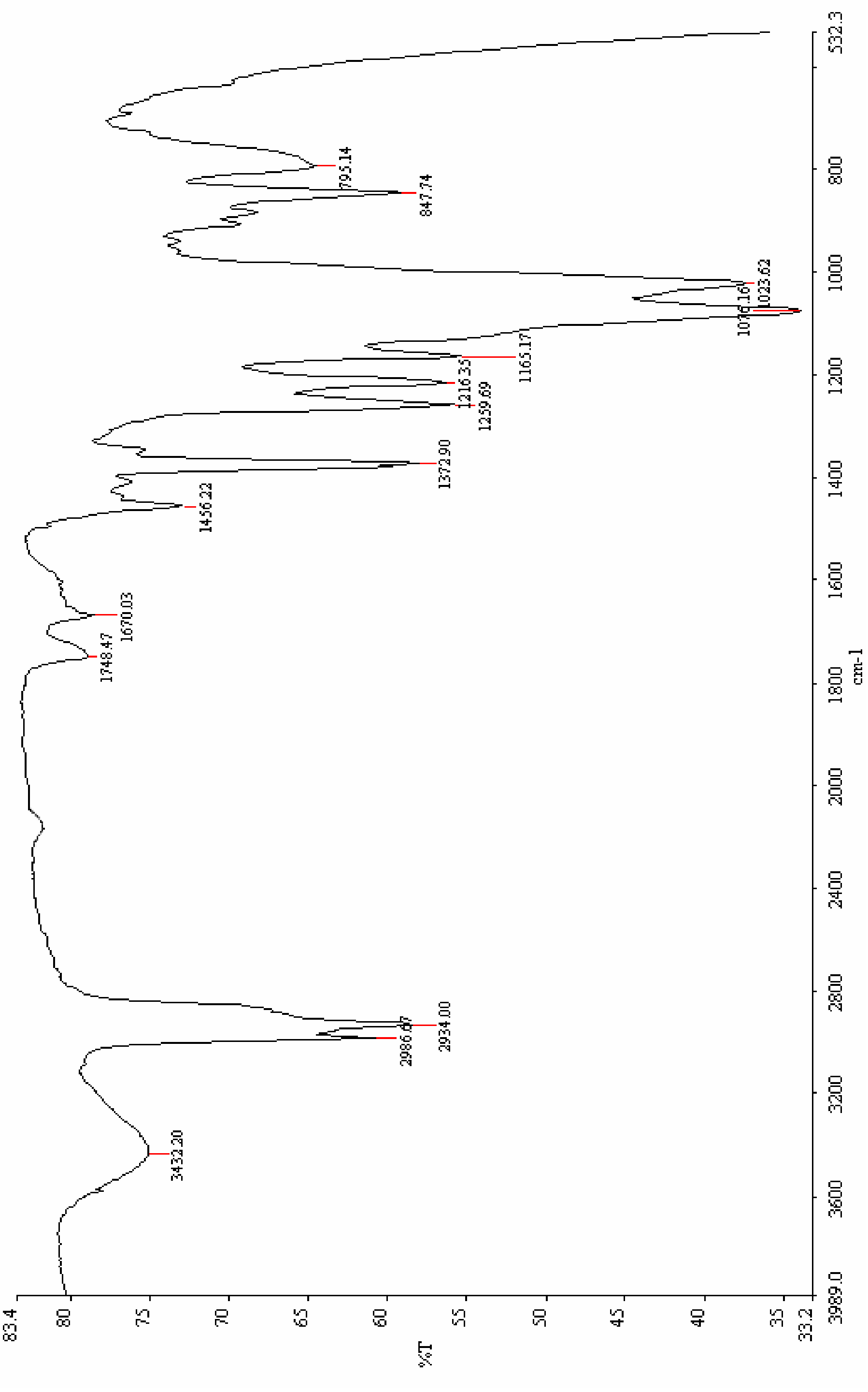


Figure 3.48 ^{1}H NMR spectrum of pure PMHS

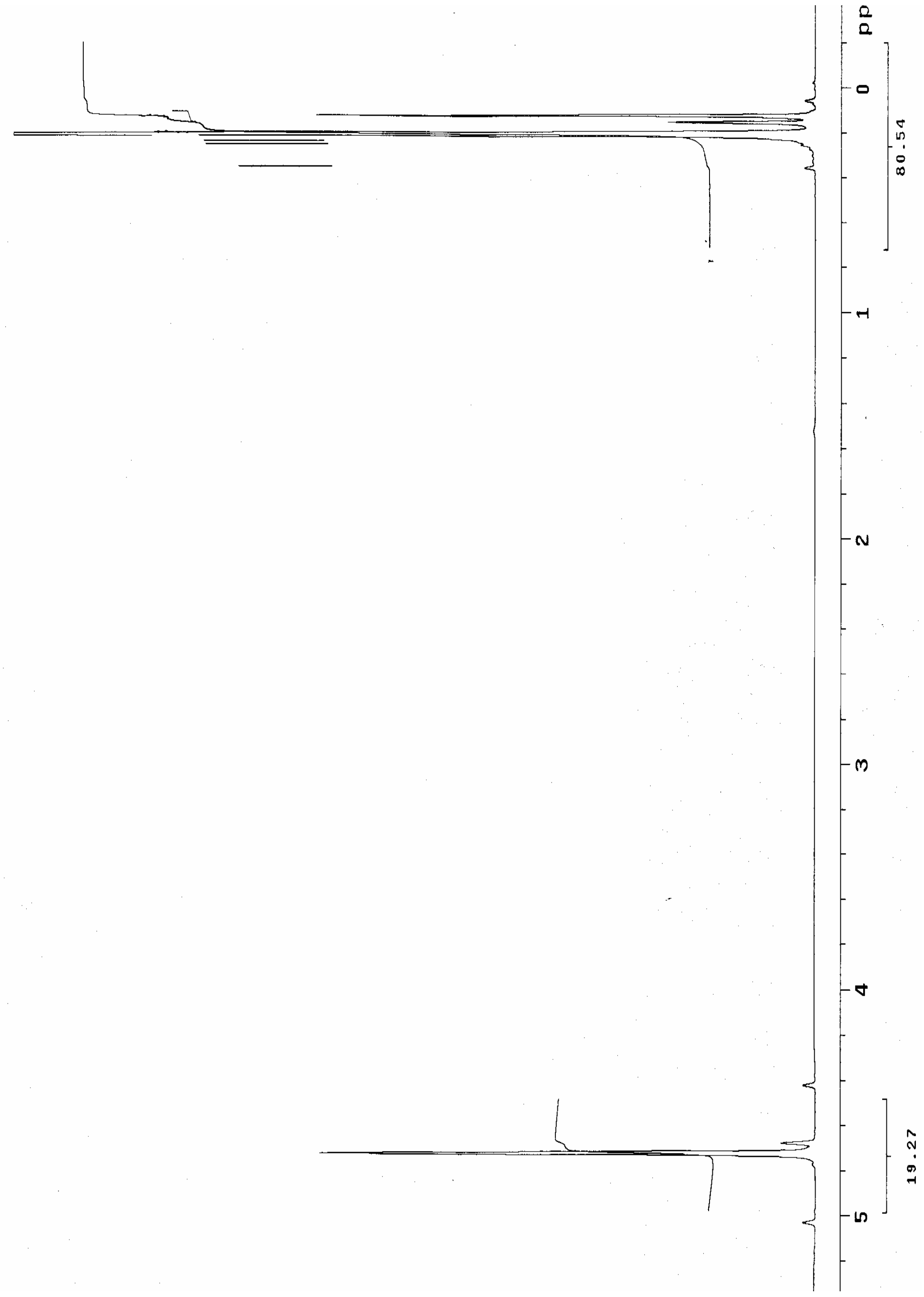
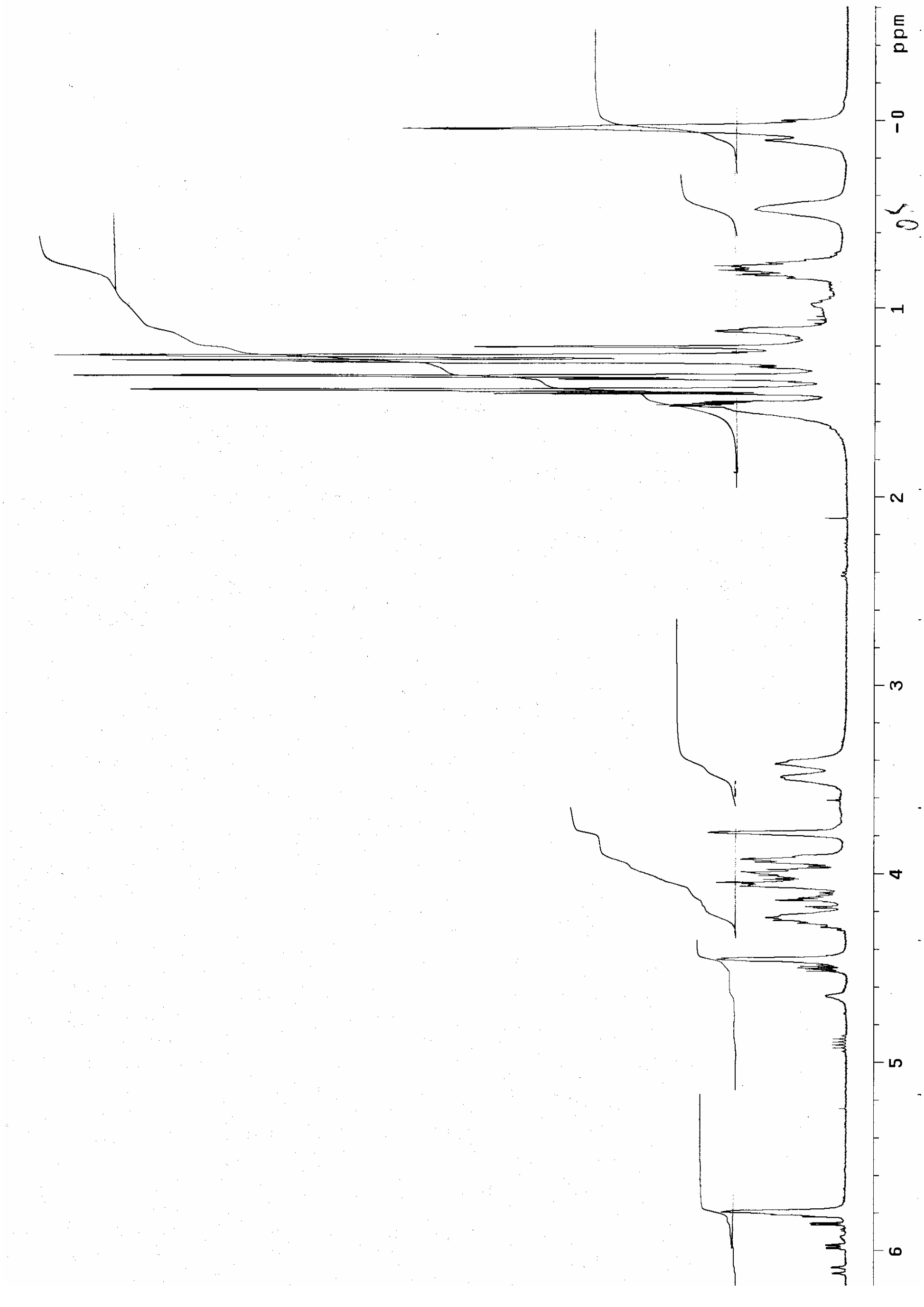


Figure 3.49 ^{1}H NMR spectrum of the compound 30



4. Results and Discussion

The aim of this study was to investigate the possibility of producing glucose based compounds which might have some surfactant properties. Glucose is one of the most abundant, sustainable natural compound and it can provide the hydrophilic "head" section to surfactants. Already some of the derivatives of glucose were discussed in the introduction section. Among, these alkylglucosides are the most important because they can be produced rather economically since there is no need to protect the sugar molecule. It is not possible to make many derivatives of sugars without using the protecting groups, therefore we decided to use a monoacetone and diacetone derivatives (1,2-*O*-isopropylidene-α-D-glucofuranose and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose respectively) as starting glucose derivatives. Diacetoneglucose can be cheaply produced from glucose and acetone with sulphuric acid as catalyst. Monoacetoneglucose can also be made similarly. Diacetoneglucose has only one free hydroxyl group therefore it is more convenient to use. For example this free hydroxyl group on C-3 of the glucose can be esterified, etherified and after inserting a leaving group it can also be used in substitution reactions. Esterification of the C-3 hydroxy group is not so easy because of the low reactivity, due to the sterical effects of the protecting groups. Also, esters are not amongst the esteemed surfactants since these are acid and base labile. Therefore we decided to make some long chain ethers. We prepared butyl (**23**), octyl (**25**) and allyl (**9**) ethers, using butyl, octyl and allyl bromide. We also prepared "3-*O*-[2',3'-epoxy-propane-1'-yl] ether (**10**) derivative, using epichlorohydrine as a reagent. Since pure enentiomeric epichlorohydrine is very expensive and difficult to obtain and this project has an industrial perspective, we decided to use the racemic reagent. The reason we decided to make this derivative was to create a new reactive site on the molecule so that we could bind new hydrophobic alkyl groups via opening the reactive epoxide ring. Thus, epichlorohydrin moiety also acted as a spacer between the main sugar molecule and the side chains. Unfortunately, using the racemic epichlorohydrine created a diastereoisomeric mixture hence caused structural assignment difficulties. We did not try to separate the diastereoisomers since our aim was to obtain products having surfactant properties and presence of stereoisomers would not impair these properties. Opening of the epoxy ring of the ether (**10**) with alcohols such as allyl, cyclohexyl, butyl, octyl, dodecyl and hexadecyl alcohols and amines such as diisobutylamine **(19)** and octylamine **(27)** were carried out. All compounds were characterized with proton and carbon NMR spectra and elemental analysis. The data were discussed in another section. Opening of the epoxy ring normally took place at the less crowded site as expected. In case of the butyl derivative, a very small amount addition on the chiral carbon (C-2) took place (as shown by the NMR spectra) but as the carbon chain gets longer this kind of addition did not took place due to the increasing sterical effect. Diastereoisomerism was only due to the chiral (C-2) carbon of epichlorohydrine. Ratio of the diastereoisomers were 50:50 as shown clearly by the H-1 signals on the ^{1}H NMR spectra.

In order to obtain surfactant properties, isopropylidene protecting groups must be removed since they make sugar molecule hydrophobic also. Removal of the isopropylidene groups is best achieved by the hydrolysis in the presence of hydrofluoric acid. This acid completely removes the isopropylidene groups. Using less strong acids will remove the 5,6-isopropylidene group but may not hydrolyse the more stable 1,2-isopropylidene rings completely. Hydrolysis and removal of the isopropylidene groups of the amino containing derivatives (**19** and **27**) was more difficult and took longer time and needed more catalyst, obviously because the acid catalyst was consumed by the amino groups.

4.1. ^{1}H NMR Spectra Overview

^{1}H NMR spectra of the furanose derivatives anomeric H-1 protons usually appear at a low field and hence they are very characteristic and distinc signals. They appear as doublets near δ 5.5 with a coupling constant $J_{1,2}$ = 3-4 Hz. Due to the twisted conformation of the furanose rings, the dihedral angle between the H-2 and H-3 protons are usually 90^o and hence, in the spectra of the glucofuranose derivatives coupling constants between H-2 and H-3 is usually zero. As a result H-2 signals are usually observed at relatively low fields as a doublet similar to H-1 doublets only at slightly higher field. With the exception of the amino derivatives (**19, 27),** all H-2 signals appeared as doublets in this thesis also. It appears that substituents with amino groups (compounds **19** and **27**) modifies the furanose ring geometry and the dihedral angles between the H-2 and H-3 protons are not 90^o anymore. Compounds **9, 23** and **25** are stereoisomerically pure compounds (no diastereoisomers exist) and therefore their spectra could be analyzed completely but others are mixture of diastereoisomers and only partial, but sufficient information could be obtained inorder to assign the structures.

4.2. ^{13}C NMR Spectra Overview

^{13}C NMR signals of acetal carbons normally appear at relatively low fields due to the two oxygen atoms bonded to the carbon atom. Di-*O*-isopropylidene derivatives of α-D-glucofuranose derivatives show 3 low field signals due to the 2 isopropylidene acetal carbons at about 105-115 ppm and due to the anomeric (C-1) carbon at about 105-110 ppm. As for the free sugars, anomeric carbon signals shift to the relatively higher fields (about 90-100 ppm) but they appear at distinctively lower field compared to the other ring carbons. Therefore either for free or protected sugars, C-1 signals can be easily identified on the spectra. (Stoddart, J.F. 1971) In the ^{13}C NMR spectra of the free sugar derivatives, reported in this thesis, two distinctive low field signals appear at near 97 ppm (for the α-anomer) and near 92 ppm (for the β-anomer). After the removal of the protecting isopropylidene groups of the furanose ring, the free sugar ring should be expected to isomerise to the much more stable “pyranose form”. Naturally, during this isomerization two different modifications of the pyranose form (α and β anomers) should be expected to form in equal amounts. Indeed , the ^{13}C NMR spectra, reported in this thesis indicates that the free sugar derivatives are a mixture of α and β anomers. In some of the compounds, there are further complications due to the formation of diastereoisomers. Therefore number of peaks exceed the expected number of signals which are expected from a pure single diasteroisomer. However, since the structures of the isomers are so similar, some of the peaks coincidentally overlap. Nevertheless, the spectra of the free sugars indicate that the protected groups are no more intact on the molecule. The findings from the spectra is supported by the elemental analysis of the products which indicate that the compounds are structurally sufficiently pure, excluding the fact that they are mixtures of the stereoisomers.

Table 4.1 ^{13}C NMR Low Field Region Shift Values for the Isopropylidene derivatives

Compound No	Isopropylidene Carbons	Anomeric Carbons	Double bond Carbons
13	112.10, 11.98, 109.50, 109.47	105.79, 105.75	NA
18	112.15, 109.55, 109.53	105.82, 105.77	NA
19	112.10, 109.47, 109.48	105.78, 105.74	NA
23*	111.91, 109.06	105.50	NA
25*	111.88, 109.04	105.49	NA
28	112.10, 111.95, 109.50, 109.46	105.63, 105.55	134.56, 134.49, 117.68, 117.60

* No stereoisomerism exist.

Table 4.2. ^{13}C NMR Anomeric Carbon Shift Values for the Free Sugars

Compound	Anomeric C (α)	Anomeric C (β)
12	97.46	92.89
14	97.48	92.89
16	97.42	92.89
20	97.42	92.91
24	97.45	92.89

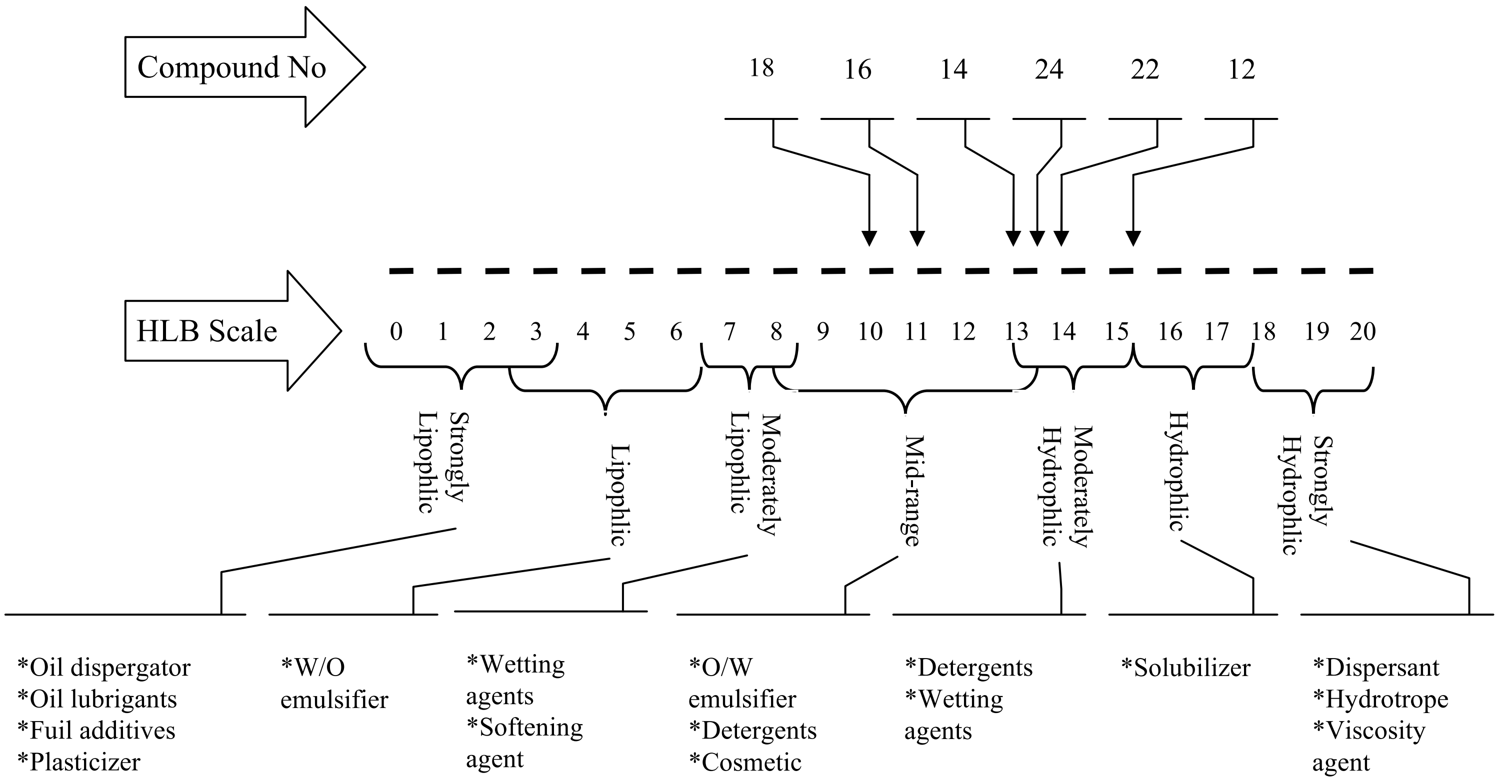
4.3. HLB Values of the Pyranose Compounds

Table 4.3 HLB values of the pyranose compounds

Compond No	HLB value*
12	15.2
14	12.9
16	11.2
18	9.9
20	N.A.
22	14.1
24	13.8
26	11.2

* HLB values is calculated by Griffin method (Griffin, W.C.; 1954)

Table 4.4. Position of the pyranose compounds on HLB scale



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