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Synthesis of Glycofuranosides

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Glycofuranosides are ubiquitous in biological structures, playing important functions in immunological response and bacterial or viral infection [1,2]. To elucidate their biological functions and their possible use in therapy, there are more and more attempts to synthesize smaller or bigger structures (glycosides, oligosaccharides, glycoconjugates) containing furanosyl units. This article describes recent advances in the development of efficient synthesis methods for glycofuranosides.

Key words: glycosylation, glycofuranosyl donors, glycofuranosides, oligofuranosides

Introduction

Glycofuranosyl moieties are widely distributed in lower organisms, including bacteria, parasites, fungi and plants [3], where they occur either as constituents of the cell wall or as exocellular polysaccharides. Pentofuranose residues are the most common of all furanoses present in this naturally occurring furanose oligosaccharides. For example, D-ribose is a component of different lipopolysaccharides (LPS), capsular polysaccharides and teichoic acid type of polymers. In all these polymers, it occurs as the β-furanosyl group or residue [4]. Occasionally, α-D-ribofuranosyl residues are found, as in α-ribasole [5] and in O-specific polysaccharide (OPS) of *Citrobacter O-1a, 1b, 1c* [6], what has been determined recently.

D-Arabinose occurs in arabinogalactans and arabinomannans produced by *Mycobacterium* species. For some arabinomannans it has been found to be furanosidic and α-linked [7]. The arabinogalactan from *Mycobacterium tuberculosis*, however, contains both α- and β-linked D-arabinofuranosyl residues [8]. It also occurs in the α-form in the LPS from *Pseudomonas maltophila* strain NCIB 9204 [9]. L-Arabinose is a component of the LPS from the purple, sulfur bacterium *Chromatium vinosum* [10]. D-Xylose, which is one of the most abundant sugars in plant polysaccharides, is a rare component of bacterial polysaccharides. It is found in the LPS of Type 1 *Neisseria gonorrhoeae* strain GC 6 [11].

Because furanose oligosaccharides do not occur in humans and, at the same time, are critical for the survival of mycobacteria and other pathogenic organisms, the enzymes containing them are ideal targets for drug action [3]. Consequently, there has been an increasing interest in the synthesis of furanose oligosaccharides and related analogues that could act as either glycosyltransferase substrates or inhibitors [1].

Numerous excellent reviews on the stereoselective synthesis of glycopyranosides have already been published [12,13], whereas methods for the construction of the furanosidic linkages have only recently begun to attract significant attention. Glycosidic bond formation is generally achieved by nucleophilic substitution at the anomeric carbon atom of the glycosyl donor. Glycosylation reaction consists usually of two steps: (1) functionalization of the anomeric hydroxyl to form an isolable glycosyl donor and (2) reaction of the donor with a promoter or catalyst to induce irreversible carbohydrate transfer to a nucleophilic acceptor. Diastereoselectivity in glycosidation is achieved mainly by exploitation of stereoselective effects, neighbouring groups participation, by the choice of a promoter, catalyst, reaction conditions (temperature, solvent) and additives (usually salts of strong acids).

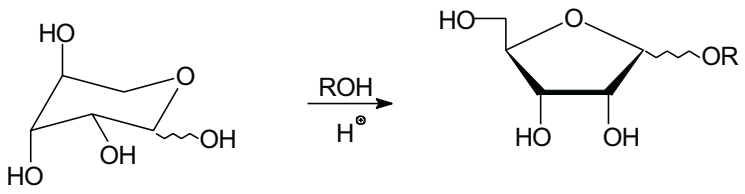
This paper presents an overview of the available methods for stereoselective synthesis of glycofuranosides. The preparation methods are based on the following classes of glycosyl donors (glycosylating agents): (I) 1-hydroxyl sugars, (II) derivatives readily available from 1-OH sugars (1-O-acyl sugars, 1-O-silylated glycosides and trichloroacetimidates), (III) thioglycosides, glycosyl thioesters and 1-Se-derivatives, (IV) glycosyl halides.

(I) Direct substitution of the glycosyl anomeric hydroxyl

Glycosylation reaction using 1-hydroxy sugars has an advantage over other glycosylations which inevitably require preparation and manipulation of reactive glycosyl donors. The main reason why glycosidation of totally O-unprotected sugars has not been yet satisfactorily developed is the undesirable generation of self-coupled products of the glycosyl donor and the deactivation of a glycosidation reagent by the free hydroxy groups of the glycosyl donor. However, the preparation of simple alkyl furanosides is most often achieved by subjecting an unprotected reducing sugar to a controlled Fischer glycosylation reaction (Scheme 1) [14]. The furanosides are kinetic products, and modest to good yields of these isomers are obtained at short reaction times. Methyl glycosides are generally synthesized by this approach [14]. One of disadvantage of these approaches is that yields depend on the sugar structure.

Direct formation of glycosidic bond from the 1-hydroxyl sugars, when all remaining hydroxyl groups are blocked by protecting groups, has an undoubtedly high efficiency

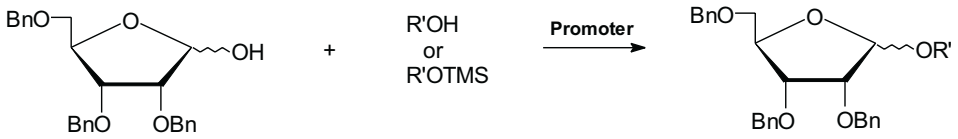
Scheme 1



+ pyranosides

in the glycosylation method. Direct anomeric 1-O-alkylation of O-protected sugars in the presence of various primary and secondary alcohols, including sugars as alkylating agents, proved to be a very convenient method for glycoside bond formation. Mukaiyama and co-workers applied 1-hydroxylribo-furanoses in the stereoselective synthesis of both 1,2-*cis*- and 1,2-*trans*-ribofuranosides [15–22] (Scheme 2).

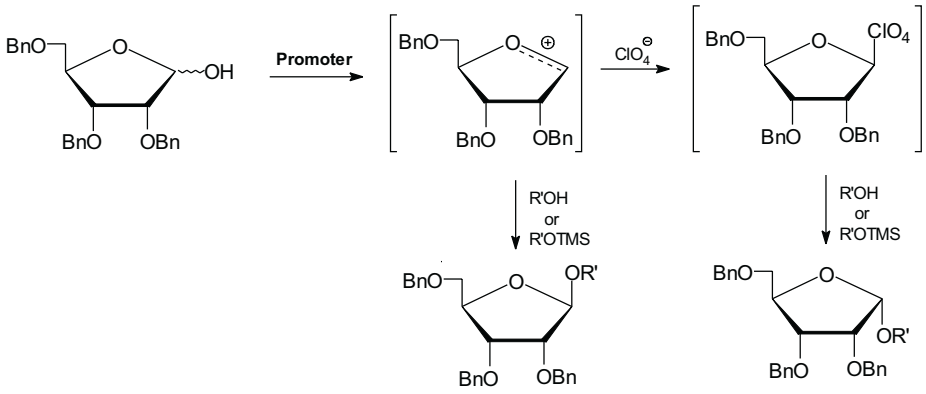
Scheme 2



1,2-cis-Ribosylation: In 1990 Mukaiyama and Suda [15] reported that the diphosphonium salt, prepared from tri-n-butylphosphine oxide ($Bu_3P=O$) and trifluoromethanesulfonic anhydride (triflic anhydride Tf_2O) is an effective reagent for stereoselective synthesis of 1,2-*cis*-ribofuranosides from 1-hydroxy sugars and alcohols or trimethylsilylated ethers. It was shown that the best result, concerning both yield and stereoselectivity, was attained when the glycosylation reaction was carried out in 1,2-dichloroethane at room temperature in the presence of diisopropylethylamine and molecular sieves 4 Å [15]. Extensive studies of the activation of the C-1 hydroxy group of 2,3,5-tri-O-benzyl-D-ribofuranose showed that 1,2-*cis* ribofuranosides can be stereoselectively synthesized in high yields by the use of catalytic systems: diphenyltin sulfide ($Ph_2Sn=S$), trifluoromethanesulfonic (triflic) anhydride and CsF (**A**) [16]; [catecholato(2-)-O,O']oxotitanium – triflic anhydride and CsF+ $^{i}Pr_2NEt$ (**B**) [17], hexamethyldisiloxane – catalytic amount of activator ($Sn(OTf)_2$, $Yb(OTf)_3$, $La(OTf)_3$ or $SnCl_2$) (**C**) [18] or catalytic amount of trityl salt ($TrClO_4$, $TrSbCl_6$, $MMTrSbCl_6$ (MM-monomethoxy), $TrB(C_6F_5)_4$) – Drierite [19] in the presence of lithium perchlorate $LiClO_4$. Reactions have been performed at room temperature with trimethylsilylated nucleophiles in dichloromethane [16,17] or free alcohols in nitromethane [18] or nitroethane [19]. The presence of perchlorate anion as a source of counter anion against oxocarbenium ion is crucial for α-selective glycosidation in the enumerated above methods.

1,2-trans-Ribosylation: In the absence of lithium perchlorate reversed selectivity was achieved – β-D-ribofuranosides were prepared predominantly in high yields [16–20]. The stereoselective direct syntheses of 1,2-trans-ribofuranosides from 1-hydroxyl-ribofuranoses and alcohols could also be effected by the combinational use of methoxyacetic acid ($MeOCH_2COOH$) and ytterbium(III) trifluoromethanesulfonate [$Yb(OTf)_3$] as a catalytic promoter [21] or in the presence of silver perchlorate ($AgClO_4$)-Lawesson's reagent or silver perchlorate ($AgClO_4$)-diphenyltin sulfide ($Ph_2Sn=S$) combined catalyst system [22].

Table 1. Stereoselective synthesis of 1,2-cis and 1,2-trans ribofuranosides from 2,3,5-tri-O-benzyl-D--ribofuranose.



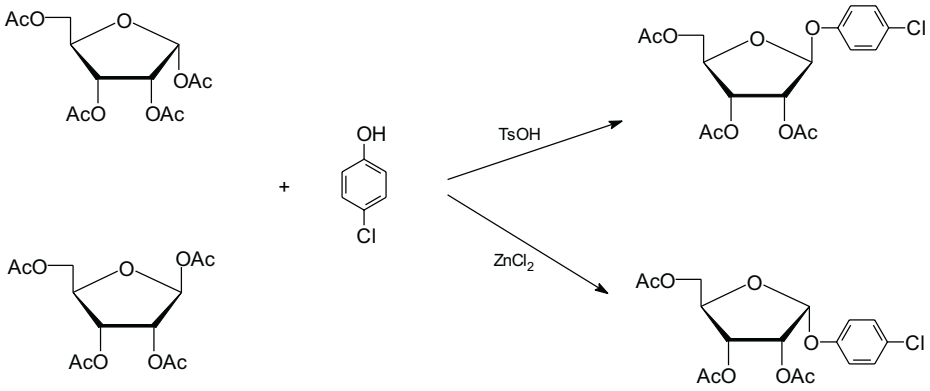
Entry	Promoter	Product	References
1	$^{n}Bu_3P{=}O$, Tf_2O, $^{i}Pr_2NEt$	1,2-*cis*	15
2	$Ph_2Sn{=}S$, Tf_2O, CsF (**A**)	1,2-*trans*	16
3	(**A**) + $LiClO_4$	1,2-*cis*	16
4	[catecholato(2-)-O,O']oxotitanium, Tf_2O, CsF, $^{i}Pr_2NEt$ (**B**)	1,2-*trans*	17, 20
5	(**B**) + $LiClO_4$	1,2-*cis*	17
6	TMS_2O, $Sn(OTf)_2$ or $Yb(OTf)_3$ or $La(OTf)_3$ or $Sn(Cl)_2$ (**C**)	1,2-*trans*	18
7	(**C**) + $LiClO_4$	1,2-*cis*	18
8	Trityl salt, Drierite (**D**)	1,2-*trans*	19
9	(**D**) + $LiClO_4$	1,2-*cis*	19
10	$MeOCH_2COOH$, $Yb(OTf)_3$	1,2-*trans*	21
11	$AgClO_4$ – Lawesson's reagent or $AgClO_4$ – $Ph_2Sn{=}S$	1,2-*trans*	22

(II) Derivatives readily available from 1-OH sugars

1-O-Acyl sugars. The simplicity of the preparation of the 1-O-acetylated glycosyl donors is undoubtedly an advantage of their use in the glycosylation method. The aryl aldofuranosides have generally been prepared by fusing the furanose acetate with an appropriate phenol in the presence of p-toluenesulfonic acid (TsOH). Lindberg and co-workers [23] have prepared phenyl β-D-furanosides of D-xylose and L-arabinose in this way. p-Chlorophenyl β-D-ribofuranoside is the product from fusion of both α and β-D-ribofuranose tetraacetate with p-chlorophenol and TsOH, but the use of zinc chloride gives α-D-ribofuranoside, instead [24] (Scheme 3).

Several efficient methods for the synthesis of both α and β-D ribofuranosides from 1-O-acetyl sugars have been reported. Alkyl β-D-ribofuranosides could be stereoselectively synthesized in high yields from 1-O-acetyl-2,3,5-tri-O-benzoyl-

Scheme 3



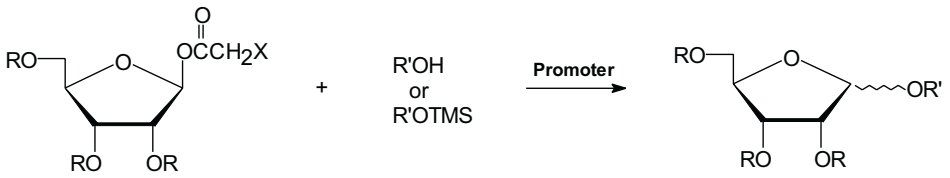
-β-D-ribofuranose and alcohols in dichloromethane at room temperature [25] or amide acetals (N,N-dimethylformamide dialkyl acetal), as the source of the aglycone, in the same solvent, but at 0°C [26], by the use of equimolar quantities of stannic chloride. Extension of this glycosidation to cyclic amide acetals derived from carbohydrates leads to effective syntheses of disaccharides containing the β-D-ribofuranosyl unit [27]. When trimethylsilyl trifluoromethanesulfonate (TMSOTf) [28,29] or boron trifluoride etherate ($BF_3 \cdot Et_2O$) [29] have been used as catalysts β-D-ribofuranosidic bonds are also formed exclusively. For example: an oligomeric fragment of the capsular polysaccharide of *Haemophilus Influenzae Type b Bacteria*, the ribosyl-ribitol moiety was stereoselectively constructed by glycosidation of tetra-O-acetyl-ribofuranoside with a suitable protected ribitol in high yield (85%) in the presence of catalytic amount of TMSOTf and molecular sieves 4 Å in 1,2-dichloroethane at room temperature (r.t. 3 h) [30]. Benzyl-protected 1-O-acetyl-β-D-ribofuranose can be effectively activated by triphenylmethyl perchlorate (trityl perchlorate,$TrClO_4$) [31]. 1,2-*trans* Ribofuranosides are formed exclusively in the reaction carried out in ethyl ether at 0°C. It has been found that the initially formed α-riboside isomerized to the β-anomer by the interaction with trityl perchlorate.

The combined use of molecular sieves 4 Å and lithium perchlorate ($LiClO_4$) has suppressed isomerization, and α-ribofuranosides are prepared predominantly in good yields [31].

The high 1,2-*cis* stereoselectivity has been also obtained in the reaction of 1-O-acetyl-2,3,5-tri-O-benzyl-β-D-ribofuranose with silylated nucleophiles by the combined use of a catalytic amount of tin(IV) chloride and tin(II) triflate with a stoichiometric amount of lithium perchlorate in dichloromethane at –23°C [32]. In some cases, addition of a catalytic amount of sodium periodate ($NaIO_4$) has improved yield [32]. Glycosyl donors carrying bromoacetyloxy and iodoacetyloxy groups at C-1 position were succesfully employed in stereoselective syntheses of α-D and β-D-ribofuranosides catalyzed by the combined use of silver salts and their

partners [22]. Thus, 1,2-*cis* ribofuranosides can be stereoselectively prepared in high yields by the reaction of 2,3,5-tri-O-benzyl-1-O-iodoacetyl-D-ribofuranose and trimethylsilylated nucleophiles in dichloromethane at room temperature by the use of silver salts in the coexistence of 3-molar amount of lithium perchlorate. By using [diphenyltin sulfide/silver salt] or [Lawesson's reagent/silver salt] combined catalyst system β-D-ribofuranosides have been predominantly obtained. The catalytic use (0.1 molar amount) of silver perchlorate ($AgClO_4$), silver hexafluoroantimonate ($AgSbF_6$) or silver triflate (AgOTf) was good enough to perform these glycosylation reactions with the best results in both yield and stereoselectivity.

Table 2. Stereoselective synthesis of 1,2-cis and 1,2-trans ribofuranosides from 1-O-acetyl sugars.



Entry	Donor	Promoter	Product	References
1	R=benzoyl, X=H	$SnCl_4$	1,2-*trans*	25, 26, 27
2	R=benzoyl, X=H	TMSOTf	1,2-*trans*	28, 29, 30
3	R=benzoyl, X=H	$BF_3 \cdot Et_2O$	1,2-*trans*	29
4	R=benzyl, X=H	$TrClO_4$	1,2-*trans*	31
5	R=benzyl, X=H	$TrClO_4$ + $LiClO_4$	1,2-*cis*	31
6	R=benzyl, X=H	$SnCl_4$ + $Sn(OTf)_2$ + $LiClO_4$	1,2-*cis*	32
7	R=benzyl, X=Br, I	AgY + $LiClO_4$ Y=ClO_4, SbF_6, OTf	1,2-*cis*	22
8	R=benzyl, X=Br, I	Ph_2Sn=S + AgY or Lawesson's reagent + AgY	1,2-*trans*	22

1-O-Silylated glycosides and trichloroacetimidates. These potentialy useful donors have been only occasionally studied**.** Mukaiyama and Matsubara have developed stereoselective reaction of 1-O-trimethylsilyl furanosides. Thus, β-D-ribofuranosides are predominantly synthesized by the glycosidation of 2,3,5-tri-O-benzyl-1-O-trimethylsilyl-D-ribofuranose and alkyl trimethylsilyl ethers in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and diphenylthin sulfide (Ph_2Sn=S) as an additive [33]. By the addition of lithium perchlorate in the above reaction conditions α-D-ribofuranosides are selectively prepared in high yields [33].

2,3,5-Tri-O-benzoyl- or -tri-O-acetyl-β-D-ribofuranosyl trichloroacetimides are excellent donors for the synthesis of oligosaccharides, especially for complex acceptors, affording disaccharides with very high yields under mild conditions in dichloromethane at 0^oC under an argon atm as phase in the presence of TMSOTf and molecular sieves 4 Å [29].

Boron trifluoride etherate at zero°C in dichloromethane has been found to be an appropriate promoter in the stereoselective synthesis of LAMPTEROFLAVIN (Figure 1), a light emitter in the luminous mushroom [34].

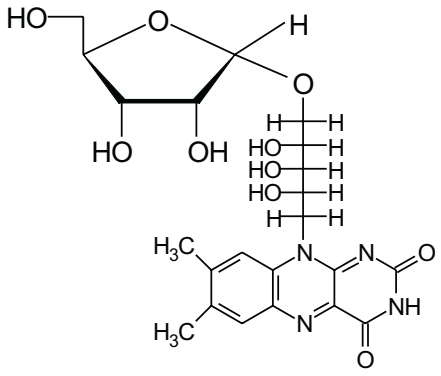


Figure 1

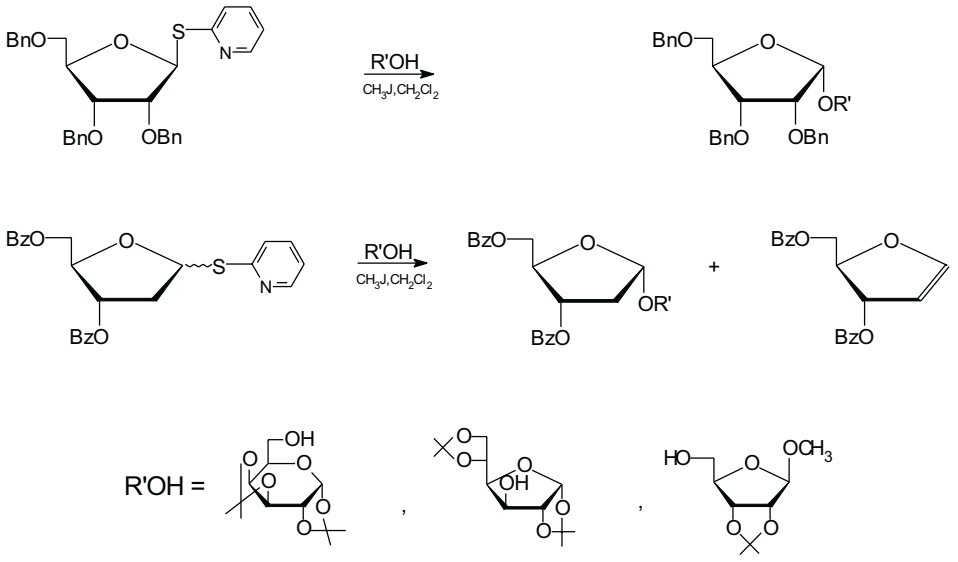
(III) Thioglycosides, glycosyl thioesters and 1-Se-derivatives

Thioglycosides have attracted considerable attention as versatile and flexible building blocks for the synthesis of simple as well as complex oligosaccharides [35]. The alkyl (aryl) thio group provides effective protection for the anomeric centre and is stable under various reaction conditions required for hydroxyl function differentiation and manipulation in protecting group chemistry. Moreover, thioglycosides can be activated with appropriate thiophilic reagents to act as potent glycoside donors. The use of S-glycosides in the synthesis of oligofuranosides was introduced by Mereyala and co-workers [36].

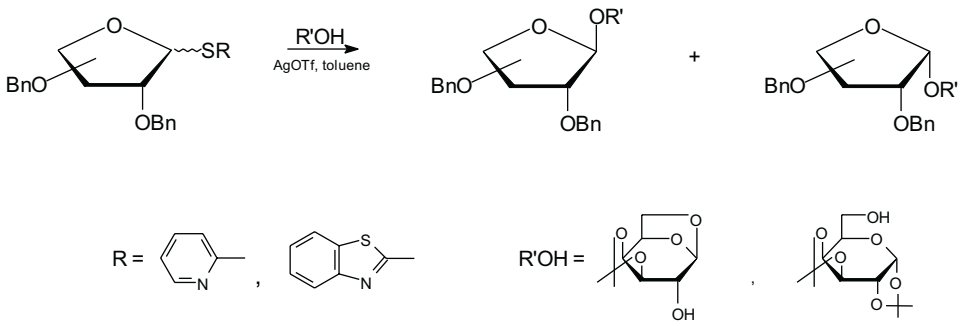
Direct activation of 2-pyridyl 2,3,5-tri-O-benzyl-1-thio-β-D-ribofuranoside and 2-pyridyl 3,5-di-O-benzoyl-2-deoxy-1-thio-α,β-D-ribofuranoside with a variety of sugar alcohols promoted by methyl iodide in methylene chloride gives exclusively 1,2-*cis* glycosidic linkages (Scheme 4). However, small amount (6–8%) of 1,4-anhydro--2-deoxy-3,5-di-O-benzoyl-D-*erythro*-pent-1-enitol is formed along with 2-deoxy-ribofurano-disaccharides with 2-pyridyl 2,5-di-O-benzoyl-2-deoxy-1-thio-α,β-D--ribofuranoside as a donor.

We introduced AgOTf as an activating agent [37]. Glycosidation of the free 2-OH and 6-OH groups in galactopyranosyl acceptors with 2-pyridyl- and 2-benzothiazolyl 1-thiofuranosides derivatives of D-ribose, D-xylose and L-arabinose, promoted by AgOTf proceeded in toluene at room temperature with moderate to high 1,2-*trans* selectivity (Scheme 5).

Scheme 4



Scheme 5

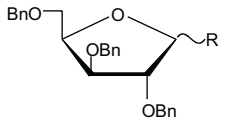


Recently, Lowary and co-workers [3] showed that coupling of per-acetylated 1-thiocresyl α-D-arabino- and α-D-lyxo-furanose with several primary and secondary carbohydrate alcohols in the presence of activating system N-iodosuccinimide/silver triflate (NIS/AgOTf) in dichloromethane (CH_2Cl_2), gave only 1,2-trans linked disaccharides in good to exellent yield.

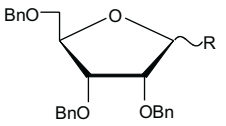
The favourable properties of other S-glycosides have been extensively studied by Bogusiak and Szeja. They have employed an anomeric S-xanthates, N,N-diethyldithiocarbamates [38] and O,O-diethyldithiophosphates [39] derivatives of benzylated D-ribo-, D-xylo- and L-arabinofuranose as a new class of thiofuranosyl donors. These functional groups can be effectively activated by silver triflate in

toluene at room temperature. Independently of the anomeric ratio of starting thioesters this glycosylation provides the 1,2-*trans* glycofuranosides with moderate to high stereoselectivity. These donors can be also converted into 1,2-*cis* glycofuranosides using the combination of silver triflate and a stoichiometric amount of polar organic compounds (DMSO, TMU, HMPA). Glycosidation reaction has been found to proceed the most stereoselectively with hexamethylphosphoric triamide (HMPA) [40,41]. Very recently we have reported that the NIS/TfOH-mediated coupling of S-glycofuranosyl dithiocarbamates with (5-nitro-2-pyridyl) 2,3,4-tri-O--benzoyl-1-thio-β-D-glucopyranoside as the acceptor gives access to valuable 1,2-*cis*-linked furanosyl-1-thiopyranosides [42]. In spite of moderate stereoselectivity at the anomeric position, this concept has opened a convenient and useful way for the block synthesis of oligosaccharides with a terminal furanosyl moiety.

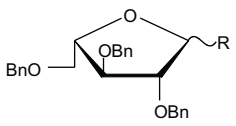
Table 3. Stereoselective synthesis of 1,2-cis and 1,2-trans pentofuranosides from 1-S- sugars



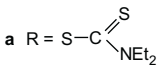
1a-c

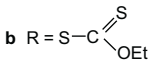


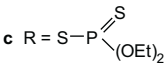
2a-c



3a-c







Entry	Donor	Promoter	Product	References
1	1a,b - 3a,b	AgOTf	1,2-*trans*	38
2	1c - 3c	AgOTf + K_2CO_3	1,2-*trans*	39
3	1 - 3	AgOTf + HMPA	1,2-*cis*	40,41
4	1a - 3a	NIS + TfOH	1,2-*cis*	42

The use of phenyl 2-O-benzoyl-3,5-di-O-benzyl-1-seleno-β-D-ribofuranoside as a potentially powerful glycosylation agent in chemoselective glycosylations of alkyl and aryl 1-thio-β-D-ribofuranosides was demonstrated by Van Boom and co-workers [43]. The only satisfactory result was obtained in NIS/TfOH-activated condensation with 4-nitrophenyl-thioribofuranoside as the acceptor. In order to exclude undesired trehalose derivatives formation and to obtain acceptable yield of desired dimer, reaction should be performed at low temperature (–50°C) using twofold excess of the donor.

(IV) Glycofuranosyl halides

By nucleophilic displacement of halide ion in the corresponding glycosyl bromides and chlorides, the stereocontrolled synthesis of 1,2-*trans* glycofuranosides can be achieved. Neighbouring group participation leads to an acyloxonium cation intermediate that reacts with an appropriate acceptor to give the 1,2-*trans*-glycoside.

When a nonparticipating benzyl group is present at C-2, the products are usually mixtures of 1,2-*trans*- and *cis*-glycosides. Treatment of crude tri-O-benzoyl-D-ribofuranosyl bromide with sodium phenoxide or methoxide in 1,2-dimethoxyethane gives phenyl [44] and methyl [45] β-D-ribofuranoside, respectively. When the 2,3,5-tri-O-benzyl-α-D-arabinofuranosyl chloride is treated with p-nitrophenol dissolved in dichloromethane in the presence of molecular sieves 4 Å as the acid acceptor, it yields the α-D and β-D p-nitrophenyl glycosides, in the ratio of 7:1 [46].

Barker and Fletcher [47] found that 2,3,5-tri-O-benzyl-D-ribofuranosyl bromide and methanol, with silver carbonate, gave mainly methyl α-D-ribofuranoside. Schmidt and Hermentin showed that 1-chloro-1-deoxy-2,3-O-isopropylidene-β-D-ribofuranuronic acid methyl ester and mono- and disaccharides with primary and secondary free hydroxylic groups gave highly stereoselectively and in high yield α-(1→5)--connected di- and trisaccharides under Koenigs-Knorr conditions, in the presence of silver oxide [48].

Low thermal stability and high sensitivity to hydrolysis of glycofuranosyl bromides and chlorides are the main disadvantages of these glycosyl donors. Mukaiyama and co-workers have demonstrated that generally much more stable perbenzylated 1,2-*trans* glycofuranosyl fluoride derivatives of D-ribo- and L-arabinofuranose can be applied to the synthesis of 1,2-cis-glycofuranosides having various aglycons [49].

In the presence of combination of stannous(II) chloride with trityl perchlorate 2,3,5-tri-O-benzyl-β-D-ribofuranosyl fluoride smoothly reacts with alcohols in ether solution at 0°C to give the corresponding ribofuranosides with high 1,2-*cis* stereoselectivity in high yields. A similar result has been observed in the reaction of 2,3,5-tri-O-benzyl-α-L-arabinofuranosyl fluoride with 3β-cholestanol [49].

Concluding remarks

Despite of the great progress recently made in the chemical synthesis of O-glycofuranosides, the procedures still remain to be improved with respect to yields, regio- and stereo-selectivity, and potential for scale-up. Formation of the glycosidic linkage is subjected to various factors such as electronic, stereoelectronic, conformational, substituent and reactivity effects generally associated with incipient oxocarbenium ions derived from carbohydrates. These factors are mostly related to glycosyl donor molecule. Additionally, the nature of the alcohol acceptor, polarity of the solvent and type of catalyst or promoter necessary to activate the leaving group at the anomeric carbon of the donor molecule should also be considered in terms of mildness, efficacy, generality and stereocontrol. The choice of the method to be used depends on the problem to be solved. Thus, the development of efficient methodologies for the construction of simple and complex glycofuranosides remains a challenging objective for synthetic chemists today, especially in view of the recent advances in glycobiology and related research fields.

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REFERENCES

1. Varki A., *Glycobiology*, **3**, 97 (1993).
2. Groisman J.F. and de Lederkremer R.M., *Eur. J. Biochem.*, **165**, 327 (1987).
3. D'Souza F.W., Cheshev P.E., Ayers J.D. and Lowary T.L., *J. Org. Chem.*, **63**, 9037 (1998) and references therein.
4. Lindberg B., *Adv. Carbohydr. Chem. Biochem.*, **48**, 279 (1990).
5. Brink N.G., Holly F.W., Shunk C.H., Peel E.W., Cahill J.J. and Folkers K., *J. Am. Chem. Soc.*, **72**, 1866 (1950).
6. Kocharova N.A., Zatonsky G.V., Shashkov A.S. and Knirel Y.A., *Abstracts of Papers*, 20th International Carbohydrate Symposium, Hamburg-Germany-August-September 1 - 2000, Poster - A-101.
7. Misaki A., Azuma I. and Yamamura Y., *J. Biochem. (Tokyo),* **82**, 1759 (1977).
8. Daffe M., Brennan P. J. and McNeil M., *J. Biol. Chem.*, **265**, 6734 (1990).
9. Wilkinson S.G., Galbraith L. and Anderton W.J., *Carbohydr. Res.*, **112**, 241 (1983).
10. Hurlbert R.E., Weckesser J., Mayer H. and Fromme I., *Eur. J. Biochem.*, **68**, 365 (1976).
11. Perry M.B., Daoust V., Diena B.B., Ashton F.E. and Wallace R., *Can. J. Biochem.*, **53**, 623 (1975).
12. Toshima K. and Tatsuta K., *Chem. Rev.*, **93**, 1503 (1993) and references cited therein.
13. Boons G.J., *Tetrahedron*, **52**, 1095 (1996) and references cited therein.
14. Green J.W., *Adv. Carbohyrd. Chem. Biochem.*, **21**, 95 (1966).
15. Mukaiyama T. and Suda S., *Chem. Lett.*, 1143 (1990).
16. Mukaiyama T., Matsubara K. and Suda S., *Chem. Lett.*, 981 (1991)
17. Suda S. and Mukaiyama T., *Bull. Chem. Soc. Jpn.*, **66**, 1211 (1993).
18. Mukaiyama T., Matsubara K. and Hora M., *Synthesis*, 1368 (1994)
19. Uchiro H. and Mukaiyama T., *Chem. Lett.*, 79 (1996).
20. Suda S. and Mukaiyama T., *Chem. Lett.*, 431 (1991).
21. Inanaga J., Yokoyama Y. and Hanamoto T., *J. Chem. Soc. Chem. Commun.*, 1090 (1993).
22. Shimomura N. and Mukaiyama T., *Bull. Chem. Soc. Jpn.*, **67**, 2532 (1994).
23. Borjeson H., Jerkeman P. and Lindberg B., *Acta Chem. Scand.*, **17**, 1705 (1963).
24. Shimidate T., *Nippon Kagaku Zasshi,* **83**, 214 (1962); *Chem. Abstracts*, **59**, 6498 (1963).
25. Hanessian S. and Banoub J., *Carbohydr. Chem.*, **59**, 261 (1977).
26. Hanessian S. and Banoub J., *Tetrahedron Lett.*, **9**, 657 (1976).
27. Hanessian S. and Banoub J., *Tetrahedron Lett.*, **9**, 661(1976).
28. Hermans J.P.G., Poot L., Kloosterman M., Van der Marel G.A., Van Boeckel C.A.A., Evenberg D., Poolman J.T., Hoogerhout P. and Van Boom J.H., *Recl. Trav. Chim. Pays-Bas*, **106**, 498 (1987).
29. Chiu-Machado I., Castro-Palomino J., Madrazo-Alonso O., Lopetegui-Palacios C. and Verez-Bencomo V., *J. Carbohydr. Chem.*, **14**, 551 (1995).
30. Hoogerhout P., Evenberg D., Van Boeckel C.A.A., Poolman J.T., Beuvery E.C., Van der Marel G.A. and Van Boom J.H., *Tetrahedron Lett.*, **28**, 1553 (1987).
31. Mukaiyama T., Kobayashi S. and Shoda S., *Chem. Lett.*, 907 (1984).
32. Mukaiyama T., Shimpuku T., Takashima T. and Kobayashi S., *Chem. Lett.*, 145 (1989).
33. Mukaiyama T. and Matsubara K., *Chem. Lett.*, 1041 (1992).
34. Tokahashi H., Isobe M. and Goto T., *Tetrahedron*, **47**, 6215 (1991).
35. Garegg P.J., *Adv. Carbohydr. Chem. Biochem.*, **52**, 179 (1997).
36. Mereyala H.B., Kulkarni V.R., Ravi D., Sharma G.V.M., Rao B.V. and Reddy G.B., *Tetrahedron*, **48**, 545 (1992).
37. Bogusiak J. and Wandzik I. unpublished results.
38. Bogusiak J. and Szeja W., *Carbohydr. Res.*, **295**, 235 (1996).
39. Bogusiak J., *Polish J. Chem.*, **73**, 619 (1999).
40. Bogusiak J. and Szeja W., *Synlett*, **6**, 661 (1997).
41. Bogusiak J. and Szeja W., *Carbohydr. Res.*, **330**, 141 (2001).
42. Bogusiak J. and Szeja W., *Tetrahedron Lett.*, **42**, 2221 (2001).

43. Sliedregt L.A.J.M., Broxterman H.J.G., Van der Marel G.A. and Van Boom J.H., *Carbohydr. Lett.*, **1**, 61 (1994).
44. Vis E. and Fletcher H.G., Jr., *J. Am. Chem. Soc.*, **79**, 1182 (1957).
45. Pedersen C. and Fletcher H.G., Jr., *J. Am. Chem. Soc.*, **82**, 941 (1950).
46. Zissis E. and Glaudemans C.P.J., *Carbohydr. Res.*, **50**, 292 (1976).
47. Barker R. and Fletcher H.G., Jr., *J. Org. Chem.*, **26**, 4605 (1961).
48. Schmidt R.R. and Hermentin P., *Chem. Ber.*, **112**, 2659 (1979).
49. Mukaiyama T., Hashimoto Y. and Shoda S., *Chem. Lett.*, 935 (1983).