1,2-cis glycosylation

Subjects: Chemistry, Organic

Contributor: Akihiro Ishiwata, Katsunori Tanaka, Yukishige Ito, Hui Cai, Feiqing Ding

Controlling the stereoselectivity of 1,2-*cis* glycosylation is one of the most challenging tasks in the chemical synthesis of glycans. There are various 1,2-*cis* glycosides in nature, such as α-glucoside and β-mannoside in glycoproteins, glycolipids, proteoglycans, microbial polysaccharides, and bioactive natural products. In the structure of polysaccharides such as α-glucan, 1,2-*cis* α-glucosides were found to be the major linkage between the glucopyranosides. Various regioisomeric linkages, 1→3, 1→4, and 1→6 for the backbone structure, and 1→2/3/4/6 for branching in the polysaccharide as well as in the oligosaccharides were identified. To achieve highly stereoselective 1,2-*cis* glycosylation, including α-glucosylation, a number of strategies using inter- and intra-molecular methodologies have been explored.

Keywords: α-glucan ; stereoselective 1,2-cis glycosylation ; α-glucosylation

1. Introduction

Stereoselective synthesis of 1,2-*cis* glycosides is one of the most challenging issues in the chemical synthesis of glycans [1][2][3][4][5][6][7]. Various 1,2-*cis* glycosides in nature have been found as α-glucoside and β-mannoside in glycoproteins, glycolipids, proteoglycans, microbial polysaccharides, and bioactive natural products. In the structure of polysaccharides such as α-glucan, 1,2-*cis* α-glucosides were found to be the major linkage between the glucopyranosides. Various regioisomeric linkages, 1→3, 1→4, and 1→6 for backbone structure, and 1→2/3/4/6 for branching in the polysaccharide as well as in the oligosaccharides were identified.

α-D-glucans

α-D-glucan is a homopolysaccharide and a simple polymer of α-D-glucopyranoside (α-D-Glc*p*) [8][9]. D-Glucose, the component of the D-glucans, is photosynthesized in plants and widespread in nature and exists in its D-glucopyranose form in α-D-glucans [10]. The most common and linear example of α-D-glucan is (1→4)-α-D-glucan (amylose), which plays an essential role as an energy source for metabolism [11]. The chain length of amylose is known to be in the order of 500–6000 glucose units, depending on its botanical origin. Three crystalline forms of amylose, A-, B-, and C- (a mixture of A and B) granules [12], containing random and short helical segments, have been reported. Crystallized structures were found in the V form [13][14][15], and each segment composed of six glucose residues formed a left-handed, single-stranded helical structure [16]. Branched (1→4)-α-D-glucans are called amylopectin and glycogen, the analogues of starch for energy storage in plants and animals, fungi, and bacteria, respectively. The structures of amylopectin and glycogen are well known to be more compact than that of linear amylose. (1→4)-α-D-glucan is biologically synthesized by glucosyltransferase [17][18][19][20] and amylosucrase (sucrose-1,4-α-glucan glucosyltransferase [21][22][23][24] and (1→4)-α-D-glucan branching enzymes [25][26][27][28][29][30]).

α-D-glucans also have extremely complex structural diversity according to various regioisomers, making non-branched and branched α-D-glucans with (1→6)-, (1→4)-, (1→3)-, and (1→2)-glycosidic linkages and molecular masses according to the degree of polymerization (**Figure 1**). The α-D-glucans have been obtained from various species, listed in **Table 1** [31][32][33][34][35][36].

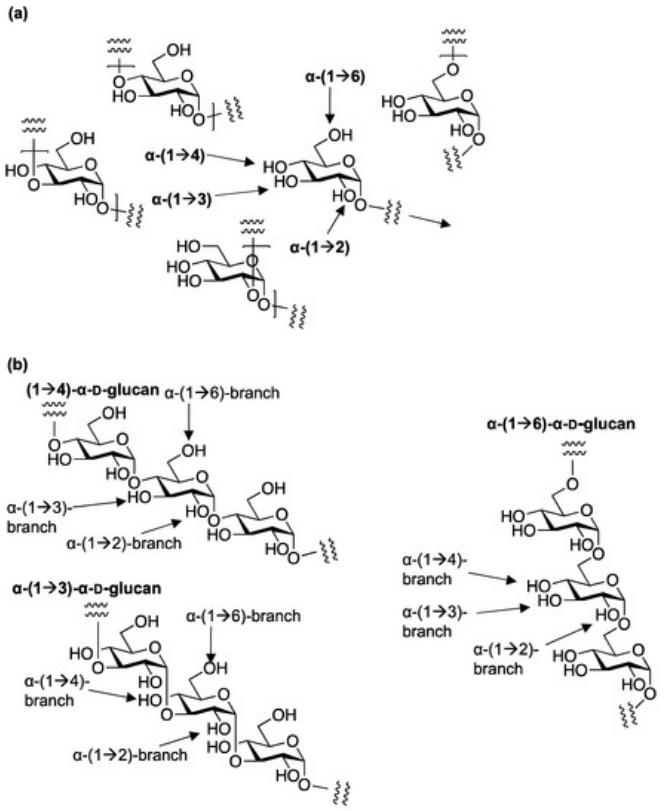

Figure 1. The linkages of α-D-glucans. (**a**) The linkages in the linear α-D-glucans; (**b**) the linkages of the branching in the various α-D-glucans.

Regioisomeric linear (1→6)-α-D-glucans (isomaltosides) were isolated from *Amillariella tabescens* and *Sarcodon aspratus* [37][38][39]. A dextran [40] obtained from lactic acid bacteria, such as *Lactobacillus*, *Leuconostoc*, *Weissella*, and *Streptococcus*, has a (1→6)-α-D-glucan backbone with up to 50% branching as α-(1→3), α-(1→4), or α-(1→2) linkages. Several glucosyl transferase (Gtf) enzymes synthesize dextrans with [41][42] and without branching [43][44][45][46][47][48]. The complex branched structures make the dextrans effective energy storage molecules that release D-glucose slowly via enzymatic hydrolysis [49][50][51][52][53].

Linear (1→3)-α-D-glucan (pseudonigan) was identified from *Aspergillus niger* [48] as a storage polysaccharide [54]. A linear (1→2)-α-D-glucan has not yet been identified. The (1→3)-α-D-glucans are major components of the cell wall of filamentous fungi [55][56][57] and dimorphic yeasts [58][59][60][61] and are synthesized via the primer for (1→3)-α-D-glucans by intracellular amylases. The structural analysis of (1→3)-α-D-glucan was reported and it was mentioned that three crystalline forms I–III of (1→3)-α-D-glucan were detected and interconverted via dehydration and hydration reactions [32][62]. Various biological functions of (1→3)-α-D-glucan were investigated such as immunological activity via Toll-like receptor 4 (TLR4) [63][64][65], which has been shown in the case of (1→4)-α-D-glucans as well as β-D-glucans [66].

More complex branching structures have been discovered in various linear glucans [33][67][68]. From dextran, NRRL B1397, an α-D-Glc-(1→2)-α-D-Glc-(1→6)-D-Glc structure [69][70][71][72][73] was identified and the D-Glc-(1→2)-branching moiety was found to be an α-glucoside to tricholomal (1→4)-α-D-glucan [74].

The most common and linear example of a stereoisomeric β-D-glucans is cellulose, composed of β-D-Glc*p*, which plays a fundamental role as a structural component of the cell wall [75][76]. As physiologically active biological response modifiers (BRMs), the structure of glucans and the biological activity relationship of β-D-glucans have been reported to be adjuvants in bacterial, viral, or protozoan infections, and potent antitumor drugs, depending on the molecular weight, degree of branching, conformation, and intermolecular associations of glucans [76][77][78][79][80][81]. In the case of the synthesis of β-D-glucans, a common methodology such as stereoselective β-D-glucopyranosylation via the effect of neighboring group participation from the 2-*O*-acyl group can be effectively used [82][83][84].

2. 1,2-*cis* glycosylation

Stereoselective *O*-glycosylation is a key step in the assembly of biologically relevant oligosaccharides. The target oligosaccharide contains 1,2-*cis*- or 1,2-*trans*-configurated *O*-glycosidic linkages to the C-2–O bond of the non-reducing side residue of the glycoside. The 1,2-*cis* linkages, such as α-glucopyranoside, α-galactopyranoside, β-mannopyranoside, β-rhamnopyranoside, and other glycosides, are found in natural glycans, including glycoconjugate such as glycoproteins,

glycolipids, proteoglycans, microbial polysaccharides, and glycosylated natural products. Controlling the stereoselectivity in the formation of 1,2-*cis* glycosides is extremely challenging in synthetic chemistry, as in the case of α-gluco (2-equatorial)- and β-manno (2-axial)-type glycoside formations, although the method for the 1,2-*trans* isomers was developed by using the effect of neighboring group participation from theC-2 acyl group as the first choice of the chemist. Various methods using inter- [85][86][87][88][89][90] and intra- [91][92][93] molecular procedures have been developed for the stereoselective synthesis of 1,2-*cis* glycosides [88][94], depending on the acceptor molecules [95][96], and further developments have been reported in recent years [97][98][99][100].

The 2-*O*-ether-protected glycosyl donors predominantly afford the axial glycosides via stereoelectronic effects [101][102][103][104][105][106][107][108] (**Figure 2**). Using this methodology, 1,2-*cis* gluco-type pyranosides were selectively obtained. However, the selectivity is not predictable, mainly because of the many controversial results reported from a variety of examinations using many types of donors suitably optimized to the demand of their targets. Based on basic observations, the solvent effect [109][110][111][112][113][114][115], the concentration effect [116][117][118][119][120], and other factors [121][122][123], including a very recent approach using an S_N2-predicting, leaving group enhanced by a coordinating acceptor [124][125], were also accepted as factors for the stereoselectivity of glycosylation. Researchers focus on two effective and stereoselective methods for glucan synthesis: the use of C2-*o*-tosylamide (TsNH)-benzyl (TAB) ether for bimodal glycosylation [126][127][128] and ZnI_2-mediated 1,2-*cis* glycosylation [129].

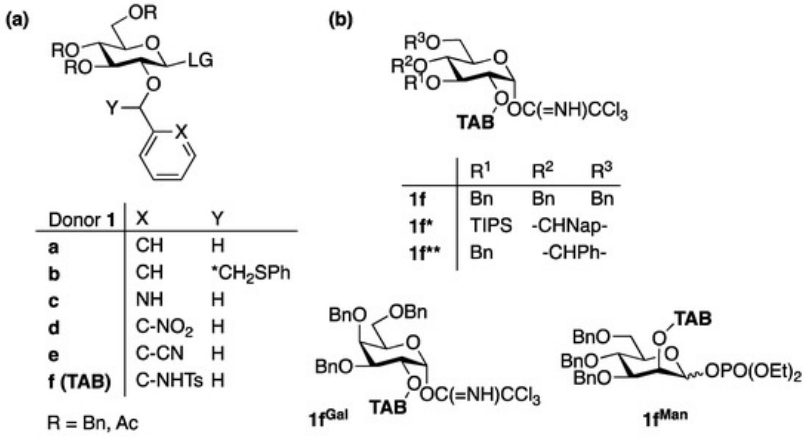

Figure 2. 2-*O*-ether-protected glycosyl donors. (**a**) The 2-*O*-ether-protected glycosyl donors for stereoselective glycosylation; (**b**) TAB-protected donors for bimodal glycosylations.

References

1. Andreana, P.R.; Crich, D. Guidelines for O-Glycoside Formation from First Principles. ACS Cent. Sci. 2021, 7, 1454–1462.
2. Gangoiti, J.; Corwin, S.F.; Lamothe, L.M.; Vafiadi, C.; Hamaker, B.R.; Dijkhuizen, L. Synthesis of novel α-glucans with potential health benefits through controlled glucose release in the human gastrointestinal tract. Crit. Rev. Food Sci. Nutr. 2020, 60, 123–146.
3. Shivatare, S.S.; Wong, C.-H. Synthetic Carbohydrate Chemistry and Translational Medicine. J. Org. Chem. 2020, 85, 15780–15800.
4. Loh, C.C.J. Exploiting non-covalent interactions in selective carbohydrate synthesis. Nat. Rev. Chem. 2021, 5, 792–815.
5. Wang, L.; Overkleeft, H.S.; van der Marel, G.A.; Codée, J.D.C. Reagent Controlled Stereoselective Synthesis of α-Glucans. J. Am. Chem. Soc. 2018, 140, 4632–4638.
6. Wang, L.; Zhang, Y.; Overkleeft, H.S.; van der Marel, G.A.; Codée, J.D.C. Reagent Controlled Glycosylations for the Assembly of Well-Defined Pel Oligosaccharides. J. Org. Chem. 2020, 85, 15872–15884.
7. Inuki, S.; Tabuchi, H.; Matsuzaki, C.; Yonejima, Y.; Hisa, K.; Kimura, I.; Yamamoto, K.; Ohno, H. Chemical Synthesis and Evaluation of Exopolysaccharide Fragments Produced by Leuconostoc mesenteroides Strain NTM048. Chem. Pharm. Bull. 2022, 70, 155–161.
8. Shetty, P.R.; Batchu, U.R.; Buddana, S.K.; Sambasiva Rao, K.; Penna, S. A comprehensive review on α-D-Glucans: Structural and functional diversity, derivatization and bioapplications. Carbohydr. Res. 2021, 503, 108297.

9. Wang, G.-L.; Li, J.-Y.; Wang, Y.; Chen, Y.; Wen, Q.-L. Extraction, Structure and Bioactivity of Polysaccharides from Tricholoma matsutake (S. Ito et Imai) Singer (Review). Appl. Biochem. Microbiol. 2022, 58, 375–381.
10. Stephens, Z.; Wilson, L.F.L.; Zimmer, J. Diverse mechanisms of polysaccharide biosynthesis, assembly and secretion across kingdoms. Curr. Opin. Struct. Biol. 2023, 79, 102564.
11. Thitipraphunkul, K.; Uttapap, D.; Piyachomkwan, K.; Takeda, Y. A comparative study of edible canna (Canna edulis) starch from different cultivars. Part II. Molecular structure of amylose and amylopectin. Carbohydr. Polym. 2003, 54, 489–498.
12. Sarko, A.; Wu, H.-C.H. The Crystal Structures of A-, B- and C-Polymorphs of Amylose and Starch. Starch 1978, 30, 73–78.
13. Helbert, W.; Chanzy, H. Single crystals of V amylose complexed with n-butanol or n-pentanol: Structural features and properties. Int. J. Biol. Macromol. 1994, 16, 207–213.
14. Bail, P.L.; Rondeau, C.; Buleon, A. Structural investigation of amylose complexes with small ligands: Helical conformation, crystalline structure and thermostability. Int. J. Biol. Macromol. 2005, 35, 1–7.
15. Rappenecker, G.; Zugenmaier, P. Detailed refinement of the crystal structure of Vh-amylose. Carbonhydr. Res. 1981, 89, 11–19.
16. Zhang, Q.; Lu, Z.; Hu, H.; Yang, W.; Marszalek, P.E. Direct detection of the formation of V-amylose helix by single molecule force spectroscopy. J. Am. Chem. Soc. 2006, 128, 9387–9393.
17. Sivak, M.N.; Preiss, J. (Eds.) Starch: Basic Science to Biotechnology. In Advances in Food and Nutrition Research; Academic Press: Cambridge, MA, USA, 1998; Volume 41.
18. Buléon, A.; Colonna, P.; Planchot, V.; Ball, S. Starch granules: Structure and biosynthesis. Int. J. Biol. Macromol. 1998, 23, 85–112.
19. Wang, T.L.; Bogracheva, T.Y.; Hedley, C.L. Starch: As simple as A, B, C? J. Exp. Bot. 1998, 49, 481–502.
20. James, M.G.; Robertson, D.S.; Myers, A.M. Characterization of the maize gene sugary1, a determinant of starch composition in kernels. Plant Cell 1995, 7, 417–429.
21. Hehre, E.J.; Hamilton, D.M.; Carlson, A.S. Synthesis of a polsaccharide of the starch glycogen class from sucrose by a cell-free, bacterial enzyme system (amylosucrase). J. Biol. Chem. 1949, 177, 267–279.
22. Potocki de Montalk, G.; Remaud-Simeon, M.; Willemot, R.-M.; Sarçabal, P.; Planchot, V.; Monsan, P. Amylosucrase from Neisseria polysaccharea: Novel catalytic properties. FEBS Lett. 2000, 471, 219–223.
23. Kim, B.-S.; Kim, H.-S.; Hong, J.-S.; Huber, K.C.; Shim, J.-H.; Yoo, S.-H. Effects of amylosucrase treatment on molecular structure and digestion resistance of pre-gelatinised rice and barley starches. Food Chem. 2013, 138, 966–975.
24. Jung, Y.-S.; Hong, M.-G.; Park, S.-H.; Lee, B.-H.; Yoo, S.-H. Biocatalytic Fabrication of α-Glucan-Coated Porous Starch Granules by Amylolytic and Glucan-Synthesizing Enzymes as a Target-Specific Delivery Carrier. Biomacromolecules 2019, 20, 4143–4149.
25. Li, Y.; Ren, J.; Liu, J.; Sun, L.; Wang, Y.; Liu, B.; Li, C.; Li, Z. Modification by α-D-glucan branching enzyme lowers the in vitro digestibility of starch from different sources. Int. J. Biol. Macromol. 2018, 107, 1758–1764.
26. Park, I.; Park, M.; Yoon, N.; Cha, J. Comparison of the Structural Properties and Nutritional Fraction of Corn Starch Treated with Thermophilic GH13 and GH57 α-Glucan Branching Enzymes. Foods 2019, 8, 452.
27. Ban, X.; Dhoble, A.S.; Li, C.; Gu, Z.; Hong, Y.; Cheng, L.; Holler, T.P.; Kaustubh, B.; Li, Z. Bacterial 1,4-α-glucan branching enzymes: Characteristics, preparation and commercial applications. Crit. Rev. Biotechnol. 2020, 40, 380–396.
28. Yu, L.; Kong, H.; Gu, Z.; Li, C.; Ban, X.; Cheng, L.; Hong, Y.; Li, Z. Two 1,4-α-glucan branching enzymes successively rearrange glycosidic bonds: A novel synergistic approach for reducing starch digestibility. Carbohydr. Polym. 2021, 262, 117968.
29. Xu, T.; Li, Z.; Gu, Z.; Li, C.; Cheng, L.; Hong, Y.; Ban, X. The N-terminus of 1,4-α-glucan branching enzyme plays an important role in its non-classical secretion in Bacillus subtilis. Food Biosci. 2023, 52, 102491.
30. Lambré, C.; Baviera, J.M.B.; Bolognesi, C.; Cocconcelli, P.S.; Crebelli, R.; Gott, D.M.; Grob, K.; Lampi, E.; Mengelers, M.; Mortensen, A.; et al. Safety evaluation of the food enzyme 1,4-α-glucan branching enzyme from the non-genetically modified Geobacillus thermodenitrificans strain TRBE14. EFSA J. 2023, 21, e07834.
31. Carbonero, E.R.; Montai, A.V.; Woranovicz-Barreira, S.; Gorin, P.A.J.; Lacomini, M. Polysaccharides of lichenized fungi of three Cladina spp.: Significance as chemotypes. Phytochemistry 2002, 61, 681–686.

32. Synytsya, A.; Novak, M. Structural analysis of glucans. Ann. Transl. Med. 2014, 2, 17–31.

33. Naessens, M.; Cerdobbel, A.; Soetaert, W.; Vandamme, E.J. Leuconostoc dextransucrase and dextran: Production, properties and applications. J. Chem. Technol. Biotechnol. 2005, 80, 845–860.

34. Zhong, X.; Wang, G.; Fang, S.; Zhou, S.; Ishiwata, A.; Cai, H.; Ding, F. Immunomodulatory Effect and Biological Significance of β-Glucans. Pharmaceutics 2023, 15, 1615.

35. Okuyama, M.; Saburi, W.; Mori, H.; Kimura, A. α-Glucosidases and α-1,4-Glucan Lyases: Structures, Functions, and Physiological Actions. Cell. Mol. Life Sci. 2016, 73, 2727–2751.

36. Synytsya, A.; Novák, M. Structural Diversity of Fungal Glucans. Carbohydr. Polym. 2013, 92, 792–809.

37. Luo, X.; Xu, X.; Yu, M.; Yang, Z.; Zheng, L. Characterisation and immunostimulatory activity of an α-(1→6)-D-glucan from the cultured Armillariella tabescens mycelia. Food Chem. 2008, 111, 357–363.

38. Han, X.Q.; Wu, X.M.; Chai, X.Y.; Chen, D.; Dai, H.; Dong, H.L.; Ma, Z.Z.; Gao, X.M.; Tu, P.F. Isolation, characterization and immunological activity of a polysaccharide from the fruit bodies of an edible mushroom, Sarcodon aspratus (Berk.) S. Ito. Food. Res. Int. 2011, 44, 489–493.

39. Painter, T.J. Details of the fine structure of nigeran revealed by the kinetics of its oxidation by periodate. Carbohydr. Res. 1990, 200, 403–408.

40. Pasteur, L. On the viscous fermentation and the butyrous fermentation. Bull. Soc. Chim. Paris 1861, 11, 30–31.

41. Leemhuis, H.; Pijning, T.; Dobruchowska, J.M.; van Leeuwen, S.S.; Kralj, S.; Dijkstra, B.W.; Dijkhuizen, L. Glucansucrases: Three-dimensional structures, reactions, mechanism, α-glucan analysis and their implications in biotechnology and food applications. J. Biotechnol. 2013, 163, 250–272.

42. van Hijum, S.A.F.T.; Kralj, S.; Ozimek, L.K.; Dijkhuizen, L.; van Geel-Schutten, I.G.H. Structure-function relationships of glucansucrase and fructansucrase enzymes from lactic acid bacteria. Microbiol. Mol. Biol. Rev. 2006, 70, 157–176.

43. Simpson, C.L.; Cheetham, N.W.H.; Jacques, N.A. Four glucosyltransferases, gtfJ, gtfK, gtfL and gtfM, from Streptococcus salivarius ATCC 25975. Microbiology 1995, 141, 1451–1460.

44. Kang, H.-K.; Oh, J.-S.; Kim, D. Molecular characterization and expression analysis of the glucansucrase DSRWC from Weissella cibaria synthesizing a α(1→6) glucan. FEMS Microbiol. Lett. 2009, 292, 33–41.

45. Mondal, S.; Chakraborty, I.; Pramanik, M.; Rout, D.; Islam, S.S. Structural studies of water-soluble polysaccharides of an edible mushroom, Termitomyces eurhizus. A reinvestigation. Carbohydr. Res. 2004, 339, 1135–1140.

46. Purama, R.K.; Goswami, P.; Khan, A.T.; Goyal, A. Structural analysis and properties of dextran produced by Leuconostoc mesenteroides NRRL B-640. Carbohydr. Polym. 2009, 76, 30–35.

47. Loesche, W.J. Role of Streptococcus mutans in human dental decay. Microbiol. Rev. 1986, 50, 353.

48. He, Q.; Kobayashi, K.; Kusumi, R.; Kimura, S.; Enomoto, Y.; Yoshida, M.; Kim, U.-J.; Wada, M. In vitro Synthesis of Branchless Linear (1→6)-α-D-Glucan by Glucosyltransferase K: Mechanical and Swelling Properties of Its Hydrogels Crosslinked with Diglycidyl Ethers. ACS Omega 2020, 5, 31272–31280.

49. Rosenfeld, E.L.; Lukomskaya, I.S. The splitting of dextran and isomaltose by animal tissues. Clin. Chim. Acta 1957, 2, 105–114.

50. Wang, R.; Dijkstra, P.J.; Karperien, M. Dextran. Biomaterials from Nature for Advanced Devices and Therapies; Wiley: Hoboken, NJ, USA, 2016; pp. 307–319.

51. Hong, M.-G.; Yoo, S.-H.; Lee, B.-H. Effect of highly branched α-glucans synthesized by dual glycosyltransferases on the glucose release rate. Carbohydr. Polymer 2022, 278, 119016.

52. Banerjee, A.; Bandopadhyay, R. Use of dextran nanoparticle: A paradigm shift in bacterial exopolysaccharide based biomedical applications. Int. J. Biol. Macromol. 2016, 87, 295–301.

53. Lamothe, L.M.; Francey, C.; Lerea-Antes, J.S.; Rytz, A.; D'Urzo, C.; Delodder, F.; Piccardi, N.; Curti, D.; Murciano Martinez, P.; Darimont, C.; et al. Effects of α-D-glucans with alternating 1,3/1,6 α-D-glucopyranosyl linkages on postprandial glycemic response in healthy subjects. Carbohydr. Polym. Technol. Appl. 2022, 4, 100256.

54. Zonneveld, B.J.M. The Significance of α-1,3-glucan of the cell wall and α-1,3-glucanase for cleistothecium development. Biochim. Biophys. Acta. 1972, 273, 174–187.

55. Johnston, I.R. The composition of the cell wall of Aspergillus niger. Biochem. J. 1965, 96, 651–658.

56. Zonneveld, B.J.M. Biochemical analysis of the cell wall of Aspergillus nidulans. Biochim. Biophys. Acta. 1971, 249, 506–514.

57. Yoshimi, A.; Miyazawa, K.; Abe, K. Function and Biosynthesis of Cell Wall α-1,3-Glucan in Fungi. J. Fungi 2017, 3, 63.

58. Van der Kaaij, R.M.; Janecek, S.; van der Maarel, M.J.E.C.; Dijkhuizen, L. Phylogenetic and biochemical characterization of a novel cluster of intracellular fungal α-amylase enzymes. Microbiology 2007, 153, 4003–4015.

59. Marion, C.L.; Rappleye, C.A.; Engle, J.T.; Goldman, W.E. An α-(1,4)-amylase is essential for α-(1,3)-glucan production and virulence in Histoplasma capsulatum. Mol. Microbiol. 2006, 62, 970–983.

60. Camacho, E.; Sepulveda, V.E.; Goldman, W.E.; San-Blas, G.; Niño-Vega, G.A. Expression of Paracoccidioides brasiliensis AMY1 in a Histoplasma capsulatum amy1 mutant, relates an α-(1,4)-amylase to cell wall α-(1,3)-glucan synthesis. PLoS ONE 2012, 7, e50201.

61. Koizumi, A.; Miyazawa, K.; Ogata, M.; Takahashi, Y.; Yano, S.; Yoshimi, A.; Sano, M.; Hidaka, M.; Nihira, T.; Nakai, H.; et al. Cleavage of α-1,4-glycosidic linkages by the glycosylphosphatidylinositol-anchored α-amylase AgtA decreases the molecular weight of cell wall α-1,3-glucan in Aspergillus oryzae. Front. Fungal Biol. 2023, 3, 1061841.

62. Jelsma, J.; Kreger, D.R. Polymorphism in crystalline (1→3)-α-D-glucan from fungal cell-walls. Carbohydr. Res. 1979, 71, 51–64.

63. Złotko, K.; Wiater, A.; Waśko, A.; Pleszczyńska, M.; Paduch, R.; Jaroszuk-Ściseł, J.; Bieganowski, A. A Report on Fungal (1→3)-α-D-glucans: Properties, Functions and Application. Molecules 2019, 24, 3972.

64. Moreno-Mendieta, S.; Guillén, D.; Hernández-Pando, R.; Sánchez, S.; Rodríguez-Sanoja, R. Potential of glucans as vaccine adjuvants: A review of the α-glucans case. Carbohydr. Polym. 2017, 165, 103–114.

65. Patra, S.; Maity, P.; Chakraborty, I.; Sen, I.K.; Ghosh, D.; Rout, D.; Bhanja, S.K. Structural studies of immunomodulatory (1→3)-, (1→4)-α glucan from an edible mushroom Polyporus grammocephalus. Int. J. Biol. Macromol. 2021, 168, 649–655.

66. Chen, R.; Xu, J.; Wu, W.; Wen, Y.; Lu, S.; El-Seedi, H.R.; Zhao, C. Structure–immunomodulatory activity relationships of dietary polysaccharides. Curr. Res. Food Sci. 2022, 5, 1330–1341.

67. Zhang, Y.; Kong, H.; Fang, Y.; Nishinari, K.; Phillips, G.O. Schizophyllan: A review on its structure, properties, bioactivities and recent developments. Bioact. Carbohydr. Diet. Fibre 2013, 1, 53–71.

68. Olennikov, D.N.; Agafonova, S.V.; Rokhin, A.V.; Penzina, T.A.; Borovskii, G.B. Branched glucan from the fruiting bodies of Piptoporus betulinus (Bull.:Fr) Karst. Appl. Biochem. Microbiol. 2012, 48, 65–70.

69. Pozsgay, V.; Nánási, P.; Neszmélyi, A. Utilisation of the d-glucopyranosyl group as a non-participating group in stereoselective glycosylation: Synthesis of O-α-D-glucopyranosyl-(1→2)-O-α-D-glucopyranosyl-(1→6)-D-glucose. Carbohydr. Res. 1979, 75, 310–313.

70. Rychener, M.; Bigler, P.; Pfander, H. Synthese und 1H-NMR-Studie der vier unverzweigten peracetylierten β-D-Glucopyranosyl-β-gentiobiosen. Helv. Chim. Acta 1984, 67, 378–385.

71. Gómez de Segura, A.; Alcalde, M.; Bernabé, M.; Ballesteros, A.; Plou, F.J. Synthesis of methyl α-D-glucooligosaccharides by entrapped dextransucrase from Leuconostoc mesenteroides B-1299. J. Biotechnol. 2006, 124, 439–445.

72. Brissonnet, Y.; Ladevèze, S.; Tezé, D.; Fabre, E.; Deniaud, D.; Daligault, F.; Tellier, C.; Šesták, S.; Remaud-Simeon, M.; Potocki-Veronese, G.; et al. Polymeric Iminosugars Improve the Activity of Carbohydrate-Processing Enzymes. Bioconjugate Chem. 2015, 26, 766–772.

73. Ahrazem, O.; Rubio-Moraga, A.; Jimeno, M.; Gómez-Gómez, L. Structural characterization of highly glucosylated crocins and regulation of their biosynthesis during flower development in Crocus. Front. Plant Sci. 2015, 6, 971–985.

74. Hoshi, H.; Yagi, Y.; Iijima, H.; Matsunaga, K.; Ishihara, Y.; Yasunara, T. Isolation and Characterization of a Novel Immunomodulatory α-Glucan-Protein Complex from the Mycelium of Tricholoma matsutake in Basidiomycetes. J. Agric. Food Chem. 2005, 53, 8948–8956.

75. Kroon-Batenburg, L.M.; Kroon, J. The crystal and molecular structures of cellulose I and II. Glycoconj. J. 1997, 14, 677–690.

76. Chawla, P.R.; Bajaj, I.B.; Survase, S.A.; Singhal, R.S. Microbial Cellulose: Fermentative Production and Applications. Food Technol. Biotechnol. 2009, 47, 107–124.

77. Brown, G.D.; Gordon, S. Immune recognition. A new receptor for β-glucans. Nature 2001, 413, 36–37.

78. Brown, G.D.; Herre, J.; Williams, D.L.; Willment, J.A.; Marshall, A.S.; Gordon, S. Dectin-1 mediates the biological effects of β-glucans. J. Exp. Med. 2003, 197, 1119–1124.

79. Zipfel, C.; Robatzek, S. Pathogen-Associated Molecular Pattern-Triggered Immunity: Veni, Vidi…? Plant Physiol. 2010, 154, 551–554.

80. Legentil, L.; Paris, F.; Ballet, C.; Trouvelot, S.; Daire, X.; Vetvicka, V.; Ferrières, V. Molecular Interactions of β-(1→3)-Glucans with Their Receptors. Molecules 2015, 20, 9745–9766.

81. Adachi, Y. Role of the 1,3-β-D-Glucan Receptor Dectin-1 in Fungal Infection and Activation of Innate and Anti-Tumor Immunity. Trends Glycosci. Glycotechnol. 2007, 19, 195–207.
82. Fesel, P.H.; Zuccaro, A. β-Glucan: Crucial Component of the Fungal Cell Wall and Elusive MAMP in Plants. Fungal Genet. Biol. 2016, 90, 53–60.
83. Vetvicka, V.; Vannucci, L.; Sima, P.; Richter, J. Beta Glucan: Supplement or Drug? From Laboratory to Clinical Trials. Molecules 2019, 24, 1251–1268.
84. Miyagawa, A. Chemical Synthesis of β-(1,3)-Glucan Oligosaccharide and Its Application. Trends Glycosci. Glycotechnol. 2018, 30, E117–E127.
85. Morelli, L.; Compostella, F.; Panza, L.; Imperio, D. Unusual Promoters and Leaving Groups in Glycosylation Reactions: The Evolution of Carbohydrate Synthesis. Carbohydr. Res. 2022, 519, 108625.
86. Singh, Y.; Geringer, S.A.; Demchenko, A.V. Synthesis and Glycosidation of Anomeric Halides: Evolution from Early Studies to Modern Methods of the 21st Century. Chem. Rev. 2022, 122, 11701–11758.
87. Ishiwata, A.; Tanaka, K.; Ao, J.; Ding, F.; Ito, Y. Recent advances in stereoselective 1,2-cis-O-glycosylations. Front. Chem. 2022, 10, 972429.
88. Takahashi, D.; Toshima, K. 1,2-cis O-glycosylation methods. In Comprehensive Glycoscience; Barchi, J., Ed.; Elsevier Science: Amsterdam, The Netherlands, 2021; Volume 2, pp. 365–412.
89. Lv, Z.; Liu, H.; Hao, H.; Rahman, F.-U.; Zhang, Y. Chemical synthesis of oligosaccharides and their application in new drug research. Eur. J. Med. Chem. 2023, 249, 115164.
90. Shadrick, M.; Singh, Y.; Demchenko, A.V. Stereocontrolled α-galactosylation under Cooperative Catalysis. J. Org. Chem. 2020, 85, 15936–15944.
91. Ishiwata, A.; Lee, Y.J.; Ito, Y. Recent advances in stereoselective glycosylation through intramolecular aglycon delivery. Org. Biomol. Chem. 2010, 8, 3596–3608.
92. Ishiwata, A.; Ito, Y. Intramolecular Aglycon Delivery. In Selective Glycosylations—Synthetic Methods and Catalysts; Bennett, C.S., Ed.; Wiley: Weinheim, Germany, 2017; Chapter II-4; pp. 81–96.
93. Ishiwata, A. Synthetic Study on Glycoconjugates Containing 1,2-cis Glycoside and Their Application. Trends Glycosci. Glycotech. 2019, 31, SE53–SE54.
94. Nigudkar, S.S.; Demchenko, A.V. Stereocontrolled 1,2-cis glycosylation as the driving force of progress in synthetic carbohydrate chemistry. Chem. Sci. 2015, 6, 2687–2704.
95. Leng, W.-L.; Yao, H.; He, J.-X.; Liu, X.-W. Venturing beyond Donor-Controlled Glycosylation: New Perspectives toward Anomeric Selectivity. Acc. Chem. Res. 2018, 51, 628–639.
96. van der Vorm, S.; Hansen, T.; van Hengst, J.M.A.; Overkleeft, H.S.; van der Marel, G.A.; Codée, J.D.C. Acceptor reactivity in glycosylation reactions. Chem. Soc. Rev. 2019, 48, 4688–4706.
97. Njeri, D.K.; Valenzuela, E.A.; Ragains, J.R. Leveraging Trifluoromethylated Benzyl Groups toward the Highly 1,2-cis-Selective Glucosylation of Reactive Alcohols. Org. Lett. 2021, 23, 8214–8218.
98. Kobayashi, Y.; Takemoto, Y. Regio- and stereoselective glycosylation of 1,2-O-unprotected sugars using organoboron catalysts. Tetrahedron 2020, 76, 131328.
99. Feng, Y.; Guo, T.; Yang, H.; Liu, G.; Zhang, Q.; Zhang, S.; Chai, Y. Ni(II)-Catalyzed Regio- and Stereoselective O-Alkylation for the Construction of 1,2-cis-Glycosidic Linkages. Org. Lett. 2022, 24, 6282–6287.
100. Ma, Z.; Hu, Y.; Li, X.; Liu, R.; Xia, E.; Xu, P.; Yang, Y. Stereoselective synthesis of α-glucosides with glucosyl (Z)-Ynenoates as donors. Carbohydr. Res. 2023, 523, 108710.
101. Szarek, W.A.; Horton, D. Anomeric Effect; American Chemical Society: Washington, DC, USA, 1979.
102. Deslongchamps, P. Stereoelectronic Effect in Organic Chemistry; Pergamon: Oxford, UK, 1983.
103. Juaristi, E.; Cuevas, G. The Anomeric Effect; CRC: Boca Raton, FL, USA, 1995.
104. Kirby, A.J. Stereoelectronic Effect; Oxford University Press: New York, NY, USA, 1996.
105. Perrin, C.L. Reverse anomeric effect: Fact or fiction? Tetrahedron 1995, 51, 11901–11935.
106. Randell, K.D.; Johnston, B.D.; Green, D.F.; Pinto, B.M. Is there a generalized reverse anomeric effect? Substituent and solvent effects on the configurational equilibria of neutral and protonated N-Arylglucopyranosylamines and N-Aryl-5-thioglucopyranosylamines. J. Org. Chem. 2000, 65, 220–226.
107. Vaino, A.R.; Szarek, W.A. An examination of the purported reverse anomeric effect beyond acetylated N-xylosyl-and N-glucosylimidazoles. J. Org. Chem. 2001, 66, 1097–1102.

108. Perrin, C.L.; Kuperman, J. Anomeric effects versus steric hindrance to ionic solvation in protonated glucosylanilines and cyclohexylanilines. J. Am. Chem. Soc. 2003, 125, 8846–8851.
109. Reichardt, C. (Ed.) Solvents and Solvent Effects in Organic Chemistry, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.
110. Lemieux, R.U.; Pavia, A.A.; Martin, J.C.; Watanabe, K.A. Solvation effects on conformational equilibria. Studies related to the conformational properties of 2-methoxytetrahydropyran and related methyl glycopyranosides. Can. J. Chem. 1969, 47, 4427–4439.
111. Eby, R.; Schuerch, C. The Use of 1-O-Tosyl-D-glucopyranose Derivatives in α-D-Glucoside Synthesis. Carbohydr. Res. 1974, 34, 79–90.
112. Schmidt, R.R.; Rücker, E. Stereoselective glycosidations of uronic acids. Tetrahedron Lett. 1980, 21, 421–1424.
113. Lemieux, R.U.; Ratcliffe, R.M. The azidonitration of tri-O-acetyl-D-galactal. Can. J. Chem. 1979, 57, 1244–1251.
114. Ishiwata, A.; Ito, Y. High throughput screening of O-glycosylation conditions. Tetrahedron Lett. 2005, 46, 3521–3524.
115. Ishiwata, A.; Munemura, Y.; Ito, Y. Synergistic solvent effect in 1,2-cis-glycoside formation. Tetrahedron 2008, 64, 92–102.
116. Chao, C.-S.; Li, C.-W.; Chen, M.-C.; Chang, S.-S.; Mong, K.-K.T. Low-Concentration 1,2-trans β-Selective Glycosylation Strategy and Its Applications in Oligosaccharide Synthesis. Chem. Eur. J. 2009, 15, 10972–10982.
117. Chao, C.-S.; Lin, C.-Y.; Mulani, S.; Hung, W.-C.; Mong, K.-K.T. Neighboring-group participation by C-2 ether functions in glycosylations directed by nitrile solvents. Chem. Eur. J. 2011, 17, 12193–12202.
118. Demchenko, A.; Stauch, T.; Boons, G.J. Solvent and other effects on the stereoselectivity of thioglycoside glycosidations. Synlett 1997, 1997, 818–820.
119. Takatani, M.; Nakano, J.; Arai, M.A.; Ishiwata, A.; Ohta, H.; Ito, Y. Accelerated glycosylation under frozen conditions. Tetrahedron Lett. 2004, 45, 3929–3932.
120. Ishiwata, A.; Sakurai, A.; Dürr, K.; Ito, Y. Effects of frozen conditions on stereoselectivity and velocity of O-glycosylation reactions. Bioorg. Med. Chem. 2010, 18, 3687–3695.
121. Csávás, M.; Herczeg, M.; Bajza, I.; Borbás, A. Protecting Group Manipulations in Carbohydrate Synthesis, Comprehensive Glycoscience, 2nd ed.; Barchi, J.J., Jr., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; pp. 464–524.
122. Ghosh, B.; Kulkarni, S.S. Advances in Protecting Groups for Oligosaccharide Synthesis. Chem. Asian J. 2020, 15, 450–462.
123. Meyer, A.G.; Bissember, A.C.; Hyland, C.J.T.; Williams, C.C.; Szabo, M.; Pearsall, M.A.; Hyland, I.K.; Olivier, W.J. Seven-Membered Rings. In Progress in Heterocyclic Chemistry; Gribble, G.W., Joule, J.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 579–633.
124. Ma, X.; Zheng, Z.; Fu, Y.; Zhu, X.; Liu, P.; Zhang, L. A “Traceless” Directing Group Enables Catalytic SN2 Glycosylation toward 1,2-cis-Glycopyranosides. J. Am. Chem. Soc. 2021, 143, 11908–11913.
125. Ma, X.; Zhang, Y.; Zhu, X.; Wei, Y.; Zhang, L. Directed SN2 Glycosylation Employing an Amide-Functionalized 1-Naphthoate Platform Featuring a Selectivity-Safeguarding Mechanism. J. Am. Chem. Soc. 2023, 145, 11921–11926.
126. Ding, F.; Ishiwata, A.; Ito, Y. Bimodal Glycosyl Donors Protected by 2-O-(ortho-Tosylamido)benzyl Group. Org. Lett. 2018, 20, 4384–4388.
127. Ding, F.; Ishiwata, A.; Ito, Y. Recent advances of the stereoselective bimodal glycosylations for the synthesis of various glucans. Stud. Nat. Prod. Chem. 2022, 74, 1–40.
128. Ding, F.; Ishiwata, A.; Zhou, S.; Zhong, X.; Ito, Y. Unified Strategy toward Stereocontrolled Assembly of Various Glucans Based on Bimodal Glycosyl Donors. J. Org. Chem. 2020, 85, 5536–5558.
129. Zhou, S.; Zhong, X.; Guo, A.; Xiao, Q.; Ao, J.; Zhu, W.; Cai, H.; Ishiwata, A.; Ito, Y.; Liu, X.-W.; et al. ZnI2-Directed Stereocontrolled α-glucosylation. Org. Lett. 2021, 23, 6841–6845.