Thiosugars of Biological Significance

Subjects: Chemistry, Organic

Contributor: Bimal Banik, Aparna Das

Thiosugars are important compounds because of their structural complexity and crucial biological activities. Therefore, a series of methods are developed for their synthesis using new methods. Unlike, oxygen sugars, thiosugars are more stable and therefore, much scope exists to alter their structures by chemical manipulations. Notably, thiosugars can act as glycosyl donors as well as acceptors. Many functionalized thiosugars occur naturally and are potential targets for therapeutics. Synthesis of thiosugars following convergent route is a challenge. Over the years, scientists have explored thiosugars through numerous green and sustainable methods. These studies are highly significant and timely since it opens the door towards carbohydrate-based drugs.

Keywords: Thiosugar ; Synthesis ; Anomer ; Therapeutics

1. Introduction

Sugar containing compounds with sulfur or nitrogen instead of oxygen in the ring have attracted considerable attention due to their pronounced biological activities compared to their parent oxygen counterparts. Among these sugar analogs, sulfur containing carbohydrate acquired special attention because its close resemblance with oxygen, as sulfur is positioned next to oxygen in periodic table. However, it is also important to note that sulfur atom is larger than oxygen, the carbon–sulfur bond is longer, the bond is weaker, and less polar than the carbon oxygen bond. The endocyclic C–S–C angle is more acute than that for a cyclic oxygen system. Sulfur-in-the-ring sugar analogues demonstrate different properties than their oxygen counterparts. These differences include anomeric effect, chemical reactivity, conformational behavior, molecular recognition by proteins, and metabolic stability.

Thiosugars and their derivatives are inhibitors of glycosidases [1]. This is due to the hydrophobic interaction between the sulfur-containing carbohydrates and the enzyme inhibitory activities [2]. Thiosugars are used as antineoplastic, [3] antidiabetic, [4] antiviral, [5] and antithrombotic compounds [6]. Some of these are precursors for the preparation of inositol and aminocyclitol derivatives [4]. Codeé *et al.* reported that the thiosugars and thio-oligosaccharides are glycosidase inhibitors [7]. Many methods are available for the preparation of thiosugars [8]. Thiosugars with sulfur atom as heteroatom or a disaccharide linked *via* a sulfur bridge are included.

2. Thiosugars: Sulfur as a Ring Heteroatom

Several groups reported the synthesis of thiosugars and its derivatives containing sulfur as a ring heteroatom [9]. Examples include 4′-thiopentofuranosyl nucleosides [10], and 5-thiopyranoses of the D-*gluco*, D-*ribo*, and D-*xylo* configuration [11].

Perlin *et al.* reported the synthesis of 5-thio-D-galactoses, anomeric methyl glycopyranosides [12]. The study examined the influences of a ring-sulfur atom on enzymes: D-galactose oxidase [13] and a- and b-D-galactosidase [14].

Gonzalez *et al*. described the uses of cyclic sulfates of *vic*-diols in the synthesis of thiosugars [15]. A series of enantiomerically pure thiosugars and their corresponding sulfoxide or sulfone were synthesized by Merrer *et al*. [16].

Haudrechy *et al.* reported a thiosubstituted ‘D-arabino’-type derivative, obtained from an open carbohydrate *via* a cascade of four consecutive transformations [17] This thiosugar was formed as a side-product [18][19].

Muraoka *et al.* isolated a new class of α-glucosidase inhibitors [20]. Among them, sulfonium salts (**10**) showed potent inhibitory activity against three enzymes [21]. Eskandri *et al.* reported the most active inhibitor in this class of molecules [22]. For the synthesis of Neoponkoranol, benzyl 2,3,4-tri-O-benzyl-D-glucopyranoside [23] was used.

Ye *et al.* reported one-pot synthesis of polyoxygenated tetrahydrothiopyrans and thiepanes from alditol derivatives[24]. The one-pot synthesis was initiated from diols, which were synthesised from natural sugars or alditols [25]. Chandrasekaran *et al.* reported an efficient method for the synthesis of biologically potent 1-deoxythiosugars [26]. The group used benzyltriethyl ammonium tetra thiomolybdate $[BnEt_3N]_2MoS_4$, [27], as an efficient sulfur transfer reagent for the synthesis of biologically active deoxythiosugars and derivatives [28] starting from aldonolactones [29]. The presence of *cis*-hydroxy groups at C_2 and C_3 was not necessary for this method.

Scanlan *et al.* reported an approach for the preparation of thiosugars and thioglycals using the intramolecular thiol-ene and thiol-yne cyclization reactions with control over regioselectivity and diastereoselectivity [30]. Utilizing the intramolecular thiol-ene cyclization pathway, both thiofuranose and thiopyranose products were attained [31]. These findings were in agreement with the report by Surzur [32].

The intramolecular thiol-yne reaction produced the 5-*exo* glycal as the major product and L-sugar gave a separable mixture of both the 5-*exo* and 6- *endo* glycals [33]. These results were in contrast with the unsubstituted pent-4-yne-1-thiol substrate where 6-*endo* cyclization was favored [32].

Yoshimura *et al*. reported the synthesis of 4'-thionucleosides as antitumor and antiviral agents [34]. To achieve the synthesis, they developed the Pummerer-type thioglycosylation reaction and the reaction was applied for the synthesis of dihydrothiopyranonucleosides.

The synthesis of 4'-thioribonucleosides [35] by constructing the skeleton of the 4-thioribose *via* a ring-contraction reaction under reductive conditions was developed**.**

Due to their increased chemical stability [36], 4-thiofuranosides and its derivatives showed biological activities, such as antiviral, [37] antibiotic, [38] and anticancer [39] activities. Madern *et al*. reported the synthesis, reactivity and stereoselectivity of 4-thiofuranosides [40].

The synthesis of 4-thiofuranosyl donors was accomplished [41]. The synthesis of the 4-thio ribosyl donor started from D-ribose.

3. Thiosugars-Sulfur Outside the Ring

Numerous naturally occurring, including the anticancer agents mithramycin, chromomycin A3, and olivomycin A as well as many of the cardiac glycosides such as digitoxin and digoxin, contained 2,6-dideoxy sugar system.

Toshima *et al.* described the synthesis of 2,6-dideoxy sugars by using 2,6-anhydro-2-thio sugars [42].

The synthesis started with the conversion of methyl α-L-glucopyranoside (**53**) [43][44]. Butler *et al.* reported the synthesis of S-nitroso derivatives of 1-thiosugar and its activity as vasodilator [45]. Witczak *et al.* designed and synthesized S-linked fucosides and were tested for the inhibition of α-L-fucosidases [46]. Hasegawa *et al.* reported the synthesis of thiosugars and thioglycosides using *p*-octyloxyphenylmethanethiol and *p*-dodecylbenzenethiol [47].

Auranofin (AF) is a gold containing drug and largely used as an antiarthritic agent. It consists of a gold(I) center linearly coordinated to triethylphosphine and to a thiosugar (3,4,5 triacetyloxy-6-(acetyloxymethyl) oxane-2-thiolate). Along with antiarthritic activity, auranofin revealed a wide range of pharmaceutical applications [48][49][50][51][52]. Ilari *et al.* described the antiparasitic activity of AF against *Leishmania infantum* [53]. Witczak *et al.* synthesized (1-4)-S-thiodisaccharides and assessed their cytotoxicity and apoptosis against human cancer cell lines [54]. The cytotoxicity of functional CARB-pharmacophore was tested at nine different concentrations on four cell lines: lung (A549), cervix (HeLa), mammary gland-breast (MCF-7) and colon carcinoma (LoVo). The FCP has four hydroxyl groups in the sugar ring protected by acetyl groups. A study showed that the hydroxyl group deprotection by removing the acetyl groups and/or substitution of glucose with galactose did not increase the cytotoxicity of compounds. Lazar *et al.* demonstrated a free-radical hydrothiolation of alkenyl sugars resulted in stable carbon-sulfur-bridges glycomimetics. Photoinduced addition of thiols to exoglycal is was demonstrated [54]. Dada *et al.* reported the synthesis, characterization and biological activity of four novel N-heterocyclic carbene-gold(I)-thiosugar complexes derived from lactose, glucose and galactose [55]. Appropriate thio-containing sugars were prepared following different procedures [56][57][58][59][60]. The α-anomeric thiol, which was known to be less nucleophilic than its corresponding β-counterpart [61], showed fairly good reactivity towards the NHC-Au(I) chloride.

Komor *et al.* reported the synthesis of 1-thiosugar with α-configuration [62]. This group also synthesized and tested biological activity of glycoconjugates analogues of acyclic uridine derivatives.

Heteroaryl-glycosides are commonly found in many compounds of enormous practical importance, ranging from natural compounds to pharmaceutical agents [63][64][65][66]. N-glycosyl quinolin-2-ones, in which a glycosyl unit is attached to a quinolin-2-one core, is one of the most important members of heteroaryl-N-glycosides family, because of its biological activity. Several studies presented quinolin-2-ones as biologically active compounds and pharmaceutical agents [67][68][69][70][71][72][73]. Thus, coupling of thiosugar derivatives with N-glycosyl quinolin-2-one nucleus had caused several changes in their features, including their chemical, physical, biochemical, and biological properties.

Redjdal *et al.* synthesized N,S-*bis*-glycosyl quinolin-2-ones *via* the palladium-catalyzed coupling of *α*- or *β*-mono-, di-, and poly-thiosugar derivatives with *α*- or *β*-3-iodo-N-glycosylquinolin-2-ones [74].

Thioglycoside are biologically important molecules [75][76][77][78][79][80][81][82][83] and are more stable than their *O*-glycosides analogs to both chemical and enzymatic degradations. Different methods are available to synthesis thioglycosides [84][85][86][87][88][89][90][91][92]. Copper-catalyzed functionalization of 1-thiosugars for the synthesis of thioglycosides was reported [93]. Metal complexes with *N*-heterocyclic carbene (NHC) ligands has wide range of applications, such as in catalysis [94], as metal-based drugs [95][96] and as materials [97]. Several groups reported potential antibiotic or anticancer activity of metal NHC complexes [98][99][100]. The synthesis of anticancer drug candidate 1,3-dibenzyl-4,5-diphenyl-imidazol-2-ylidene gold(I) chloride (NHC*-AuCl) and its derivative 2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl-1'-thiolate (NHC*-AuSR) [101][102][103] was described [104]. NHC*-AuCl and NHC*-AuSR were tested *in vitro against* NCI-60 cancer cell panel and both compounds showed very good activity against a wide range of human cancer cell lines.

4. Naturally Occurring Thiosugars

Many of functionalized thiosugars occur naturally. A few examples are salacinol and kotalanol, tagetitoxin, thiolactomycin and analogues, mycothiol and analogues, and S-nitrosothiols. Among them many are used as a potential target for the development of carbohydrate-based therapeutics. 5-Thio-D-mannose is the first naturally occurring free thiosugar and was isolated from the marine sponge Clathria pyramida [105]. 1,4-thioanhydrosugar, salacinol and kotalanol, is a class of thiosugar that possess potent sucrase inhibition, which bear a sulfonium salt-containing heterocycle in their skeleton [106]. Yoshikawa *et al.* synthesized a-glucosidase inhibitor salacinol with unique thiosugar sulfonium sulfate structure [107]. It was extracted from the water-soluble fraction from the dried roots of *salacia reticulata* by silica gel column chromatography and repeated various HPLC. Yoshikawae *et al*. isolated also kotalanol (**98**), another potent a-glucosidase inhibitor from the roots and stems of *Salacia reticulate* [108], molecular structure is shown in **Scheme 24**.

4-O-acetyl-3-amino-1,6-anhydro-3-deoxy-D-gulose 2-phosphate commonly known as Tagetitoxin (**99**) is a bacterial phytotoxin [109]. Tagetitoxin is produced by the plant pathogenic bacteria, *Pseudomonas syringae pv. tagetis*. By specifically inhibiting chloroplast RNA polymerase, tagetitoxin induces chlorosis in the apex of the host plant making it potentially useful as herbicide [110]. Oishi *et al.* isolated thiolactomycin (**100**) from *Nocardia sp.* [111]. It has unique pharmacological activity against parasitic and bacterial organisms. *In vitro* studies showed that thiolactomycin is active against a wide range of *Mycobacterium tuberculosis* strains. It selectively inhibited the mycobacterial acyl carrier protein-dependent type II FAS (FAS-II) but not the multifunctional type I FAS (FAS-I) present in mammals [112][113].

The low molecular weight thiol found in most actinomycetes, including mycobacteria and strepto-mycetes, is the Mycothiol (**101**) [114]. It was isolated first in 1996 and is a conjugate of N-acetylcysteine, glucosamine, and myo-inositol, produced by most of actinomycetes but not by other bacteria or eukaryotes [115]. Lee *et al.* reported the first total synthesis of mycothiol and its disulfide [116]. Different methods and protocols are now available to synthesize mycothiol [117][118][119].

5. Conclusions

Many aspects of synthesis as well as biological activities associated with thiosugars are extensively reviewed in this chapter. Thiosugars with sulfur atom as heteroatom or a disaccharide linked *via* a sulfur bridge were treated separately and the data were taken from recent literatures. New methodologies and techniques to synthesize almost all representatives of functionalized analogs of thiosugars, oligosaccharides including thiodisaccharides and simple functionalized thiosugars, were illustrated.

Contributors

Aparna Das[1] and Bimal Krishna Banik[2]

[1] Department of Mathematics and Natural Sciences, College of Sciences and Human Studies, Prince Mohammad Bin Fahd University, Al Khobar, Kingdom of Saudi Arabia; Email: adas@pmu.edu.sa

[2] Department of Mathematics and Natural Sciences, College of Sciences and Human Studies, Deanship of Research, Prince Mohammad Bin Fahd University, Al Khobar, Kingdom of Saudi Arabia; Email: ; bimalbanik10@gmail.com; bbanik@pmu.edu.sa

Acknowledgement: BKB is grateful to the USA NIH, USA NCI and USA Private Research Foundation. BKB and AD also thank Prince Mohammad Bin Fahd University for encouragement.

References

1. T. Kajimoto, K. K.-C. Liu, R. L. Pederson, Z. Zhong, Y. Ichikaw, J. A. Jr. Porco, C.-H. Wong, J.Am.Chem.Soc.113 (1991) 6187.
2. H.Yuasa, Y. Nakano, H. Hashimoto, Carbohydr. Lett.2 (1996) 23.
3. [a] Y. Yoshimura, M. Endo, S. Sakata, Tetrahedron. Lett.40 (1999) 1937; [b] S. Miura, Y. Yoshimura, M. Endo, H. Machi da, A.Matsuda, M. Tanaka, T. Sasaki, Cancer Lett. 129 (1998) 103.
4. T. Hudlicky, J. D. Price, F. Rulin, T. Tsunoda, J. Am. Chem.Soc.112 (1990) 9439.
5. [a] R. F.Schinazi, C. K. Chu, A. Peck, A. McMillan, R. Mathis, D. Cannon, L. S. Jeong, J. W. Beach, W. B.Choi, S. Yeol a, Antimicrob. Agents Chemother.36 (1992) 672; [b] J. A. Coates, N. Cammack, H. J. Jenkinson, A. J. Jowett, Jowett, B. A. Pearson, C. R. Penn, P. L. Rouse, K. C. Viner, J. M. Cameron, Antimicrob. Agents Chemother. 36 (1992) 733; [c] J. W. Beach, L. S. Jeong, A. J. Alves, D. Pohl, H. O. Kim, C. N. Chang, S. L. Doong, R. F. Schinazi, Y. C. Cheng, C. K. Ch u, J. Org. Chem. 57 (1992) 2217.
6. E. Bozo, S. Boros, J. Kuszmann, Carbohydr. Res. 311 (1998) 191. [6b] E. Bozo, T. Gati, A. Demeter, J. Kuszmann, Car bohydr. Res.337 (2002) 1351.
7. S. Mohan, B. M. Pinto, Carbohydr. Res. 342 (2007) 1551.
8. [a] H. Yuasa, Y. Izukawa, H. Hashimoto, Curr. Top. Med. Chem.9 (2009)76. [b] I. Robina, P. Vogel, Z. Witczak, J. Curr. Org. Chem.5 (2001) 1177; [c] I. Robina, P. Vogel, Curr. Org. Chem. 6(2002) 471.
9. [a] D. Horton, D. H. Hijtson, Adv. Carbohydr. Chem. 18 (1963) 123; [b] H. Paulsen, K. Todt, Adv. Curbohydr. Chem. 23 (1968) 115; [c] R. L. Whittier, W- C. Lake, Methods Carbohydr. Chem. 6 (1972) 286.
10. E. J. Reist, L. V. Fisher, L. Goodman, J. Org. Chem. 33 (1968) 189.
11. [a] M. J. Purrs, M. Chemelews, M. S. Chen, M. M. A. Abd El-Rahman, R. L. Whisiur, Arch. Eiochem. Biophys. 169 (197 5) 384; [b] M.S. Chen, R.L. Whistler, Arch. Biochem. Biophys. 169 (1975) 392; [c] C. J. Clayton, N. A. Hughes, Curbohy dr. Res. 27 (1973) 89.
12. J. E. Nam Shin, A. S. Perlin, Carbohydrate Research 76 (1979) 165.
13. [a] S. Guillarme, K. Plé, A. Haudrechy, J. Org. Chem.71 (2006) 1015; [b] S. Guillarme, A. Haudrechy, Tetrahedron Lett. 46 (2005) 3175.
14. (a)A. Maradufu, G. M. Cree, A. S- Perlin, Con. J. Chem., 49 (1971) 3429; (b) A. Maradufu, A. S. Pewn, Curbohydr. Res. 32 (1974) 93.
15. J. E. N. SHIN, Ph.D. Thesis, McGiil University, Montreal, Canada, 1978.
16. F. G. Calvo-Flores, P. G.-Mendoza, F. H.-Mateo, J. I.-Garcıa, F. S.-Gonzalez, J. Org. Chem. 62 (1997) 3944.
17. Y. L. Merrer, M. Fuzier, I. Dosbaa, M.-J. Foglietti, J.-C. Depezay, Tetrahedron 53 (1997) 16731.
18. A. Martinez, E. Hénon, C. Coiffier, A. Banchet, D. Harakat, J.-M. Nuzillard, A. Haudrechy, Carbohydrate Research 345 (2010) 1088.
19. A. Banchet, S. Guillarme, A. Haudrechy, Synlett (2007) 1467.
20. W. Xie, G. Tanabe, J. Akaki, T. Morikawa, K. Ninomiya, T. Minematsu, M. Yoshikawa, X. Wu, O. Muraoka, Bioorganic & Medicinal Chemistry 19 (2011) 2015.
21. B. D. Johnston, H. H. Jensen, B. M. Pinto, J. Org. Chem.71 (2006) 1111.
22. R. Eskandari, D. A. Kuntz, D. R. Rose, B. M. Pinto, Org. Lett. 12 (2010) 1632.
23. L. Wallach, N. Latifeh, D. T. Scott, Carbohydr. Res. 340(2005) 1213.
24. J. Zhang, Y. Niu, X. Cao, X.-S. Ye, Tetrahedron 68 (2012) 4242.
25. M. Violante de Paz Banez, J. A. A. Moreno, J. A. J. Galbis, Carbohydr. Chem. 27 (2008) 120.

26. T. Gunasundari, S. Chandrasekaran, Carbohydrate Research 382 (2013) 30.

27. [a] John Wiley and Sons Ltd.:Benzyl triethylammonium Tetrathiomolybdate: e-EROS Encyclopedia of Reagents for Organic Synthesis Chichester, UK, 2001; [b] T.-L. Ho, M. Fieser, L. Fieser, Benzyltriethylammonium Tetrathiomolybdate: Fieser and Fieser's Reagents for Organic Synthesis; John Wiley and Sons, (2006); [c] K. R. Prabhu, N. Devan, S. Chandrasekaran, Synlett (2002) 1762; [d] D. Sureshkumar, K. Srinivasa Murthy, S. Chandrasekaran, J. Am. Chem. Soc.127(2005) 12760; [e] D. Sureshkumar, T. Gunasundari, V. Ganesh, S. Chandrasekaran, J. Org. Chem. 72 (2007) 2106.

28. (a) P. Ramu Sridhar, K. R. Prabhu, S. Chandrasekaran, Eur. J. Org. Chem. (2004) 4809; (b) T. Gunasundari, S. Chandrasekaran, J. Org. Chem. 75 (2010) 6685.

29. [a] T. Gunasundari, S. Chandrasekaran, Eur. J. Org. Chem. (2012) 6986; [b] I. Lundt, Top. Curr. Chem. 187 (1997) 117.

30. [a] E. M. Scanlan, V. Corce, A. Malone, Molecules 19 (2014) 19137; [b] L. McSweeney, F. Dénès, E. M. Scanlan, Eur. J. Org. Chem (2016) 2080.

31. A. Malone, E. M. Scanlan, Org. Lett. 15 (2013)504.

32. J. M. Surzur, React. Intermed. 2 (1982) 121.

33. V. Corce, L. McSweeney, A. Malone, E. M. Scanlan, Chem. Commun. (2015) 8672.

34. Y. Yoshimura, Y. Saito, Y. Natori, H. Wakamatsu, Chem. Pharm. Bull. 66 (2018) 139.

35. Y. Yoshimura, H. Wakamatsu, Y. Natori, Y. Saito, N. Minakawa, J. Org. Chem.14 (2018) 1595.

36. M. I. Elzagheid, M. Oivanen, R. T. Walker, J. A. Secrist, Nucleosides Nucleotides 18 (1999) 181.

37. [a] M. Bobek, A. Bloch, R. L. Whistler, J. Med. Chem. 15 (1972) 168; [b] M. R. Dyson, P. L. Coe, R. T. Walker, J. Chem. Soc., Chem. Commun. (1991) 741.

38. J. A. Secrist, K. N. Tiwari, J. M. Riordan, J. A. Montgomery, J. Med. Chem. 34 (1991) 2361.

39. N. Ototani, R. L. Whistler, J. Med. Chem. 17 (1974) 535.

40. J. M. Madern, T. Hansen, E. R. van Rijssel, H. A.V. Kistemaker, S. van der Vorm, H. S. Overkleeft, G. A. van der Marel, D. V. Filippov, J. D.C. Codeé, J. Org. Chem.84 (2019) 1218.

41. N. Minakawa, D. Kaga, Y. Kato, K. Endo, M. Tanaka, T. Sasaki, A. Matsuda, J. Chem. Soc. Perk. T. 1 (2002) 2182.

42. K. Toshima, T. Yoshida, S. Mukaiyama, K. Tatsuta, Carbohydrate Research 222 (1991) 173.

43. L. Kocourek, Curbohydr. Res. 3 (1967) 502.

44. A. B. Foster, J. M. Duxbury, T. D. Inch, J. M. Webber, Chem. Commun. (1967) 881.

45. A. R. Butler, R. A. Field, I. R. Greig, F. W. Flitney, S. K. Bisland, F. Khan, J. J. F. Belch, NITRIC OXIDE: Biology and Chemistry 1 (1997) 211.

46. Z. J. Witczak, D. Boryczewski, Bioorganic & Medicinal Chemistry Letters 8 (1998) 3265.

47. J. Hasegawa, M. Hamada, T. Miyamoto, K. Nishide, T. Kajimoto, J. Uenishi, M. Node, Carbohydrate Research 340 (2005) 2360.

48. P. N. Fonteh, F. K. Keter, D. Meyer, Biometals 23 (2010) (2) 185.

49. R. E. Kast, Cent Eur Neurosurg 71 (2010) 139.

50. W. F. Kean, I. R. Kean, Inflammopharmacol 16 (2008)112.

51. M. Navarro, C. Gabbiani, L. Messori, D. Gambino, Drug Discov Today 15 (2010) 1070.

52. S. Prast-Nielsen, M. Cebula, I. Pader, E. S. Arner, Free Radic Biol Med 49 (2010) 1765.

53. A. Ilari, P. Baiocco, L. Messori, A. Fiorillo, A. Boffi, M. Gramiccia, T. Di Muccio, G. Colotti, Amino Acids 42 (2012) 803.

54. Z. J. Witczak, J. Sarnik, A. Czubatka, E. Forma, T. Poplawski, Bioorg. Med. Chem. Lett. 24 (2014) 5606.

55. O. Dada, G. S.-Sanz, M. Tacke, X. Zhu, Tetrahedron Letters 59 (2018) 2904.

56. X. Zhu, R.T. Dere, J. Jiang, L. Zhang, X. Wang, J. Org. Chem. 76 (2011) 10187.

57. H. Wang, X. Zhu, Org. Biomol. Chem. 12 (2014) 7119.

58. M.B. Haque, B.P. Roberts, D.A. Tocher, J. Chem. Soc., Perkin Trans. 1 (1998) 2881.

59. D.A. Fulton, J.F. Stoddart, J. Org. Chem. 66 (2001) 8309.

60. M. Cerny, J. Vrkoc, J. Stanek, Collect. Czech. Chem. Commun. 24 (1959) 64.

61. R. Smith, H. Müller-Bunz, X. Zhu, Org. Lett. 18 (2016) 3578.

62. R. Komor, G. P.-Gawolek, E. Krol, W. Szeja, Molecules 23 (2018) 2017.

63. R.A. Dwek, Chem. Rev. 96 (1996) 683.

64. A. A.-H. Abdel-Rahman, S. H. El Ashry, R. S. Richard, Carbohydr. Res. 315 (1999) 106.

65. J. Ren, C. Bailly, J. -B. Chaires, FEBS Lett. 470 (2000) 355.

66. M. Rajesh, J. Pengei, S. Rohit, S. Dmitri, B. Ila, N. Natsuko, C. Ying, P. Sandra, Int. J. Nanomed. 8 (2013) 3991.

67. P. Hewawasam, N. Chen, M. Ding, J. T. Natale, C. G. Boissard, S. Yeola, V. K. Gribkoff, J. Starrett, S. I. Dworetzky, Bio org. Med. Chem. Lett. 14 (2004) 1615.

68. K.H. Raitio, J.R. Savinainen, J. Vepsäläinen, J.T. Laitinen, A. Poso, T. Järvinen, T. Nevalainen, J. Med. Chem. 49 (200 6) 2022.

69. P. Hewawasam, W. Fan, M. Ding, K. Flint, D. Cook, G.D. Goggings, R.A. Myers, V.K. Gribkoff, C.G. Boissard, S.I. Dwor etzky, J. Med. Chem. 46 (2003) 2819.

70. P. Hewawasam, W. Fan, J. Knipe, S.L. Moon, C.G. Boissard, V.K. Gribkoff, J.E. Starret, Bioorg. Med. Chem. Lett. 12 (2 002) 1779.

71. A.A. Cordi, P. Desos, J.C. Randle, J. Lepagnol, Bioorg. Med. Chem. 3 (1995) 129.

72. P. Desos, J.M. Lepagnol, P. Morain, P. Lestage, A.A. Cordi, J. Med. Chem. 39 (1996) 197.

73. R.W. Carling, P.D. Leeson, K.W. Moore, J.D. Smith, C.R. Moyes, I.M. Mawer, S. Thomas, T. Chan, R. Baker, A. Foster, J. Med. Chem. 36 (1993) 3397.

74. W. Redjdal, N. Ibrahim, B. Benmerad, M. Alami, S. Messaoudi, Molecules 23 (2018) 519.

75. C. S. Rye, S. G. Withers, Carbohydr. Res. 339 (2004) 699.

76. B. B. Metaferia, B. J. Fetterolf, S. Shazad-ul-Hussan, M. Moravec, J. A. Smith, S. Ray, M.-T. Gutierrez-Lugo, C. A. Bewl ey, J. Med. Chem. 50 (2007) 6326.

77. F. Castaneda, A. Burse, W. Boland, R. K.-H. Kinne, Int. J. Med. Sci. 4 (2007) 131.

78. F. Castaneda, A. Burse, W. Boland, R. K. H. Kinne, Int. J. Med. Sci. 4 (2007) 131.

79. J. Rodrigue, G. Ganne, B. Blanchard, C. Saucier, D. Giguere, T. C. Shiao, A. Varrot, A. Imberty, R. Roy, Org. Biomol. C hem. 11 (2013) 6906.

80. G. H. Elgemeie, A. B. Farag, K. M. Amin, O. M. El-Badry, G. S. Hassan, Med. Chem. 4 (2014) 814.

81. M. R. Aouad, Nucleosides Nucleotides Nucleic Acids 35 (2016) 1.

82. E. Kato, H. Nagano, S. Yamamura, M. Ueda, Tetrahedron 59 (2003) 5909.

83. M. Schnabelrauch, A. Vasella, S. G. Withers, Helv. Chim. Acta. 77 (1994) 778.

84. R. Furneaux, R. Ferrier, Methods Carbohydr. Chem. 8 (1980) 251.

85. K. C. Nicolaou, J. L. Randall, G. T. Furst, J. Am. Chem. Soc. 107 (1985) 5556.

86. S. K. Das, J. Roy, K. A. Reddy, C. Abbineni, Carbohydr. Res. 338 (2003) 2237.

87. C.-A. Tai, S. S. Kulkarni, S.-C. Hung, J. Org. Chem. 68 (2003) 8719.

88. S. K. Das, J. Roy, K. A. Reddy, C. Abbineni, Carbohydr. Res. 338 (2003) 2237.

89. G. Agnihotri, P. Tiwari, A. K. Misra, Carbohydr. Res. 340 (2005) 1393.

90. E. Fischer, K. Delbruek, Ber. Dtsch. Chem. Ges. 42 (1909) 1476.

91. M. Blanc-Muesser, J. Defaye, H. Driguez, Carbohydr. Res. 67 (1978) 305.

92. M. Apparu, M. Blanc-Muesser, J. Defaye, H. Driguez, Can. J. Chem. 59 (1981) 314.

93. N. Ibrahim, M. Alami, S. Messaoudi, Asian J. Org. Chem. 7 (2018) 2026.

94. D. Zhao, L. Candish, D. Paul, F. Glorius, ACS Catal. 6 (2016) 5978.

95. W. Liu, R. Gust, Coord. Chem. Rev. 329 (2016) 191.

96. T. Zou, C. T. Lum, C.-N. Lok, J.-J. Zhang, C.-M. Che, Chem. Soc. Rev. 44 (2015) 8786.

97. L. Mercs, M. Albrecht, Chem. Soc. Rev. 39 (2010) 1903.

98. M. Tacke, J. Organomet. Chem. 782 (2015) 17.

99. S. A. Patil, S. A. Patil, R. S. Keri, S. Budagumpi, G. Balakrishna, M. Tacke, Fut. Med. Chem. 7 (2015) 1305.

100. F. Hackenberg, M. Tacke, Dalton Trans. 43 (2014) 8144.
101. S. Patil, A. Deally, B. Gleeson, H. Müller-Bunz, F. Paradisi, M. Tacke, Metallomics 3 (2011) 74.
102. F. Hackenberg, H. Müller-Bunz, R. Smith, W. Streciwilk, X. Zhu, M. Tacke, Organometallics 32 (2013) 5551.
103. M. Tacke, O. Dada, C. O'Beirne, X. Zhu, H. Müller-Bunz, Acta Cryst. C72 (2016) 857.
104. M. Tacke, Slovak Chemical Society, Bratislava 2019.
105. R. J. Capon, J. K. MacLeod, J Chem Soc Chem Commun 15 (1987)1200.
106. H. Matsuda, T. Morikawa, M. Yoshikawa, Pure Appl Chem 74 (2002) 1301.
107. M. Yoshikawa, T. Murakami, H. Shimada, H. Matsuda, J. Yamahara, G. Tanabe, O. Muraoka,Tetrahedron Letters 38 (19 97) 8367.
108. M. Yoshikawae, T. Muraksmi, K. Yashiro, H. Matsuda, Chem. Pharm. Bull. 46 (1998) 1339.
109. R. E. Mitchell, R. D. Durbin, Physiol Plant Pathol 18 (1981) 157.
110. D. E. Mathews, R.D. Durbin, J Biol Chem 265 (1990) 493.
111. H. Oishi, T. Noto, K. Suzuki, T. Hayashi, H. Okazaki, K. Ando, M. Sawada, J Antibiot 35 (1982) 391.
112. R. A. Slayden, R. E. Lee, J. W. Armour, A. M. Cooper, I. M. Orme, P. J. Brennan, G. S. Besra, Antimicrob Agents Chem other, 40 (1996) 2813 .
113. [114] L. Kremer, J. D. Douglas, A. R. Baulard, C. Morehouse, M. R. Guy, D. Alland, L. G. Dover, J. H. Lakey, W. R. Jr. J acobs, P. J. Brennan, D. E. Minnikin, G. S. Besra, J. Biol. Chem. 275(2000) 16857.
114. G. M. Nicholas, C. A. Bewley, Curr Med Chem Anti- Infect Agents 3 (2004) 221.
115. G. L. Newton, K. Arnold, M. S. Price, C. Sherrill, S. B. delCardayre, Y. Aharonowitz, G. Cohen, J. Davies, R. C. Fahey, C. Davis, J Bacteriol, (1996) 178.
116. S. Lee, J. P. N. Rosazza, Org Lett 6 (2004) 365.
117. M. P. Patel, J Am Chem Soc 120 (1998) 11538.
118. M. A. jardine, H. S. C. Spies, C. M. Nkambule, D. W. Gammon, D. J. Steenkamp, Bioorg Med Chem 10 (2002) 875.
119. G. M. Nicholas, P. Kovac, C. A. Bewley, J Am Chem Soc 124 (2002) 3492.
