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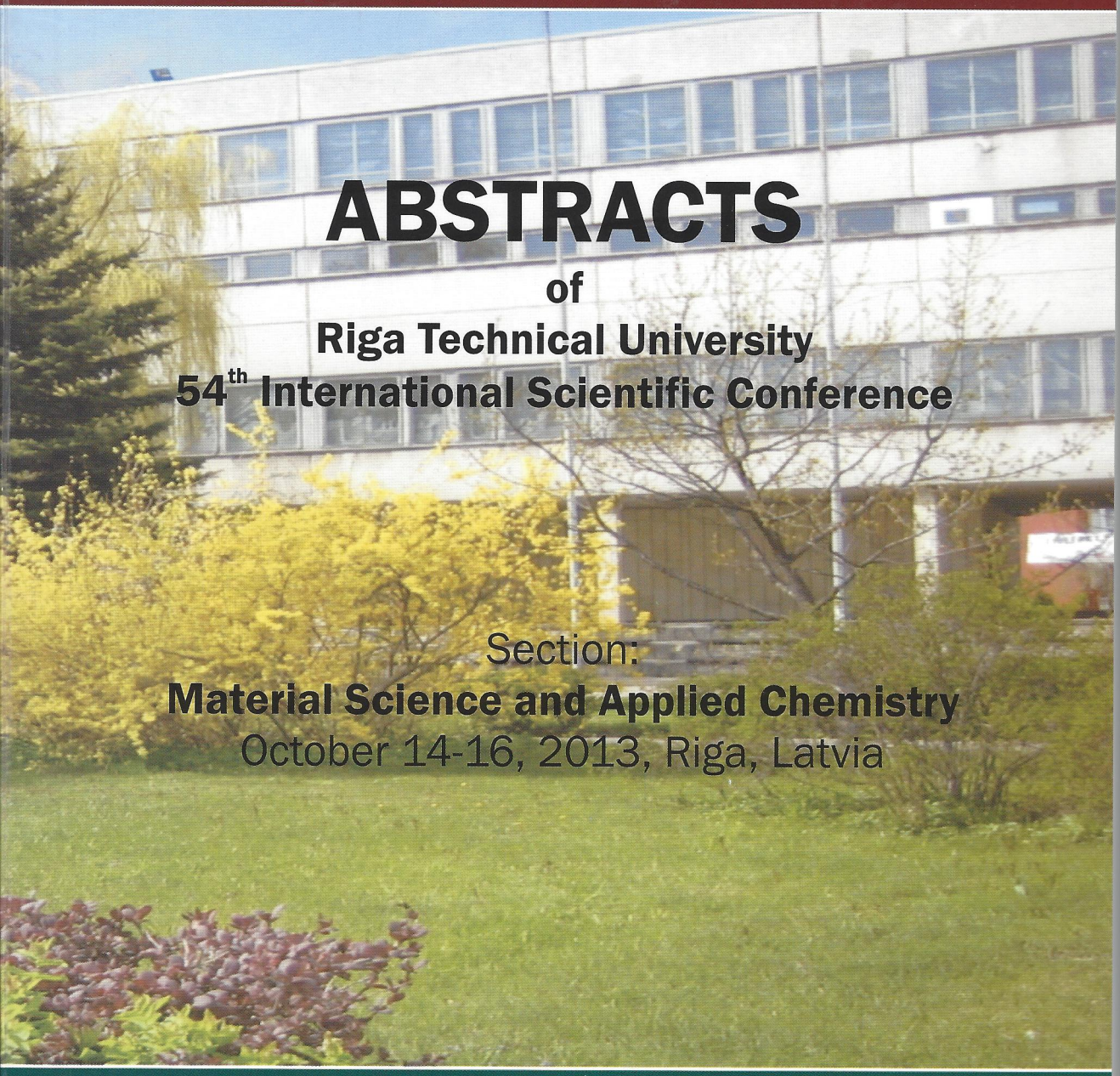
Faculty of Material Science and Applied Chemistry



ABSTRACTS

of

Riga Technical University

54th International Scientific Conference

Section:

Material Science and Applied Chemistry

October 14-16, 2013, Riga, Latvia

Riga 2013

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Synthesis and Analysis of Novel Sugar Amino Acid-based Saccharopeptides

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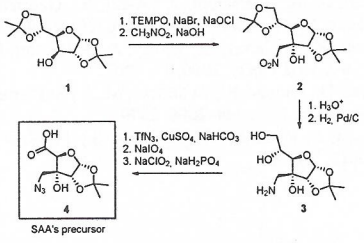
Keywords **– glycoconjugates, oligosaccharide chemistry, sugar amino acids, foldamers, γ-peptides.**

INTRODUCTION

Sugar amino acids (SAAs) represent a structurally diverse class of compounds that can be used in foldamer synthesis and as multifunctional monomeric building blocks for drug design. Oligomers of such monosaccharide hybrid molecules frequently adopt secondary structures in relatively short sequences. [1]

RESULTS AND DISCUSSION

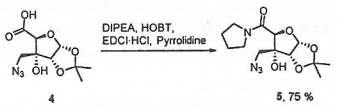
We have developed a synthetic strategy towards a novel furanoid γ-SAA with *ribo* configuration. Commercially available diacetone-α-D-glucose **1** was used as a starting material in a multistep synthesis. The process started with TEMPO catalyzed oxidation affording corresponding ketone. [2] Further synthesis included a sequence of modifications at carbohydrate C(3) position. First, diastereomerically pure nitromethyl product **2** was prepared by the Henry reaction. After treatment with Brønsted acid and the reduction of the nitro group, deprotected aminomethylalcohol **3** was obtained. Azide functionality was introduced by diazotransfer reagent TfN_3. Finally, SAA precursor – γ-azidoacid **4** was prepared by two subsequent oxidation reactions, first with sodium periodate followed by Pinnick oxidation. Product **4** can be easily transformed into corresponding γ-amino acid by reduction of its azido group. Synthesis of **4** included six steps starting from diacetone-α-D-glucose **1** with an overall yield of 23% (Scheme 1).



Scheme 1. Synthesis of SAA precursor 4

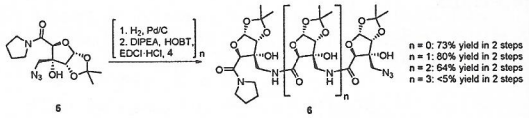
Some derivatives of compound **4** were synthesised in order to obtain a fully protected monosaccharide unit that could be used as a starting material in the synthesis of corresponding homooligopeptides. An appropriate orthogonal protection/deprotection strategy for liquid phase synthesis has been developed.

We have discovered that in our case the use of isopropyl ester as a protecting group for carboxyl termini is inappropriate since intramolecular cyclization occurs, once free amine is obtained. Hence, we focused on the linear homooligomer synthesis strategy. While the azido group was used as *N*-protection, the *C*-end was protected as a pyrrolidine amide (Scheme 2).



Scheme 2. Synthesis of SAA amide **5**

Compound **5** was further used for oligomer synthesis *via* standard solution phase peptide synthesis. Short-chain oligopeptides were obtained in adequate yields (Scheme 3).



Scheme 3. Oligopeptide synthesis

The presence of intramolecular hydrogen bond in the obtained SAA homooligopeptides was detected by ^{1}H-NMR-titration of their $CDCl_3$ and CD_3CN solutions with DMSO-*d6*. It has been concluded that tetramer **6** (n=2) and pentamer (n=3) form at least one intramolecular hydrogen bond in CD_3CN solution.

We assume that further elongation of the obtained oligomers will lead to new artificial peptides that will form well-ordered secondary structures.

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[1] Edwards, A. A.; Alexander, B. D.; Fleet, G. W. J.; Tranter, G. E. *Chirality* **2008**, *20*, 969.
[2] Ostrovskis, P.; Mackeviča, J.; Kumpiņš, V.; Turks, M. *Carbohydr. Chem.: Proven Synth. Methods* **2013**, *2*. In press.

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New Approac

Irina Novosjolova[1],

Keywords **– purine nucleosides derivatives, 1,3-dipolar cycl aromatic substitution, fluorescenc**

INTRODUCT

Modified purine derivatives anticancer and antiviral drugs significant applications also as of adenosine receptors [2].

Since 2002, many different n derivatives containing 1,2,3-tria synthesised and investigated. N literature reports deal with eithe yl)-purine nucleosides [3]. In process of synthesis of new adenine derivatives [4].

RESULTS AND DI

A straightforward way to the sy triazol-1-yl)-purine nucleosides developed from 2,6-diazidop various terminal alkynes (for e 4-bromophenylacetylene, 4-*tert*-methyl-3-butyn-2-ol and others)

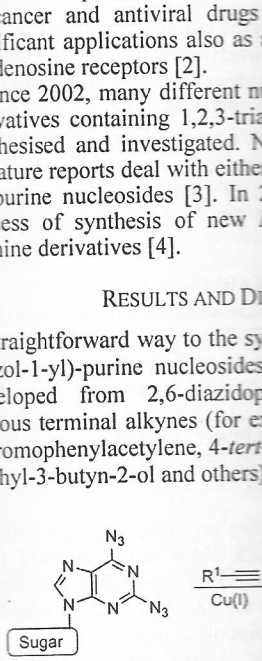

Figure 1. General synthesis of bis-t

We have discovered that tri the purine base undergoes nucleophilic substitution with nucleophiles. The substitutio proven by X-ray analysis (Figu

Recently, we have discove between 2,6-diazidopurine nu nucleophile we obtain C(2) sul following "click" reaction give