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REVIEW ON NMR LIBRARIES OF NATURAL AND SYNTHETIC MONOSACCHARIDES, OLIGOSACCHARIDES AND GLYCOSIDES†

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†This article is dedicated to Prof. Mrs Anakshi Khare Ex Head Department of Chemistry, Lucknow University, Lucknow

Abstract: The carbohydrates are made up of small monosaccharide units but their identification is a real challenge for an organic chemist. Since NMR is the only non-invasive and physicochemical technique for compound identification but limitation of this technique is, limited due to overlapping resonating range of chemical shift of protons and carbons of various monosaccharides in their spectra. Although a number of two and multidimensional NMR experiments have been developed for enhancing the resolution in other frequency dimension, for resolving chemical shift dispersion arising due to structural complexities of these molecules. However, no detailed and comprehensive library of chemical shifts and other related data of monosaccharide units which are present in the oligosaccharide moiety is available. A minute change in the structure of oligosaccharide i.e. anomeric configuration, linkage, sequence and position of appended groups causes a marked difference in the chemical shift of involved carbon and proton of that monosaccharide unit in the oligosaccharide. To overcome these problems a NMR library of oligosaccharides, has been developed which covers the data of monosaccharide, disaccharides, trisaccharides and up to oligosaccharide level. Besides the NMR data of known oligosaccharides and glycosides isolated from various sources, various monosaccharide i.e. glucose, mannose, rhamnose, fucose etc. have also been taken and their substituted derivatives at various positions (1to 6) have been synthesized and their NMR data have been arranged in tabular form. Further, utilization of various ^{1}H and ^{13}C chemical shifts with respect to linkages and sequence have been given, which will help in precise prediction of the chemical shifts in oligosaccharides and glycosides. The ^{1}H NMR data which is available in the literature and procured from synthetic compounds and natural products have been compiled.

Keywords: NMR, Monosaccharides, Disaccharides, Glycosides, Oligosaccharides.

Introduction

Structure elucidation of natural compounds with meager amount became possible only after the invention of nuclear magnetic resonance[1,2] which is a non-invasive tool for the structure assignment of natural products and synthetic compounds. After the introduction of Fourier Transformation (FT) technique, Nuclear Magnetic Resonance (NMR) spectroscopy has undergone a vast change which reduces the requirement of large quantities of the compounds required for the structure elucidation. NMR has been used to study bioactive molecules of synthetic and natural origin. During the synthesis and structural characterization[3] studies of synthetic and natural products, various experiments of NMR are performed. Earlier, only ^{1}H NMR studies were performed which were later aided by ^{13}C NMR and presently 2D NMR techniques like ^{1}H-^{1}H COSY, NOESY, HSQC, HMBC and multidimensional NMR experiments are performed to unambiguously assign complex overlapped transitions which aids in structural determination of oligosaccharides. NMR spectral data provides detailed information about the structures, functional groups, conformation and stereochemistry of a compound. Presently a large number of NMR experiments are available to chemists many of which use pulse field gradient[4] which has wide application in structural, conformational and stereo chemical studies on any type of chemical compounds

During the course of investigation, it was found that the field of carbohydrate chemistry, which is presently covered under the umbrella of glycobiology[5] is the most challenging field. Among the natural products carbohydrates and carbohydrate containing moieties like glycosides, glycoprotein, oligosaccharides[6] and glyconjungates have emerged as an important class of compounds for various biological purposes. For knowing the stereoscopic structures of these compounds, one has to carry conformational and configurational analysis of these compounds using especially designed NMR experiments.

The role of carbohydrates in biological recognition processes[7,8], in development of diseases[9] and in the food and other industries is enormous. Still the function of carbohydrates and their role in causing these events are poorly understood. Amongst the various biomolecules, carbohydrates are the least exploited compounds. Carbohydrates are difficult to synthesize and manipulate[10] and their limited availability makes it difficult to study their biological function in detail. Carbohydrates often differ from each other in stereochemistry and the pattern of inter residue linkages which can be very heterogeneous[11]. The information capacities of carbohydrates are much larger than proteins, particularly due to branched structure of the former. It has been claimed that carbohydrate contain hidden code to biological recognition[12,13]. Since addition of carbohydrate to any organic moiety increases its solubility in water and the resultant could be absorbed easily in biological system and causes decreased toxicity therefore it is advisable to study carbohydrate mediated biologically active compounds. For the development of carbohydrate based therapeutics, it is necessary to investigate the behavior and mechanism of carbohydrate function. Recent advances in glycochemistry have helped to solve some of the problems associated with large scale synthesis of complex carbohydrates for drug development. The structure determination of complex oligosaccharides is a difficult but challenging task and NMR spectroscopy is the technique[14-18] which is currently being applied in the identification of known and unknown oligosaccharides and glycons. Therefore, it seems most appropriate to review the latest techniques and applications.

Classical NMR Methods

For performing a primary structural analysis of a mono-, oligo-or polysaccharide, there are various methods and approaches through NMR spectroscopy. `Structural-reporter-group' concept was introduced by Vligenthart et. al., in which the bulk region (3-4 ppm) was emphasized in the ^{1}H NMR spectra of carbohydrates. Various data bases like CASPER[19] and SUGABASE[20] were developed by different workers for prediction of proton and carbon chemical shifts and coupling constants for structure determination of various oligosaccharides.

NMR Spectroscopy[21-23]

A typical NMR spectroscopy analysis of oligosaccharide sample involves the following steps-

1. **Number of sugar residues-** In the structural analysis of oligosaccharides, the chemical shift of anomeric proton and anomeric carbon plays an important role. By counting the number of anomeric protons or anomeric carbons and the integration of the anomeric resonances we can get an initial estimate of the number of different monosaccharide residues present. The anomeric proton resonances are found in the shift range δ4.4-5.5 ppm in ^{1}H NMR[21]. Additionally, the number of anomeric C-1 resonances present in a ^{13}C NMR spectrum confirm the number of monosaccharide units in the oligosaccharide molecule which are present in the chemical shift range of δ90-110 ppm.

2. **Constituent monosaccharides-** After knowing the number of sugar residues in the oligosaccharide, the next step is to know the constituent monosaccharide unit present in the oligosaccharide. By combining the data of ^{1}H and ^{13}C anomeric chemical shifts, one can easily distinguish the monosaccharide present in the oligosaccharide. For sialic acid moiety which does not have anomeric protons, the characteristic signal of the H-3ax and H-3eq proton are a good starting point for the assignment. 2D homonuclear co-relation spectroscopy (COSY, HOHAHA)[23], ^{13}C NMR[21], ^{1}H-^{1}H TOCSY[24-25] and ^{1}H-^{13}C correlation spectroscopy[26-29] are also useful in the identification of individual monosaccharide residues.

3. **Anomeric configuration-**In oligosaccharide molecule normally a α-anomer resonates downfield compared to the β-anomer in D-pyranose in $^{4}C_{1}$ conformation. If H-1 and the H-2 are both in an axial configuration in pyranose structure, a large coupling constant (8-10 Hz) is observed, whereas if they are equatorial-axial, there is a smaller coupling constant ($J_{1,2}$ ~ 4Hz), and for equatorial-equatorial oriented protons, even smaller coupling constants are observed (<2Hz)[30]. The J value 6-9 Hz showed the presence of β-configuration whereas J value 3-4 Hz showed the presence of α-configuration.

4. **Linkages and sequence-** The ^{1}H and the ^{13}C chemical shifts give an indication of the linkage of complete oligosaccharide moiety. The effect of glycosylation depends on the linkage type, and the changes in the chemical shift are in general larger at the glycosylation site than at the neighboring positions. The Heteronuclear Multiple Bond Correlation (HMBC) and inter-residue NOEs experiment give information about the glycosidic linkage. An effective way of knowing the glycosidic linkage between two monosaccharide residues is by monitoring the nuclear overhauser effect (NOE) from the signal for an anomeric group to the hydrogen of the substituted position in the adjacent ring[31,32].

5. **Position of appended groups-** A non-carbohydrate group like a methyl, acetyl, sulfate, or a phosphate group shifts the

proton and carbon where the appended group is located. In the case of acetyl group attached, the methine proton corresponding to reducing sugar is downfield shifted by ~1.0-1.2 ppm whereas the neighboring protons are downfield shifted by 0.1-0.2 ppm. In other cases, downfield shifts of ~ 0.2-0.5 ppm[33] were observed in δ values for protons where appended group is attached. This entire process places these resonances in a less crowded area of the spectra and helped in the identification of appended groups.

6. **Structure Reporter Group-** Since the NMR data of oligosaccharides is highly complex, Vligenthart et.al. Introduced the "structural reporter group" (SRG)[34,35] concept, which was based on signals outside the bulk region (δ 3-4) in the ^{1}H NMR spectra of the oligosaccharide. This structural reporter group concept helped in the identification of novel residues and characterization of oligosaccharides.

Different NMR techniques in structure elucidation of oligosaccharides

The structure of milk oligosaccharides has been determined by comparing NMR data of the new isolated compound with the reference data of different core units found in milk oligosaccharides. While comparing the chemical shift values it is important that the reference data is measured at the same temperature and is based on the same internal reference or is one that can be correlated in a simple manner. The different NMR experiments useful in structure elucidation of oligosaccharides are as follows-

^{1}H NMR Spectroscopy of oligosaccharides

The ^{1}H NMR is the most basic and important experiment of NMR series. It provides maximum information regarding configuration and conformation of monosaccharides present in the oligosaccharide. The high resolution ^{1}H NMR spectra gives valuable information about qualitative and quantitative aspects of the oligosaccharide structure. The chemical shift of a particular anomeric proton and its splitting pattern gives an idea of the monosaccharide units presents their in, simultaneously it also fixes the configuration of sugar linkage and conformation of that monosaccharide unit. The proton NMR spectroscopy of carbohydrates suffers from severe spectral overlap, because most of the monomer residues differ only in their stereochemistry and their magnetic properties are little influenced by their position in the chain. Since the chemical shift of anomeric protons and methine protons of different sugars are confined to the region δ 4.3-5.5 and δ 3.0-4.2 respectively hence it requires expert interpretation of spectra for monosaccharide identification. The analysis of reducing oligosaccharides showed that the anomeric configuration of the reducing end sugar also exerts its influence on the spectral parameters of residues in its spatial neighborhood, being sometimes even the non-reducing end sugar. To resolve the spectral complexities of oligosaccharides, Vligenthart et.al. introduced the "structural reporter group" concept, which was based on signals outside the bulk region (3-4) in the ^{1}H NMR spectra of the oligosaccharide[35]. This approach is used to identify individual sugars or sequence of residues. These structural reporter groups include anomeric protons, equatorial protons, deoxy protons and the distinct functional group such as the amide group. ^{1}H NMR gives anomeric protons at 4.3-5.9 ppm, methyl doublets of 6-deoxy sugars at 1.1-1.3 ppm, methyl singlet of acetamido groups at 2.0-2.2 ppm and various others with distinctive chemical shift. In D-pyranoses $^4C_1$ conformation the α-anomer resonates downfield in comparison to β-anomer[21]. The chemical shift value for α-anomer lies in the range of 4.9-5.4 ppm and for β-anomer in the range of 4.4-4.8 ppm. The α-anomeric doublet showed

coupling constant J = 3-4 Hz whereas the β-anomeric doublet showed J value of 6-9 Hz. All these values were correlated with known structures to yield relevant information in terms of monosaccharide units and their relative abundance. The structure of different linkages can be defined in terms of NMR parameters of their structural reporter groups. In case of milk oligosaccharides, the anomeric proton resonances are found in the chemical shift range of 4.3-5.5 ppm and the remaining ring proton resonances are found in the range of 3.0-4.2 ppm. But in case of acetylated oligosaccharides, acetyl groups induce a strong downfield shift of protons which are directly linked to acetylated carbons. Hence the signals of methine protons occur downfield in the region of 4.0-5.2ppm. The resonances of protons linked to the non-acetylated carbons at the site of glycosidic linkage and at the ring C-5 occur in the chemical shift range between 3.5 and 3.9 ppm.

Some of the common spectral features of the ^{1}H NMR **structural reporter groups** of milk oligosaccharides are given below[36-40]

1- In the ^{1}H NMR spectra the reducing Glc residue is characterized by the H-1 signals for its α and β anomers at δ5.221 ($J_{1,2}$ 3.7 Hz) and δ 4.688 ($J_{1,2}$ 8.0 Hz) respectively in the ratio of 7:10.

2- The 4-substituted reducing Glc shows anomeric signals for both the α- and the β-anomers at δ 5.22 and 4.66 ppm, with H-2 of the β-form in the range of δ3.2-3.3 ppm as triplet.

3- The 3,4-disubstituted reducing Glc shows anomeric signals from both the α- and the β-anomers at δ 5.22 and 4.66 ppm, with H-2 of the β-form at a typical downfield shift above δ3.35 ppm.

4- The 3-substituted β-linked Gal shows signal for H-1 at 4.4 ppm and H-4 of β-linked Gal showed at a typical downfield shift around δ 4.13-4.15 ppm due to substitution at the 3-position.

5- The H-4 of (1→6) linked β-Gal appeared at δ 3.8-3.9 ppm and H-4 of (1→3) linked β-Gal at δ 3.9-4.2 ppm.

6- Signal for H-1 of the unsubstituted Gal residue appears around 4.44-4.47 ppm.

7- β-linked GlcNAc residues with anomeric signals appear at δ 4.6-4.7 ppm and CH_3 signals in the range of δ 2.02-2.08 ppm. H-1 of the (1→6) linked GlcNAc appears at lower chemical shift value (δ 4.6 ppm.) than the (1→3) linked GlcNAc residue (4.7ppm). A splitting of the anomeric doublets is due to the anomerization of the reducing terminal.

8- The H-2 of β-GlcNAc appeared at 3.6-3.8 ppm and H-2 of β-GalNAc appeared at 3.8-4.2ppm.

9- Presence of anomeric signal with a integration of two protons at 4.44-4.6 ppm suggests a LNT structure in which one β-Gal is attached to Glc by (1→4) linkage while another β-Gal unit is attached to β-GlcNAc or β-Glc by (1→3) linkage i.e. β-Gal(1→3) β-GlcNAc(1→3/6) β-Gal (1→4) Glc or β-Gal(1→3) β-Glc (1→3/6) β-Gal(1→4) Glc moieties are present.

10- α-linked Gal residue appeared at δ4.94-5.2 ppm. The (1→4) linked α-Gal residues showed anomeric signal at δ 5.02 ppm, (1→2) linked α-Gal residues showed anomeric signal at δ 5.20 ppm and (1→3) linked α-Gal residues showed anomeric signal between δ 5.02-5.20 ppm.

11- α-linked Fuc residues anomeric signals appeared at δ5.02-5.43 ppm. The presence of fucose subunit could be inferred by the presence of CH_3 doublet at δ 1.1-1.3, H-5 at δ 4.2-4.9 and the anomeric doublet at δ5.02-5.4 ppm.

12- Generally (1→4) linked fucose occurs near δ4.98ppm, (1→2) linked fucose occurs near δ5.38ppm and (1→3) linked fucose occurs between the two.

13-The presence of sialic acid residue could be ascertained by the characteristic resonances

of H-3 axial and equatorial protons at 1.78 and 2.75 ppm respectively. The location of Neu5Ac residue can be deduced as follows. (a) the signal for H-3a and H-3e of Neu5Ac residue can be used to discriminate between (2-3) and (2-6)-α-linkage to Gal. (b) for an α-Neu5Ac(2-3)-β-Gal-(1- sequence, the signal for H-3 of Gal residue is shifted downfield by 0.6 ppm of the ring protons.

14- The 3,6-disubstituted β-linked Gal shows signal for H-1 at 4.4ppm and H-4 at a typical downfield shift around 4.13-4.15 ppm, due to substitution in the 3- position by a β -linked GlcNAc residue.

15- The location of Neu5Ac residue can be deduced as follows –

(a)The signal for H-3a and H-3e of the Neu5Ac residue can be used to discriminate between (2-3) and (2-6)-α - linkages to Gal .

(b)For an α-Neu5Ac(2-3)- -Gal-1- sequence, the signal for H-3 of the Gal residue is shifted down field of the ring protons by 0.6 ppm.Also , in a β-GlcNAc-(1-3)-β-Gal-1- sequence, the signal for H-4 0f the Gal residue appears at 4.15ppm.

16- The presence of α-Gal subunit could be inferred by the presence of the anomeric doublet at 5.14-5.25ppm and H-4 doublet at 4.09-4.25.

17-Linkage of Gal(S_4) to GlcNAc(S_3) in LNT and LNeoT is confirmed by the chemical shift value of Gal(S_4).If the chemical shift value of Gal(S_4) is exactly similar to that of lactose Gal(S_2) than it would be 1-4 linked to GlcNAc(S_3)otherwise it would be 1-3 linked to GlcNac(S_3).

18-The 4-substituted reducing Glc shows anomers signals for both the α- and β-anomeric at δ5.22 and 4.46ppm, with H-2 for the β-form in the range of δ 3.2-3.3ppm as triplet.

^{1}H NMR data of common glycopyranoses of oligosaccharides found in milk[21]

Sugar	H-1	H-2	H-3	H-4	H-5	H-6	$NHCOCH_3$
β-D-Glc	4.64	3.25	3.50	3.42	3.46	3.72,3.90	-
α-D-Glc	5.23	3.54	3.72	3.42	3.84	3.76,3.84	-
β-D-Gal	4.53	3.45	3.59	3.89	3.65	3.64,3.72	-
α-D-Gal	5.22	3.78	3.81	3.95	4.03	3.69,3.69	-
β-L-Fuc	4.55	3.46	3.63	3.74	3.79	1.26	-
α-L-Fuc	5.20	3.77	3.86	3.81	4.20	1.28	-
β-D-GlcNAc	4.72	3.65	3.56	3.46	3.46	3.75,3.91	2.06
α-D-GlcNAc	5.21	3.88	3.75	3.49	3.86	3.77,3.85	2.06
β-D-GalNAc	4.68	3.90	3.77	3.98	3.72	3.82,3.84	2.06
α-D-GalNAc	5.28	4.19	3.95	4.05	4.13	3.79,3.79	2.06

^{13}C NMR Spectroscopy of oligosaccharides[41-43]

The ^{13}C NMR provides information about configuration and conformation of monosaccharides present in the oligosaccharides. ^{13}C NMR Spectroscopy has enormous potential for carbohydrates and glycosides because of its greater chemical shift dispersion and lack of complexities arising from spin-spin coupling and overlapping resonances with those arising from solvents. In contrast to rather crowded and poorly resolved ^{1}H NMR spectrum, the ^{13}C NMR spectrum is usually well resolved and has few overlapping lines and therefore is comparatively easy to interpret. The anomeric signals for carbon appear in the region 90-110 ppm in the case of O-glycosides[21]. In the case of C-glycosides which are the monomeric signal for carbon appears in the chemical shift range of 70-80 ppm. The appearance of anomeric resonances in a well separated chemical shift range of 90-112 ppm help greatly in determining the number of O-linked monosaccharides. The C-1 resonances of a reducing hexose absorbs at 5-10 ppm upfield relative to the chemical shift of C-1 glycosidic residue. The C-1 of reducing end residue appears in the region 90-98 ppm and other non-reducing monosaccharide units appear at 98-112 ppm[21]. The rest of methine and methylene resonances absorb between 51-

86 ppm. The appearance of methine resonances between 52-57 ppm[44] is generally associated with amino substituted carbon signals at an amino sugar residue. Low field absorption in the region 170-176 ppm[45] reflects the presence of a carboxylic group of hexapyranoic acids or the carbonyl group of acetamido sugars. The presence of an acetaamido sugar may further be complemented by the appearance of methyl resonances in the region 20-24 ppm. The spectral region between 57-64 ppm[51] contains signals for all the unsubstituted hydroxy methylene resonances C-6, whereas methyl resonances of 6-deoxy sugars generally appear in the region 16-19 ppm[46-47].

Since naturally occurring monosaccharides are generally hexoses or pentoses therefore, each hexose and pentose unit introduces either six or five resonances, respectively. Accordingly in a well-resolved ^{13}C NMR spectrum, in most cases the number of monosaccharide residues can be easily ascertained by simply dividing the total number of signal absorbing between 60-85 ppm either by five or four or by combination of both. In a hexose monosaccharide besides the anomeric signal it give rise to five resonances whereas in case of 6-deoxy hexose and pentose it give rise to four resonances in the above mentioned chemical shift range[22]. The coupling pattern for GalNAc and GlcNAc in ^{1}H NMR is similar to Gal and Glc respectively but in ^{13}C NMR an upfield shift of $\delta_{C2\alpha}$55.4, $\delta_{C2\beta}$~58ppm for GlcNAc and an upfield shift of $\delta_{C2\alpha}$~51.4, $\delta_{C2\beta}$~54.9ppm for GalNAc has been reported. In the chemical shift analogy method the chemical shifts of carbon atoms in identical residues of similar oligosaccharide structure will be influenced only by glycosylation shifts, primarily by the δ shift (approximately 8 ppm downfield) for a substituted carbon atom and secondarily by the β shift (1-2 ppm upfield) for those carbon atoms adjacent to the linkage position. The ^{13}C chemical shift reveals the anomeric configuration in a manner similar to the proton chemical shift but most importantly the one bond ^{13}C-^{1}H coupling constant in pyranoses can be used to determine the anomeric configuration. For D sugars in the $^{4}C_{1}$ conformation a $J_{C1,H1}$~170 indicates an α-anomeric sugar whereas $J_{C1,H1}$~160 indicates an β-anomeric sugar configuration[48].

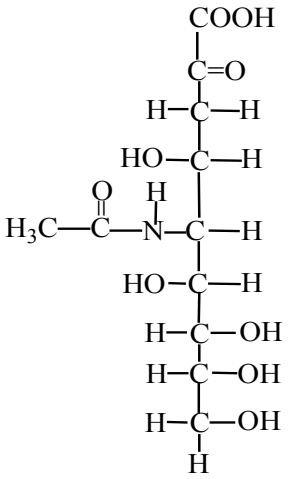
NMR library

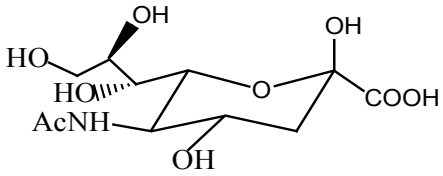
Carbohydrates form an important family of biomolecules as simple or complex carbohydrates; they play a significant role in biological recognition processes, in development of diseases and in many important areas of food and technical industry. More recently, role of carbohydrates in biological events has been recognized in glycobiology, which has emerged as a new and challenging area of research at the interface of biology and chemistry. This upcoming field of glycobiology mainly concentrates on the biological specificities of various moieties containing carbohydrates in them i.e. glycoconjugates, oligosaccharides, avermectins, anthraycyclins, macrolide antibiotics etc. The glycoconjugates, present at the cell surface display diversity in glycosydation pattern between species, which appear to be driven by evolutionary selection pressure. Further oligosaccharides are known to play structural and physical roles but are recognized specifically by lectin receptors. Of special interest of the carbohydrate mediated recognition events that play a role in important biological phenomenon involving cell-cell interaction such as fertilization, bacterial infection, inflammatory processes cell growth etc. Moreover the role of carbohydrates and carbohydrate containing moieties are increasing day by day. They are being used as antibiotics, anti cancer, anti tumor and anti-inflammatory agentsand provide lead for most of these diseases, and are found to be natural in origin. The function of glycan part of these biomolecules and their detailed mechanism are still poorly

^{13}C NMR data of common glycopyranoses of oligosaccharide found in milk[21]

Sugar	C-1	C-2	C-3	C-4	C-5	C-6	MeCONH
β-D-Glc	96.8	75.2	76.7	70.7	76.7	61.8	-
α-D-Glc	93.0	72.4	73.7	70.7	72.3	61.8	-
β-D-Gal	97.4	72.9	73.8	69.7	75.9	61.8	-
α-D-Gal	93.2	69.3	70.1	70.3	71.3	62.0	-
β-L-Fuc	97.2	72.7	73.9	72.4	71.6	16.3	-
α-L-Fuc	93.1	69.1	70.3	72.8	67.1	16.3	-
β-D-GlcNAc	95.9	57.9	74.8	71.1	76.8	61.9	23.1,175.5
α-D-GlcNAc	91.8	55.0	71.7	71.3	72.5	61.8	22.9,175.1
β-D-GalNAc	96.3	54.8	72.0	68.9	76.0	61.9	23.1,175.8
α-D-GalNAc	92.0	51.2	68.4	69.6	71.4	62.1	22.9,175.4

The presence of sialic acid residue could also be well determined by ^{13}C NMR spectroscopy. The anomeric signals (C-2) appear at δ 100-101 ppm while signal for –COOH group appears at δ 174 ppm. The other characteristic signals of sialic acid are as below-





N-acetyl Neuraminic acid[49]
(5-amino-3,5-dideoxy-D-glycero-D-galacto-2-nonulosonic acid)

^{13}C and ^{1}H NMR values of Sialic acid residue found in Milk[49]

Sialic acid residue	^{1}H Chemical Shift	^{13}C Chemical Shift
α- Neuraminic- 5Ac 1	-	174.0-174.6
2	-	100.2-101.0
3 ax	1.693-1.801	40.5-41.0
3 eq	2.668-2.762	-
4	3.56-3.68	69.0-69.3
5	3.79-3.85	52.5-52.7
6	3.63-3.71	73.3-73.7
7	3.55-3.65	69.0-69.3
8	3.86-3.90	72.5-72.7
9	3.64	63.3-63.9
9’	3.87-3.88	-
C=O	-	175.7-175.8
CH_3	22.8-22.9	2.025-2.038

understood. For better understanding of the mechanism of these molecules, it is necessary to have the three dimensional structure of these glycans. Till date the researches do not have any sufficient method available, which facilitates stepwise structural assignment of carbohydrates. However, for the structural assignment of these biologically important molecules Nuclear Magnetic Resonance is the only non-invasive, successful and powerful direct experimentation method. The only limitation of this experimentation is the limited range of chemical shifts of proton and carbons of various monosaccharides in their spectra. Although a number of two and three dimensional spectral experimentation have been developed for relieving the structural complexity of these molecules but no detailed and comprehensive library of the chemical shifts and other related data of monosaccharide units present in the oligosaccharides moiety are available. A minute change in the structure of oligosaccharide (i.e. anomeric configuration, linkage, sequence and position of appended groups) causes a marked difference in the chemical shift of involved carbon and proton of that monosaccharide unit in the oligosaccharide. To overcome these problems a NMR library of oligosaccharides, has been developed which covers the data of monosaccharides, disaccharides, trisaccharides and up to oligosaccharide level. Besides, the NMR data of known oligosaccharides which was being generated from the structure of various oligosaccharides isolated from various sources, various monosaccharides i.e. glucose, mannose, rhamnose, fucose etc. have also been taken and their mono substituted derivatives at various positions (1 to 6) have been synthesized and have been collected in tabular form. Further, utilization of various ^{1}H and ^{13}C chemical shifts with respect to linkages and sequence, an algorithm will be developed which would help

in precise prediction of the chemical shifts in oligosaccharides. The ^{1}H NMR data which is available in the literature and procured from synthetic compounds and natural products has been compiled in the following tables.

Results obtained from the Oligoglycosides isolated from Plants

The glycon moieties present in the pregnane derivative gave the characteristics splitting pattern and coupling constants of anomeric proton thus revealing the configuration of glycosidic linkage and also the size and conformation of monosaccharides. The anomeric protons of α-glycosides usually resonate 0.3-0.5 ppm downfield from those

^{1}H Chemical shifts and coupling constant of D-aldohexoses[50]

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-6'
D-Hexopyranoses							
α-glucose	5.09 (J=3.6)	3.41 (J=9.5)	3.61 (J=9.5)	3.29 (J=9.5)	3.72	3.72 (J=2.8)	3.63 (J=5.7, 12.8)
β-glucose	4.51 (J=7.8)	3.13 (J=9.5)	3.37 (J=9.5)	3.30 (J=9.5)	3.35	3.75 (J=2.8)	3.60 (J=5.7, 12.8)
α-galactose	5.16 (J=3.8)	3.72 (J=10.0)	3.77 (J=3.8)	3.90 (J=1.0)	4.00	3.70 (J=6.4)	3.62 (J=6.4)
β-galactose	4.48 (J=8.0)	3.41 (J=10.0)	3.56 (J=3.8)	3.84 (J=1.0)	3.61	3.70 (J=3.8)	3.62 (J=7.8)
α-mannose	5.05 (J=1.8)	3.79 (J=3.8)	3.72 (J=10.0)	3.52 (J=9.8)	3.70	3.74 (J=2.8)	3.63 (J=6.8, 12.2)
β-mannose	4.77 (J=1.5)	3.85 (J=3.8)	3.53 (J=10.0)	3.44 (J=9.8)	3.25	3.74 (J=2.8)	3.60 (J=6.8, 12.2)
β-allose	4.76 (J=8.5)	3.30 (J=3.3)	4.05 (J=3.2)	3.51 (J=9.5)	3.66	3.76 (J=2.4)	3.57 (J=6.0, 12.8)
β-gulose	4.76 (J=8.3)	3.52 (J=3.6)	3.95 (J=3.6)	3.70 (J=0.8)	3.92	3.62 (J=6.0)	3.58 (J=6.0)

^{1}H Chemical shifts and coupling constant of D-aldopentoses[51-53]

Compound	H-1	H-2	H-3	H-4	H-5a	H-5e
D- Pentopyranoses						
β-xylose	4.47 (J=7.8)	3.14 (J=9.2)	3.33 (J=9.0)	3.51	3.82 (J=5.6)	3.22 (J=10.5, 11.4)
α-xylose	5.09 (J=3.6)	3.42 (J=9.0)	3.48 (J=9.0)	3.52	3.58 (J=7.5)	3.57 (J=7.5)
β-arabinose	5.12 (J=3.6)	3.70 (J=9.3)	3.77 (J=9.8)	3.89	3.54 (J=2.5)	3.91 (J=1.7, 13.5)
α-arabinose	4.40 (J=7.8)	3.40 (J=9.8)	3.55 (J=3.6)	3.83	3.78 (J=1.8)	3.57 (J=1.3, 13.0)
β-ribose	4.75 (J=2.1)	3.71 (J=3.0)	3.83 (J=3.0)	3.77	3.82 (J=5.3)	3.50 (J=2.6, 12.4)
α-ribose	4.81 (J=6.5)	3.41 (J=3.3)	3.98 (J=3.2)	3.77	3.72 (J=4.4)	3.57 (J=8.8, 11.4)
β-lyxose	4.89 (J=4.9)	3.69 (J=3.6)	3.78 (J=7.8)	3.73	3.71 (J=3.8)	3.58 (J=7.2, 12.1)
α-lyxose	4.74 (J=1.1)	3.81 (J=2.7)	3.53 (J=8.5)		3.84 (J=5.1)	3.15 (J=9.1, 11.7)

^{1}H Chemical shifts and coupling constant for methyl-D-pentosides[54-56]

Compound	H-1	H-2	H-3	H-4	H-5e	H-5a	OMe
D-pentopyranosides							
α-arabinose	4.16 (J=8.0)	3.43 (J=10.0)	3.57 (J=3.9)	3.85	3.82 (J=2.8, 13.8)	3.57 (J=1.0)	3.44
β-arabinose	4.72 (J=2.8)	3.74 (J=10.0)	3.72 (J=3.0)	3.89	3.55 (J=2.3, 13.0)	3.77 (J=1.0)	3.30
α-lyxose	4.58 (J=3.2)	3.77 (J=3.8)	3.68 (J=4.0)	3.76	3.69 (J=4.8, 12.0)	3.42 (J=9.0)	3.32
β-lyxose	4.51 (J=2.2)	3.14 (J=3.8)	3.60 (J=7.5)	3.75	3.89 (J=4.0, 12.5)	3.23 (J=7.5)	3.37
α-ribose	4.51 (J=3.0)	3.70 (J=3.2)	3.86 (J=3.2)	3.72	3.47	3.68	3.35
β-ribose	4.52 (J=5.1)	3.51 (J=3.4)	3.91 (J=3.4)	3.79	3.74 (J=3.5, 12.5)	3.61 (J=7.0)	3.37
α-xylose	4.67 (J=3.4)	3.44 (J=10.0)	3.53	3.47	3.59 (J=5.0, 11.0)	3.39 (J=11.0)	3.30
β-xylose	4.21 (J=7.9)	3.14 (J=9.5)	3.33 (J=9.5)	3.51	3.88 (J=5.5, 12.3)	3.21 (J=11.0)	3.44

^{13}C chemical shifts for Aldoses[57]

D-Hexopyranoses						
Compound	**C-1**	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**
α-Allose	93.7	67.9	72.0	66.9	67.7	61.6
β-Allose	94.3	72.2	72.0	67.7	74.4	62.1
α-Altrose	94.7	71.2	71.1	66.0	72.0	61.6
β-Altrose	92.6	71.6	71.3	65.2	75.0	62.5
α-Galactose	93.2	69.4	70.2	70.3	71.4	62.2
β-Glactose	97.3	72.9	73.8	69.7	76.0	62.0
α-Glucose	92.9	72.5	73.8	70.6	72.3	61.6
β-Glucose	96.7	75.1	76.7	70.6	76.8	61.7
α-Gulose	93.6	65.5	71.6	70.2	67.2	61.7
β-Gulose	94.6	69.9	72.0	70.2	74.6	61.8
α-Idose	93.2	73.6	72.7	72.6	73.6	59.4
β-Idose	93.9	71.1	68.8	70.6	75.6	62.1
α-Mannose	95.0	71.7	71.3	68.0	73.4	62.1
β-Mannose	94.6	72.3	74.1	67.8	77.2	62.1
α-Talose	95.5	71.7	70.6	66.0	72.0	62.4
β-Talose	95.0	72.5	69.6	69.4	76.5	62.2

D-Pentoopyranoses	**C-1**	**C-2**	**C-3**	**C-4**	**C-5**
α-Arabinose	97.6	72.9	73.5	69.6	67.2
β-Arabinose	93.4	69.5	69.5	69.5	63.4
α-Lyxose	94.9	71.0	71.4	68.4	63.9
β-Lyxose	95.0	70.9	73.5	67.4	65.0
α-Ribose	94.3	70.8	70.1	68.1	63.8
β-Ribose	94.7	71.8	69.7	68.2	63.8
α-Xylose	93.1	72.5	73.9	70.4	61.9
β-Xylose	97.5	75.1	76.8	70.2	66.1

D-Pentopyranosides	C-1	C-2	C-3	C-4	C-5	OMe
α-Arabinose	107.0	73.9	75.6	71.5	69.3	60.0
β-Arabinose	103.0	72.1	70.1	71.4	65.7	58.1
α-Lyxose	102.0	70.4	71.6	67.4	63.3	55.9
α –Ribose	100.4	69.2	70.4	67.4	60.8	56.7
β –Ribose	103.1	71.0	68.6	68.6	63.9	57.0
α –Xylose	100.6	72.3	74.3	70.4	62.0	56.0
β –Xylose	105.1	74.0	76.9	70.4	66.3	58.3

^{1}H NMR Data for Monosaccharide derivatives (Synthetic)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Allyl 2-3-di-O-benzoyl -α-D-glucopyranoside	δ 5.21 d $J_{1,2}$=3.6 Hz	δ 5.26-5.19 m	δ 5.69 t $J_{2,3,4}$= 9 Hz	δ 3.92-3.84 m	δ 3.92-3.84 m	δ 3.92-3.84 m	7.92 (d, 4H, J=6Hz, Ph-H) δ7.46 (t, J = 6 Hz, Ph-H) δ7.31(t, J = 6 Hz, Ph-H) δ5.83-5.73 (m, -OHC$_2$-CH=CH$_2$) δ5.26-5.19 (m, -OHCH$_2$-CH=CH$_2$) δ5.09 (d, J=10 Hz, -OCH-CH=CH$_2$) δ4.18 (dd, J = 10 Hz, -OCH$_2$-CH=CH$_2$) δ3.97(dd, J=6Hz, OCH$_2$-CH=CH$_2$)
Allyl 2-3-di-O-benzoyl -β-D-glucopyranoside	δ 4.78 d $J_{1,2}$=8Hz	δ 5.42 t $J_{2,3,4}$=9 Hz	δ 5.47 t $J_{2,3,4}$= 9 Hz	δ 4.01 t $J_{3,4,5}$=9 Hz	δ 3.62-3.56 m	δ 3.92 dd J = 3 Hz J = 12 Hz δ 3.95 m	δ7.98 (d, J=6 Hz, Ph-H) δ7.53 (t, J = 7 Hz, Ph-H) δ7.38 (t, J = 7 Hz, Ph-H) δ5.84-5.74 (m, -OHC$_2$-CH=CH$_2$) δ5.26-5.19 (m, -OCH$_2$-CH=CH$_2$) δ5.28-5.12 (m, , -OCH-CH=CH$_2$) δ4.37-4.16 (2dd, J = 6 Hz, -OCH$_2$-CH=CH$_2$)
Allyl 2-3-di-O-methyl -6-O-trityl-α-D-glucopyranoside	δ 5.03 d $J_{1,2}$=3Hz	δ 3.25 dd $J_{2,3}$=9 Hz	δ 3.52 t $J_{2,3,4}$= 9 Hz	δ 3.48 t $J_{3,4,5}$=9 Hz	δ 3.90-3.84 m	δ 3.38-3.33 m (2H)	7.47 (d, J = 6 Hz, Ph-H) δ7.36-7.23 (m, 13H, Ph-H) δ6.04-5.19 (m, -OCH2-CH=CH$_2$) δ5.39-5.22 (m, -OHC$_2$-CH=CH$_2$) δ4.23-4.09 (2dd, J = 6 & 12H, -OCH$_2$-CH=CH$_2$) δ3.63, 3.50 (2s, 6H, MeO)
Allyl 4-O-acetyl-2,3-di-O-methyl -6-O-trityl-α-D-glucopyranoside	δ 5.09 d $J_{1,2}$=3Hz	δ 3.36 dd $J_{2,3}$=9 Hz	δ 3.57 t $J_{2,3,4}$= 9 Hz	δ 4.88 t $J_{3,4,5}$=9 Hz	δ 3.92-3.84 m	δ 3.11-3.05 m (2H)	7.46 (d, 6H, J = 6 Hz, Ph-H) δ7.30 (t, 7H, J = 7 Hz, Ph-H) δ7.22 (d, 2H, J = 7 Hz, Ph-H) δ6.08-5.97 (m, 1H –OCH$_2$-CH=CH$_2$) δ5.42-5.24 (m, 2H, -OCH$_2$-CH=CH$_2$) δ4.34-4.28 (2dd, J = 6 & 12 Hz, -OCH$_2$ –CH=CH$_2$) δ3.54, 3.50 (2s, 6H, 2MeO)
Allyl 6-O-acetyl-2,3-di-O-methyl -α-D-glucopyranoside	δ 5.03 d $J_{1,2}$=3Hz	δ 3.26 dd $J_{2,3}$=3 & 9 Hz	δ 3.41 t $J_{2,3,4}$= 9 Hz	δ 3.40 m $J_{3,4,5}$ =9 Hz	δ 3.85-3.80 m	δ 4.22-4.19 m δ 4.25 dd J=2 & 12Hz	δ6.01-5.90 (m, -OCH$_2$-CH=CH$_2$) δ5.38-5.23 (m, -OCH$_2$-CH=CH$_2$) δ4.48 (dd, J = 6 & 12 Hz, -OCH$_2$ –CH=CH$_2$) δ4.10 (dd,-OCH$_2$-CH=CH$_2$) δ2.13 (s, 3H, AcO)
Allyl 2,3,6-tri-O-acetyl -α-D-glucopyranoside	δ 4.98 d $J_{1,2}$=4Hz	δ 4.78 dd $J_{2,3}$= 9 Hz	δ 5.30-5.14 m	δ 3.50 t $J_{3,4,5}$= 9.5 Hz	δ 3.85-3.81 m	δ 3.99-3.92 m δ 4.22 dd J=3.5Hz	5.87-5.77 (m, -OCH$_2$-CH=CH$_2$) δ5.30-5.14 (m, -OCH$_2$-CH=CH$_2$) δ4.39 (dd, J = 6 Hz, -OCH$_2$ –CH=CH$_2$) δ4.12 (dd, J = 6 Hz, -OCH$_2$-CH=CH$_2$) δ2.08, 2.05, 2.02 (s, 9H, AcO)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Methyl 4,6,-O-benzylidene-2-deoxy-α-D-glucopyranoside	δ 4.813 d J=3.3Hz	δ1.845 dd δ 2.173 dd	δ 4.114 m	δ 3.487 t J = 9.9 Hz	δ 3.800 m	δ 4.173 m δ 4.114 m	3.358 s (3H) OMe δ 7.389 m (5H) C_6H_5 δ 5.582 s (1H) CH C_6H_5
Methyl 3-O-acetyl 4-6-O- benzylidene-2-deoxy-α-D-glucopyranoside	δ 4.810 d J=3.1Hz	δ1.829 dd δ 2.25 dd	δ 4.26 m	δ 4.493 t J = 9.3 Hz	δ 3.756 m	δ 4.283 m δ 4.261 m	5.581 s (1H) CH C_6H_5 δ 7.378 m (5H) C_6H_5 δ 3.357 s (3H) OMe δ 2.01 s (3H) OAc
Methyl 3-O-acetyl -6-O-benzylidene-2-deoxy-α-D-glucopyranoside	δ 4.811 d J=3.3Hz	δ2.228 dd δ1.830 dd	δ 4.198 m	δ 3.485 t J = 9.0 Hz	δ 3.798 m	δ 4.248 m δ 4.260 m	3.357 s (3H) OMe δ 2.009 s (3H) OAc δ 7.488 m (5H)C_6H_5 δ 4.162 d $\underline{CH_2}C_6H_5$, J = 12.1 Hz
Methyl 6-O-trityl -2-deoxy-α-D-glucophyranoside	δ 4.178 d J=3.3Hz	δ2.041 dd δ2.253 dd	δ 3.882 m	δ 3.39 t J = 9.6 Hz	δ 3.471 m	δ 3.943 m δ 3.882 m	3.30 s (3H) OMe δ 7.175 m (15H) C_6H_5
Methyl 3,4-Di-O-acetyl-6-O- trityl -2-deoxy-α-D-glucopyranoside	δ 4.178 d J=3.3Hz	δ2.041 m δ2.253 dd	δ 4.406 m	δ 4.381 t J = 9.6 Hz	δ 3.469 m	δ 3.945 m δ 4.082 M	3.30 s (3H) OMe δ 7.175 m (15H) C_6H_5
Methyl 3,4-di-O-acetyl-6-O-trityl -2-deoxy-α-D-glucopyranoside	δ 4.850 d J=3Hz	δ1.821 dd δ2.265 dd	δ 5.313 m	δ 5.003 t J = 9.9 Hz	δ 3.959 m	δ 3.093 dd δ 4.319 dd	2.098 s (3H) OAc δ 2.039 s (3H) OAc δ 3.354 s (3H) OMe

Compound name	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Allyl 4,6,-O-benzylidene-2,3-di-O-methyl-α-D-glucopyranoside	δ 5.01 d $J_{1,2}$=3.7Hz $J_{2,3}$ = 9.1Hz	δ 3.32 dd $J_{1,2}$=3.7Hz	δ 3.52 t $J_{2,3,4}$= 9.4Hz	δ 3.75-3.68 m (2H)	δ 3.88-3.83 m (1H)	δ 3.75-3.68 m δ 4.28 dd J = 4.7 & 12 Hz	δ 6.02-5.95 (m, - OCH_2-$\underline{C}H$=CH_2) δ 5.38-5.26 (m, OCH_2-CH=$\underline{C}H_2$) δ 4.25-4.20 (m, - O$\underline{C}H_2$-CH=CH_2) δ 4.08 (dd, - O$\underline{C}H_2$-CH=CH_2) δ 3.64, 3.53 (2s, 6H, 2Meo) δ 5.55 (s, CH-C_6H_5) δ 7.51-7.35 (m, 5H, Ph-H)
Allyl 4,6,-O-benzylidene-2,3-di-O-methyl-β-D-glucopyranoside	δ 4.46 d $J_{1,2}$=7.6Hz	δ 3.15 t $J_{1,2,3}$= 9 Hz	δ 3.43-3.32 m (2H)	δ 3.58 t $J_{3,4,5}$=9.6 Hz	δ 3.43-3.32 m (2H)	δ 3.85-3.73 m (2H)	6.02-5.87 (m, -OCH_2-$\underline{C}H$=CH_2) δ 5.40-5.16 (m, 2H, OCH_2-CH=$\underline{C}H_2$) δ 4.35 (dd, J = 5.9 Hz, -O$\underline{C}H_2$-CH=CH_2) δ 4.15 (dd, J = 6 Hz, -O$\underline{C}H_2$-CH=CH_2) δ 5.54 (s, -CH-C_6H_5) δ 7.51-7.31 (m, 5H, Ph-H) δ 3.64-3.62 (2s, 6H, 2MeO)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6/6′	Appended group's proton
Allyl 2-3-di-O-benzoyl-4-6-O-benzylidene-α-D-glucopyranoside	δ 5.20 d $J_{1,2}$=3.5 Hz	δ 5.31 dd $J_{1,2}$=3.5 Hz	δ 5.74 t $J_{2,3,4}$ = 9 Hz	δ 4.31 t $J_{3,4,5}$=9 Hz	δ 3.98 m	δ 4.37 dd J = 3 Hz J = 12 Hz δ 4.11-4.08 m	δ7.96 (d, 4H, J=6Hz, Ph-H) δ7.56 (m, 7H, Ph-H) δ7.32 (t, J = 6 Hz, Ph-H) δ5.84-5.72 (m, -OCH2-CH=CH_2) δ5.55 (s,1H, -CH, C_6H_5) δ5.92-4.92 (m,2H,-OCH2-CH=CH_2) δ4.46-4.13 (2dd, J=6, -OCH_2-CH=CH_2)
Allyl 2-3-di-O-benzoyl-4-6-O-benzylidene-β-D-glucopyranoside	δ 4.86 d $J_{1,2}$=7.8 Hz	δ 5.51 dd $J_{1,2}$=8 Hz $J_{2,3}$=9 Hz	δ 5.79 t $J_{2,3,4}$ = 9.4 Hz	δ 3.99-3.67 m	δ 3.75-3.80 m (1H)	δ 3.99-3.80 m δ 4.42-4.33 m (2H)	δ8.12 (d, 6H, J=7Hz, Ph-H) δ7.96 (d, J = 7 Hz, Ph-H) δ7.62 (t, J = 7.6 Hz, Ph-H) δ7.45 (t, 4H, J=7.4 Hz, Ph-H) δ7.42 (m, 2H, Ph-H) δ5.77 (m, 1H,-OCH2-CH=CH_2) δ5.55 (s, 1H, -CH-C_6H_5) δ5.28-5.11 (m, 2H, -OCH_2-CH=CH_2) δ4.42-4.33 (m,2H, -OCH_2-CH=CH_2)
1,2; 5, 6-Di-O-isopropylidene α-D-glucofuranose	δ 4.93 d $J_{1,2}$=3.6 Hz	δ 4.52 d J= 3.6 Hz	δ 4.35-4.31 m (2H)	δ 4.06 dd J=3.7 & 6.5 Hz	δ 4.35-4.31 m (2H)	δ 4.16 d J = 6.2 & 8.5 Hz	δ 1.49, 1.44, 1.36, 1.31 (4s, 12H, 4Me)
1,2, 5, 6-Di-O-isopropylidene-3-O-methyl-α-D-glucofuranose	δ 5.86 d $J_{1,2}$=3.5 Hz	δ 4.56 d J= 3.6 Hz	δ 3.78 d J = 3 Hz	δ 4.12-4.06 m (2H)	δ 4.02 dd J = 6 Hz J = 8 Hz	δ 4.33-4.26 (m, 1H) δ 4.12-4.06 (m, 2H)	δ 3.45 (s, 3H, MeO) δ1.49, 1.43, 1.38, 1.32 (4s, 12H, 4Me)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
1,2-O-Isopropylidene-α-D-glucofuranose	δ 5.84 d $J_{1,2}$=3.7Hz	δ 4.46 d J=3.6 Hz	δ4.22 d J = 2.7 Hz	δ3.78-3.68 m (2H)	δ 3.61-3.53 m	δ3.78-3.68 M δ4.01 dd J -7.6 Hz	1.39, 1.25 (2s, 6H, 2Me)
1,2-O-Isopropylidene-3,5,6-tri-O-methyl-α-D-glucofuranose	δ 5.87 d $J_{1,2}$=3.5Hz	δ 4.55 d J=3.5 Hz	δ3.78 d J = 3.1Hz	δ3.51 t J = 5.1 Hz	δ 3.64-3.58 m	δ3.75 dd J = 2 & 11 Hz δ4.12 dd J = 9.7 Hz	δ3.48, 3.45, 3.39 (3s, 9H, MeO) δ1.48, 1.32 (2s, 6H, 2Me)
3,4,5-Tri-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose	δ 5.91 d $J_{1,2}$=3.5Hz	δ 4.61 J=3 Hz	δ4.12 d J = 3Hz	δ3.72-3.67 m J = 3 Hz	δ 4.10-4.04 m	δ3.95-3.89 m δ4.31 dd J = 9 Hz	7.45-7.27 (m, 15H, Ph-H) δ4.83, 4.50 (2d, 2H,-CH_2-C_6H_5) δ4.72-4.52 (m, 2H,-CH_2-C_6H_5) δ4.60 (s, -CH_2-C_6H_5) δ1.51, 1.32 (2s, 6H, 2Me)

Compound name	**H-1**	**H-2**	**H-3**	**H-4**	**H-5**	**H-6/6/**	**Appended group's proton**
Allyl-α-D-mannopyranoside	δ 4.62 d $J_{1,2}$ = 1 Hz	δ 3.38 dd $J_{1,2}$ = 1 Hz $J_{2,3}$ = 2.4 Hz	δ 3.46-3.41 m 2 Hz	δ 3.28-3.22 m	δ 3.16-3.41 m 2H	δ 3.69-3.58 m 2H	5.96 – 5.83 (m, 1H, -OCH_2-C<u>H</u>-CH_2) δ 5.26 – 5.11 (m, 2H, -OCH_2-CH = <u>C</u>H_2) δ 4.10 (dd, 1H, J = 4.9 & 12 Hz - O<u>C</u>H_2-CH=CH_2) δ 3.90 (dd, 1H, J = 5.7 & 13.3 – O<u>C</u>H_2-CH=CH_2)
Allyl 4,6-0-benzylidene-α-D-mannopyranoside	δ 4.92 s 1 Hz	δ 3.81 d $J_{2,3}$ = 2.6 Hz	δ 3.84 dd $J_{2,3}$ = 2.6 Hz $J_{3,4=}$ 8 Hz	δ 4..08-3.96 m 3H	δ 3.92-3.89 m 1H	δ 4.08-3.96 m 3H	5.99 – 5.86 (m, 1H, -OCH_2-<u>C</u>H-CH_2) δ 5.56 – 5.20 (m, 2H, -OCH_2-CH = <u>C</u>H_2) δ 4.32 – 4.16 (m, 2H, - O<u>C</u>H_2-CH=CH_2) δ 5.83 (s, 1H, – <u>C</u>H-C_6H_5) δ 7.53- 7.30 (m, -CH=Ph-H)
Allyl 2,3-0-benzylidene-α-D-mannopyranoside	δ 5.14 s	δ 3.91 d $J_{2,3}$ = 3.5 Hz	δ 4.06 dd $J_{2,3}$ = 3.5 Hz $J_{3,4=}$ 9 Hz	δ 3.76-3.70 m 2H	δ 3.76-3.76 m 2H	δ 4.22-4.14 m 2H	5.93 – 5.83 (m, 1H, -OCH_2-<u>C</u>H-CH_2) δ 5.34 – 5.19 (m, 2H, -OCH_2-CH = <u>C</u>H_2) δ 4.48 (dd, 1H, J= 5.5 & 12.8 -O<u>C</u>H_2-CH=CH_2) δ 4.23 (dd, 1H, J= 6.1 & 10.3 Hz – OCH_2-CH=CH_2) δ 7.46-7.26 (m, 5H, Ph-H)
Compound name	**H-1**	**H-2**	**H-3**	**H-4**	**H-5**	**H-6/6/**	**Appended group's proton**
Allyl 4,6-di-0-acetyl -2,3-0-benzylidene-α-D-mannopyranoside	δ 5.18 s 1H	δ 4.22-4.16 m 3H	δ 4.22-4.16 m 3H	δ 5-32-5.20 m 3H	δ 4.00-3.92 m 1H	δ 4.22-4.16 m δ 4.58 ($H\text{-}6^1$) dd J = 5.3 & 10 Hz	5.98 – 5.82 (m, 1H, -OCH_2-<u>C</u>H-CH_2) δ 5.32-5.20 (m, 3H, -OCH_2-CH = <u>C</u>H_2) δ 4.13-4.02 (m, 1H, -O<u>C</u>H_2- CH= CH_2) δ 6.21 (s, 1H, C<u>H</u>-C_6H_5) δ 7.46-7.31 (m, 5H, Ph-H) δ 2.119 – 2.114 (2s, 6H, 2AcO)
Allyl 4,6-di-0-acetyl -α-D-mannopyranoside		δ 3.98 d J = 2Hz	δ 3.96-3.91 m 1H	δ 5-04 t $J_{3,4,5}$=9 Hz	δ 4.05-4.00 m 1H	δ 4.12 dd J = 2 & 12 Hz δ 4.33 dd J = 12 Hz ($H\text{-}6^1$)	5.96 – 5.85 (m, 1H, -OCH_2-CH-CH_2) δ 5.33-5.21 (m, 2H, -OCH_2-CH = <u>C</u>H_2) δ 4.33 (33, 2H, -<u>O</u>CH_2- CH = CH_2) δ - 4.29 dd, 1H, -OCH_2-CH=CH_2 δ 2.14-2.10 (2s, 6H, 2AcO)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6/6′	Appended group's proton
Allyl 2,3-di-O-benzyl-4-6-O-benzylidene-α-D-mannopyranoside	δ 4.75 s	δ 3.85 d $J_{2,3}$ = 2 Hz	δ 4.02-3.86 m	δ 4.02-3.86 m	δ 4.02-3.86 m	δ 4.30-4.10 m	δ7.52-7.22 (m, 15H, Ph-H) δ5.93-5.76 (m, -OCH_2-$\underline{CH}$=CH_2) δ5.26-5.14 (m, OCH_2-$\underline{CH}$=CH_2) δ5.4.30-4.10 (m, 4H, -O$\underline{CH_2}$-CH=CH_2) δ5.65 (s, -$\underline{CH}$-C_6H_5) δ4.87 (m, 3H, -$\underline{CH_2}$, C_6H_5) δ4.69 (d, J = 6.3 Hz, -$\underline{CH_2}$-C_6H_5)
Allyl 2,3-di-O-benzyl-α-D-mannopyranoside	δ 4.90 s	δ 3.83 d $J_{2,3}$ = 2.5 Hz	δ 3.73-3.86 dd $J_{3,4}$ = 9 Hz	δ 4.01 t $J_{3,4,5}$=9 Hz	δ 3.68-3.63 m	δ 3.91-3.85 m δ 4.18 dd	δ7.38-7.28 (m, 10H, Ph-H) δ5.92-5.82 (m, -OCH_2-$\underline{CH}$=CH_2) δ5.28-5.18 (m, 2H, OCH_2-CH=$\underline{CH_2}$) δ4.67 (s, 2H, $\underline{CH_2}$-C_6H_5) δ4.18 (dd, 2H, -$\underline{OCH_2}$ –CH_2=CH_2) δ3.96 (dd, -O$\underline{CH_2}$-CH=CH_2) δ4.62, 4.48 (2d, J = 11 Hz, -CH_2-C_6H_5)
Allyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside	δ 5.06 s	δ 5.62 dd $J_{1,2}$ = 10 Hz $J_{2,3}$ = 3 Hz	δ 5.85 dd $J_{3,4}$= 10 Hz	δ 3.95 t $J_{3,4,5}$ = 10 Hz	δ 4.20-4.08 m (2H)	δ 4.20-4.08 m δ 4.40-4.25 m	δ8.10, 7.62 (2dd, 6H, J = 6 Hz, Ph-H) δ7.91 (d, J = 7 Hz, Ph-H) δ7.52-7.30 (m, 8H,Ph-H) δ5.68 (s, -$\underline{CH}$-C_6H_5) δ6.01-5.91 (m, -OCH_2 –$\underline{CH_2}$=CH_2) δ5.42-5.26 (m, 2H, -OCH_2-CH=$\underline{CH_2}$) δ4.40-4.25 (m, -O$\underline{CH_2}$-CH=CH_2)

Compound name	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Allyl 2,3-di-O-benzyl -α-D- mannopyranoside	δ 5.40 s	δ 5.64-5.57 m	δ 5.64-5.57 m	δ 4.37 t $J_{3,4,5}$ = 9 Hz	δ 3.93-3.87 m	δ 3.93-3.87 m	δ8.02, 7.92 (2d, 4H, J = 7 Hz, Ph-H) δ7.62, 7.35 (2t, 3H, Ph-H) δ7.50 (dd, 3H, J = 7Hz, Ph-H) δ6.01-5.90 (m, 2H, -OCH_2 –$\underline{CH}$-CH_2) δ5.34-5.24 (m, 2H, -OCH_2 –CH=$\underline{CH_2}$) δ4.28 (dd, J = 5 & 12Hz, -O$\underline{CH_2}$-CH=CH_2) δ4.09 (dd, J = 6 & 12 Hz, -OCH_2-CH=CH_2)
Allyl 6-0-Benzyl-2,3-di-O-methyl -α-D-mannopyranoside	δ 4.98 d $J_{1,2}$=1Hz	δ 3.63 dd $J_{2,3}$=3 Hz	δ3.58-3.51 m (2H)	δ3.84 t $J_{3,4,5}$ = 10 Hz	δ 3.58-3.51 m	δ 3.81-3.72 m (2H)	7.38-7.32 (m, 5H, Ph-H) δ5.98-5.83 (m, 1H, -OCH_2 –$\underline{CH}$-CH_2) δ5.34-5.19 (m, 2H, -OCH_2 –CH=$\underline{CH_2}$) δ4.62 (d, 2H, J = 6 Hz, –$\underline{CH_2}$-C_6H_5) δ4.23,4.01 (2dd, J = 12 Hz, -O$\underline{CH_2}$ –CH=CH_2) δ3.49 (s, 6H, 2 MeO)

Compound name	H-1	H-2	H-3	H-4	H-5	6-CH_3	OMe	Appended group's proton
Methyl-4-O-Acetyl-α-L-Rhamnopyranoside	δ 4.44 s 1H	δ 3.672 d J = 3Hz	δ 3.762 m 2H	δ 4.86 t J = 9.6Hz	δ 3.762 m 2H	δ 1.276 d J = 6 H	δ 3.56 s 3H	$\underline{OAc}$ δ 2.12 s 3H
Methyl-4=O=Acetyl-2,3-di-O-Benzoyl-α-L-Rhamnopyranoside	δ 4.857 s	δ 5.592 d J = 1.8Hz	δ 5.622 dd 2H J=3.3 & 6.3 Hz	δ 5.408 t J = 9.9 Hz	δ 4.032 m	δ 1.352 d J = 6.6Hz	δ 3.470 s	$\underline{OBz}$ δ 7.881 m
Methyl-2,3-Di –O-Benzoyl-α-L-Rhamno-Pyranoside	δ 4.833	δ 5.567 d J = 1.8Hz	δ 5.621 dd J=3.3 & 6.3	δ 3.899 t J = 9.9Hz	δ 4.032 m 1H	δ 1.322 d J = 6.1Hz	δ 3.461 s	$\underline{OBz}$ δ 7.881 M, 10H
Methyl-2-O-Acetyl-α-L-Fucopyranoside	δ 4.725 d J=3.3Hz	δ 4.859 dd J = 3 & 6.3Hz	δ 3.339 dd J=4.2 & 6.3Hz	δ 3.446 dd	δ 4.021 m	δ 1.336 d J = 6Hz (3H)	δ 3.441 s (3H)	$\underline{OAc}$ δ 2.01 s
Methyl-3,4-O-isopropylidene-α-L-Fucopyranoside	δ 4.716 d J=3.6Hz	δ 3.862 dd J = 3 & 6.6Hz	δ 3.839 dd J=4.2 & 6.3Hz	δ 4.046 dd	δ 4.021 m	δ 1.332 d J = 6.6Hz	δ 3.440 s	$\underline{CH_3}$ δ 1.357 s
Methyl-2,3-O-isopropylidene-α-L-Fucopyranoside	δ 4.85 s	δ 4.054 m	δ 4.14 m	δ 4.054 m	δ 3.651 m	δ 1.252 d J = 6.9	δ 3.390 s	$\underline{CH_3}$ δ 1.35 s

^{1}H NMR Data for Disaccharide derivatives (Synthetic)

Compound's name	S_1/S_2	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Acetyl 2,3,4, 6-tetra –O-acetyl -β-D-glucopyranosyl (1-6) -2,3,4-tri-O-acetyl -D-glucopyranoside	S_1	δ 5.413 d $J_{1,2}$ = 3.1 Hz	δ 5.17 dd J = 9.3 Hz	δ 5.452 bt J= 9.9 Hz	δ 4.994 bt J = 9.9 Hz	δ 3.802 m	δ 3.956 dd J=11.1, 5.4 Hz δ 3.584 dd J = 11.1 & 7.8 Hz	δ 2.006, 2.002, 2.028, 2.039, 2.079, 2.095, 2.114 (7s, 24H, 8OAc)
	S_2	δ 4.532 d J = 6.9Hz	δ 5.197 dd J = 8.1Hz	δ 5.197 2t J = 9.6 Hz	δ 5.197 2t J = 9.3 Hz	δ 3.681 m	δ 4.249, dd J 12.3, 7.8 Hz δ 4.140, dd J = 12.3, 4.8 Hz	
2,3,4, 6 -tetra –O-acetyl- -β-D-glucopyranosyl (1-6)-2,3,4-tri-O-acetyl -D-glucopyranose	S_1	δ 5.435 d $J_{1,2}$ = 3.1 Hz	δ 4.973 dd J = 9.6 Hz	δ 5.411 t J= 9.9 Hz	δ 5.128 bt J = 9.9 Hz	δ 3.873 m	δ 3.413, dd J=11.0, 5.4 Hz δ 3.601, dd J = 11.0, 7.8 Hz	δ 2.010, 2.032, 2.047, 2.072, 2.083, (7s, 21H, 7OAc)
	S_2	δ 4.5872 d J = 7.8Hz	δ 4.973 dd J = 8.1Hz	δ 5.188 2t J = 9.6 Hz	δ 5.188 2t J = 9.3 Hz	δ 3.711 m	δ 4.282, dd J 12.1, 7.5 Hz δ 4.173, dd J = 12.1, 4.5 Hz	

Compound name	S_1/S_2	H-1	H-2	H-3	H-4	H-5	H-6	Appended group's proton
Allyl 6-0-(2,3,4,-tri-O-acetyl-α-L-rhamnopyranosyl)-4-O-acetyl-2,3-di-O-methyl-β-D glucopyranoside	S_1	δ4.36 d $J_{1,2}$=8.5 Hz	δ 3.11 t $J_{1,2,3}$ = 9 Hz	δ 3.26 t $J_{2,3,4}$ = 9 Hz	δ 4.75 t $J_{3,4,5}$ = 9 Hz	δ 3.58-3.53 m	δ 3.58-3.53 m	δ 5.98 – 5.87 (m, -OHC$_2$-CH = CH$_2$) 5.37 – 5.32 (m, -OHC$_2$-CH = CH$_2$) δ 5.27-5.18 (m, 2H, -OCH$_2$-CH = CH$_2$) δ 4.33-4.11 (2dd, J= 6 & 12 Hz, -OCH$_2$-CH = CH$_2$) δ 3.59, 3.51 (2s, 6H, 2MeO) δ 2.13, 2.11, 2.04, 1.98 (4s, 12H, 4Aco) δ 1.21 (d, J = 6 Hz, Me-6′
	S_2	δ 4.83 s	δ 5.28 d $J_{2,3}$=2.5Hz	δ 5.27-5.18 m (2H)	δ 5.05 t $J_{3,4,5}$ = 9 Hz	δ 3.89-3.81 m	δ 3.64-3.61 m	
Allyl 6-0-(2,3,4-tri-0-acetyl-α-L-rhamnopyranosyl)-4-O-acetyl-2,3-di-O-benzoyl-α-D-glucopyranoside	S_1	δ 5.31 d $J_{1,2}$ = 3.5 Hz	δ 5.20 dd $J_{2,3}$ = 9 Hz	δ 6.00 t $J_{2,3,4}$ = 10 Hz	δ 5.09 T $J_{3,4,5}$ = 9 Hz	δ 3.68-3.62 m	δ 3.72-dd J = 3 & 12 Hz	δ7.98 (t, 4H, J = 7 Hz, Ph-H) δ7.60-7.35 (m, 6H, Ph-H) δ5.92 (m, -OCH$_2$-CH=CH$_2$) δ5.38-5.32 (m, 3H, -OCH$_2$-CH=CH$_2$) δ5.18-5.15 (m, -OCH$_2$-CH=CH$_2$) δ4.08 (dd, J = 6 Hz, 12 Hz, -OCH$_2$-CH=CH$_2$) δ1.25 (d, $J_{5,6}$ = 6 Hz, Me6') δ2.17, 2.07, 2.01, 1.98 (4s, 12H, 4AcO)
	S_2	δ 4.85 s	δ 5.30 d $J_{2,3}$ = 3 Hz	δ 5.38-5.32 m (3H)	δ 5.25 t $J_{1,2,3}$ = 9 Hz	δ 3.95-3.87 m	δ 4-22-4.15 m	

Compound name	S_1/S_2	H-1	H-2	H-3	H-4	H-5′	H-6	Appended group's proton
Allyl 6-0-(2,3,4,6-tetra-0-acetyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-D-glucopyranoside	S_1	δ 5.03 d $J_{1,2}$ = 3 Hz	δ 3.26 dd $J_{2,3}$ = 3 Hz	δ 3.53 t $J_{2,3,4}$ = 9 Hz	δ 3.39 t $J_{3,4,5}$ = 9 Hz	δ 3.85-4.05 m (2H)	δ 4.12 4.05 m (2H)	δ 6.01 – 5.92 (m, -OHC$_2$-CH =CH$_2$) δ 4.47 – 5.24 (m, 2H, -OHC$_2$-CH = CH$_2$) δ 4.47 (dd, J = 6 Hz –OCH$_2$-CH = CH$_2$) δ 3.65-3.49 (s, 3 Meo) δ 2.19, 2.13, 2.08 (3s, 12H, 4AcO)
	S_2	δ 4.25 d $J_{1,2}$ = 8.5 Hz	δ 1.13-4.03 m (5H)	δ 4.23-4.03 m (3H)	δ 5.52 t $J_{3,4,5}$ = 9 Hz	δ 3.85-3.71 m (2H)	δ 4.12-4.05 m δ 4.23-4.03 m	
Allyl 6-0-(2,3,4-tri-0-acetyl-α-L-rhamnopyranosyl)-2,3-di-O-benzoyl-α-D-glucopyranoside	S_1	δ 5.26 d $J_{1,2}$ = 3.5 Hz	δ 5.28 dd $J_{1,2}$ = 3.5 Hz $J_{2,3}$ = 9 Hz	δ 5.73 t $J_{2,3,4}$ = 9 Hz	δ 5.11 t $J_{3,4,5}$ = 9 Hz	δ 3.81-3.75 m	δ 4.11-3.86 m (4H)	δ8.00 (t, 3H, J = 6 Hz, Ph-H) δ7.52 (t, 2H, J = 7 Hz, Ph-H) δ7.38 (t, 5H, J = 7 Hz, Ph-H) δ5.93-5.82 (m, -OCH$_2$-CH=CH$_2$)
	S_2	δ 4.88 s	δ 5.39-5.31 m (3H)	δ 5.39-5.31 M (3H)	δ 3.88 t $J_{3,4,5}$ = 9 Hz	δ 4.11-3.86 m (4H)	δ 4.11-3.86 (4m)	δ5.39-5.31 (m, -OCH$_2$-CH=CH$_2$) δ5.20-5.15 (m, -OCH$_2$-CH=CH$_2$) δ4.28 (dd, J = 5.5 Hz, -OCH$_2$-CH=CH$_2$) δ1.24 (d, 3H, J = 6 Hz, Me6′) δ2.19, 2.11, 2.03 (3s, 9H, 3AcO)

Allyl 6-0-(2,3,4,6-tetra-0-acetyl-β-D-galactopyranosyl)-2,3-di-O-methyl-α-D-mannopyranoside	S_1	δ4.95 s	δ 3.65 d $J_{2,3}$ = 2.5 Hz	δ 3.79-3.72 m	δ 3.93 t $J_{3,4,5}$ = 9 Hz	δ 3.79-3.72 m	δ 4.24-4.12 m	5.97 – 5.85 (m, -OHC$_2$-CH =CH$_2$) δ 5.37 – 5.28 (m, 2H, -OHC$_2$-CH = CH$_2$) δ 4.3` (dd, J = 6 Hz –OCH$_2$-CH = CH$_2$) δ 3.49, 3.48 (s, 6H, 3Meo) δ 2.21, 2.17, 2.08, 2.06 (4s, 12H, 4AcO)
	S_2	4.60 d $J_{1,'2'}$ = 8.6 Hz	δ 5.25 t $J_{1,2',3'}$=9Hz	δ 5.03 dd $J_{2',3}$=10Hz	δ 5.39 d $J_{3,'4'}$ = 3.5 Hz	δ 4.01-3.96 m	δ 4.24-4.12 m	
Allyl 6-0-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-4-O-di-acetyl-2,3-di-O-methyl-α-D-mannopyranoside	S_1	4.92 d $J_{1,2}$ = 1 Hz	δ 3.48 dd $J_{2,3}$ = 2 Hz	δ 3.58 dd $J_{3,4}$ = 9 Hz	δ 4.32 t $J_{3,4,5}$ = 9 Hz	δ 3.91-3.81 m	δ 3.62 dd J = 2 & 12 Hz	5.95-5.77 (m, -OHC$_2$-CH-CH$_2$) δ 5.38-5.32 (m , -OHC$_2$-CH = CH$_2$) δ 5.07 -4.95 (m, 2H, -OCH$_2$-CH = CH$_2$) δ 3.96 (dd, J = 6 & 1 Hz, -OCH$_2$,-CH =CH$_2$) δ 3.53, 3.43 (2s, 6H, 2MeO) δ 2.15, 2.08, 2.05, 1.98 (5s, 15H, 5AcO)
	S_2	4.53 d $J_{1,2}$=8.5 Hz	δ 5.24 t $J_{1,2,3}$=9Hz	δ 5.07-4.95 m	δ 5.39 d	δ 4.22-4.08 m	δ 4.22-4.08 m	

Allyl 6-0-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,-di-O-benzyl-α-D-mannopyranoside	S_1	δ4.92 d $J_{1,2}$=1.5 Hz	δ 3.83 d $J_{2,3}$ = 2.5 Hz	δ 3.78-3.70 m	δ 3.92 t $J_{3,4,5}$ = 9 Hz	δ 3.78-3.70 m	δ 4.24-4.12 m	δ 7.37 – 7.29 (m, 10H, Ph-H) 5.94 - 5.82 (m, -OHC_2-$\underline{CH}$ = CH_2) δ 5.21 – 5.09 (m, 2H, -OCH_2-CH = $\underline{CH_2}$) δ 4.72 -4.60 (m, 3H, $\underline{CH_2}$-C_6H_5) δ 4.52-4.44 (m, 1H, $\underline{CH_2}$-C_6H_5) δ 4.24-4.12 (m, -$\underline{OCH_2}$-CH=CH_2) δ 2.15, 2.05, 1.98, 2.01 (4s, 12H, 4AcO)
	S_2	δ4.58 d $J_{1,2}$=8 Hz	δ 5.26 t $J_{1,2,3}$ = 9 Hz	δ 5.02 dd $J_{2,3}$ = 9 Hz	δ 5.39 d $J_{3,4}$ = 3.5Hz	δ 4.00-3.95 m	δ 4.24-4.12 m	
Allyl 6-0-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-2,3,-di-O-benzyl-α-D-mannopyranoside	S_1	δ4.92 s	δ 3.82 d $J_{2,3}$ = 2.5 Hz	δ 3.75-3.67 m	δ 3.79 T $J_{3,4,5}$ = 9 Hz	δ 3.75-3.67 m	δ 4.05-3.87 m	δ 7.40 – 7.28 (m, 10H, Ph-H) 5.97 - 5.86 (m, -OHC_2-$\underline{CH}$ = CH_2) δ 5.24 – 5.11 (m, -OCH_2-CH = $\underline{CH_2}$) δ 4.31, 4.22 (dd, J = 6 & 12Hz, --$\underline{OCH_2}$-CH=CH_2) δ 4.72-4.56 (m, 3H, $\underline{CH_2}$-C_6H_5) δ 4.43 (d, 1H, J = 12 Hz, $\underline{CH_2}$=C_6H_5) δ 2.15, 2.03, 1.98, 1.21 (3s, 3H, $J_{5,6}$ = 6 Hz, Me-6′)
	S_2	δ4.87 s	δ 5.32 d $J_{2,3}$ = 2 Hz	δ 5.30 dd $J_{3,4}$ = 9 Hz	δ 5.07 t $J_{3,4,5}$ = 9 Hz	δ 4.05-3.87 m	δ 4.05-3.87 m	

Compound name	**S_1/S_2**	**H-1**	**H-2**	**H-3**	**H-4**	**H-5**	**H-6**	**Appended group's proton**
Allyl 2-0-(2,3,4-tri-0-acetyl-α-L-rhamppyranosyl)-4,6-di-O-acetyl -α-D-mannopyranoside	S_1	δ 4.95 s	δ 4.00 d $J_{2,3}$ = 3 Hz	δ 3.97-3.92 m (2H)	δ 5.08 T $J_{3,4,5}$ = 10 Hz	δ 3.97 m (2H)	δ 4.18-4.15 m (3H)	δ 5.95 – 5.85 (m, OHC_2-$\underline{C}$H =CH_2) δ 5.30-5.22 (m, 3H, -OHC_2-CH = $\underline{C}H_2$) δ 4.28 (dd, 2H, J = 4.7 Hz –$O\underline{C}H_2$-CH = CH_2) δ 4.18-4.15 (m, $O\underline{C}H_2$-CH=CH_2) δ 1.28 (d, 3H, $J_{5,6}$ = 6 Hz, Me-6′) δ 2.18, 2.14, 2.07, 2.02 (4s, 15H, 5AcO)
	S_2	δ 4.91 s $J_{1,2}$ = 8.5 Hz	δ 5.32 d $J_{2,3}$=3 Hz	δ5.30-5.22 m (3H)	δ 5.12 t $J_{3,4,5}$ = 9.7 Hz	δ 4.06-4.01 m (1H)	δ 4.28 dd J = 4.7 Hz J = 12 Hz	
Allyl 3-0-(2,3,4-tri-O-acetyl-α-L-rahmnopyranosyl)2,4,6-tri -O-acetyl-α-D-mannopyranoside	S_1	δ4.87 s (2H)	δ 5.26 d $J_{2,3}$ = 2 Hz	δ 3.87-3.81 m (2H)	δ 5.03 t (2H)	δ 3.87-3.81 m (2H)	δ 4.22-3.99 m (3H)	δ 6.01 – 5.81 (m, -$\underline{OHC_2}$-CH = CH_2) δ 5.38 – 5.27 (m, -$\underline{OHC_2}$-CH = $\underline{CH_2}$) δ 5.13-5.07 (m, 3H, -OCH_2-CH = $\underline{CH_2}$) δ 4.28 (dd, J = 5.1 Hz, -OCH_2,-CH =CH_2) δ 4.22-3.99 (m, -$O\underline{CH_2}$-CH=CH_2) δ 1.21 (d, 3H, $J_{5,6}$= 6Hz, Me-6) δ 2.20, 2.15, 2.12, 2.11, 2.04, 1.97(6s, 18H, 6AcO)
	S_2	δ 4.88 s	δ 5.23 d	δ 5.13-5.07 m (3H)	δ 5.03 t $J_{2,3,4}$ = 9 Hz	δ 3.99-3.91 m (1H)	δ 4.22-3.99 m (3H)	

Allyl 2-0-(2,3,4-tri-O-acetyl-α-L-rahmnopyranosyl)-3,4,6-tri- -O-acetyl-α-D-mannopyranoside	S_1	δ4.90 s	δ 4.08 d $J_{2,3}$ = 2 Hz	δ 5.33 dd (2H) $J_{2,3}$=2H	δ 5.09 t (2H) $J_{3,4,5}$=9 Hz	δ 4.06-4.00 m (2H)	δ 4.17 dd J = 4 Hz J = 12 Hz	δ 5.96 – 5.85 (m, -OHC_2-CH - CH_2) δ 5.29 – 5.21 (m, 2H, -OHC_2-CH = CH_2) δ 4.26 (dd, J = 6 Hz, -OCH_2-CH = CH_2) δ 4.15-4.11 (m, 1H, -OCH_2,-CH =CH_2) δ 1.21 (d, 3H, $J_{5,6}$= 6 Hz, Me-6′) δ 2.16, 2.10, 2.09, 2.04, 2.00 (5s, 18H, 6AcO)
	S_2	δ 4.81 s	δ 5.37 d $J_{2,3}$=2 Hz	δ 5.33 dd (3H) $J_{2,4}$ = 9Hz	δ 5.09 t (2H)	δ 4.06-4.00 m (2H)	δ 4.24-4.19 m (1H)	
Allyl 2-0-(2,3,4-tri-O-acetyl-α-L-rahmnopyranosyl)-2,3-di- O-methyl-α-D-mannopyranoside	S_1	δ4.91 s	δ 3.58 D $J_{2,3}$ = 2 Hz	δ 3.66-3.61 m (3H)	δ 3.69 t (2H) $J_{3,4,5}$=8 Hz	δ 3.66-3.61 m (3H)	δ 3.88 dd J = 5 Hz J=12Hz	δ 5.94 – 5.83 (m, -OHC_2-CH - CH_2) δ 5.32 – 5.25 (m, 2H, -OHC_2-CH = CH_2) δ 8.14 (dd, J = 6 & 12 Hz, -OCH_2-CH = CH_2) δ 4.00-3.93 (m, 2H, -OCH_2,-CH =CH_2) δ 3.41 (s, 6H, 2MeO) 1.24 (d, $J_{5,6}$= 6Hz, Me-6′) δ 2.07, 1.97, 1.90 (5s, 18H, 6AcO)
	S_2	δ 4.81 s	δ 5.21 d $J_{2,3}$=2 Hz	δ 5.18 dd (2H) $J_{2,3}$=2H $J_{3,4}$=9Hz	δ 5.00 t $J_{3,4,5}$ = 9Hz	δ3.66-3.61 m (3H)	δ 4.00-3.93 m (2H)	
Methyl 3,0 (2,3,4,6-tetra-O-acetyl--β-D-glucopyranosyl-(1-6)2,3,4-tri-O-acetyl β-D- glucopyranosyl)-4-6-0-benzlidene-2-deoxy-α-D-glucopyranoside	S_1	δ 4.839 d $J_{1,2}$ = 3.3 Hz	δ 1.787 ddd J = 16.1, 2.3 Hz δ 2.247 dd J = 16.1, 3.9 Hz	δ 5.193 m	δ 3.542 t J = 9 Hz	δ 4.289 m	δ 3.947 m (2H, a, b)	δ 3.352 (s, 3H, -OMe) δ 5.5762 (s, CH C_6H_5) δ 7.480 (s, 5H, C_6H_5) δ 2.106, 2.087, 2.070, 2.042, 2.032, 2.020 (6s, 21H, 7OAc)
	S_2	δ 5.672 d J = 8.1Hz	δ 5.054 dd J = 10.2Hz	δ 5.256 t J = 9.9 Hz	δ 5.021 t J = 9.3 Hz	δ 4.289 m	δ 3.650 m δ 3.597 dd J = 12.0, 4.5 Hz	
	S_3	δ 4.527 d J = 7.8Hz	δ 5.054 dd J = 4.2Hz	δ 5.224 2t J = 9.3 Hz	δ 5.224 2t J = 9.6 Hz	δ 3.650 m	δ 4.274 dd J 12, 5.4 Hz δ 4.225 dd J = 12, 4.8 Hz	

Methyl 4,0 (2,3,4,6-tetra-O-acetyl--β-D-glucopyranosyl-(1→6)2,3,4-tri-O-acetyl β-D- glucopyranosyl)-3-0-acetyl-6-0-benzyl-2-deoxy-α-D-glucopyranoside	S_1	δ 4.851 d $J_{1,2}$ = 2.7Hz	δ 1.7922 dd J = 16.3, 8.9, 2.7 Hz δ 2.310 dd J = 16.3, 3.6 Hz	δ 5.269 m	δ 5.054 t J = 8.9 Hz	δ 3.969 m	δ 4.20 dd δ 4.254 dd J = 5.9 Hz	δ 3.580 (s, 3H, -OMe, S-1) δ 4.120 (d, $\underline{CH_2}$ C_6H_5) δ 7.381 (s, 5H, C_6H_5, S-1) δ 2.020, 2.032, 2.042, 2.070, 2.087, 2.106 (7s, 24H, S-1, S-2, S-3, 8OAc)
	S_2	δ 5.722 d J = 8.4Hz	δ 5.080 dd J = 10.1Hz	δ 5.452 t J = 9.9 Hz	δ 4.63 bt J = 9.3 Hz	δ 3.947 m	δ 3.969 m δ 3.398 dd J = 11.1, 4.8 Hz	
	S_3	δ 4.539 d J = 7.8Hz	δ 5.107 dd J = 10.3Hz	δ 5.193 bt J = 9.3 Hz	δ 5.153 bt J = 9.6 Hz	δ 3.729 m	δ 4.315 dd J 12.1, 4.5 Hz δ 4.274 d J = 5.9 Hz	

Methyl 6-0-(2,3,4,6-tetra-O-acetyl--β-D-glucopyranosyl-(1→6)2,3,4-tri-O-acetyl β-D-glucopyranosyl)-3,4-di-O-acetyl -2-deoxy-α-D-glucopyranoside	S_1	δ 4.8539 d $J_{1,2}$ = 2.7Hz	δ 1.804 ddd J = 16.1, 9.3, 2.7 Hz δ 2.234 dd J = 16.1, 3.7 Hz	δ 5.301 m	δ 5.301 m	δ 3.947 m	δ 5.021 dd J = 12.3, 5.4 Hz δ 4.503 dd J = 12.3, 4.5 Hz	δ 3.349 (s, 3H, -OMe, S-1) δ 1.998, 2./006, 2.013, 2.020, 2.034, 2.087, 2.093 (7s, 21H, S-2, S-3, 7OAc)
	S_2	δ 5.672 d J = 8.4Hz	δ 5.054 dd J = 10.3Hz	δ 5.411 bt J = 9.6 Hz	Nd	δ 3.796 m	δ 3.947 m δ 3.580 dd J = 12.1, 5.7 Hz	
	S_3	δ 4.527 d J = 7.8Hz	δ 5.193 dd J = 10.1Hz	δ 5.224 2t J = 9.3 Hz	δ 5.224 2t J = 9.6 Hz	δ 3.657 m	δ 4.225, dd J 12.3, 4.5 Hz δ 4.087, d J = 12.3, 2.1 Hz	

Allyl 6-0-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-4-O-di-acetyl-2,3-di-O-methyl-α-D-glucopyranoside	S_1	5.04 d $J_{1,2}$ = 3 Hz	δ 3.34 dd $J_{1,2}$ = 3 Hz $J_{2,3}$ = 8 Hz	δ 3.62 t $J_{2,3,4}$ = 8 Hz	δ 4.95 t $J_{3,4,5}$ = 9 Hz	δ 3.95-3.88 m (2H)	δ 4.04 dd J = 2 & 11 Hz	δ 6.01 – 5.91 (m, -$\underline{OHC_2}$-$\underline{C}$H - CH_2) δ 5.38 – 5.24 (m, 2H, -$\underline{OHC_2}$-CH = $\underline{C}H_2$) δ 4.30 - (dd, J = 6 Hz, -O$\underline{C}H_2$-CH = $\underline{C}H_2$) δ 4.21-4.14 (m, 2H -O$\underline{C}H_2$,-CH =CH_2) δ 4.21-4.14 (m, 2H, -O$\underline{C}H_2$,-CH =CH_2) δ 3.53, 3.51 (2s, 6H, 5 MeO) δ 2.13, 2.11, 2.10, 2.06, 2.04 (5s, 15H, 5AcO)
	S_2	δ 4.22 d $J_{1,2}$=8 Hz	δ 4.13-4.07 m (3H)	δ 4.13-4.07 m (3H)	δ 5.51 t $J_{3,4,5}$ = 9 Hz	δ 3.95-3.88 m (2H)	δ 4.21-4.14 m (2H) δ 4.27-4.2 m (H-6‴)	
	S_2	δ 4.84 s	δ 5.30 d $J_{2,3}$=2Hz	δ 5.38-5.31 m (2Hz)	δ 5.08 t $J_{3,4,5}$=9Hz	δ 3.67-3.47 m (2H)	δ 4.02-3.91 m (3H)	
Allyl 4-0-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-6-O-(2,3,4-tri-O-acetyl-α-D-rhamnopyranosyl)-2,3-di-benozyl-α-D-glucopyranoside	S_1	δ 5.30 d $J_{1,2}$ = 3.5 Hz	δ5.35-5.25 m	δ 6.01 t $J_{2,3,4}$ = 9 Hz	δ 3.72 dd $J_{3,4}$= 8Hz $J_{4,5}$= 9Hz	δ 3.90-3.83 m	δ 4.12-3.97 m	δ8.04 (d, 2H, J = 7 Hz, Ph-H) δ7.95 (d, 2H, J = 7 Hz, Ph-H) δ7.50 (t, 2H, J = 6 Hz, Ph-H) δ7.41-7.33 (m, 4H, Ph-H) δ5.90-5.80 (m, -OCH_2-$\underline{CH}$=CH_2) δ5.35-5.25 (m, -OCH_2-CH=$\underline{CH_2}$) δ5.21-5.16 (m, -OCH_2-CH=$\underline{CH_2}$) δ4.30-4.22 (dd, 2H, J = 6 Hz, -$O\underline{CH_2}$-CH=CH_2) δ1.29 (6H, Me-6′) δ2.19, 2.17, 2.11, 2.06, 2.00, 1.98(6s,18H,6AcO)
	S_2	δ 4.87 s	δ 5.12 d $J_{2,3}$ = 3 Hz	δ5.10-5.02 m	δ 4.91 t $J_{3,4,5}$= 9Hz	δ 4.112-3.97 m	δ 4.12-3.97 m	
	S_3	δ 4.87 s	δ 5.14 d $J_{2,3}$ = 3 Hz	δ5.10-5.02 m	-nd-	δ 4.112-3.97 m	-nd-	
Allyl 4-0-(2,3,4, tri-O-acetyl-α-L-rhamnopyranosyl)-2,3-di-O-methyl-β-D glucopyranoside	S_1	δ4.34 d $J_{1,2}$=8 Hz	δ 3.25-3.09 m	δ 3.25-3.09 m	δ 3.25-3.09 m	δ 3.40-3.35 m	δ 3.18-4.09 m (3H)	δ 5.99 – 5.88 (m, -OHC_2-$\underline{CH}$ - CH_2) 5.23 – 5.01 (m, -OHC_2-CH = $\underline{CH_2}$) δ 4.18-4.09 (m, -$\underline{OCH_2}$-CH = CH_2) δ 3.63-3.60 (2s, 6H, 2MeO) δ 1.21, (d, 3H, $J_{5,6}$= 6 Hz, 2Me6″) δ 1.19 (d, $J_{5,6}$ = 6 Hz, Me6′) δ 2.16, 2.14, 2.07, 2.06, 2,.03, 2.02 (6s, 18H, 6AcO)
	S_2	δ 4.82 s	δ 5.32 d $J_{2,3}$=2.5Hz	δ 5.23 dd $J_{2,3}$= 2.5 Hz $J_{3,4}$= 9 Hz	δ 5.23-5.01 m (4H)	δ 3.76-3.69 m (2H)	δ 4.18-4.09 m (3H)	
	S_3	δ 4.86 s	δ 5.37 d $J_{2,3}$=2 Hz	δ 5.28 dd $J_{2,3}$= 2 Hz $J_{3,4}$= 9 Hz	δ 5.23-5.01 m (4H)	δ 3.76-3.69 m (2H)	nd	
Allyl 4-0-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-6-0-(2,3,4,-tri-O-acetyl-α-L-rhamnopyranosyl)-2,3-di-O-benzyl-α-D-mannopyranoside	S_1	δ4.86 d $J_{1,2}$=1.5	δ 3.87 d $J_{2,'3'}$ = 2.5 Hz	δ 3.81-3.79 m	δ 3.57 dd $J_{3,4}$ = 8 Hz	δ 3.81-3.79 m	δ 4.14-4.03 m	δ 7.38 – 7.28 (m, 10H, Ph-H) 5.90 – 5.83 (m, -$\underline{OHC_2}$-$\underline{CH}$ = CH_2) δ 5.19 – 5.08 (m, -OCH_2-CH = $\underline{CH_2}$) δ 4.19 (dd, J = 6 & 12Hz, -$\underline{OCH_2}$-CH=CH_2) δ 4.79-4.69 (m, $\underline{CH_2}$-C_6H_5) δ 4.61, 4.52 (2d, J = 11 Hz, $\underline{CH_2}$=C_6H_5) δ 2.23,2.16, 2.14, 2.12, 2.08, 2.06 (6s, 18H, 6 AcO) δ 1.24 (d, 3H, $J_{5,6}$=6 Hz, Me-6′) δ 1.20 (d, 3H, $J_{5,6}$= 6Hz, Me-6′)
	S_2	δ4.84 s	δ 5.30 d $J_{2,3}$ = 3 Hz	δ 5.25 dd $J_{3,4}$=9 Hz	δ 5.04-4.90 m	δ 4.00-3.91 m	-nd-	
	S_3	δ4.84 s	δ 5.33 d $J_{2,3}$ = 3 Hz	δ5.25 dd	δ 5.04-4.90 m	δ 4.00-3.91 m	δ 4.14-4.03 m	

of the corresponding β-glycosides. In case of normal sugars (2-hydroxy) anomeric proton appears as a doublet while the anomeric proton of 2-deoxy sugar appears as a double doublet in the region of δ4.3-5.5 ppm[59]. In case of normal sugar, if the H-2 is axial, as it is for gluco-and galacto-stereochemistry, then a small coupling constant of 2-4 Hz is observed as a result of gauche conformation of H-1 and H-2 following the Karplus relation (digedral angle 60°). The trans diaxial relationship of H-1 and H-2 in β-anomers of sugars with a gluco-and galacto-configuration leads to larger (8-10 Hz) coupling constant (dihedral angel 180°). The equatorial orientation of H-2 in mannose result in a small dihedral angle and thus a small coupling constant for both α- and β- anomers, therefore making assignment of the anomeric configuration more difficult. The splitting pattern of the anomeric proton of normal sugars depends on the conformation of H-1 as well as that of H-2 i.e. when H-1 are trans to each other, the resultant coupling observed in the anomeric proton signal would be large (J = 3-8 Hz). A downfield glycosidation shift[60] of 0.6-1 ppm is observed in the anomeric proton signal of glycosidically linked sugars with respect to the free sugars. In 2-deoxy sugars if the coupling constants of the double doublet is of 7-10 Hz and 1-2 Hz then it confirms the presence of β-glycosidic linkage in $^4C_1$ conformation and H-1 is axial, where as smaller coupling of 3-4 Hz and 1 Hz indicates the nature of glycosidic linkage as α where the sugar is in $^1C_4$ conformation and H-1 is in equatorial position.

The high frequency spectra are also well resolved in the higher field and give characteristic splitting pattern for 6-deoxy and 2,6 dideoxy sugar[61-63]. The 2-deoxy and 2,6-dideoxy sugars exhibit their methylene protons (H-2) and two sets of multiplets for equatorial and axial protons in the region of δ2.0 - 2.5 and 1.5 – 2.0 respectively. Their assignment can be easily ascertained by double resonance experiments[64]. The signals of H-3, H-4 and H-5 in hexose appear as multiplets in region δ3.0 – 4.5. The characteristic signals of secondary methyl group (6-CH_3) of 6-deoxy sugars appear as doublets (J=6Hz) between δ1.0 – 1.5.

The ^{1}H NMR spectrum of compounds having methoxy groups shows singlets for three protons of –OCH_3 in the range of 3.5 – 4.4 ppm, depending on the type of carbon attached. The signal of the proton to which other substituents are present varies from 3.05 – 5.76 ppm depending on the nature of ethereally linked substituents[65]. Due to presence of aromatic substituent, the multiplet of attached methine proton shifted to downfield and the signal of the aromatic protons falls in the range 7.1–8.2 ppm. The information regarding the number of primary and a secondary hydroxyl groups present which are acylable can be obtained by counting the methyl group peak of acetate group between δ 2.1 – 2.3 of acylated hydroxyl groups and while the number of tertiary hydroxyl group can be determined by D_2O exchange and the addition of trichloroacetyl isocyanate reagent (TAI). There are various decoupling experiments which are very helpful in confirming the assignments of the anomeric protons and other functional group in the moiety. These experiments can be used for conforming the assignments of the signal due to H-1, H-2 and H-5 of the 2, 6 dideoxy sugars besides the C-20 methine and secondary methyl protons present in the side chain of the pregnane aglycon. Proton spin decoupling and correlated spin-spin coupling experiments have been used for establishing the structure of constituents hexose of glycosides.

Results obtained from the ^{1}H NMR of Milk Oligosaccharides

The ^{1}H NMR of some of the milk oligosaccharides are given in the tabular form in the following pages. By going through the

literature of ^{1}H NMR values of various ring and anomeric protons it was revealed that there were certain markers which give us information about the position of glycosidic linkages and

^{1}H NMR Data of Glycosides Isolated From Plants

Isolated compound	S_1	H-1	H-2	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
12, 20 di-O-cinnamoylsarcostin-3-O-β-D-cymaroside	S_1	δ 4.79 dd J = 9.5 & 1.5 Hz	δ 2.17-2.19 m(aq) δ 2.05-1.71 m (ax)	δ 3.58 m	δ 3.22 m	δ 3.66 m	δ 1.30 d J = 6 Hz (3H)	7.97-7.28(10H, m, armoatic) δ 6.47 (1H, d, J = 16 Hz, H-21) δ 6.29 (1H, d, J = 16 Hz, H -22) δ 4.88 (1H, q, J = 6 Hz, H-20) δ 3.44 (3H, s, OCH_3-H-3') δ 1.27 (3H, s, CH_3 -18) δ 1.37 (3H, d, J= 6 Hz, CH_3 -21) δ 1.13 (3H, s, CH_3 -19)

Isolated compound	S_1-S_2	H-1	H-2	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
Uzarigenin-3-O-β-D-xylopyranosyl (1→4)- O-β-D-digitalopyranoside	S_1	δ 4.97 d J=7.5 Hz	δ 3.22 dd J= 8 Hz	δ 3.66 d (3H, OMe)	-nd-	δ 4.10-4.02 m	δ 1.32 d J=6 Hz (3H, Me)	Aglycon δ 5.88 (1H, s, H-22) δ 4.86 (3H, s, J = 16 Hz, H-21) δ 1.28 (3H, s, H-18) δ 1.22 (3H, s, H-19)
	S_2	δ 4.81 d J = 8 Hz	δ 3.12 dd J = 8 Hz	-nd-	δ 3.46-3.38 m	δ 3.92-3.86 m(ax) δ 4.10-4.02 m(eq)	-	
Periplogenin-3-O-β-doexy-D-glucopyranosyl (1→4)-O-α-D-digitalopyranoside	S_1	δ 4.35 d J=8Hz	δ 3.28 dd J =9 & 3 Hz	δ 3.66 s (3H, OMe)	δ 3.46-3.38 (2H) m	δ 3.94-3.84 m	δ 1.31 d J = 7 Hz	5.90 (1H, s, H-22) δ 4.81 (1H, d, J=16 Hz, H-21) δ 2.78 (1H, H-17) δ 1.26 (3H, s, H-18) δ 0.91 (3H, s, H-19)
	S_2	δ 4.23 d J=3 Hz	δ 3.14 t J =8 Hz	δ 3.94 m	δ 3.46-3.38 (2H)	δ 3.94 – 3.89 m	δ 1.31 d J=7Hz	
12, 20 di-O-cinnamoyl sarcostin-3-O-α-L-oleandropyranosyl (1→4)-O-β-D-cymaropyranoside	S_1	δ 4.50	δ 2.99-2.15 m(aq) δ 2.15-1.70(ax)	δ 3.61-3.45 m	δ 3.35-3.23 m	δ 3.93-3.84 m (2H)	δ 1.33 d J = 6 Hz (3H)	7.96-7.92 (Arom.proton) δ 3.53 (3H, s, OCH_3) δ 3.43 (3H, s, OCH_3) δ 1.27 (3H, s, CH_3-18) δ 1.22 (3H, s, CH_3-19) δ 4.88 (1H, m, J = 6 Hz)
	S_2	δ 4.23 dd J= 9 & 1.3 Hz	δ 2.49-2.15 m (eq.) δ 2.15-1.70 m (ax)	δ 3.61-3.45 m	δ 3.35-3.23 m	δ 3.93-3.84 m (2H)	δ 1.24 d J=6 Hz (3H)	

Isolated compound	S_1-S_2	H-1	H-2 (eq/ ax)	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
Calogenin-3-O-3-O-α-D-galactopyranosyl- (1→4)- O-β-D-digitoxopyranoside	S_1	δ 4.64 dd J=9 & 2 Hz	δ 2.11-2.17 (eq) m δ 1.75-1.01 (ax) m	δ 3.57-3.62 m (2H)	δ 3.43-3.47 m	α 3.67-3.73 m	δ 5.28 m (1H)	δ 3.49 (3H, s, OMe) δ 1.22 (3H, d, J = 7 Hz, 7Hz, Me, s, -6)) δ 1.19 (3H, d, J = 6Hz, 21 Me) δ 0.93 (3H, s, 18 Me) δ 0.90 (3H, s, 19 Me)
	S_2	δ 4.82 d J = 2 Hz	δ 3.29-3.47 m (2H)	δ 3.43-3.47 m (2H)	δ 3.29-3.35 m (2H)	δ 3.57-3.62 m (2H)	δ 3.67-3.73 m (3H)	
11α, 12β-di-O-acetyl-orgogenin -3-O-β-D-cymaropyranosyl-(1→4)-O-β-D-cymaropyranosyl (1→4)-O-β-D-cymaropyranoside	S_1	δ 4.57 dd J=7 & 1.5 Hz	δ 2.29-2.36 (eq) m δ 1.81-1.86 (ax) m	δ 3.53-3.57 m (3H)	δ 3.13-3.21 m (3H)	δ 3,57-3.62 m (2H)	δ 3.67-3.73 m (3H)	3.50 (3H, s, OMe) δ 3.44 (3H, s, OMe) δ 3.34 (3H, s, OMe) δ 2.18 (3H, s, $COCH_3$) δ 2.16 (3H, s, OAc) δ 2.07 (3H, s, OAc) δ 0.98 (3H, s, 18 CH_3) δ 0.84 (3H, s, 19 CH_3)
	S_2	δ 4.87 dd J=2 & 9 Hz	δ 2.29-2.36 (eq) m δ 1.81-1.86 (ax) m	δ 3.53-3.57 m (3H)	δ 3.13-3.21 m (3H)	δ 3.82 – 3.87 m (3H)	δ 1.24 d (CH_3-6') (3H) J=6 Hz	
	S_3	δ 4.87 dd J = 9 & 2H	δ 2.29-2.36 (eq) m δ 1.81-1.86 (ax) m	δ 3.53-3.57 m (3H)	δ 3.13-3.21 m (3H)	δ 3.82 – 3.87 m (3H)	δ 1.32 d (CH_3-6') (3H) J=6 Hz	

Isolated compound	S_1-S_3	H-1	H-2 (eq/ax)	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
Calogenin-3-O-β-D-glucopyranosyl (1→4)- O-β-D-glucopyranosyl (1→4)O-β-D-Cymaropyranoside	S_1	δ 4.45 dd J=9 & 2 Hz	δ 2.28 eq. m δ 1.84 ax. M	δ 3.63-3.58 m	δ 3.13-3.18 m	δ 3.63-3.58 m	δ 1.29 d (CH_3) J = 6 Hz	δ 3.52 (3H, s, OMe-3) δ 1.25 (3H, d, J = 6 Hz, 21 Me) δ 1.0 (3H, s, 18 CH_3) δ 0.88 (3H, s, 19 CH_3)
	S_2	δ 4.32 d J= 8 Hz	δ 3.29-3.36 m	δ 3.41-3.45 m	δ 3.56-3.58 m	δ 3.46-3.50 m	δ 3.68-3.72 m	
	S_3	δ 4.32 d J= 8 Hz	δ 3.29-3.36 m	δ 3.41-3.45 m	δ 3.37-3.41 m	δ 3.46-3.50 m	δ 3.68-3.72 m	
Sarcogenin-3-O-β-D-thevetopyranosyl (1→4)- O-β-D-glucopyranosyl (1→4)O-β-D-Oleandropyranoside	S_1	δ 4.86 dd J= 2 Hz	δ 2.28-2.10 (eq.) m δ 2.04-1.84 (ax.) m	δ 3.43-3.36 m	δ 3.32-3.28 m	δ 3.92-3.83 m	δ 1.22 d (Me-6') J = 6 Hz	δ 2.26 (3H, s, COMe) δ 3.66 (3H, s, J = OMe, S-1) δ 3.48 (3H, s, OMe S-2) δ 3.46 (3H, s, OMe, S-3) δ 1.28 (3H, s, Me) δ 1.29 (3H, s, Me)
	S_2	δ 4.80 dd J= 2 & 9 Hz	δ3.28-2.10 m δ 2.04-1.84 m	δ 3.43-3.36 m	δ 3.32-3.28 m	δ 3.92-3.83 m	δ 1.28 d (Me-6')	
	S_3	δ 4.35 d J= 8 Hz	δ 3.54 t J = 7.5 Hz	-nd-	δ 3.29 m	-nd-	δ 1.31-d (Me-6') J=5.4 Hz	

Isolated compound	S_1-S_4	H-1	H-2 (eq/ ax)	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
12-O-Cinnamoyl sarcostin-3-O-α-L-oleandropyranosyl (1→4)-O-α-L-oleandropyranosyl-(1→4)-O-α-L-oleandropyranosyl-1→4)-O-β-D-cymaropyranoside	S_1	δ 4.51 dd J = 9.5 & 1.5 Hz	δ 2.36-2.97 m(aq) δ 2.02-1.80 m (ax)	δ3.62-3.51 m	δ 3.27-3.14 m	δ 3.93-3.84 m	δ 1.35-d J = 6 Hz	δ 7.95-7.92(2H, m, aromatic) δ 7.44-7.30 (3H, m, aromatic) δ 3.46-3.40(12H, s, J=4.0 Me) δ 1.23(3H, s, J =Me-18) δ 1.11(3H, d, J=6 Hz, Me-21) δ 1.18 (3H, s, Me-19)
	S_2	δ 4.86 dd J = 3 & 1 Hz	δ 2.36-2.97 m(aq) δ 2.02-1.80 m (ax)	δ3.62-3.51 m	δ 3.27-3.14 m	δ 3.93-3.84 m	δ 1.33-d (3H) J = 6 Hz	
	S_3	δ 4.86 dd J = 3 & 1Hz	δ 2.36-2.97 m(aq) δ 2.02-1.80 m (ax)	δ3.62-3.51 m	δ 3.27-3.14 m	δ 3.93-3.84 m	δ 1.33-d (3H) J = 6 Hz	
	S_4	δ 4.88 brd J = 3 Hz	δ 2.36-2.97 m(aq) δ 2.02-1.80 m (ax)	δ3.62-3.51 m	δ 3.27-3.14 m	δ 3.93-3.84 m	δ 1.24-d J = 6 Hz	

Isolated compound	S_1-S_4	H-1	H-2 (eq/ ax)	H-3	H-4	H-5	H-6	Aglycon part/ Appended group
3-Epiuzarigenin-3-O-β-D- cymaropyranosyl (1→4)- O-β-D-thevetopyranosyl (1→4) O-β-D-Cymaropyranoside (1→)-O-β-D-digitoxopyranoside	S_1	4.94 dd J= 2.5 & 8 Hz	δ 2.14-2.08 (eq.) m δ 1.94-1.84 (ax.) m	δ 3.90-3.78 m	δ 3.30-3.18 m	δ 4.28-4.20 m	δ 1.35 d (3H) J = 5.4 Hz	δ 3.45 (3H, s, OMe) δ 3.43 (3H, s, OMe) δ 0.87 (3H, s, Me) δ 0.78 (3H, s Me)
	S_2	δ 4.94 d J= 2.5 & 8 Hz	δ 2.14-2.08 (eq.) m δ 1.94-1.84 (ax.) m	As above	As above	As above	δ 1.31 d (Me-6') J =5 .4 Hz	
	S_3	δ 4.48 d J= 8 Hz	δ 2.76 t J = 7.5 Hz	As above	As above	As above	1.30 (3H) J 6.5 Hz	
	S_4	δ 4.35 dd J= 2.5 & 8 Hz	δ 2.14-2.08 (eq.) m δ 1.94-1.84 (ax.) m	As above	As above	As above	δ 1.31 d (Me-6) J = 5.4 Hz	

Isolated compound	**S_1-S_4**	**H-1**	**H-2 (eq/ax)**	**H-3**	**H-4**	**H-5**	**H-6**	**Aglycon part/ Appended group**
Kidjolanin-3-O-β-D-cymaropyranosyl (1→4)- O-β-D-thevetopyranosyl (1→4)O-β-D-cymaropyranoside (1→)-O-β-D-digitoxopyranoside	S_1	4.76 dd	δ 2.19-1.86 (eq.) m δ 1.70-1.52 (ax.) m	δ 3.40-3.20 m	δ 3.25-3.15 m (3H)	δ 3.93-3.74 m	δ 1.20 d	δ7-98-7.95 (arom) δ 7.55-7.35 (arom) δ 6.29 (CH=CH) δ 2.22 (COMe) δ 1.40 (18 Me) δ 1.13 (3H, d, 19 Me)
	S_2	δ 4.84 dd J= 9 & 2 Hz	δ 2.19-1.86 (eq.) m δ 1.70-1.52 (ax.) m	δ 3.40-3.20 m	δ 3.25-3.15 m (3H)	δ 3.93-3.74 m	δ 1.20 d	
	S_3	δ 4.30 d J= 2 Hz	δ 3.50 m	δ 3.45 m	δ 3.30 m (3H)	-nd-	δ 1.28 d	
	S_4	δ 4.8.4 dd J= 9 & 2 Hz	δ 3.50 m	δ 3.45 m	δ 3.30 m (3H)	δ 3.93-3.74 m	δ 1.30 d	

Isolated compound	**S_1-S_4**	**H-1**	**H-2 (eq/ax)**	**H-3**	**H-4**	**H-5**	**H-6**	**Aglycon part/ Appended group**
Calogenin-3-O-β-D-cymaropyranosyl (1→4)-O-3-O- methyl-α-D-glactoyranosyl (1→4) O-β-D- digitoxopyranoside (1→)-O-β-D- cymaropyranosyl	S_1	δ 4.73 dd J= 9 & 21 Hz	δ 2.30 (eq.) m δ 1.01 (ax.) m	δ 3.70-3.74 m	δ 3.55-3.61 m	δ 4.09-4.15 M	δ 1.29 d (3H) J = 6 Hz	δ 3.52 (OMe) δ 3.49 (OMe) δ 3.46 (OMe) δ 0.75 (3H, s, 19 Me) δ 1.0 (3H, s, 18 Me) δ 1.27 (d, J = 7 Hz, 21 Me)
	S_2	δ 4.77 dd J= 2 & 8 Hz	δ 2.30 (eq.) m δ 1.01 (ax.) m	δ 3.70-3.74 m	δ 3.55-3.61 m	δ 4.09-4.15 M	δ 1.27 d J =7 Hz	
	S_3	δ 5.14 d J= 4 Hz	δ 3.35-3.61 m	δ 3.70-3.74 m	δ 3.55-3.61 m	δ 4.09-4.15 M	δ 4.26-4.36 (3H)	
	S_4	δ 4.73 dd J= 9 & 2 Hz	δ 2.30 (eq.) m δ 1.02 (ax.) m	δ 3.70-3.74 m	δ 3.55-3.61 m	δ 4.09-4.15 M	δ 1.32 d (3H) J = 6 Hz	

nature of monosaccharides present in the oligosaccharides. They are termed as structure reporter groups,which were described earlier.

Besides the structure of four compounds i.e. Bosiose, Bovisose, Grunniose, Vakose given in tabular forms of this review article some of the other oligosaccharide were also isolated from milk of Mare, Donkey, Goat, Black Cow, Sheep and Camel milk namely Aminose[68], equinose[69], Asinose[69] caprose[70], bosonose[71], dicose[72] and madalose[73] and their structure were elucidated by incorporating the results obtained from ^{13}C and 2D NMR like COSY, TOCSY, HSQC and

Compound (Bosiose)[66]

Isolated Compound	S_1-S_3	H-1	H-2	H-3	H-4	NHAc
GlcNAc(1-6)GalNAc(1-4)Glc	S_1	5.27 [d, 1H, J=3.6 Hz, α-Glc] 4.57 [d, 2H, J=8.0Hz, β-Glc]	3.32 [t, 1H, J=7.2 Hz, β-Glc(S-1), H-2]			
	S_2	4.50 [d, 1H, J=8.0Hz, β-GalNAc]			3.82 [β-GalNAc (S-2), H-4]	2.04[s, 3H NHCO$\underline{CH_3}$, β-GalNAc (S_2)].
	S_3	4.57 [d, 2H, J=8.0Hz, β-GlcNAc]				2.05[s, 3H, NHCO$\underline{CH_3}$, β-GlcNAc (S_3)],

Compound (Bovisose)[66]

Isolated Compound	S_1-S_6	H-1	H-2	H-3	H-4	NHAc
Galβ(1-3)GlcNAcβ(1-6)Galβ(1-3)GlcNAcβ(1-3)Galβ(1-4)Glc	S-1	5.25 [d, 1H, J=3.6Hz, -Glc] 4.59 [d, 1H, J=7.6Hz, β-Glc	3.32 [t, 1H, J=8.1Hz, β-Glc(S-1), H-2],			
	S-2	4.48 [d, 2H, J=8.0Hz, β-Gal			4.16 [β-Gal (S-2), H-4]	
	S-3	4.69 [d, 1H, J=8.0Hz, β-GlcNAc]				2.02 [s, 3H, NHCO$\underline{CH_3}$, β-GlcNAc (S-3)]
	S-4	4.48 [d, 2H, J=8.0Hz, β-Gal (S-4) H-1],				
	S-5	4.61 [d, 1H, J=7.6Hz, β-GlcNAc (S-5) H-1]				2.03 [s, 3H, NHCO$\underline{CH_3}$, β-GlcNAc (S-5)]
	S-6	4.55 [d, 1H, J=8.0Hz, β-Gal (S-6) H-1]				

Compound (Grunniose)[67]

Isolated Compound	S_1-S_5	H-1	H-2	H-3	H-4	NHAc
Galα(1-3)GlcNAcβ(1-6)Galβ(1-4)Glc (GalNAcα(1-3))	S_1	5.21 [d, 1H, J=3.6Hz, α-Glc (S-1) H-1] 4.66 [d, 1H, J=7.8Hz, β-Glc (S-1) H-1]	3.58 [t, 1H, J=8.7Hz, β-Glc(S-1), H-2],			
	S_2	4.44 [d, 1H, J=7.2Hz, β-Gal (S-2) H-1]			3.92 [β-Gal (S-2), H-4]	
	S_3	4.55 [d, 1H, J=6.3Hz, β-GlcNAc (S-3) H-1]				1.99 [s, 6H, $NHCOCH_3$, β-GlcNAc (S-3)&
	S_4					
	S_5	5.25 [d, 1H, J=3.6Hz, α-GalNAc (S-5) H-1]				1.99α-GalNAc (S-5)].

Compound (Vakose)[67]

Isolated Compound	S_1-S_7	H-1	H-2	H-3	H-4	NHAc
Glcβ(1-3)Galβ(1-3)GlcNAcβ(1-6)Galβ(1-3)GlcNAcβ(1-3)Galβ(1-4)Glc	S_1	5.26 [d, 1H, J=3.6 Hz, α-Glc (S-1), 4.71 [d, 2H, J=7.5 Hz, β-Glc (S-1)				
	S_2	4.49 [d, 2H, J=7.8Hz, β-Gal (S-2)	3.30 [t, 1H, J=8.4Hz, β-Glc(S-1), H-2],		4.18 [β-Gal (S-2), H-4]	
	S_3	4.71 [d, 2H, J=7.5 Hz, β-GlcNAc (S-3) H-1]				2.03 [s, 3H, $NHCOCH_3$, β-GlcNAc (S-3)].
	S_4	4.49 [d, 2H, J=7.8Hz, β-Gal (S-2) & β-Gal (S-4) H-1]			3.89 [β-Gal (S-4), H-4]	
	S_5	4.59 [d, 1H, J=9.0 Hz, β-GlcNAc (S-5)				2.05 [s, 3H, $NHCOCH_3$, β-GlcNAc (S-5)],
	S_6	4.56 [d, 1H, J=7.6Hz, β-Gal (S-6) H-1]			4.13 [β-Gal (S-6), H-4]	
	S_7	4.64 [d, 1H, J=7.8 Hz, β-Gal C, H-1]]				

HMBC experiments.

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