# PAC Review

Pure and Applied Chemistry (PAC) is the official journal of IUPAC. It publishes the main invited lectures of symposia sponsored by the Union; the recommendations of its Commissions on nomenclature, symbols and units, and technical reports on standardization, recommended procedures, collaborative studies and data compilations. Summaries of the most recent IUPAC recommendations on nomenclature and symbols, and technical reports appearing in PAC are published in Chemistry International in the section Recent Reports. In this section we take a brief look at symposia and lectures published in recent issues of PAC.

# Lectures from Symposia and Conferences

#### Carbohydrates

The September 1997 issue of *Pure and Applied Chemistry*, **69**(9), contains texts of the plenary lectures presented at the 18th International Carbohydrate Symposium held in Milan, Italy, 21–26 July 1996. The Symposium was organized by the Organic Chemistry Division in conjunction with the International Carbohydrate Organization, the International Union of Biochemistry and Molecular Biochemistry, the Italian Chemical Society, the Italian Biochemical Society and the Italian Research Council (CNR).

The Whistler Award Lecture was presented by Constant van Boeckel of Organon Scientific Development Group in the Netherlands. His theme was heparinfrom the original 'soup' to well-designed heparin mimetics. His lecture traces the history of heparin—from the introduction of heparinotherapy in 1937—to present day. He covers the use of heparin in clinics of the late 1930s, the structure of anti-factor Xa oligosaccharides obtained from heparin, first generation synthetic pentasaccharides and finally second generation synthetic pentasaccharides. He concludes that the chemical synthesis approach has been very fruitful in terms of both understanding the mode of action of heparin and production of potential active substances for new drugs. It is clear, he says, that the interaction of the complex polysaccharide and AT III depends on the presence of a very precise array of sulfate and carboxylate groups that induce a conformational change necessary and

sufficient to inhibit blood coagulation factor Xa. More importantly, it is possible to obtain in a pure state all the heparin mimetics desired. These synthetic products constitute active principles for new drugs the biological profile of which can be adapted at will to reproduce some of the many activities of heparin.

The other lectures covered: the emerging importance of oligosaccharide synthesis; the use of low molecular weight carbohydrates as organic raw materials; the information capacity of the carbohydrate code; structural glycobiology; recent progresses in the glycodrug area; shapes and motions of polysaccharide chains; a challenge to the riddle of the carbohydrate chain; heparan sulfate; cell-type specific expression on gangliosides in the central nervous system; and microbial exopolysaccharides.

## Physical organic chemistry

The September issue also contains the special and plenary lectures presented at the 13th International Conference on Physical Organic Chemistry held in Inchon, Korea, 26–29 August 1996. The Conference was organized by the Organic Chemistry Division in conjunction with Inha University and the Korean Chemical Society and timed to coincide with the 50th anniversary of the Korean Chemical Society.

The opening paper, a special lecture presented by George Hammond of Bowling Green State University, Ohio, and Georgetown University, Washington DC, provides a historical perspective of physical organic chemistry. It is followed by nine plenary lectures, illustrating

both old and new trends in physical organic chemistry.

Marie-Françoise Rausse of the University of Paris, France, describes organic reactions in microorganized media. The effect of ion exchanges at the micellar interface in cationic micelles and the electrophilicity of water in reverse micelles are discussed. The chemistry of stable enols is presented by Zvi Rappoport of the Hebrew University, Jerusalem. The detailed pathway of enol formation by the addition of amines to a ketene, mechanism of enantiomerization of chiral triarylenols, and the pK values of the enols are discussed.

Derek Barton of the Texas A&M University summarizes the use of Gif chemistry in the selective functionalization of saturated hydrocarbon. His lecture illustrates how physical organic concepts can be applied to invent a new organic reaction. Yoshiteru Sakata of Osaka University, Japan, describes the basic principles of how electron transfer can be controlled and utilized to convert solar energy to chemical energy based on model studies, a tool used mostly by physical organic chemists.

Biological science is a new frontier of physical organic chemistry. The thiamin chemistry described by Ronald Kluger of the University of Toronto, Canada, demonstrates how analysis of products, study of reactive intermediates and kinetics can be utilized to understand enzymatic catalysis. The human brain defines a major challenge in all fields of science. Structure–function studies on the nicotinic acetylcholine receptor by Dennis Dougherty of the California Institute of Technology shows that physical organic chemistry can also be applied to the chemistry of the brain.

further lectures were developed supramolecular chemistry. Peter Stang of the University of Utah described self-assembly of molecular squares and rectangles based on square-planar complexes, iodonium species and metallocenes connected by bidentate ligands. Fraser Stoddart of the University of Birmingham, UK, showed that slippage of  $\pi$ -electron deficient bipyridinium-based polyethers through the  $\pi$ electron hydroquinone-based dioxynaphthalene-based macrocyclic polyethers can self-assemble [n]rotaxane. Two-dimensional organization of molecules is presented by Toyoki Kunitake of Kyushu University, Japan. He shows that mixed monolayers and multicomponent monolayers can be produced at the air-water interface by utilizing complementary hydrogen bonding.

#### Carotenoids

The October 1997 issue of *Pure and Applied Chemistry*, **69**(10), contains texts of the main lectures presented at the 11th International Symposium on Carotenoids, held in Leiden, the Netherlands, 18–23 August 1996. A total

#### Synthesis of peridinin

of 21 lectures are published, dealing with aspects ranging from stereochemistry to commercial opportunities for production by biotechnology.

In a preface, Symposium Editor George Britton, of the School of Biological Sciences, University of Liverpool, UK, recalls that the first International Symposium on Carotenoids was held 30 years earlier (1966) in Trondheim, Norway; the expansion and diversification in the carotenoid field is reflected by the fact that, in Leiden, almost ten times as many participants were registered as attended the first meeting. The Leiden Symposium also marked the beginning of a new era for the carotenoid field, with the foundation of a new International Carotenoid Society. The Society will seek to promote carotenoid science and will take responsibility for future International Symposia.

Stereochemical aspects of carotenoids are of importance not just for stereoselective total synthesis and structure elucidation of naturally occurring carotenoids, but also have an impact on biochemical and biological phenomena. Such aspects were dealt with by Synnove Liaanen-Jensen of the Norwegian University of Science and Technology, with examples selected from his own research. Particular emphasis was placed on the interdisciplinary aspects of stereochemistry, and the application of different methods—spectroscopy (VIS, CD, ¹H NMR), HPLC, total and partial synthesis, oxidative degradation, derivatization including partial resolution and enzymatic reactions, iodine-catalysed stereomutation and proof of natural occurrence.

Hanspeter Pfander of the University of Berne, Switzerland, presented a progress report on carotenoid synthesis, covering the period 1990–96. This is a continuation of the review given at the 9th International Symposium on Carotenoids held in Kyoto. As 'outstanding achievements' he points to the total synthesis of peridinin and fucoxanthin. Rodney Ausich of Kemin Foods of Des Moines, Iowa, focused on commercial biosynthesis, particularly for carotenoids that cannot easily be synthesized or cannot be produced economically by chemical synthetic techniques. With the new power of biotechnology and recombinant DNA technology, the biosynthetic capability of organisms to produce carotenoids can be enhanced, he says.

A discussion of the role of dietary carotenoids as po-

#### Synthesis of fucoxanthin

tential cancer preventive agents was provided by John Bertram of the Cancer Research Center of Hawaii. He presents evidence that three major dietary carotenoids, beta-carotene, lutein and lycopene, can increase connexin 43 gene expression in 10T1/2 cells and in human keratinocytes in organotypic culture. He continues to suggest that the conversion of dietary carotenoids to compounds which can increase gap junctional communication may play a role in the protective action of carotenoid-rich foods.

Other lectures included E/Z isomeric carotenes, the fate of carotenoids in sediments, model systems for observing photoreox reactions of carotenoids, photophysics and photochemical properties, carotenoid levels in human lymphocytes, bioavailability of carotenoids, molecular genetics of the carotenoid biosynthesis pathway in plants and algae.

#### Coordination chemistry

The October issue also contains texts of the six plenary lectures presented at the 31st International Conference on Coordination Chemistry, held at Vancouver, Canada, 18–23 August 1996. The Conference was organized by the Inorganic Chemistry Division in conjunction with the Canadian Society of Chemistry.

Included is a lecture by Leonard Lindoy of the University of Sydney, New South Wales, on the development of alternate strategies for achieving metal—ion recognition. He considers an important aspect of the research to have been the investigation of metal ion complexation over a range of related macrocycles, incorporating different macrocyclic ring sizes, donor atom

set combinations and/or degree of ring substitution and the search for stability maxima at different points in this range. His methodology includes assessment of the possible factors influencing any observed metal-ion recognition behaviour, followed by structural modification of particular ligand systems in an attempt to 'tune up' such behaviour. In particular instances he says it has proved possible to modify a ligand type progressively, using several 'tuning' cycles, such that very considerably enhanced discrimination towards a metal ion of interest has been achieved. In this manner, he says it has also proved possible to elucidate the subtle factors underlying different discrimination mechanisms.

The other five lectures covered: a structural model for silicotungstate monolayers on silver(111); macrocyclic metal com-

plexes for selective recognition of nucleic acid bases and manipulation of gene expression; high oxidation state coordination chemistry with triamidoamine tungsten and molybdenum complexes; X-ray absorption spectroscopic studies of metal centres in biology and developments of relevant synthetic analogues; and coordination chemistry and catalytic conversions of H<sub>a</sub>S.

### **Chemical thermodynamics**

The November issue of *Pure and Applied Chemistry*, **69**(11), contains texts of the plenary and invited lectures presented at the 14th International Conference on Chemical Thermodynamics held in Toyonaka, Osaka, Japan, 25–30 August 1996. The Conference was organized by the Physical Chemistry Division in conjunction with the Science Council of Japan, the Chemical Society of Japan, the Japan Society of Calorimetry and Thermal Analysis and the Atomic Energy Society of Japan.

Included is the text of the 11th Rossini Lecture, presented by Robert Alberty of the Massachusetts Institute of Technology. His theme is Legendre transforms, used to introduce intensive variables as natural variables in the fundamental equations of thermodynamics. Prof. Alberty explains that natural variables are important because, when a thermodynamic potential can be determined as a function of its natural variables, all the other thermodynamic properties of the system can be obtained by taking partial derivatives. It is usually more convenient to use thermodynamic potentials that have intensive natural variables because they are often more easily controlled than the conjugate extensive variables. This is illustrated, he says, for chemical reaction systems in which it is of interest to specify the chemical

#### Production of phenylacetylcarbinol (PAC)

potential of a species (for example, the pH in a biochemical system). Since the electric potentials of phases in a multi-phase system are not natural variables of the Gibbs energy, it is useful to define a transformed Gibbs energy, for which electric potentials of phases are natural variables. The use of Legendre transform brings in a new set of thermodynamic properties, new Maxwell equations, Gibbs—Duhem equations and Gibbs-Helmholtz equations.

#### **Environmental biotechnology**

The November issue also contains selected proceedings of an International Conference on Environmental Biotechnology '96 held in Palmerston North, New Zealand, 1–4 September 1996. The published conference papers offer a wide-ranging analysis of the potential of biotechnology to waste treatment, specific perspectives on environmental damage and remediation, industrial research on pollutant mitigation, research into the area of upflow anaerobic sludge blanket reactors, the biological treatment of food industry wastes and two examples of cleaner technology for developments from the pharmaceutical and paper industries.

The cleaner technology examples included produc-

ity improvements and waste minimisation. L-Phenylacetylcarbinol is a precursor for the synthesis of L-ephedrine and D-pseudoephedrine, two pharmaceuticals with nasal decongestant properties. L-Phenylacetylcarbinol is generated biologically through the pyruvate decarboxylase-mediated condensation of added benzaldehyde with acetaldehyde generated metabolically from feed stock sugars via pyruvate. Some of the added benzaldehyde is converted through the action of alcohol dehydrogenase(s) to benzyl alcohol, an undesired by-product. L-Phenylacetylcarbinol extracted from the fermentation broth is converted chemically by hydroamination in the presence of methylamine and hydrogen to L-ephedrine, and then by isomerization to p-pseudoephedrine. Bruce Anderson and colleagues at the Royal Melbourne Institute of Technology present a dual approach strategy to enhance the ratio of product to by-product generated and to minimize the waste treatment burden of the spent fermentation broth. He explains that benzaldehyde delivery to the fermentation has been modified to ensure that sufficient raw material is available, together with pyruvate, during peak periods of pyruvate decarboxylase activity, and that benzaldehyde is less available during periods of high alcohol dehydrogenase activity. The inorganic content of the spent fermentation broth has been reduced substantially by the partial substitution of raw sugar for molasses in the medium, with a reduction of molasses content by 60% resulting in an increase of phenylacetylcarbinol production. Further work on the optimization of the concentration of carbohydrate, nitrogen and phosphate in the fermentation has been conducted and has led, he claims, to further productivity increases, together with reduced waste generation, resulting in an L-phenylacetylcarbinol process which is considerably 'cleaner' than the parent process.

tion of phenylacetylcarbinol by yeast through productiv-