Polish J. Chem., **79**, 155–161 (2005)

Professor Aleksander Wiesław Zamojski 1929–2004

OBITUARY*

Aleksander Wiesław Zamojski was born in Poznań on 1st September 1929. His father Szczepan was a medical doctor. Alex received his early education in elementary school in Smigiel near Poznań and then in Aleksandrów near Łódź. During the Second World War he attended hidden education in Łódź. In 1948 Alex graduated from high-school with a special mathematics-physics program and began his chemical education at the Chemistry Department of the Technical University of Łódź. In 1952 he obtained the degree of engineer and then in 1954, M.Sc. in chemistry. The same year he moved to Warsaw, where he was appointed as a teaching assistant at the Chemistry Department of Warsaw University and started his Ph.D. program under the supervision of Professor Osman Achmatowicz on reactions of carbonyl cyanide $CO(CN)_2$. This very reactive compound had been synthesized by Professor Roman Małachowski before the Second World War. Alex demonstrated the extremely high reactivity of carbonyl cyanide as a heterodienophile in the Diels-Alder reaction leading to dihydropyran derivatives. He also showed that diethyl mesoxalate was an even better dienophile. In 1959 he defended his Ph.D. thesis entitled '*Diene reactions of carbonyl cyanide and diethyl mesoxalate*'. In 1959–61 he received a Rockefeller fellowship to work as a post-doctoral at the ETH in Zurich in the laboratory of the future Nobel Prize laureate Professor Vladimir Prelog, where he was engaged in a project directed to the structure determination of two antibiotics – narbomycin and lankacidin.

After returning to Poland, he began to work as a senior research associate in the Department of Chemistry of Warsaw University under direction of Professor Achmatowicz and continued the program which he had started with Prelog. In 1965 Dr. Zamojski defended the habilitation thesis entitled '*Structures of narbomycin and related macrolide antibiotics*' and obtained the D.Sc. (habilitation) degree. The same year he moved to the newly formed Institute of Organic Chemistry of the Polish Academy of Sciences (IOC) in Warsaw, first as a Docent (Associate Professor) and since 1973 as a full Professor until his retirement. In 1968 he succeeded Professor Osman Achmatowicz as the head of the Department of the Synthesis of Natural Products. After reorganization of the Institute and the departure of the alkaloid laboratory to Poznań, he became the head of the laboratory responsible for the synthesis of mono- and oligosaccharides. Between 1979 and1982 he served as the Research Director of the Institute.

After retirement at the age of seventy, he continued his association with the Institute as Professor Emeritus.

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* This obituary was also published in *Advances in Carbohydrate Chemistry and Biochemistry*.

Professor Zamojski was very much engaged in the education of Ph.D. students in the Institute. He was a true scholar. Together with Dr. Osman Achmatowicz Jr., son of his former supervisor, he was the organizer of the first Ph.D. Study program in Poland; located in the Institute, it resembled post-graduate studies in western hemisphere universities. At that time, a scientific career in Poland was based on the long-established way of doing a Ph.D. degree, usually taking many years. Ph.D. study at the Institute of Organic Chemistry, even now, represents a model of training Ph.D. students, which in Poland deserves imitation. As a part of the graduate students' training, he delivered a two-semester course on the stereochemistry of organic compounds. In the middle 60's he was the initiator of the introduction of stereochemistry to the advanced course of organic chemistry and was a popularizer of the famous books of Ernest Eliel , '*Stereochemistry of Carbon Compounds*' and '*Conformational Analysis*'. He was a founder of the Section of Stereochemistry of the Polish Chemical Society, which under his presidency (1973–82) was a model of activity for other sections of the Society. Since 1973, he was the organizer of Schools on Stereochemistry which took place in the beautiful palace in Jabłonna located in close vicinity to Warsaw where he and his coworkers taught a basic course of modern stereochemistry. At the end of each school an invited eminent stereochemist delivered a lecture related to the program. In 1975 Alex organized the First National Symposium on Stereochemistry.

The first research project that Alex undertook in the Institute was directed to the chemistry of the macrolide anitbiotic, erythromycin. Chemical modifications led him to the preparation of a new interesting derivative, 8-hydroxyerythromycin. The patent on the synthesis of this compound was purchased by a well known pharmaceutical company. At the same time Alex initiated studies on the total synthesis of monosaccharides from the Diels-Alder adduct of 1-methoxy-1,3-butadiene and butyl glyoxylate. As Alex used to say: '*I started to think about the concept of the synthesis as early as the beginning of the 60's during my post-doctoral stay with Professor Prelog*'. Total synthesis of sugars dominated the work of the Zamojski's group for almost two decades, establishing his high position among the Polish, as well as, international carbohydrate societies.

The group continued research not only in the synthesis and transformation of Diels-Alder cycloadducts, but also in the study of spectral properties and conformations of substituted dihydropyrans and the corresponding epoxides. The pioneering work of Professor Zamojski on the diastereoselective transformations of cycloadducts allowed him to propose a new, original, and general method for the preparation of racemic monosaccharides. During early years of this program, he competed with Professor Robert Brown's group from Edmonton, Canada, who at the same time started the total synthesis of racemic monosaccharides from acrolein dimer. In both methods the crucial step involved rearrangement of epoxides into allylic alcohols. Brown's group used butyl lithium promoted rearrangement whereas Alex performeda more versatile sequence of simple, high yielding reactions which consisted of opening of the epoxide with dimethyl amine, followed by oxidation of the dimethylamino

Department of the Synthesis of Natural Products of the Institute of Organic Cheistry, PAS in 1976

From left to right
Sitting: Ewa Dudek, Halina Burzyńska, Barbara Szechner, Osman Achmatowicz Jr., Aleksander Zamojski, Hanna Banaszek-Rułko, Janina Wach, Maria Zajączkowska.
Standing: Sławomir Jarosz, Marek Pietraszkiewicz, Tomasz Koźluk, Waldemar Priebe, Grzegorz Grynkiewicz, Janusz Jurczak, Andrzej Konował, Jan Szymoniak, Konstanty Belniak, Marek Chmielewski

group to N-oxide and finally a Cope degradation. Zamojski's total synthesis of monosaccharides was also the beginning of modern organic synthesis in Poland. Alex clearly demonstrated to the Polish scientific community that the target compounds could be synthesized by a sequence of reactions in which every step has been very carefully planned, leading to the desired product with high stereoselectivity and in high yield. This project led his group to syntheses of all of the stereoisomeric methyl glycosides of pentoses, hexoses, and hexuronic acids, as well as many deoxy sugars, aminodeoxy sugars, components of aminoglycoside antibiotics, and higher sugars.

Together with Professor Osman Achmatowicz Jr., Alex elaborated another approach to monosaccharides which utilized furfuryl alcohols as the starting material. The crucial step of this method consisted in the oxidation of the furan ring followed by a subsequent rearrangement of the dihydrofuran skeleton into dihydropyranone.

The transformation, which is known in the literature as the Achmatowicz rearrangement, has caused a big resonance in the chemical literature since it allowed for syntheses, not only of a number of pentoses, hexoses and 6-deoxyhexoses, but also introduced an attractive new method to general organic synthesis. The Achmatowicz rearrangement and its many versions have been commonly used in variety of sophisticated syntheses of natural products.

Alex spent two sabbaticals in Canada with Professor Walter Szarek (1971–72 and 1984–85) and turned his attention to the newly discovered Mitsunobu reaction; it was later widely applied in sugar chemistry by his collaborators Janusz Jurczak, Grzegorz Grynkiewicz and Edward Grochowski. They discovered attractive new applications of the Mitsunobu reaction and managed to explain mechanistic aspects.

The success in transformations of the dihydropyran and furan skeletons into monosaccharides led Alex to study the photochemical reaction of furan with alkyl glyoxylates, leading to a new route to carbohydrates. Paterno-Bűchi reaction followed by opening of the oxetane ring provided a convenient synthesis of 3-substituted furans, which is still regarded as one of the best method of the preparation of these molecules which are otherwise difficult to obtain. The preparation of an anti-biotic sugar, racemic 3-deoxy-DL-streptose was the final success of this project.

Following research trends, Zamojski began to study the synthesis of optically active monosaccharides. Early work with his Ph.D. student Janusz Jurczak directed attention to chiral optically pure glyoxylates and to diastereoselective formation of their Diels-Alder adducts. Although asymmetric inductions obtained at that time were not very attractive, this pioneering work provided a sound base for later successful investigations of this reaction performed by the Professor Jurczak's group involving separation of enantiomers, diastereoselective, and finally catalytic enantioselective cycloadditions, carried out under atmospheric and high pressure.

Based on the methodology of the synthesis of racemic monosaccharides, Alex elaborated an entry to oligosaccharides in the form of rhamnobioses and rhamnotrioses. In the beginning of the 90's he proposed also a convenient strategy for the synthesis of the 11-carbon atom sugar tunicamine. In order to simplify the ^{1}H NMR spectra of per-O-benzyl derivatives, he performed an elegant synthesis of α,α-dideuteriobenzyl chloride and bromide, compounds used for the protection of the free hydroxyl groups in sugars. The NMR spectra of such deuterated compounds were much simpler than 'normal' benzylated molecules.

In the middle 80's the work of Alex was concentrated on the synthesis of bacterial sugars. The first convenient method of the preparation of L-*glycero*-D-*manno*-heptose, a sugar occurring in bacterial lipopolysaccharides, was realized in 1986. Synthesis of mono-phosphates of L-*glycero*-D-*manno*-heptose and methyl L-*glycero*-D-*manno*-heptopyranoside, as well as the study on hydrolysis and migration of the phosphate moiety rationalized the knowledge on the location of the phosphate group in bacterial heptoses. These investigations have attracted the interest of many biochemists. Alex started a close collaboration with Professor Helmut Brade from the Borstel Research Center, Germany. Common studies on the synthesis of biologically important oligoheptoses were sponsored by Polish Academy of Sciences and Deutsche Forschung Gemeinschaft.

A new project, related to complexes of cyclopentadienyl-carbonyl-triphenylphosphin-acyl iron(II) was initiated at the end of the 80's. Alex was particularly interested in the reactivity of anions generated from the acyl fragment towards electrophiles. This led to elaboration of a new method for the synthesis of deoxysugars from 'acyliron' and sugar aldehydes.

In the last period of his research activity Alex was engaged in an elongation of monosaccharides by reaction of terminal sugar aldehydes with the C_1-Grignard reagents, $ROCH_2MgCl$. Synthesis of higher deoxysugars prompted him to investigate an entry to indolizidine type iminosugars from aminodeoxyoctitol derivative. This led him to the new synthesis of castanospermine epimers. Alex developed also a synthesis, free of unpleasant odors, of thiosugars and thioglycosides, which proceeded *via* sugar thiocyanates followed by their reaction with Grignard reagents.

The activity of Alex Zamojski was highly acknowledged by the scientific community. He was twice invited as a "visiting scientist" to the Department of Chemistry, Queen's University, Kingston, Canada (co-operation with Professors J.K.N. Jones and W.A. Szarek). He delivered plenary and invited lectures to numerous international conferences (*e.g.* Carbohydrate Symposia in Madison, Bratislava, Sewilla, and Sydney; *ACS* meetings in Philadelphia and Montreal, Symposia in Bratislava, Rostock, Borstel, Warna). He also presented a number of plenary lectures at the annual meetings of the Polish Chemical Society. He has visited many Universities in the USA, Canada, Germany, France, Hungary, Spain, Denmark, and Switzerland presenting the important results from his own work.

Professor Zamojski was a supervisor for 19 Ph.D. students. Five of his co-workers accomplished habilitation (D.Sc.) and six of them became full Professors. Two of his former students (Professors Janusz Jurczak and Marek Chmielewski) are members of the Polish Academy of Sciences. Professor Zamojski published about 200 scientific papers, and was a co-author of 13 patents. He also wrote 10 chapters and reviews, including a landmark article in *Advances of Carbohydrate Chemistry and Biochemistry*. It should be mentioned that Alex was a great master in the Polish language and taught his students how to write and how to present consistently and clearly their Ph.D. theses and scientific papers.

Aleksander Zamojski served on many committees of academic societies and the Ministry of Science and the Ministry of Education. He was member of the Presidium of the Polish Chemical Society (1976–82), served as President of the Society (1988–1991) and was given honorary membership by the Society in 2000. He served as a member of the Council of Polish Scientific Societies and a member of Executive Committee of Federation of European Chemical Societies FECS (1992–1995 and 1998–2001). He was the chairman of the Section of Chemistry of the State Committee for Scientific Research in 1992–1994 and 1998 till November 2003. He was an expert and a member of the Committee for Popularization of Science of the State Committee for Scientific Research (1993–1994 and 1995–2000). He was a member of the Editorial Advisory Boards of: "*Carbohydrate Research*" (1976–1996), "*Chemtracts – Organic Chemistry*" (since 1989 r.) and the vice-chairman and then chairman of the

Editorial Board of "*Wiadomości Chemiczne*" (1981–1990), written in Polish. Since 1991 he was the founder and Editor in Chief of an informative journal of the Polish Chemical Society '*Orbital*'. He represented Poland in the "*International Carbohydrate Organization*" (1976 –2000), Polish representative to the carbohydrate group in COMECON (East European Carbohydrate Organization coordinated by Professor N.K. Kochetkov; 1976–1991).

He was the Chairman of the Organizing Committee of *7th European Carbohydrate Symposium (EUROCARB 7th)* in Kraków (22–27.VIII.1993) and then the President of the "*European Carbohydrate Organization*" (1993–1995).

He was a member of many Research Councils of institutes of the Polish Academy of Sciences. In particular, he was the Chairman of the Council of the Institute of Bioorganic Chemistry in Poznań (1993–1998) and a member of the councils of the Institutes: Organic Chemistry (Warsaw), Physical Chemistry (Warsaw), and Center of Molecular and Macromolecular Studies (Łódź).

Aleksander Zamojski's achievements have been recognized by many scientific awards, including the Polish Chemical Society Award (1956), Award of the 3rd Division of the Polish Academy of Sciences (1972), 4 Awards of the Scientific Secretary of PAS, and a prestigious Kostanecki Medal of the Polish Chemical Society (1984). In 1984 he was awarded the *Polonia Restituta* Cavalier Cross by the President of Poland.

Alex enjoyed having personal contacts with his coworkers and students. All of us remember every day five o'clock tea in the Institute, collective volley-ball games and traditional picnics organized every autumn thirty kilometers out of Warsaw, while eating and drinking we were talking on day-to-day problems. Having broad interests in organic chemistry and spectroscopy of organic compounds, he has always had time for scientific discussions with his students and colleagues. In 1999 we celebrated his 70th birthday in Ustroń, a small resort located in southern Poland. A large group of his friends from Poland and abroad attended the event presenting lectures on topics related to fields of Alex interests, having friendly discussions and enjoying a social program. After retirement at the age of seventy Alex was active and full of energy. As a Professor Emeritus he has been associated with the Institute having courses with Ph.D. students. He collaborated also with State Committee for Scientific Research being an active member of its two commissions. Alex's rich and rewarding life ended in Warsaw on February 23rd 2004 when he passed away at the age of 74 after losing a battle with cancer.

Professionally, he will be remembered as a creative and enthusiastic scientist and inspiring teacher, for his contributions to carbohydrate chemistry, for his service to the Institute of Organic Chemistry of the Polish Academy of Sciences, to the Polish Chemical Society, to the State Committee for Scientific Research, and to International and European Carbohydrate Organizations.

Sławomir Jarosz
Marek Chmielewski

Polish J. Chem., **79**, 163–178 (2005) **REVIEW ARTICLE**

Oxidative Nucleophilic Substitution of Hydrogen in Nitroarenes. A Short Review

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(Received December 8th, 2004)

Recent results of oxidative nucleophilic substitution of hydrogen in nitroarenes with carbon, nitrogen, oxygen *etc*. nucleophiles and discussion of oxidants used in these reactions are presented.

Polish J. Chem., **79**, 179–209 (2005) **REVIEW ARTICLE**

Progress of Understanding Liquid Crystals Made of Bent-Shaped Molecules

by J. Mieczkowski and J. Matraszek

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(Received October 28th, 2004)

Many strongly bent, so-called banana mesogenes have been synthesized and examined. These liquid crystalline materials are very attracted due to their unique properties and possible applications. In this paper we gathered information about bent-core mesogenes reported in the literature and described connections between molecular structure and polymorphism.

Polish J. Chem., **79**, 211–222 (2005)

Synthesis of Novel Mannose-based Crown Ethers

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(Received September 25th, 2004)

A novel class of chiral crown ether analogues incorporating carbohydrate subunits can be easily prepared from methyl α-D-mannopyranoside. By a short reaction sequence involving either alkylations using a dibutylstannane intermediate or by phase transfer catalyzed etherification well defined disaccharide mimetics were obtained, which are suitable starting materials in Richman-Atkins cyclizations. The combination of several various reaction partners led to structurally interesting ring systems differing in ring size, number of carbon and hetero atoms (20–40) as well as kind of sugar subunits.

Polish J. Chem., **79**, 223–230 (2005)

Synthesis and Determination of Alkali Metal Binding Selectivities of Chiral Macrocyclic Bissulfonamides Derived from D-Mannitol and L-Threitol

by M.M. Gruza[1], A. Pokrop[1] and J. Jurczak[1,2]

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(Received October 4th, 2004)

Four chiral macrocyclic bissulfonamides derived from D-mannitol and L-threitol, possessing C_2 symmetry, were obtained by a macrocyclization reaction under high-dilution conditions. Their applications for alkali metal binding processes were studied using ESI-MS technique.

Polish J. Chem., **79**, 231–238 (2005)

Functionalization of the Homoallylic Bridge in Higher Sugar Precursors

by S. Jarosz[1], K. Szewczyk[1], A. Gaweł[1], A.M. Gomez[2] and J.C. Lopez[2]

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(Received September 30th, 2004)

The Barton reduction of the sugar homoallylic xanthate did not afford the expected hydrocarbon, but led to two cyclic products resulting from the attack of initially formed radical onto the olefin fragment of the homoallylic system. The mechanism of such cyclization is discussed.

Polish J. Chem., **79**, 239–249 (2005)

Synthesis of Iminosugars from α,β-Unsaturated Lactones and *N*-Benzyl Nitrone

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(Received October 22nd, 2004)

1,3-Dipolar cycloadditions of *N*-benzyl nitrone **12** to *D-glycero* γ-lactone **13** and to *D-threo* δ-lactone **14** proceed with excellent stereoselectivity to provide only one adduct in each case, **16** and **17**, respectively. The same reaction performed with *L-erythro* δ-lactone **15** afforded two stereoisomers **18** and **19** in the ratio *ca.* 2.5:1. Cycloadducts **16–19** were subsequently subjected to a sequence of reactions involving hydrogenolysis of the N–O bond and intramolecular alkylation of the nitrogen atom by C-4 or C-5 carbon atom of the sugar backbone to afford 1,2-dideoxy iminosugars **25**, **31**, **38**, **44** and **50** with a protected hydroxymethyl group at C-2 carbon atom.

Polish J. Chem., **79**, 252–265 (2005)

Synthesis of *C*-Glycosidic Galacturonates Suitable as Glycosyl Acceptors

by C. Vogel[1], M. Farouk[1], M. Michalik[1], H. Reinke[1] and S. Jarosz[2]

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(Received November 22nd, 2004)

Methyl 3,4,5-tri-*O*-acetyl-2,6-anhydro-7,8,9-trideoxy-D-*glycero*-L-*galacto*-non-8-enonate (**5**) was obtained by different routes starting from D-galactose and D-galacturonic acid, respectively. Exploring several protecting group manipulations, an effective route was found out for the preparation of methyl 2,6-anhydro-5-*O*-benzyl-7,8,9-trideoxy-D-*glycero*-L-*galacto*-non-8-enonate (**15**) which is one of the key compounds in this synthetic program. Finally, selective benzylation *via* 3,4-*O*-butylstannyl intermediates resulted in methyl (**16**) and benzyl (**17**) 2,6-anhydro-4,5-di-*O*-benzyl-7,8,9-trideoxy-D-*glycero*-L-*galacto*-non-8-enonate both suitable as acceptors in glycosylation reactions. The chemical structure of a great number of intermediates was investigated by X-ray diffraction studies.

Polish J. Chem., **79**, 267–273 (2005)

The Structure of the O-Specific Polysaccharide of the Lipopolysaccharide from *Acinetobacter* Strain 44 (DNA Group 3)

by E. V. Vinogradov[1], L. Brade[1], H. Brade[1] and O. Holst[2]

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(Received September 30th, 2004)

Extraction of dry bacteria of *Acinetobacter* strain 44 (DNA group 3) by phenol/water gave a polymer that was identified by means of serological studies as S-form lipopolysaccharide (LPS). Mild acetic acid hydrolysis degraded the O-specific polysaccharide, thus, its structure was investigated by compositional analyses and NMR spectroscopy after de-*O*-acylation and Smith degradation of the LPS. The structure of the O-specific polysaccharides was

3)-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-β-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→
2
↑
1
α-L-Rha*p*-(1→4)-β-D-Glc*p*A-(1→2)-α-L-Rha*p*

After immunization of BALB/c mice with *Acinetobacter* strain 44, monoclonal antibody S48-26 (IgG_3 isotype) was obtained which reacted in Western blot with this LPS and characterized it as S-form.

Polish J. Chem., **79**, 275–286 (2005)

A Short and Simple Synthesis of Branched Mannooligosaccharides with [1-^{13}C]-Labelled Terminal Mannose Units

by E.A. Ivlev, L.V. Backinowsky, P.I. Abronina, L.O. Kononov and N.K. Kochetkov

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(Received October 5th, 2004)

Mannosylation with 2,3,4,6-tetra-*O*-benzoyl-α-D-[1-^{13}C]mannopyranosyl bromide as a glycosyl donor has been used for the synthesis of 3,6-branched mannotri- and -pentaoside bearing labelled terminal mannopyranose units. Methyl 2,4-di-*O*-benzoyl-α-D-mannopyranoside was used as the glycosyl acceptor for the synthesis of the trisaccharide and also converted into a disaccharide precursor for the pentasaccharide.

Polish J. Chem., **79**, 287–295 (2005)

Repeating Unit Structure of *Enterobacter sakazakii* ZORB A 741 *O*-Polysaccharide

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(Received October 10th, 2004)

The O-specific polysaccharide from *Enterobacter sakazakii* cell was isolated and structurally characterized. Lipopolysaccharide (LPS) was obtained from cell mass by hot phenol-water extraction procedure. Mild acid hydrolysis followed by gel filtration provided pure O-antigen (OPS). Two-stage sugar analysis detected tyvelose, rhamnose and galactose in the molar ratio of 1:1:2, and their linkages were established by means of methylation analysis. Sugar configurations, D or L, were determined by gas-liquid chromatography on an achiral liquid phase for (*S*)-(+)-2-butyl glycosides. D configuration was determined for galactose and 3,6-dideoxy-mannose (tyvelose), but L for rhamnose. Repeating unit structure was deduced by analysis of ^{1}H and ^{13}C NMR spectra. ^{1}H and ^{13}C NMR resonances have been assigned by homonuclear (COSY, TOCSY) and heteronuclear (HSQC, HMBC) correlations spectra. Anomeric configurations were determined from anomeric proton chemical shifts and $^{3}J_{H1\text{-}H2}$ and $J_{C\text{-}H}$ coupling constants. Sugar sequences were established from comparisons of specific carbon chemical shifts with those in literature, two-dimensional nuclear Overhauser effect spectroscopy (NOESY), and heteronuclear multiple-bond correlation experiments (HMBC). The repeating unit structure of *Enterobacter sakazakii* was found to be as:

$$\begin{array}{c} \alpha\text{-Tyv}p \\ \downarrow 2 \\ \rightarrow 3)\text{-}\alpha\text{-L-Rha}p\text{-}(1\rightarrow 3)\text{-}\alpha\text{-D-Gal}p\text{-}(1\rightarrow 3)\text{-}\alpha\text{-D-Gal}p\text{-}(1\rightarrow \\ \uparrow 6 \\ \text{O-Ac} \end{array}$$

Polish J. Chem., **79**, 297–307 (2005)

A Facile Synthesis of the Fucosylated *N*-Linked Glycan Core and Its Application to Solid-Phase Synthesis of CD52 Glycopeptide

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(Received August 29th, 2004)

An efficient synthesis of the fucosylated *N*-linked core hexasaccharide (**23**) and its asparagine conjugate (**26**), as well as their applications to the solid-phase synthesis of an extensively protected glycopeptide (**1**) of CD52 antigen containing the hexasaccharide, is described. The difficult β-mannosidic and α-fucosidic linkages were achieved by the Crich and *in situ* anomerization protocols respectively, which offered excellent results. An especially acid-sensitive resin, 2-chlorotrityl resin, was used in the solid-phase synthesis, and the target glycopeptide **1** could be released from the resin by 10% HOAc without affecting the acid-labile protecting groups and fucosidic bond.

Polish J. Chem., **79**, 309–315 (2005)

A Purification Strategy for Oligosaccharide Synthesis on Soluble Polymer Supports

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(Received October 4th, 2004)

Removal of deficient sequences in the synthesis of oligosaccharides on soluble polymer supports can be efficiently achieved by selective esterification of the soluble support-bound incomplete glycosylation products with a conveniently functionalized insoluble resin.

Polish J. Chem., **79**, 317–322 (2005)

DDQ-Mediated Regioselective de-*O*-Benzylation of Pyranosides Stilted by a 4,6-O-(2-Phenylsulfonyl)ethylidene (PSE) Clip

by E. Cabianca[1,2], A. Tatibouët[1] and P. Rollin[1]

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(Received November 22nd, 2004)

A model study on diverse 4,6-acetalated O-benzylated D-glucopyranosides was performed to evaluate DDQ-mediated regioselective de-*O*-benzylation in connection with structural rigidity.

Polish J. Chem., **79**, 323–328 (2005)

New Complexes of Ribose Derivatives

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(Received November 19th, 2004)

D-(+)-Ribono-1,4-lactone (**1**) and methyl β-D-ribopyranoside (**5**) can form stable crystalline complexes with NaBr. The organic and inorganic components can be separated only by chemical methods.

Polish J. Chem., **79**, 329–333 (2005)

Stereoselective and Effective Synthesis of Alkyl α-D-Gluco- and α-D-Galactopyranosides

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(Received November 29th, 2004)

Practical, improved synthesis of alkyl α-D-glycopyranosides by reaction of *O*-gluco- or *O*-galactopyranosyl *N*-allyl thiocarbamate with bromine followed by addition of alcohol is described. This process proceeded very fast to give the glycosides in good yields and excellent stereoselectivity.

Polish J. Chem., **79**, 335–347 (2005)

Synthesis of 1-*O*-Silylated 3-Azido- and 3-*N*-Trifluoroacetamido-2,3,6-trideoxy-L-*arabino* and L-*lyxo*-hexopyranoses, Convenient Glycosyl Donors for Preparation of Anthracycline Antibiotics and Related DNA-Binding Agents

by G. Grynkiewicz[1], I. Fokt, P. Skibicki[2], T. Przewloka[3], W. Szeja[4] and W. Priebe

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(Received December 9th, 2004)

Over the years our studies have been aimed at the preparation of DNA-binding agents containing L-daunosamine, L-acosamine, or their derivatives, and we have found 1-*O*-silylated 2-deoxy-hexopyranoses to be very valuable as synthetic intermediates and glycosyl donors. We present here efficient strategies for the synthesis and separation of 1-*O*-silylated 3-azido- and 3-amino-2,3,6-trideoxy-L-hexopyranoses and the design of suitable glycosyl donors towards synthesis of doxorubicin analogs modified at C-4′ and C-14. By using a set of known reactions, we generated a mixture of 3-azido-hexopyranoses with L-*arabino* and L-*ribo* configurations, hitherto practically unexplored as glycosylating reagents. Two new approaches are described for producing efficient and scaleable resolution of 1-*O*-silylated azides (epimeric at C-3). The selection of 4-*O*-protecting groups able to withstand glycosylation conditions, yet suitably labile to allow deprotection under acidic or mild basic conditions, led to strategically important glycosyl donors that allow preparation of previously inaccessible doxorubicin-based DNA-binding glycosides. The described use of 3-azido-2,3,6-trideoxyhexoses constitutes a new strategy for pre- and postglycosylation functionalization of anthracycline antibiotic precursors.

Polish J. Chem., **79**, 349–359 (2005)

New Strategies Towards Synthesis of Doxorubicin Analogs

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(Received December 9th, 2004)

Most of the new drug candidates in the anthracycline class of antitumor antibiotics are a result of synthetic efforts involving modification of both the aglycone and sugar moieties. In such an approach, formation of a glycosidic bond is an important step that often becomes a limiting factor in the preparation of certain target structures and can also affect the efficiency of synthetic processes for obtaining analogs of anthracycline antibiotics of clinical interest. We have developed a general approach to *de novo* glycosylation of anthracycline aglycones leading to doxorubicin analogs with L-*lyxo*- and L-*arabino*-monosaccharides. Such glycosylation procedures are also effective in preparation of daunorubicin congeners. Specifically, we have explored the use of 1-*O*-silylated 3-azido-2,3,6-trideoxy-hexopyranoses as stable glycosyl donors and have successfully demonstrated the practical use of the 3-azido group to generate an amino function during the last steps of synthesis to allow easy generation of doxorubicin analogs. We have also shown that other known glycosyl donors can be conveniently generated from 1-*O*-silylated-hexopyranoses and can be used effectively to take advantage of a particular glycosidation and deprotection strategy. We describe two standard glycosylation procedures that were designed to attain the desired level of α-glycoside stereoselectivity and overall efficiency. Different glycosylation procedures were selected depending on the sugar synthon configuration and sensitive C-14 substitution in the target anthracycline aglycone. These achievements are exemplified by the use of previously unreported 3-azidosugar synthons of L-*lyxo*- and L-*arabino*- configuration protected by a 4-*O*-chloroacetyl group or an acid-labile triethylsilyl (TES) protecting group.

Polish J. Chem., **79**, 361–367 (2005)

Regioselective Glycosylation of Unprotected Mannosides: A Convenient Access to High-Mannose Type Saponins

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(Received October 14th, 2004)

3-*O*-Acetyl- and 28-*O*-acetyl-betulin were mannosylated with tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate. Debenzoylation of the monosaccharide obtained followed by treatment with 2 equiv of tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate selectively gave *O*-3,*O*-6-linked trimannosides.

Polish J. Chem., **79**, 369–386 (2005)

New Glycoside Derivatives of 6*H*-Indolo[2,3-*b*]quinolines

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(Received November 24th, 2004)

The series of carbohydrate derivatives of 6*H*-indolo[2,3-*b*]quinoline was obtained. Carbohydrate units (2-deoxy-D-glucose, 2-deoxy-D-lactose and 2-deoxy-L-rhamnose) were coupled *via* a glycosidic bond to a hydroxyl group placed in a side chain at selected positions of indoloquinoline. Increased solubility was noted for all obtained products. Some of them exhibit also increased *in vitro* cytotoxicity.

Polish J. Chem., **79**, 387–399 (2005)

Chirality Probing of Chlorotetrabutyratodiruthenium(II,III) Complexes with *vic*-Amino Alcohols by Circular Dichroism Spectroscopy

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(Received November 10th, 2004)

The circular dichroism (CD) spectra of a variety of *vic*-amino alcohols in the presence of chlorotetrabutyratodiruthenium(II,III) as an auxiliary chromophore were measured in acetonitrile and chloroform. The method was tested in several model compounds containing acyclic and cyclic amino alcohols, and among them biologically important adrenergic drugs and amino sugars. The study demonstrated that the sign of the Cotton effects obtained is determined by the preferred helicity of the O–C–C–N unit in the chiral complex formed *in situ*. On this basis, a rule was formulated that correlates a positive (negative) sign of the O–C–C–N torsional angle with a positive (negative) Cotton effect arising around 350 nm and/or with negative (positive) signs of CD spectra bands occurring around 300 and 400 nm.

Polish J. Chem., **79**, 401–412 (2005)

Chiroptical Properties of the Guanidine Chromophore

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(Received October 5th, 2004)

The CD spectra of 15 α-guanidino-acids, derived from 15 proteinaceous amino acids were measured and analysed. Using L-amidino-proline, L-amidino-prolinol, and L-amidino-4-hydroxyproline as standards the sector rule for prediction of the sign of the Cotton effect at 190–195 nm, attributed to the guanidine chromophore, was constructed. X-ray analysis of crystal structures of L-amidino-4-hydroxyproline and L-amidinomethionine was also performed.

Polish J. Chem., **79**, 413–428 (2005)

Synthesis of the Enantiomer of 1α,25-Dihydroxy Vitamin D_3 (Calcitriol) and a Diastereomer of 1α,25-Dihydroxy Vitamin D_3 Differing from Natural Product in Configuration at All but One Asymmetric Carbon Atoms

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(Received October 22nd, 2004)

Convergent synthesis of *ent*-1α,25-dihydroxyvitamin D_3 (*ent*-calcitriol, **2**) and (1*S*,3*S*, 13*S*,14*S*,17*S*,20*S*) – 1α,25-dihydroxyvitamin D_3 (**5**) using the ring A building blocks, **6** and **7**, respectively, and rings CD building block **8**, is described. Building block **6** was obtained starting from vitamin D_3 *via* dihydroxylation of the C7–C8 double bond, Mitsunobu inversion at C3, diastereoselective hydroxylation at C1 and cleavage of the C7–C8 bond. Building block **7** was prepared from known synthetic intermediate, **16a**(1*R*,3*S*) *via* benzylation of the primary hydroxy group, mono-deprotection of bis-silyl ether **16b** and Mitsunobu inversion of the configuration at C3 in **19**. Synthetic building blocks were combined using Julia-Kocienski olefination reaction.

Polish J. Chem., **79**, 429–440 (2005)

Oxidation of *o*-Isopropylphenol with Lead Tetraacetate: Synthesis of the Unit of Celastroidin Terpenes by the Diels-Alder Condensation

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(Received October 15th, 2004)

Lead tetraacetate oxidation of *o*-isopropyl phenol under various conditions led to the dienone acetate which, when dimerized, represents a central part of the celastroidin penta- and hexa-terpenes (natural products from the Mexican shrub *Hippocratea Celastroides*). Six oxidation products formed in this reaction (the iso-propyl dienolone acetate, two dimers, benzoquinone, and two phenol acetates) were identified with help of 2D and 3D NMR, GC and LC-MS. From this, we concluded that the dimer skeleton observed for the dienolone acetate in natural products corresponded to the product from the photochemical pathway, and that the synthetic dimer has the opposite geometry; this was verified by molecular modelling. The oxidation of the second compound, *o*-cresol, leads to a similar profile of products.