Conference paper

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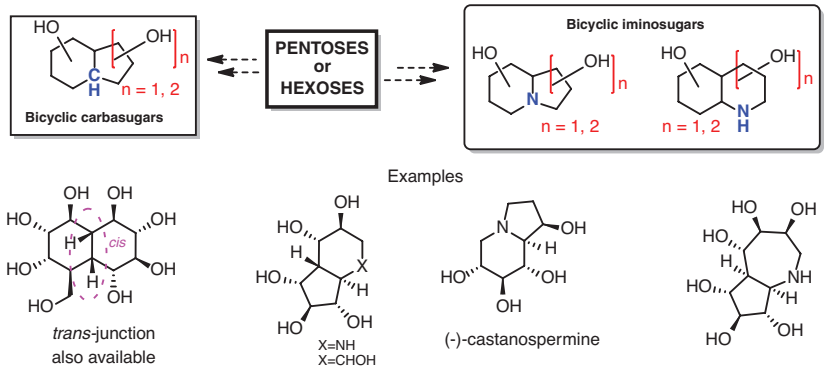
Stereoselective synthesis of sugar mimetics from simple monosaccharides

https://doi.org/10.1515/pac-2019-0116

Abstract: A number of bicyclic imino- and carba-sugars (examples are presented in the Scheme) can be obtained from simple monosaccharides (hexoses or pentoses) by various methods.



Keywords: carbasugar; ICS-29; iminosugar; stereoselective synthesis.

Introduction

Iminosugars are inhibitors of glycosidases which usually display potent activity; carbasugars have similar properties. The most known group of sugar mimetics are undoubtedly iminosugars, i.e. compounds closely related to sugars, with the endocyclic oxygen atom replaced by a nitrogen atom [1–10]. Such compounds are recognized by appropriate enzymes but, since they are not metabolized, block their active center(s) [11, 12]. Several derivatives of iminosugars, e.g. miglitol and miglustat, have found an application in a clinical use. They are active forms of medicinal drugs: Glyset™ and Zavesca™; both are analogs of deoxynojirimycin (DNJ), probably the most recognized iminosugar. When the oxygen atom in the sugar ring is replaced by the CH_2 group (or other substituted carbon moiety), another class of compounds – carbasugars – is obtained. (Fig. 1) [13–16].

The representative derivatives from this group also possess interesting biological activities similar to iminosugars [17]. The synthesis of mono-carbocyclic carbasugars is well explored; the carbo-bicyclic analogs, however, are less known. They strongly resemble natural inhibitors of glycosidases [18–20] being at the same time the analogs of bicyclic imino sugars (a in Fig. 2) and the analogs of 'normal' (i.e. monocyclic) carbasugars with the rigid structure (b). The bicyclic nature of such compounds can secure the unfavorable conformation

Article note: A collection of invited papers based on presentations at the 29th International Carbohydrate Symposium (ICS-29), held in the University of Lisbon, Portugal, 14–19 July 2018.

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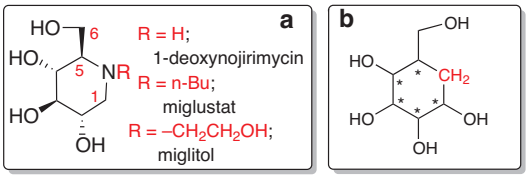


Fig. 1: Examples of (a) iminosugars; (b) carbasugars.

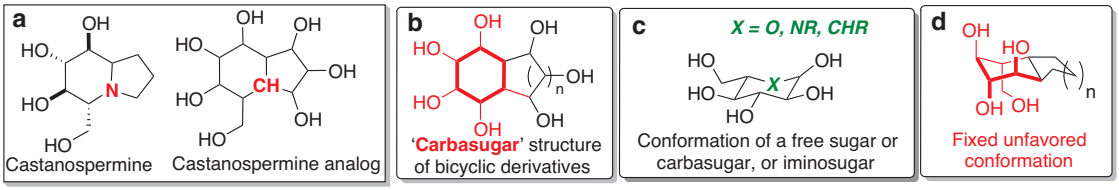


Fig. 2: Similarity of polyhydroxylated bicyclic derivatives to iminosugars and conformational analysis of carbasugars.

of the mimetics. For example, the low-energy conformation c of a monocyclic sugar (iminosugar, carbasugar) can be '*converted*' into not favored one, when an additional ring with the *trans*-relation of the substituents is introduced to the molecule (d in Fig. 2). Such compound may be treated either as a bicyclic mimetic or regarded as the analog of a monocyclic derivative with a rigid structure [17]. The '*inverted*' conformation could be sometimes beneficial to interact with enzymes.

In this review, the synthesis of bicyclic imino- and carbasugars with special emphasis on the results obtained in the laboratory of the authors will be presented. We have already proposed several useful routes, alternative to previously described, which allow preparing different imino sugars either 'natural' i.e. existing in Nature or 'unnatural'. According to our methodology, a number of stereoisomeric 'natural' and 'unnatural' alkaloids as well as bicyclic carbasugars can be prepared.

Synthesis of bicyclic carba- and iminosugars from sugar allyltins

Our interest in the synthesis of bicyclic carbasugars came from the *incidental* observation made during the study on the preparation of higher carbon sugars (HCS), i.e. polyhydroxylated derivatives with a long (>10 *C*-atoms) carbon chain. Such compounds can be conveniently prepared by a connection of two, properly functionalized monosaccharides [21–23]. One of the most reliable methods was based on the reaction of sugar derived phosphoranes (**1**) or phosphonates (**2**) with aldehydes (**3**), which allow to connect two sugar rings *via* a proper linker (Fig. 3).

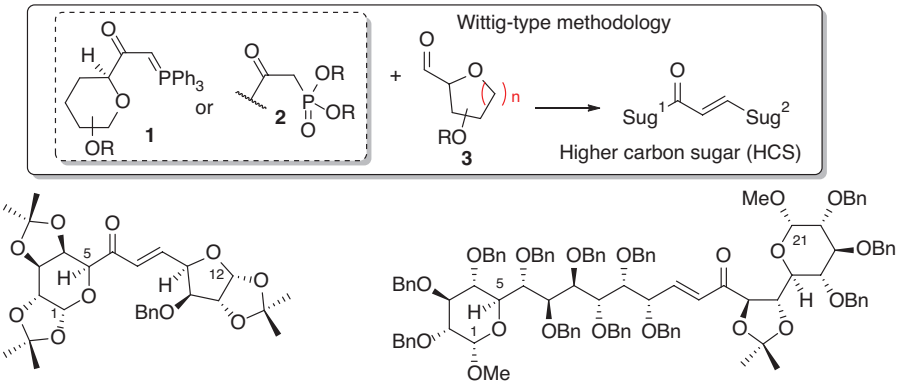
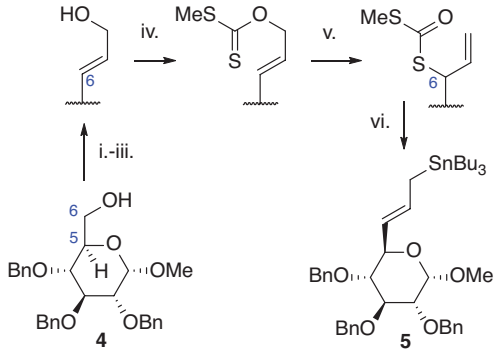


Fig. 3: Examples of C12 and C21 monosaccharides.

We also proposed another method of a construction of a HCS skeleton from sugar allyltin derivatives. Convenient synthesis of such organometallics is presented in Scheme 1. Protected methyl α-D-glucopyranoside **4** was converted, in few well defined steps, into allyltin derivative **5**; this was the first synthesis of such organometallics with sugar core reported in the literature [24].

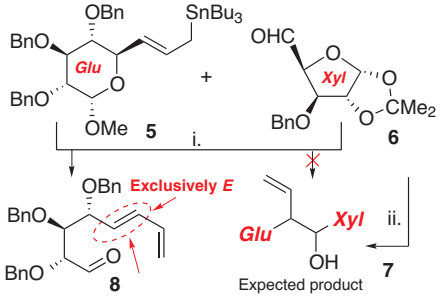
Organometallic derivative **5**, upon reaction with sugar aldehyde **6** catalyzed with a strong Lewis acid ($TiCl_4$), should afford the HCS skeleton **7**. However, slow addition (syringe pump) of a Lewis acid to a mixture of both sugar reagents (**5** and **6**) resulted only in the fragmentation of starting sugar allyltin (Scheme 2). The product of this unexpected reaction, dienoaldehyde **8** with the *E*-configuration across the internal double bond [25], was isolated in very good yield from the post-reaction mixture [24]. The desired higher carbon sugar derivative **7** could be, however, obtained upon fast addition of a Lewis acid to the reaction mixture.

The dienoaldehydes obtained from D-mannose and D-galactose are also available (Fig. 4), thus opening a route to a variety of configurationally different bicyclic carbasugars [26].



i. [O]; ii. $Ph_3P{=}CHCO_2Me$; iii. LAH; iv. 1. NaH, 2. CS_2, 3, MeI; v. xylene, 140 °C, 2 h; vi. Bu_3SnH, 140 °C, 1 h;

Scheme 1: Synthesis of allyltin compound **5**.



i. Slow addition of $TiCl_4$; ii. Fast add. of $TiCl_4$

Scheme 2: Reaction of allyltin compound **5** with carbohydrate aldehyde **6**.

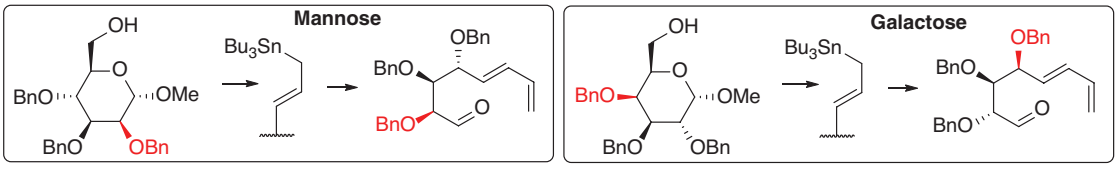


Fig. 4: Dienoaldehydes prepared from D-mannose and D-galactose.

Such dienoaldehyde were used as a starting material for the preparation of complex bicyclic carba- and imino-sugars.

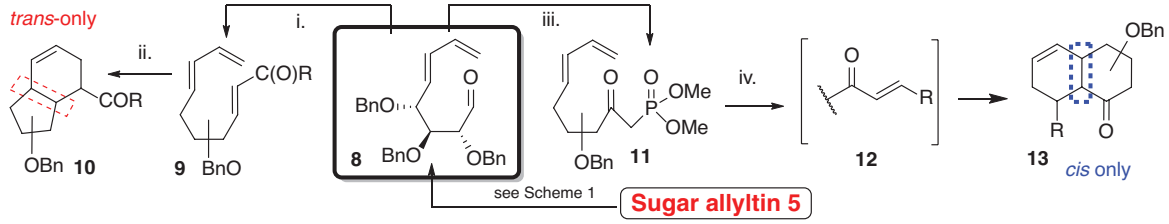
Stereoselective synthesis of bicyclic carbasugars from sugar allyltin derivatives

We have proposed a convenient route to polyhydroxylated carbobicyclic derivatives from such organometallics [21–23, 27]; an example derived from D-glucose is shown in Scheme 3. Dienoaldehyde **8**, obtained from sugar allyltin **5** as depicted in Scheme 2, was converted into triene **9** in the reaction with the corresponding phosphorane (Wittig reaction) or phosphonate (Horner–Wadsworth–Emmons reaction).

Diels-Alder cyclization of **9**, induced with a Lewis acid or high pressure (10 000 atm.), afforded hydrindane derivative **10** with the *trans*-ring junction, which resulted from the *endo*-transition state of the Diels-Alder cyclization. Selectivity of this [4 + 2] cycloaddition was dependent on the configuration of the starting dienoaldehyde (derived from D-glucose, D-mannose, or D-galactose) [21–23]. Alternatively, **8** was converted into phosphonate **11**, which – by reaction with aldehydes – underwent a conversion into triene **12**, which spontaneously cyclized to decalin **13** with the *cis*-ring junction (Scheme 3) [28].

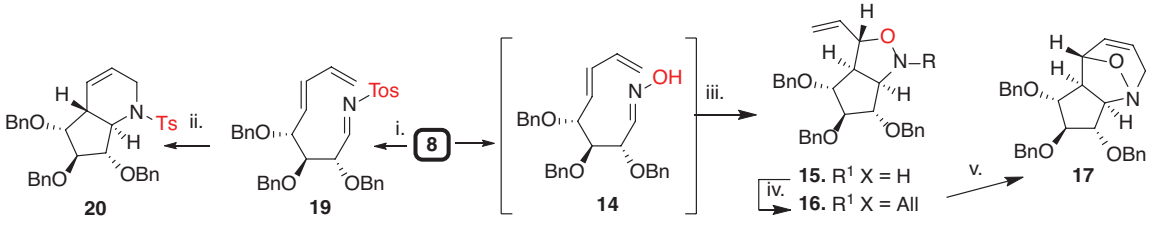
Stereoselective synthesis of bicyclic iminosugars from sugar allyltin derivatives

Dienoaldehyde **8** served also as a convenient precursor of rare imino sugars (Scheme 4). It was thus converted into oxime **14**, which underwent – instead of the expected hetero Diels-Alder process – the 1,3-dipolar cycloaddition providing **15**. Allylation of the nitrogen atom (→**16**) followed by a ring-closing metathesis (RCM) reaction afforded **17**, which finally was converted into iminosugar **18** (shown in Fig. 5) [29].



i. Ph_3P=CHCOR or $MeP(O)(OMe)_2$; ii. 10 kbar or $AlCl_3$; iii. 1. [O] 2. CH_2N_2 3. $^{(-)}CH_2P(O)(OMe)_2$; iv. RCHO, PTC

Scheme 3: Application of sugar allyltins in the preparation of bicyclic carbasugars.



i. $TsNH_2$; ii. cyclization; iii. NH_2OH; iv. AllBr; v. RCM

Scheme 4: Application of sugar allyltins in the preparation of sugar rare bicyclic iminosugars.

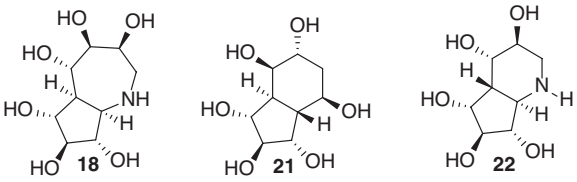


Fig. 5: Examples of sugar mimetics prepared in our laboratory.

On the other hand, reaction of **8** with tosyl amine afforded **19**, which underwent the hetero Diels-Alder reaction providing the expected product **20** [30]. This is consistent with the results obtained by Herczegh who proved that oximes similar to **14**, in which the hydroxyl group was protected, readily underwent the [4 + 2]-cyclization (Scheme 4) [31]. Functionalization of all intermediates shown in Schemes 2 and 3 yielded polyhydroxylated bicyclic derivatives, such as **18**, **21**, **22** (Fig. 5).

Preparation of carba- and imino-sugars *via* different methodologies

Our tin-methodology towards sugar mimetics presented above has several disadvantages. First, it is not environmentally friendly; organic stannanes are toxic, thus application of them in pharmacy, even as starting materials, is not recommended. Second, the synthesis is long and tedious, which results mostly from a multistep conversion of starting glycosides into allyltin derivatives (such as **5**). Moreover, we are able to obtain only *cis*-decalin and *trans*-perhydroindane systems, which is a consequence of the stereochemistry of the intramolecular Diels-Alder reactions of intermediate trienes (**9**→**10**-*trans* and **12**→**13**-*cis*).

Preparation of the alternative bicyclic derivatives: *trans*-decalins and *cis*-perhydroindanes required another solution(s). First, most obvious, possibility lays in changing the geometry of the reacting molecules. The elaboration of the convenient procedure for the preparation of dienes with the *Z*-configuration across the internal double bond is, therefore, needed. The access to such dienes would open a useful route to bicyclic derivatives with a different geometry at the ring junction (Fig. 6).

Recently we have proposed a useful method allowing the preparation of *Z*-dienes, which may-be used as precursors of trienes shown in Fig. 6; this procedure was applicable also for the selective preparation of the *E*-dienes as shown in Scheme 5.

Methyl α-D-glucoside was converted in a few, well-defined steps into the protected derivative **24**. Its reaction with pinacol (*E*)-1-(trimethylsilyl)-1-propene-3-boronate (**25**) provided adduct **26** as a mixture of two isomers with the relative *anti*-configuration. Treatment of **26** with potassium hydride gave diene **27** with the *Z*-configuration across the internal double bond, while treatment with sulfuric acid furnished the *E*-diene **28**. Both isomers were deprotected at the anomeric center affording hemiacetals **29** and **30**, respectively, which were converted into oxazolines **31** and **32** as shown in Scheme 5 [32].

Second approach, quite different from the cyclization route proposed in Fig. 6, was based on a concept in which the *trans*-relation between the substituents was built ***before*** cyclization [33]. The synthesis of *trans*-decalin system was initiated from cyclohexenone **33** [33], readily prepared from 6-iodoglucoside **34** according to the methodology shown in Scheme 6.

1,4-Addition of vinylmagnesium bromide to **33** afforded intermediate **35** [34] which – upon *in situ* treatment with unsaturated aldehyde **(*R*)-36** – provided adduct **37** with the *trans*-relation between both

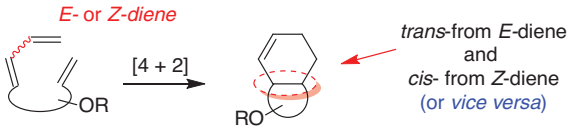
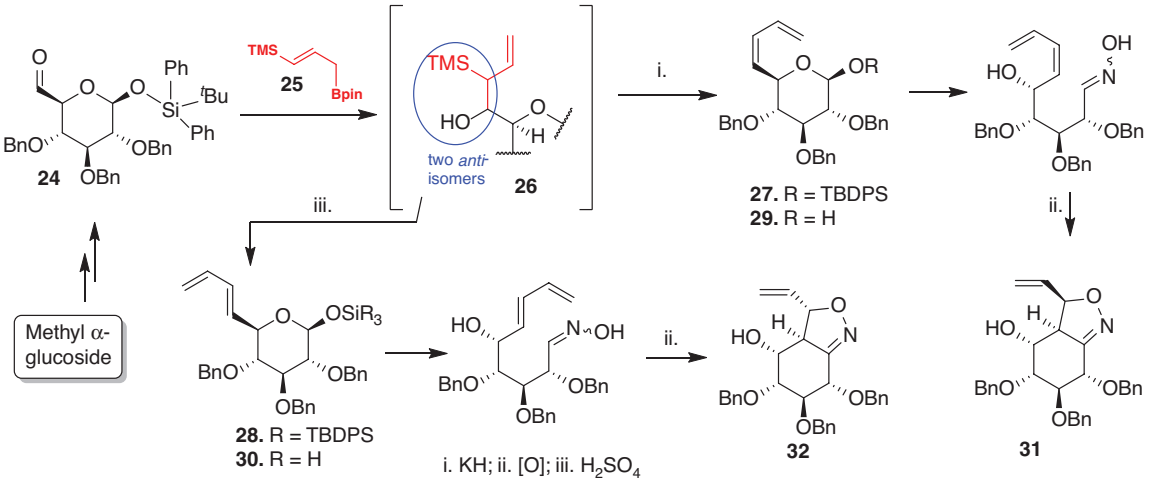
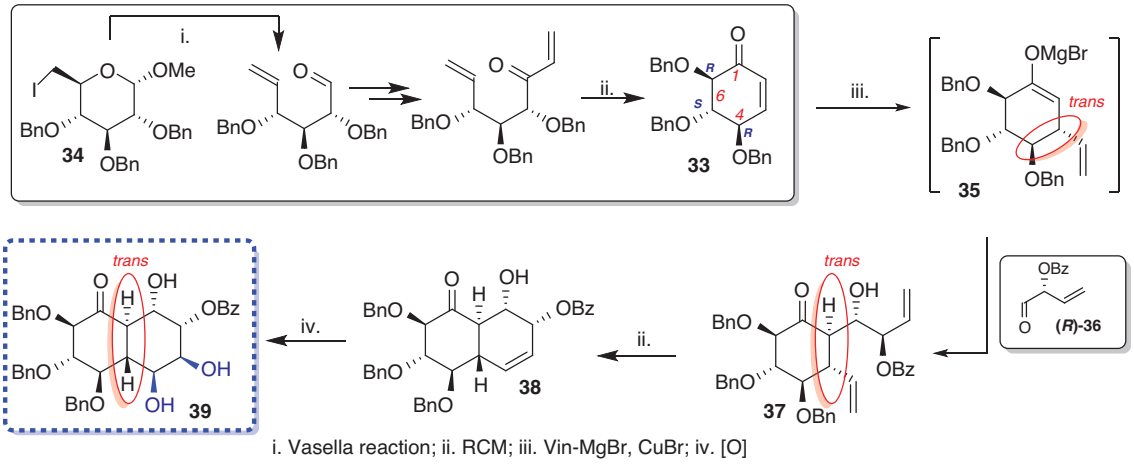


Fig. 6: Synthesis of different steroisomers of bicyclic targets.



Scheme 5: Stereoselective preparation of sugar dienes from the same precursor and their further conversion into isoxazolines.



Scheme 6: Synthesis of highly oxygenated *trans*-decalins from D-glucose.

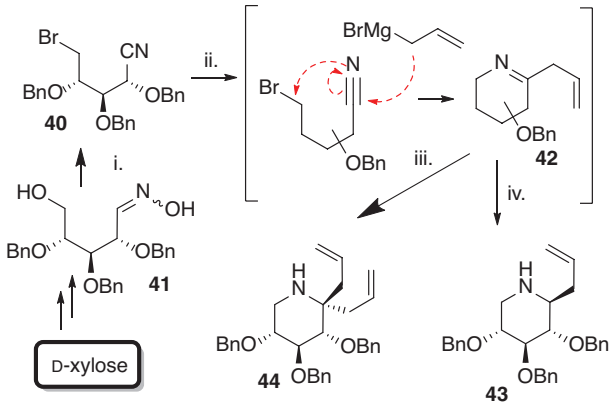
newly introduced substituents. The 6-membered ring was constructed in the *RCM* reaction; the resulting endocyclic olefin **38** was then *cis*-dihydroxylated to afford the fully hydroxylated *trans*-decalin **39** [33].

We have proposed also a useful route to iminosugars excluding toxic organotin intermediates. The general idea, shown in Scheme 7, is based on a cascade addition of a Grignard reagent to halonitriles and subsequent spontaneous cyclization [35]. Addition of allylmagnesium bromide to bromonitrile **40** – readily obtained from the corresponding oxime **41** – afforded cyclic intermediate **42** which was reduced either to piperidine **43** or reacted with another equivalent of All-MgBr to **44**. The selectivity (mono *versus* double allylation) was dependent on the polarity of the solvent used, and could be controlled.

Compounds **43** and **44** were used as staring materials for the preparation of bicyclic iminosugars as shown in Scheme 8. After introduction of the second unsaturated unit to **43**, the resulting derivative **45** was cyclized under the RCM conditions to afford bicyclic derivative **46**, which finally was converted to **47**. Alternatively, cyclization of a 'double' adduct induced by the Grubbs' catalyst gave the spiro-derivative **48** and finally diol **49**.

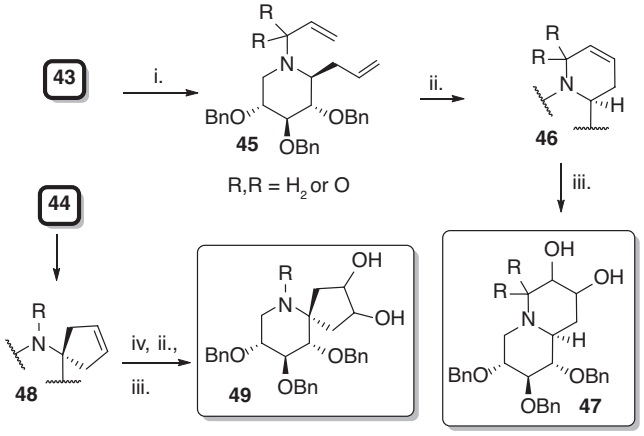
Compounds **46** and **48** were *cis*-dihydroxylated providing the corresponding iminosugars **47** and **49** [35].

The effectiveness of this approach was documented by our recent synthesis of the enantiomer of natural alkaloid castanospermine as shown in Scheme 9.



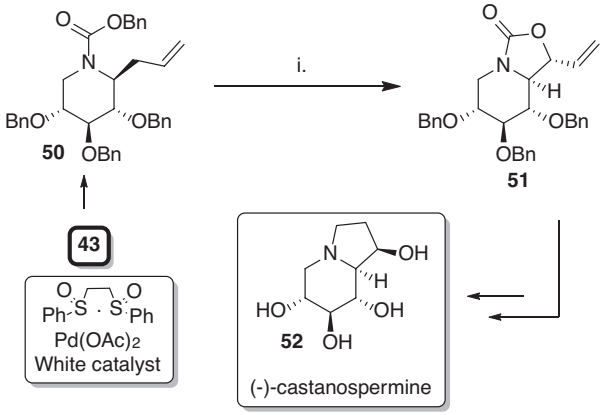
i. Ph_3P/CBr_4; ii. All-MgBr; iii. excess All-MgBr, THF/DMPU; iv. $NaBH_4$, toluene.

Scheme 7: Preparation of monocyclic iminosugars from sugar-derivatives.



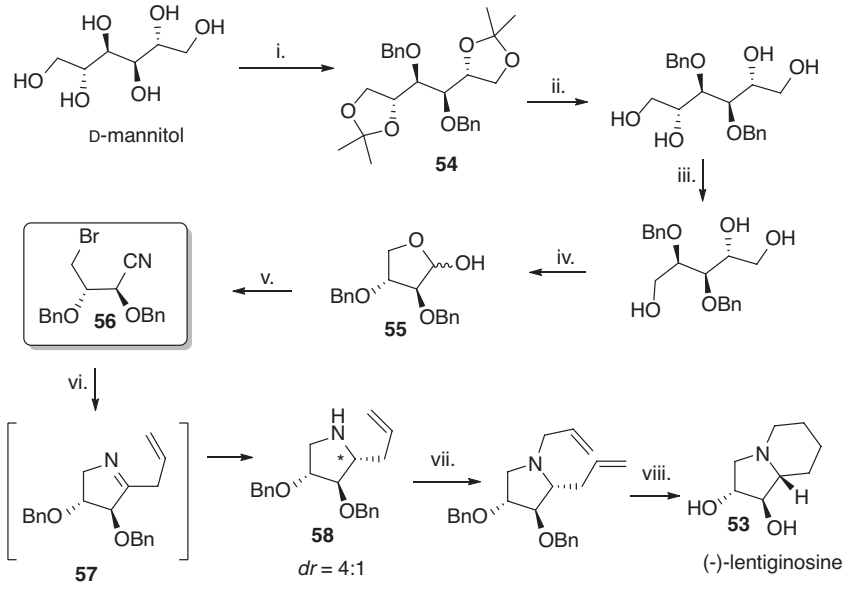
i. All-X or CH_2=CH-COX; ii. RCM; iii. OsO_4; iv. protection of NH

Scheme 8: Preparation of bicyclic iminosugars.



i. White catalyst, $Yb(OTf)_3$, benzoquinone

Scheme 9: Synthesis of the enantiomer of natural castanospermine.



i. ref. 39; ii. HCl/MeOH; iii. $NaIO_4$ then $NaBH_4$; iv. $NaIO_4$; v. NH_2OH then Ph_3P/CBr_4; vi. All-MgBr, $Zn(BH_4)_2$; vii. AllBr; viii. RCM, then [H]

Scheme 10: Synthesis of (-)-lentiginosine.

Adduct **43** was protected at the nitrogen atom with benzyl chloroformate and allylic position in the resulting carbamate **50** was oxidized in the presence of the White's catalyst [36], which is a powerful tool for the oxidation of the allylic position [37]. The intermediate derivative **51** was then converted into unnatural (-)-castanospermine **52** [38].

This convenient methodology of the synthesis of 'normal' (i.e. **43** or **47**) as well was 'strange' (e.g. **44** or **49**) iminosugars can be applied for the preparation of a variety of iminosugars differing in the structure [39]. An example of the synthesis of (-)-lentiginosine (**53**) by this methodology, shown in Scheme 10, is a good illustration of this concept.

D-Mannitol was converted into known [40] functionalized derivative **54**, which – in a few standard steps – was converted into tetrose **55** and finally into bromonitrile **56** (as shown in Scheme 10) [41]. Reaction of this bromonitrile with allylmagnesium bromide followed by reduction of the intermediate imine **57** with zinc borohydride provided pyrrolidine **58** as a mixture of two diasteroisomers in a 4.3:1 ratio. Allylation of the nitrogen atom followed by RCM and hydrogenation provided natural (-)-lentiginosine (**53**) in good overall yield.

This latter approach – successfully applied to the synthesis of unnatural castanospermine and natural lentiginosine – may be also used for the preparation of other configurationally different alkaloids as shown in Fig. 7 [41].

In this short review, various approaches to imino- and carbasugars developed in our laboratory were presented. As already mentioned (see Refs. [1] and [2]) the synthesis of sugar mimetics is well explored; these results are already described in a number of excellent reviews.

Miscellaneous

We have presented several methodologies for the preparation of imino- and carbasugars especially bicyclic ones. They have general applications, thus the proper methodology might be chosen to prepare the desired derivative. However, there is still need for the development of new methods for the preparation of carba- and iminosugars, especially leading to 'strange' skeletons with different ring(s) and/or various position of the nitrogen atom.

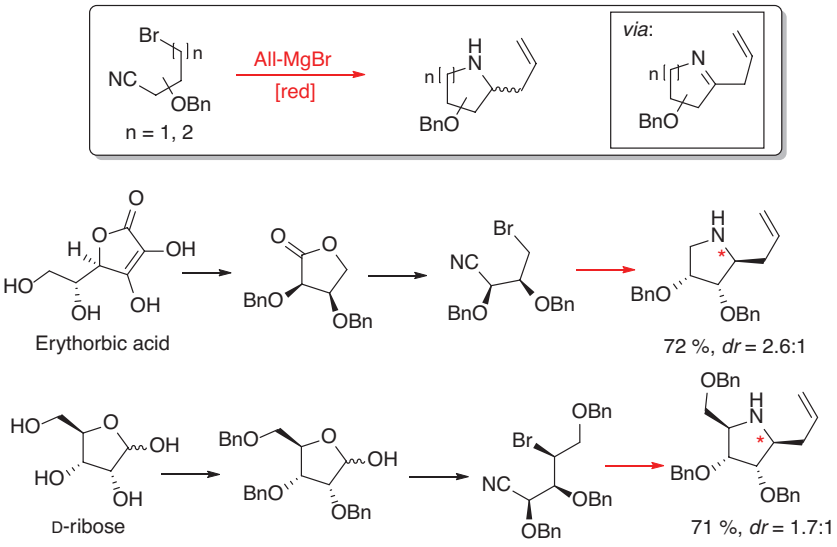


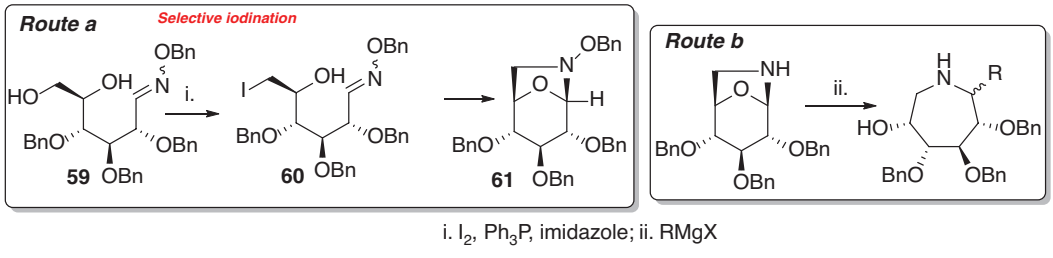
Fig. 7: Preparation of various polyhroxylated pyrrolidines from the corresponding bromonitriles.

Recently we have found that iodination of the primary hydroxyl group in protected oxime-diol **59** can be performed selectively at the primary position. The resulting product **60** undergoes cyclization providing bicylic iminosugar **61** (***route a*** in Scheme 11)[1]. This compound may be used, eventually, as a precursor of 7-membered iminosugars as proposed recently by Bleriot and co-workers (***route b*** in Scheme 11) [42].

In this Section we will present also very recent syntheses of strange iminosugars performed in other laboratories.

Recently, in a series of papers, Baskaran and co-workers [43–48] proposed the efficient routes to complex iminosugar *C*-glycosides. For example, treatment of D-ribose tosylate **62** with aliphatic amines and subsequent stereoselective arylation of the *in situ* generated iminium ions with aryl nucleophile, resulted in functionalized iminosugar *β*-*C*-glycosides as single products. Electron-rich arenes (resorcinol, pyrogallol, *m*-aminophenol) and heterocycles (indole and pyrrole) have been used as aryl nucleophiles. Thus, reaction of **62** with benzyl amine followed by treatment of an intermediate **63** with coumarine – which is present in many natural as well as in synthetic drug molecules [49] – allowed to prepare fused iminosugars such as e.g. **64**. This method was successfully expanded to a library of various complex *C*-aryl iminosugars [43]. Alternatively, the use of tryptamine (**65**) provided the fused product **66** (Scheme 12) [44].

Other compounds prepared by this methodology are shown in Scheme 12. The intermediate β-*C*-alkynylglycoside **68**, obtained from iminium ion **67** and terminal acetylene, under the Grubbs ring-closing metathesis (RCM) conditions provided **69** spontaneously oxidized to **70** [45]. A family of other complex iminosugars: **71** [45], **72** [46], **78** [47], and **80** [48], which are shown in Fig. 8, were prepared from simple monosaccharides.



Scheme 11: Selective iodination of sugar derived diols and its application in the synthesis of bicyclic iminosugars.

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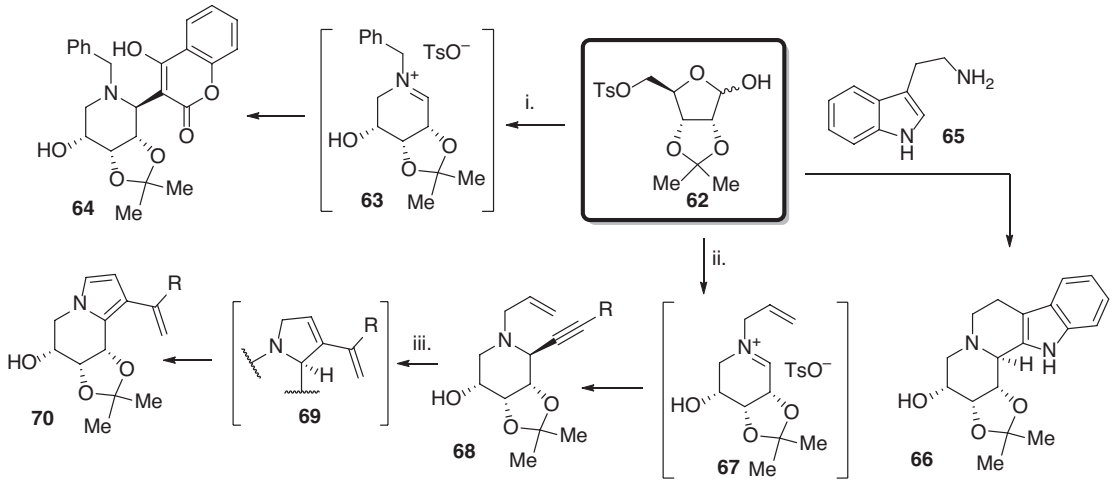


Scheme 12: Diversity oriented one-pot synthesis of novel iminosugar *C*-aryl glycosides.

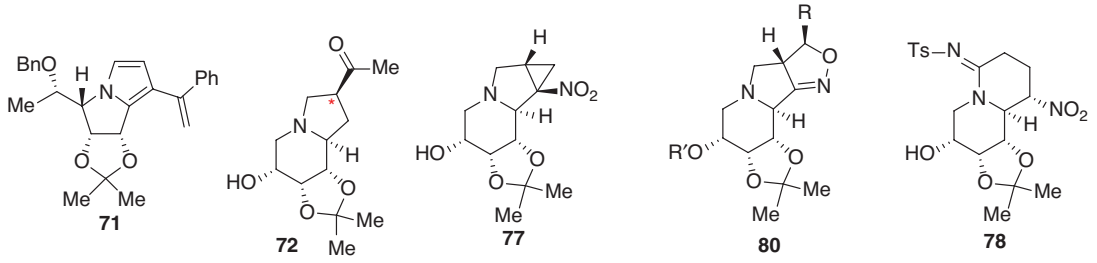
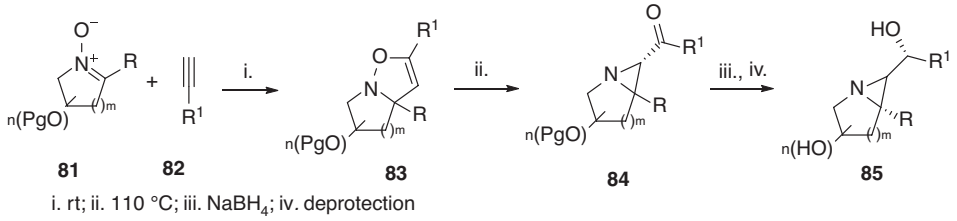


Fig. 8: Examples of 'strange' iminosugars prepared by Baskaran and co-workers.



Scheme 13: Aziridination of cyclic nitrones targeting constrained iminosugars.

Another approach to 'strange' iminosugars was recently proposed by French scientists [50]. It is based on the stereoselective (1,3)-cycloaddition of cyclic nitrones (**81**) and acetylenes (**82**) which provides 4-isoxazolines (**83**). The latter, undergo the Baldwin rearrangement [51] affording bicyclic 2-acylaziridines **84**, which finally are converted into iminosugars **85** (Scheme 13).

Conclusion

The methodologies elaborated in our laboratory allow for efficient syntheses of complex fused-bicyclic (six-six and six-five) carba- and imino-sugars having different structures. This is, however, limited only to compounds having two six-membered or five- and six-membered rings. In the recent literature there are

examples of the synthesis of bicyclic iminosugars with different ring sizes. These syntheses were presented briefly in the last part of this short review.

There is of course a need to predict the structure of the mimetic, preferably by the *in silico*, and then propose the proper method to prepare this derivative in an efficient way. Having so many methodologies which were shown in this review it should be possible to choose the proper one.

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