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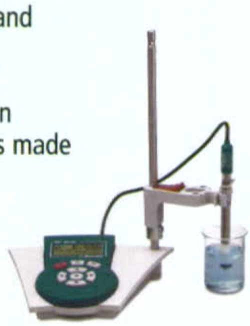

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# Seeing Things in a New Light: Synchrotron Science and the Australian Synchrotron Project

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## Introduction

Significant advances in scientific knowledge are often driven by the discovery of new techniques and new ways of examining the building blocks of the world around us. Chadwick's discovery of the neutron was predicated on Wilson's 1911 invention of the cloud chamber. In a similar manner the invention of the spectroscope which briefly became a party amusement,[1] became the vital tool in the study of everything from atomic structure to the composition of stars.

The spectroscopists dream is a radiation source which provides useful photon intensities across as wide a range of wavelengths as possible, and thus accesses many modes of interaction with atoms, molecules, and structures. Perhaps the closest thing we currently have to such an ideal source is the synchrotron. Since the early 60s it has provided increasingly powerful, broad spectrum sources across a huge part of the electromagnetic spectrum and has opened up a new range of techniques, and extended the capabilities of many laboratory-based spectroscopic methods, in addressing many areas of application. The extreme brightness, energy selectivity, time structure, and polarisation options provide powerful tools in materials and biological sciences, medical imaging, and fundamental spectroscopy. The synchrotron radiation source has developed to become the dominant method used in large molecule crystallography, the only technique which can readily access the far IR, which is the best hard X-ray source for investigating materials structure and increasingly a tool for medical imaging and potentially therapies. Indeed the *coming of age* of synchrotron science might be seen in the sharing of the 2003 Chemistry Nobel prize by Roderick MacKinnon largely based on his synchrotron based work on ion channels.[2] The formal participation of NZ research institutions in the Australian Synchrotron project will soon bring the power of these techniques to our doorstep. The nature of synchrotron radiation and several applications of synchrotron-based methods are outlined below.

In July 2004 an announcement was jointly made by the NZ and Victoria State Governments that NZ was to be part of the consortium which constructs the initial suite of beamlines on the Australian Synchrotron.[3] This prompted the question of the role of access to synchrotron-based techniques and how it would fit into the NZ science strategy, given that the costs involved - small in terms of the overall project - are significant in terms of the NZ research budget.

The June 2001 announcement on the construction of the Australian Synchrotron was in many ways a logical progression for a community that now numbers in excess of 140 principal investigators and 400 users. This community, covering fields from protein crystallography, materials, bio- and environmental sciences, medical imaging, and pure spectroscopy, has grown strongly over the past decade in particular, based on Australian investments in, and access to, beamlines at the Photon Factory in Tsukuba, the Advanced Photon Source (APS) in Chicago, and more recently a soft X-ray line at the NSSRC in Taiwan. They have provided a ready, low cost, mechanism for access to the facilities on the basis of peer reviewed merit access.[4] Importantly, the peer reviewed merit access is decided from a strategic perspective within the borders of Australia.

The arguments for an Australian synchrotron were based strongly around the impacts in research, technology, and economic activity, emphasising the desire to be (and stay) internationally competitive in science across a wide range of applications, especially in biotechnology and materials science.[5] Synchrotrons have been perceived as central to these goals in a number of countries; Canada and Taiwan provide interesting and very different examples of this philosophy. Establishment of the Canadian synchrotron was driven largely by a strong spectroscopy community, while the Taiwanese Government made the decision to build a synchrotron against much of the advice of its scientists, because of a commitment to a high technology future.[6] Thus an indigenous synchrotron has been a logical consequence of Australia's increasing use of and dependence on such facilities; there are also major practical advantages, *e.g.* in the handling of potential bio-hazard materials, and avoidance of shipping such materials internationally.

The Australian facility (Fig.1) is now under construction at a cost, in its initial configuration of ~11 beamlines, of $NZ240 M. Of this, the Government of Victoria has provided the $175 M for the storage ring itself, with a consortium of partners (including NZ) contributing to the beamline construction consortium. The building to house the synchrotron was formally handed over to the project team in March, and hand-over of the facility to the operators, with at least four operational beamlines, is targeted for April '07. Thus the synchrotron is well advanced and will provide a major frontline science facility for Australasia, whether NZ chooses to maximise this opportunity or not.

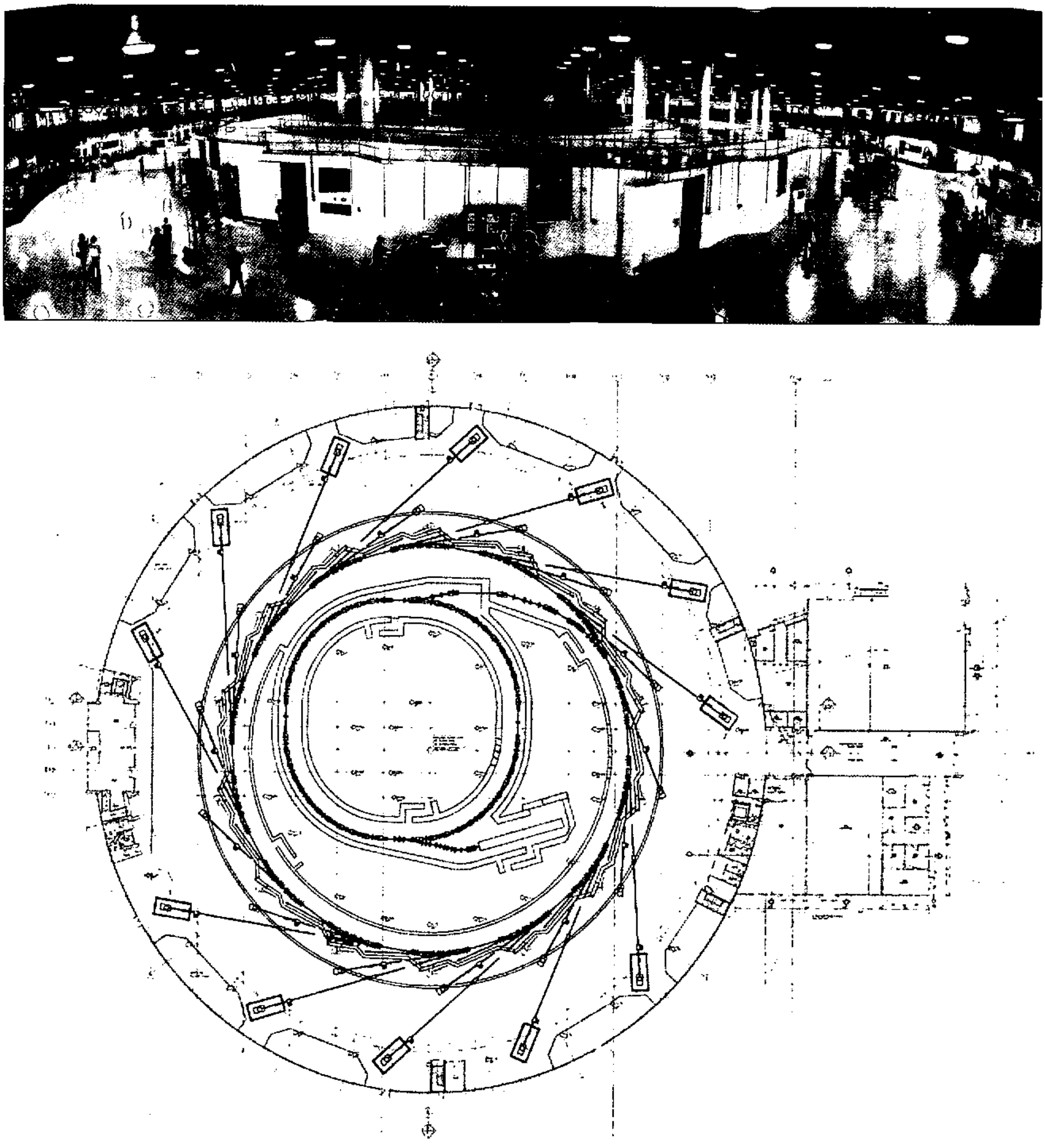

**Fig. 1.** (a) Wide-angle image (Mar. '05) of the interior of the building for the Australian Synchrotron. The interior shield walls are visible while the open floor area will eventually contain the beamlines; (b) the floor plan showing the first suite of beamlines extending tangentially from the ring (Reproduced courtesy Australian Synchrotron Project).

## Synchrotron Light

The acceleration of electrons produces electromagnetic radiation. Synchrotrons are electron storage rings that exploit this effect. Bunches of electrons orbit at near the speed of light (*c*); in the case of the 3 GeV (giga electron volts) Australian ring, >99.9999% c) and are accelerated or *bent* through a series of magnets that are separated by straight sections. The acceleration through the bend results in a flattened cone of radiation that is emitted tangentially to the bend and captured in a beamline extending along the tangent (Fig. 2). The radiation covers a continuous spectrum from the far IR to a cut-off energy determined by the energy of the orbiting electrons and the radius of

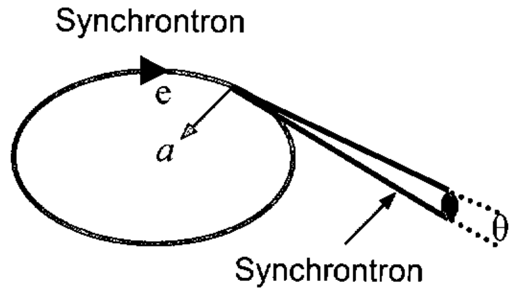

**Fig. 2.** Flattened radiation cone emitted tangentially to the bend when electrons are accelerated in the magnetic field of a bend magnet.

the bend. The power radiated by the accelerated electron is given by:[7]

$$P = \frac{2}{3}\frac{e^2\gamma^2}{m_0^2c^3}\left|\frac{dp}{dt}\right| \quad \text{.........} (1)$$

where $m_o$ is the rest mass of the electron, $e$ is the electron charge, and $c$ the speed of light; $p = m_o v$ *is the momentum* and $(1/m_o).(dp/dt)$ is the acceleration; $\gamma$ is the ratio of the mass of the relativistic electron to its rest mass $m_o$ and is given by:

$$\gamma = \frac{E}{m_0c^2} = 1957\,E[\mathrm{GeV}] \quad \text{..........}(2)$$

Thus for the 3 GeV Australian Synchrotron, $\gamma$ is 5,871 while for the 7 GeV Chicago APS, $\gamma$ = 13,699. For electrons circulating at a fixed radius, $r$, the energy lost (as synchrotron radiation) by the circulating electrons per orbit is given by:

$$\Delta E[keV] = 88.5\frac{E^4[GeV^4]}{r[m]} \quad \text{..........}(3)$$

Because the intensity of the emitted radiation follows the fourth power of the ring energy, higher energy gives significantly more synchrotron radiation. The frame of reference effect for these relativistic electrons means this radiation is forward projected more strongly, leading to higher effective brightness of the source. The loss of this energy requires the positioning of an RF cavity in the ring to provide an energy kick to the orbiting electrons, thus restoring their orbital energy. In typical operation the ring current (200 mA in the case of the Australian ring) decays steadily due to scattering and other losses, and the beam current is topped up, sometimes continuously, but generally by injection of *electron bunches* at several scheduled points in an operating day.

The ring energy and bend radius also determine a *critical* energy above which, by definition, half the radiated power is given off. In practice this leads to a relatively rapid drop in flux above this threshold:

$$\varepsilon_c = \frac{2.218E^3}{\rho} = 0.665BE^2 \quad \text{..........}(4)$$

$\rho$ is the radius of the bend at the magnet in metres, $E$ the ring energy in GeV, and $B$ is the magnetic field in Tesla. The intensity curve from a bend magnet calculated for the Australian 3 GeV ring (216 m circumference) is shown in Fig. 3. The shape of the curve implies that useful intensity is generally obtained up to ca. 4 x $\varepsilon_c$. The use of *wigglers* and *undulators* positioned in the straight sections of the synchrotron improves performance, both in brightness and by extending the energy range, as discussed below. The calculated flux from a 30 pole 1.9 Tesla wiggler on a straight of the Australian ring is shown in Fig. 4.

In the so called *third generation rings* as is the Australian facility, increasing emphasis is placed on radiation obtained by the wiggling of the electron beam by lines of magnets placed along the straight sections of the ring. If the period of this wiggle is short, the radiation is again a continuous spectrum (although usually extends to higher energy due to tighter radius of the oscillation) and is multiplied in intensity by the number of magnet pairs (and thus oscillations induced) – so called *wiggler radiation*. Longer oscillation periods produce an interference pattern with a characteristic series of *harmonics* producing very high intensities at specific energies. These energies are tuned usually by adjusting the magnet separation and thus the tightness of the oscillation. These undulators are an increasingly favoured source, *e.g.* in protein crystallography.

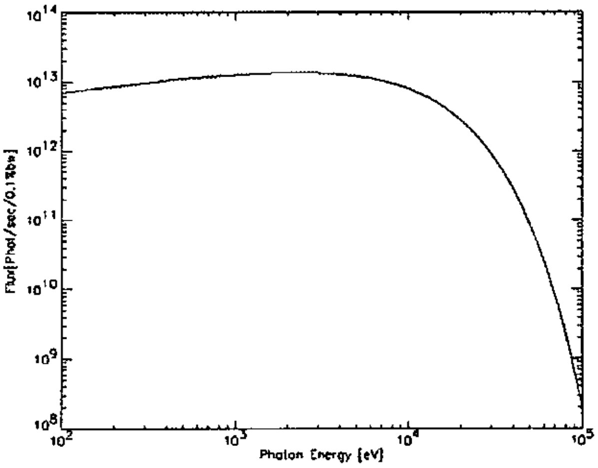

**Fig. 3.** Intensity curve from a bend magnet calculated for the Australian 3 GeV ring of 216 m circumference.

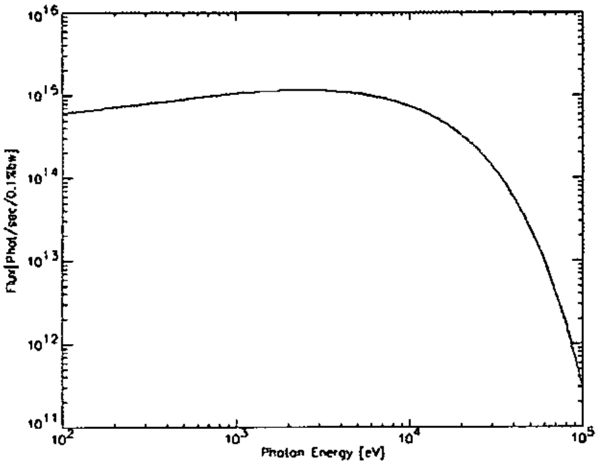

**Fig. 4.** Calculated flux from a 30 pole 1.9 Tesla wiggler on a straight of the Australian ring.

Synchrotron radiation was first observed in 1947 by scientists at the GE laboratories,[8] but it took time before the utility of this light source was appreciated. Second generation synchrotron sources were constructed from the early 80s specifically to use bending magnet radiation rather than the parasitic radiation from particle accelerators; a major step in utility and accessibility. Third generation rings date from the early 90s and have exploited increasingly the very intense radiation from the insertion devices – the wigglers and undulators described above – on the straight sections of the ring.

Two key attributes have driven the development and exploitation of these radiation sources. The first is the extreme brightness where a figure of a billion times the brightness of the sun is widely quoted, but this is somewhat energy dependent; certainly practical intensities of a million times conventional laboratory X-ray sources are realistic. The second is the very broad span of energies which are accessible at most facilities by construction of appropriate beamlines to capture selected windows across this energy spectrum. There are other additional characteristics that can be usefully exploited, such as the variable polarisation and time resolved nature of the beam.[7] However, the synchrotron itself is simply a light source from which dedicated beamlines capture a window of this radiation. Very few experiments (notably in lithography and imaging work) use the *white light beam.* A beam transport system is required to select the requisite wavelength(s), and transport (and perhaps focus) it to a position in an experimental station that may consist of a conventional IR spectrometer, a PE microscope, a single crystal diffractometer, or many other devices. Thus a huge range of quite distinct experiments, in different energy regimes, are operating at any point in time in a mature synchrotron facility.

A very reasonable and frequently asked question, particularly in light of the NZ participation in the Australian ring, is what will the synchrotron do for these experiments beyond that which a laboratory-based diffractometer can do for a fraction of the cost? There are two key considerations. Firstly, there exist a variety of techniques that are only possible using synchrotrons, such as the X-ray absorption spectroscopies in which the primary beam energy is scanned. Secondly, many experiments are either prohibitively time consuming, or too difficult to be carried out in any other way. Typical examples of the first case are Extended X-ray Absorption Fine Structure (EXAFS) and Diffraction Enhanced medical imaging, while the second case is best exemplified by large molecule crystallography and far IR spectroscopy. In the latter case, the comparative flux of a synchrotron source in this region is shown in Fig. 5.

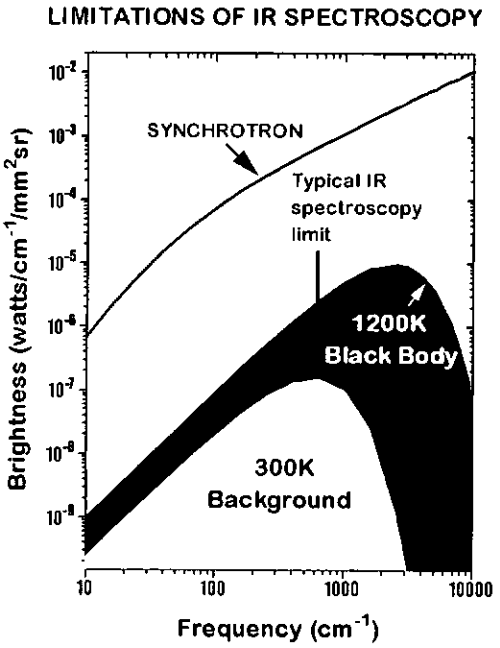

**Fig. 5.** Comparison of photon intensity in the IR region for a synchrotron and a conventional source. The several orders of magnitude more intensity from the synchrotron make it the only viable source in the far infrared (Reproduced courtesy Richard Garrett, ASRP)

In protein crystallography, the primary advantage is the order of magnitude reduction in time and the far greater number of reflections that can be collected – a function of the photon intensity. However, even more fundamental is the phase information available in the experiment as this allows exploitation of the so called *Multiple Anomalous Dispersion* (MAD);[9] *ca.* 98% of structures currently being registered on the protein crystallography database are collected on synchrotrons.[10]

The Australian ring is a 3rd generation synchrotron, the design of which is detailed on the synchrotron website,[11] and is one of about 18 such facilities built or under construction. It has an evolutionary design based on previous experience with 3 GeV rings, *e.g.* the CLS currently being commissioned in Saskatoon.[12] Comparison with the CLS or the UK Diamond ring (Table 1) shows that individual machines with a similar energy range may be optimised for different applications and capacities within the usual constraint of overall cost. However, use of 3 GeV is emerging internationally as a useful intermediate energy which, when coupled with increasingly powerful insertion devices in the straight sections, provides access to all but a few specialist high energy (≥ 70 keV) applications. Similar energy facilities are also planned for rings under construction in Shanghai (3.5 GeV) and Barcelona (3 GeV).

**Table 1.** Comparison of synchrotrons currently under construction.

| Parameter | Australian | Diamond (UK) | CLS (Canada) | SPEAR III (USA) |
|---|---|---|---|---|
| Lattice Energy (GeV) | 3.0 | 3.0 | 2.9 | 3.0 |
| Periodicity | 14 | 24 | 12 | 18 |
| Useable Straights[a] | 12 | 22 | 10 | 16 |
| Circumference (m) | 216.0 | 561.6 | 170 | 234 |
| Current (mA)[b] | 200 | 300 | 200 | 500 |
| Emittance (nm-rad)[c] | 7 | 2.7d | 18.1 | 18 |
| Lifetime (h) at max. current | >20 | 10 – 20 | ~50 | |
| Beam Size in straights[d] (height/ width; μm) | 389/20 | 123/6.4 (5 m)[d]<br>178/12.7 (8 m)[d] | | |

[a] The number of useable straights determines how many high performance insertion devices can be installed.

[b] Facilities generally start up with 200 mA but some plan to increase current after several years of operation; this option is available for the Australian synchrotron.

[c] The emittance specifies the size of the electron beam in the straight sections. The smaller the number the higher the brightness of the photon beams.

[d] Diamond has straights with two different lengths – 5 m and 8 m.

## Beamlines

The beamlines and end-stations provide the experimental devices where the power of the synchrotron is harnessed. Initially, the experience with and preponderance of crystal monochromators meant that energies above 3-5 kV dominated synchrotron applications. For example, X-ray crystallography and X-ray absorption spectroscopy - particularly the use of the EXAFS - matured rapidly in geochemistry and materials science.[13,14] The advantages of tuneable energy and extreme brightness soon found application in large molecule crystallography and this field has now emerged to dominate demand for beamtime in many facilities (Fig. 6).

The chemical richness in the near edge structure of the X-ray Absorption spectrum (XANES), especially of the softer X-ray lines (below 2 kV) has also become more widely appreciated with the development of the spherical and plane grating monochromator beamlines now available at most facilities. This variant of classical PE spectroscopy makes the utility of the synchrotron apparent. In addition to a monochromatic source of tuneable energy, and perhaps 50 meV resolution, *cf.* monochromatised Al $K_\alpha$ at 1486.6 eV and 0.4 eV resolution of a laboratory instrument at best, which can be selected to control depth resolution, the source energy can be scanned across the absorption edge to reveal the fine structure in the Near Edge Spectrum. Thus in resolution, speed, control of analysis depth, access to bound states above the ionisation threshold, the advantages of synchrotron radiation are enormous.

Over the past decade, one of the fastest developing areas of application of synchrotron radiation has been medical imaging and therapy. At a workshop in Auckland (Aug. '04) Dr. F. Arfelli, who leads a group based at the Italian Synchrotron in Trieste, discussed clinical applications in mammography, where the enhanced resolution at lower dose accessible on the synchrotron beamline can be utilised in difficult cases associated with dense tissue imaging.[15,16] Several characteristics of the synchrotron radiation make it very useful in this respect. Firstly, the beam is highly collimated, thus the optical advantages are considerable, *e.g.* in increasing beamline lengths (and thus demagnification factors) often to greater than 100 m. Secondly, phase information is retained giving the potential for applications such as phase-contrast imaging that is simply not accessible with other approaches.[15] In the therapy area, energy tunability becomes a huge advantage, *e.g.* in radiotherapy where the beam energy can be tuned specifically to the absorption edge of, say, platinum contained in anticancer drugs; the bulk of the radiation

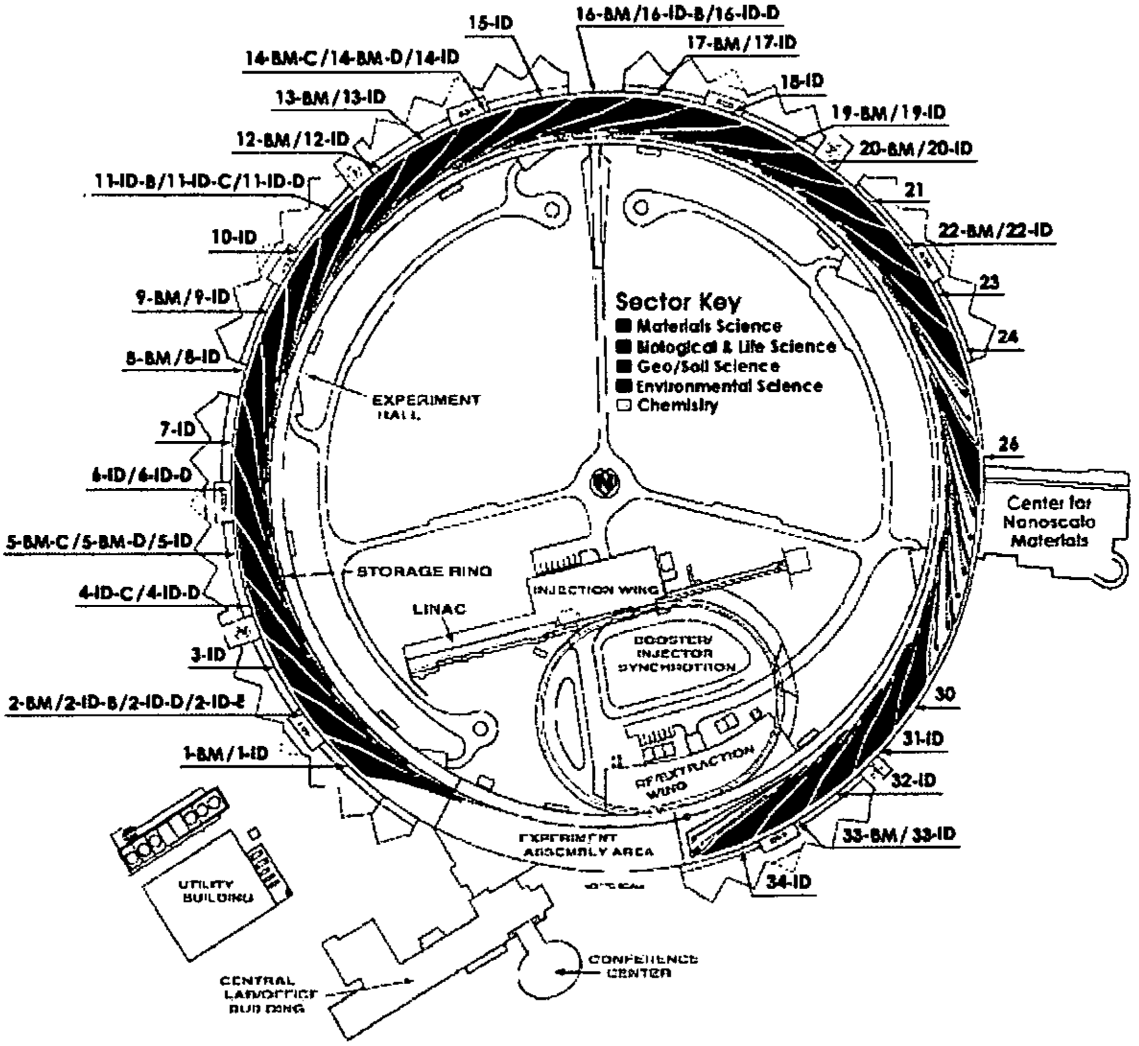

**Fig. 6.** Distribution of beamlines at APS Chicago; the website version of this diagram identifies the biological-life sciences (mostly protein crystallography) beamlines in blue. These now constitute around one third of the beamlines. (Taken from the APS website).

dose is then delivered only in the location of the drug.[16]

The Australian ring has the capacity to support more than 30 beamlines but cost constraints will limit the first phase of construction to perhaps 10 or 11. The current, ambitious plan is to have at least four of these lines operational by April '07 when the facility is handed over to its operator. The selection of the initial tranche of beamlines was addressed following extensive consultation with the user community, including that in NZ. It seeks to balance established need, *e.g.* in protein crystallography, EXAFS, X-ray microprobe, lithography, soft X-ray and IR spectroscopies, *etc.*, with the capacity to push beamline performance and enable quite novel science. For example, as indicated above, major interest is emerging in the area of medical imaging, but beamlines of 100 m of more in length are needed to best exploit the advantages of the synchrotron source. The technical difficulties are considerable but the results emerging in this area is stunning (see below), and extend into the potential use of the beam in medical therapy. A more complete discussion of individual beamline design and capability is available from the National Science Case for the Australian Synchrotron.[5]

## Applications

To date, synchrotron use in NZ has been dominated by crystallography, and surface and materials science. Much of our own work has utilised soft X-ray lines in the 70 eV to 5 keV range at the Canadian Synchrotron Radiation Facility in Madison. The most useful of these has been the 200-800 eV spherical grating monochromator (SGM) line for the characterisation of amorphous GaN thin films,[17-19] with a stunning demonstration being the resolution of the XANES spectrum to observe the vibrational structure of the nitrogen molecule trapped in interstitial sites within the films (Fig. 7). However, the complete story emerges when studies of the photoemission spectra of these samples are also included to allow examination of the band structure below the band gap.[19] A combination of synchrotron experiments in the US and Germany are routinely used to characterise these materials.

Spectra collected at the sulfur L edge (≈ 164 eV) from a series of model compounds used as standards in a recent study of sulfur speciation in aluminium smelting anodes[20] are shown in Fig. 8. The spectra allow differentiation of the 5-membered heterocycle from the 6-membered ring, and comparison with model compounds has been successfully in examining S speciation in carbon anodes containing ~1% sulfur.[20] This speciation information is critical in understanding the mechanism by which O=C=S is generated at the face of the anode during electrolysis.[21] This has environmental implications because the gas is sufficiently stable kinetically to allow a small proportion to be released into the duct gases at aluminium smelters, and eventually to the atmosphere. Soft X-ray XANES has also been used in the development of new cathode materials for Li ion batteries,[22-24] and is being applied to the characterisation of a range of semiconductor materials and refractories.

The growing power and diversity of these methods is illustrated in several international examples, firstly in the

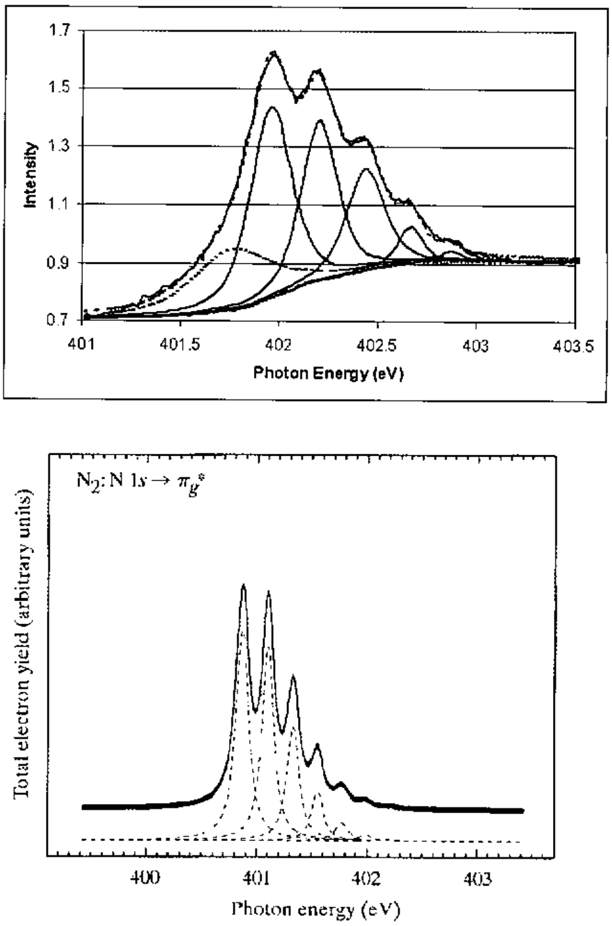

**Fig. 7.** (a) The X-ray Absorption Near Edge spectrum at the nitrogen K edge from an IAD-deposited amorphous GaN thin film showing gas phase $N_2$ trapped in interstitial sites within GaN – see refs. 17-19.; (b) the XANES spectrum from gas phase $N_2$.

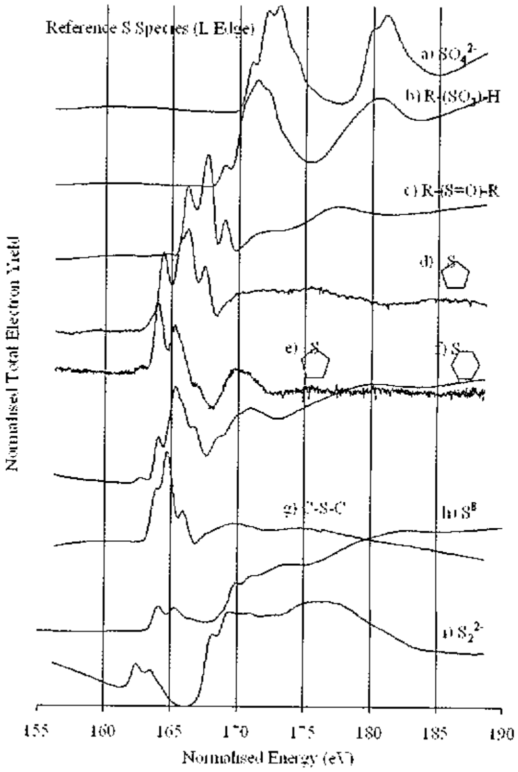

**Fig. 8.** Spectra collected on the Canadian SGM line at the sulfur L edge (≈ 164 eV) from a series of model compounds used as standards in a study of sulfur speciation in aluminium smelting anodes – see refs. 20 and 21.

reading of ancient manuscripts and secondly from cutting edge studies of bone development in animals. The Stanford website[25] recently featured an epic detective story in which Stanford synchrotron (SSRL) X-ray fluorescence was used to completely read the Archimedes Palimpsest, the only source of at least two previously unknown treatises thought out by Archimedes in the 3rd century BC. The palimpsest is a 1,000-year old parchment made of goat skin containing Archimedes' work as laboriously copied down by a 10th century scribe. Due to the value of the parchment, two centuries later the documents were erased, the parchment scrapped down with pumice and written over to make a prayer book. Parts of the document were even painted over some centuries later (as ancient parchments became increasingly valuable to art forgers). However, the residue from the original iron gall inks gave a sufficient signal in the XRF spectrum than when the parchment was scanned across the micro-focused synchrotron beam, the characters could be read! The second example, at the cutting edge of medical imaging, is taken from the work of Whitley and Lewis at the Victorian Department of Primary Industries and Monash University, respectively. Here interest is in the early development of lungs in mammals and the images shown in Fig. 9 follow the calcification of bones in the chest of wallaby from 1 to 22 days of growth.[26]

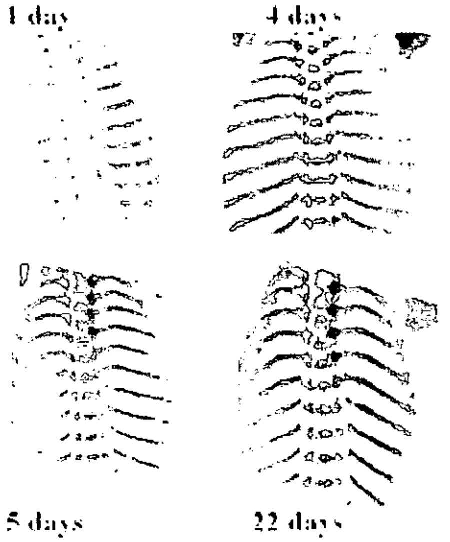

**Fig. 9.** Clacification of bones in the chest of a wallaby during early stages of development from data collected on the largest synchrotron, Spring8 (Japan) [Reproduced courtesy of Dr. J. Whitley (Victorian Department of Primary Industry) and Prof. R. Lewis, (Monash University)].

## The NZ Situation

The RSNZ was commissioned by MoRST in 2003 to prepare a detailed report on the case for formal NZ involvement in the Australian Synchrotron. Much of this was released[27] in Dec. '03 providing a review of then current and anticipated use of synchrotrons by NZ-based researchers and examines the nature of the opportunity presented by the Australian initiative. What is perhaps surprising is that NZ has activity across most spheres of mainstream synchrotron application, especially in protein crystallography, materials science, and IR spectroscopy. However, the regular community of about 12 regular users compares to 400 or so users across some 140 groups in Australia.

The vehicle for the growth and increasing sophistication of the Australian user community has been the Australian Synchrotron Research Programme (ASRP), a scheme mirrored in most developed countries, *e.g.* by the Canadian Synchrotron Radiation Facility (CSRF) initially based at the Madison synchrotron *Aladdin*, and supported by a Canadian *Major Facilities Access Fund*. The difficulty for NZ is that our fully costed research funding regime provides a poor fit with the way international science is carried out, particularly in the operation of very large science facilities, *e.g.* the APS in Chicago (Fig. 6) provides Australians access to four beamlines. These are billion dollar facilities for which the fully costed access regime is clearly inappropriate.

The local funding regime has in the past prevented any *as of right* synchrotron access for NZ users through an ASRP-type arrangement. Thus use has been restricted to relatively experienced scientists with international contacts through whom beamtime can be secured, typically by competitive, peer-assessed application. There is no doubt that this is highly cost effective since the international operational model is invariably that where *photons are free*. However, favourable costs must be balanced against the strategic limitations of relatively scarce access, and the external selection of NZ science to gain access to such frontline facilities. A further consideration is a perception of poor citizenship of our users who, in terms of the development and operation of such facilities, are able to contribute very little. Nevertheless, there is strongly growing use and awareness of the power of these techniques within NZ science. The Royal Society report identifies a number of notable examples of recent applications from the Baker group (Auckland), Jameson (Massey), Gainsford (IRL), and from our own work.

An industry-based example lies the development of new cathode materials for Li ion batteries by Pacific Lithium. This is an excellent case study of the evolution of materials from the initial Al- and Cr-doped Li manganate spinels, into much superior materials in battery performance, especially in cycle life. This systematic development has been based heavily on hard X-ray, EXAFS spectroscopy, and soft X-ray Absorption Near Edge Spectroscopy (XANES), using synchrotrons in France, the US and Taiwan.[22]

There is a wide, but currently very small, synchrotron user community in NZ. The challenge over the next few years is to develop the funding initiatives that will allow for rapid growth of a much stronger and more diverse user community; something of a catch-up on other nations. This is essential in order to make best use of the opportunities the Australian facility will provide and, more importantly, to ensure that this access has the maximum impact in enhancing NZ science and technology.

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Chemistry in New Zealand December 2005

# Cheminanotechnology: Nanotechnology for Chemistry and Chemical Engineering

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A well known scientist was recently heard to comment that the word *nano* is Greek for funding. How much truth is there in this jest – is nanotechnology just marketing hype to make the work of some scientists sound trendy and new or is there some merit to the term? Is it just a new name to an old concept or is it, as many claim, a revolutionary way of thinking that will change the face of science and technology? There are claims that billions of dollars are spent worldwide on nanotechnology research. But where has all this research suddenly appeared from? What were these people doing before the term nanotechnology came into widespread use and became favoured by the funding agencies? A cynic might rightly be amused at how so many people have managed to reinvent themselves.

At this point I will have to confess that I fall into the category of someone who may have benefited from using the term nanotechnology in funding applications and also someone who is reinventing themselves as a nanotechnologist even to the extent of offering the first nanotechnology degree in New Zealand. But is this a blatant piece of marketing or is there some substance to this claim? *If* I am part of the nanotechnology fraternity how can I be trusted to give an unbiased answer anyway? The reader will have to make this judgement.

Here I give my opinion on these issues. For those who choose to buy into this approach, I would also like to define a new term, *cheminanotechnology*, to represent the most pervasive nanotechnology which is that which applies to chemical processes.

Most commentaries on nanotechnology start with reference to Eric Drexler,[1] who is credited with coining the term, and then proceed to discuss physicist Richard Feynman's assertion that *there is plenty of room at the bottom*,[2] by which he meant the advances that remain to be made in manipulating and controlling things on the small scale. After this point, views diverge. Nanotechnology can mean little machines that will pump miniscule volumes of liquid, or it can refer to some new development in fabrics that repel water. Many people understand nanotechnology to refer only to miniature electromechanical devices. Some try to separate nanotechnology from nanoscience. Most would agree that nanotechnology deals with the very small scale - things measured in nanometres.

So how does nanotechnology apply to chemistry and chemical engineering? Chemistry can be loosely described as the study of the formation, properties, and interactions of molecules, while chemical engineering is the control of chemical processes on a large scale. It has been known since at least the time of Lord Kelvin[3] and J.Williard Gibbs[4] that the thermodynamic properties of a chemical substance are not constant but are in fact affected by the size of the piece of the substance being studied. It appears that some people have not been taught this in their undergraduate courses or they have forgotten these details. For example, everyone *knows* that at 1 atm pressure water boils at 100 °C. However, this is true only of relatively large volumes of water. A droplet of water of 5 nm radius will boil at 95.9 °C.[5] The physics behind this has been understood for over a hundred years. Similarly, melting points are affected by size; gold, which normally melts at 1064 °C, will melt at temperatures as low as 350 °C when it is a 2 nm particle.[6]

At the nanoscale, not only do these physical properties change but enthalpies of fusion, vaporisation, and chemical reaction change. These can affect the equilibrium of a chemical reaction or can lead to chemical reactions being possible that do not take place on larger particles. An early example is the observed change in the nickel-nickel carbonyl equilibrium.[7] A more recent example is the discovery that small particles of gold exhibit catalytic behaviour.[8,9] Previous studies on larger particles of gold showed no catalytic activity, and the change is known to be chemical rather than depend upon the increase in surface area per mass as a substance is divided up into smaller pieces. Properties thought to be characteristics of the substance start to become inconstant at small sizes, and at the nanometre level the effects have dramatic results.

It is not only chemical reactions but also fluid flows that change at small size. When dealing with liquids at small scales, that indispensable engineering concept, the Reynolds number (the dimensionless ratio of viscosity to momentum) is usually less than unity, and handling fluids becomes quite a different task with the intuitive notions of the flow and behaviour of a liquid being overturned.[10,11]

Most of these changes to the properties of substances at small scales have been known to chemists and chemical engineers for many years. What, then, has changed that enables us to claim the term nanotechnology for our work? There are two key areas where there have been changes that justify the application of the term nanotechnology to chemical research.

We now have techniques that can look at, or work with, single molecules to establish the properties of molecules individually rather than as an average of a collection. A good example here is the scanning probe microscope (SPM) that enables us to visualise single atoms and even electron waves[12] in a way we may never have thought possible. Now we can see defects in surfaces at which catalysis may be occurring,[13] whereas previously we knew that they must exist but could only infer their properties by other means. We can stretch single molecules and obtain directly physical properties[14,15] and thermodynamic data from force measurements on the single molecule rather than the large numbers of molecules in a calorimeter or a spectrophotometer.[14] We can look at the effect of possible new drugs on a single live bacterium rather than on a whole population of bacteria.[16]

Not only do we have new techniques but we have new materials that were not available previously. Challenges still lie in determining how these new products can be used, but they are providing opportunities for new and innovative exploration into fields ranging from medicine to mineral processing. Examples include carbon nanotubes[17] (people were wondering what could be done with these but applications are now appearing) and titanium dioxide nanotubes.[18] We can now use our understanding of the adhesion forces we observe in nature, such as a gecko clinging to a wall soley by means of van der Waals forces,[19] and mimic these structures in synthetic adhesive materials.[20] A further spectroscopic technique of interest to chemists is surface-enhanced Raman spectroscopy whereby the signals can be enhanced up to $10^{15}$ times for molecules adsorbed onto clusters of small particles of gold or silver.[21]

The blurring of the traditional disciplinary boundaries between chemistry, physics, and chemical engineering is reflected in the lack of clear distinctions between the branches that make up nanotechnology. Nevertheless, cheminanotechnology can be delineated as a subset of nanotechnology that is focused on understanding the effect that very small size has on chemical reactions, and the subsequent use of this understanding in new product and process development.

So, while at times I am a nano-cynic, I think the emphasis on nanotechnology is a useful guide to one's thinking and has at least some basis in actual practice. Although much of the science relating to nanotechnology may not be entirely new it reflects a major change in the tools and techniques available for studying materials and processes at the nano scale. New materials and methods have been developed utilising the peculiar properties of the nanoscopic realm and many applications remain to be discovered or developed.

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# Chemistry and Chemical Ecology of some of the Common Opisthobranch Molluscs Found on the Shores of NE New Zealand

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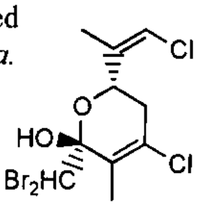
Opisthobranchs, sea hares and nudibranchs commonly known as sea slugs, are soft bodied marine invertebrates. Molluscs with a greatly reduced shell, the opisthobranchs, lack a physical defence mechanism and are potentially vulnerable to carnivorous predators. Loss of the shell in these animals is compensated for by several behavioural, anatomical, and physiological adaptations. Many opisthobranchs are cryptic and nocturnal, some can discard body parts when attacked, and some display an effective camouflage by sequestering pigments from their preferred foods. However, the most effective defence mechanism displayed by these organisms is a chemical one. Opisthobranchs are a rich source of cytotoxic, antimicrobial, antifungal, neurotoxic, and antimitotic natural products which have been shown to deter feeding by many natural predator species.[1] These defensive natural products are also known as secondary metabolites. Unlike the primary metabolites such as nucleic acids and proteins implicated in essential growth and differentiation processes, secondary metabolites are not directly involved in the basic maintenance functions of an organism. They do however play an important role in enhancing an organism's survival. Marine natural products have been assigned various ecological roles such as predator deterrence, mediation of competition, facilitation of reproduction, inhibition of overgrowth, protection from ultraviolet radiation, defense against pathogens and the induction of settlement.[2] Secondary metabolites are either diet-derived or made *de novo* by direct synthesis. Sea hares are herbivores that forage on red algae and sequester algal secondary metabolites into their own tissues. Nudibranchs can both sequester their prey's secondary metabolites and biosynthesise their own.

Over the past six years we have studied the secondary metabolite chemistry of several common local opisthobranch mollusc species; namely the sea hares *Aplysia parvula*, *A. dactylomela* and *Bursatella leachii*, and nudibranchs *Dendrodoris denisoni* and *Ceratosoma amoena*. In addition, by screening local species of algae we have identified possible dietary sources of these compounds and have established and quantified the anatomical distribution of secondary metabolites in selected organisms.

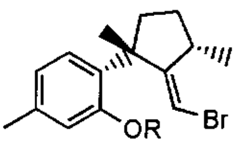
## Natural product chemistry of sea hares

Sea hares are small, slow moving molluscs with a soft shell buried in the mantle tissue. They feed on micro and macro algae and display similar colouration patterns to their dietary plants. Most of the compounds isolated in our work on sea hares are either algal natural products or slightly modified derivatives. For example, the sea hare *Aplysia parvula* at the time of collection was feeding on the red alga *Plocamium costatum*. Costatone, the main metabolite in this sea hare is a known terpene natural product found both in an Australian collection and our own study of the alga *P. costatum* (Chart 1).[3] A comparison on the relative concentration of costatone between the sea hare and the alga, as quantified by $^1H$ NMR spectroscopy, revealed that costatone is fourteen times more concentrated in the sea hare (Fig. 1).

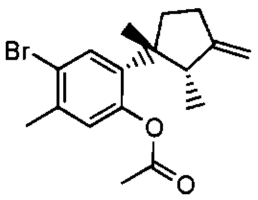
**Chart 1.** Natural products isolated from the sea hare *Aplysia parvula.*



Costatone



Isolaurenisol, R=H
Isolaurenisol acetate, R=Ac



Allolaurinterol acetate

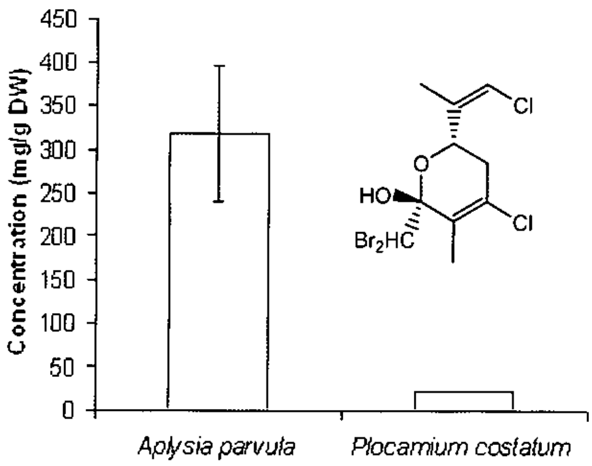
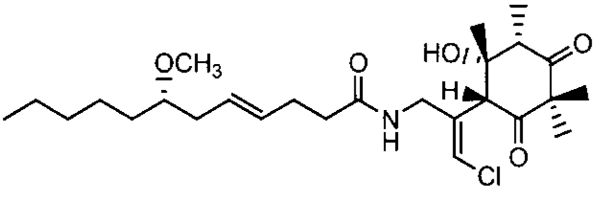


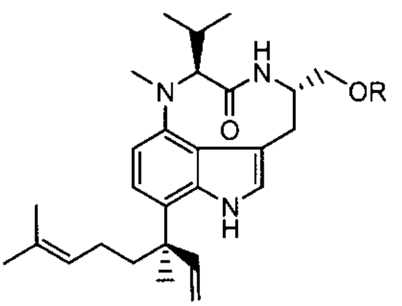
Fig. 1. Concentration of costatone in *Aplysia parvula* and its dietary plant *Plocamium costatum*; values quantified by $^1H$ NMR; data for *A. parvula* are presented as mean ± SD, n = 4.

Studies of the sea hare *Bursatella leachii* and its documented preferred food, the blue-green alga *Lyngbya majuscula*, yielded a new alkaloid malyngamide S as well as two other known natural products lyngbyatoxin A and its acetate (Chart 2).[4,5] Upon comparison of the sea hare and the dietary alga chemistry, compounds malyngamide S and lyngbyatoxin A were present in both organisms whereas lyngbyatoxin A acetate was never detected in the blue-green alga. Such acetylation adducts are common in opisthobranch natural product chemistry. Neither the allolaurinterol acetate or isolaurenisol acetate that we have found in *Aplysia parvula* and *A. dactylomela* are true algal metabolites (Chart 1). The free phenol compounds, allolaurinterol and isolaurenisol have been reported from local collections of red algae *Laurencia distichophylla* and *Hymenea variolosa*.[6] Acetylation of the phenol group is thought to occur in the sea hare, most likely as a detoxification mechanism or a by-product of the acidic digestive system environment.[7]

**Chart 2.** Natural products isolated from the sea hare *Bursatella leachii.*



Malyngamide S



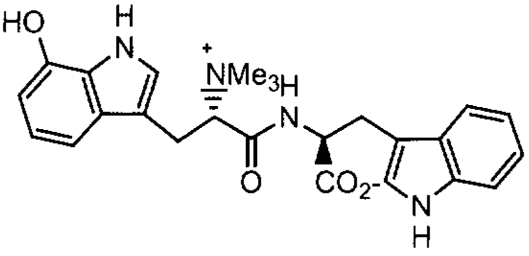
Lyngbyatoxin A, R=H

Lyngbyatoxin A acetate, R=Ac

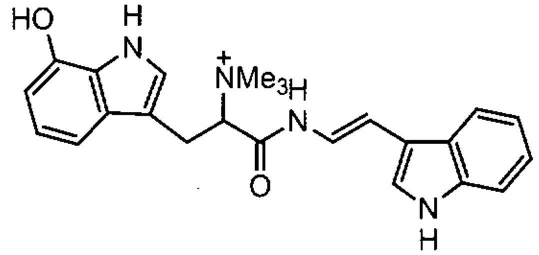
*Aplysia dactylomela*, apart from having known terpene metabolites allolaurinterol acetate and isolaurenisol acetate, was also the source of two new natural products dactylamides A and B (Chart 3).[8] Amino acid-derived metabolites have never previously been reported from the genus *Aplysia*. Dactylamides A and B were found in only a single specimen of *A. dactylomela* and it is yet to be resolved whether the sea hare acquires these tryptophan-derived dipeptides through diet or biosynthesis.

Our investigations have included both the sea hares and their dietary algae which were selected either because they were a previously documented dietary source or by our own field observations at the time of collection. We have shown that sea hares accumulate and concentrate selected algal metabolites in their own tissues. Gratifyingly, our secondary metabolite chemistry studies have found evidence of each sea hare dietary alga relationship established in previous ecological work.[5]

**Chart 3.** Natural products isolated from the sea hare *Aplysia dactylomela.*



Dactylamide A



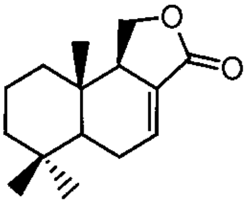
Dactylamide B

## Natural product chemistry of nudibranchs

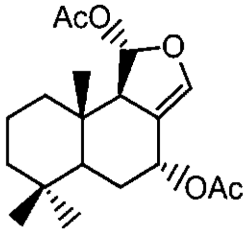
Nudibranchs are characterized by a complete loss of the shell. They are carnivores that prey on soft bodied invertebrates and sponges. As well as sequestering defensive metabolites from their prey, nudibranchs can also biosynthesize the same or very similar compounds themselves, a process known as de novo synthesis.[9] We have investigated the natural product chemistry of several local species: *Dendrodoris denisoni, Ceratosoma amoena, Tambja verconis* and *T. morosa.*

In the case of *Dendrodoris denisoni*, we have examined specimens collected from three different sites: Rabbit Island off the coast of the Coromandel Peninsula, Great Barrier Island and Matheson Bay. Cinnamolide, the major compound found in this species has previously been reported from a terrestrial plant but never a marine organism (Chart 4).[10] Interestingly, cinnamolide was detected in all the *D. denisoni* specimens that we have screened to date, independent of age or geographical location. The consistent occurrence of a compound in an organism throughout its range is considered an indicator of *de novo* synthesis.[11] During the isolation and purification work of the three minor *D. denisoni* metabolites, we found that olepupuane undergoes allylic methanolysis to give the methoxy acetal that decomposes into polygodial (Chart 4). All three compounds are common secondary metabolites of the genus *Dendrodoris* worldwide, and several species are able to biosynthesise olepupuane and polygodial when injected with the radiolabeled precursor, $^{14}$C-mevalonic acid.[12] As very little is known about the ecology and the diet of this species and previous studies of the local ascidians and sponges have never found cinnamolide, olepupuane or related compounds, we suspect that *D. denisoni* might be synthesizing cinnamolide and possibly olepupuane de novo, rather then acquiring these compounds through diet.

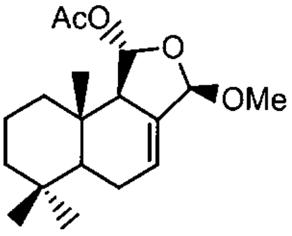
**Chart 4.** Natural products isolated from the nudibranch *Dendrodoris denisoni.*



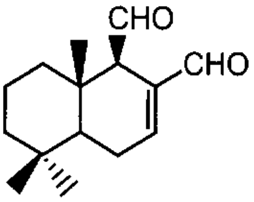
Cinnamolide



Olepupuane



Methoxy acetal



Polygodial

In contrast, another nudibranch species, *Ceratosoma amoena*, yielded an interesting ecological observation. At the time of collection the nudibranch was observed on the red alga *Hymenea variolosa*. We found a known red algal terpenoid secondary metabolite, allolaurinterol (Chart 1), in both the alga and the nudibranch. Nudibranchs are an exclusively carnivorous group of animals and do not have the digestive system physiology to break down algal tissues.[13] Therefore, *C. amoena* was not foraging on *H. variolosa* and sequestering its metabolites and an alternative explanation for the allolaurinterol in *C. amoena* might be that the nudibranch is preying upon some other organism that sequesters this compound from the alga. Locally, both *Aplysia dactyomela* and *A. parvula* are known to sequester allolaurinteriol, but since both sea hare species are significantly larger than *C. amoena* it seems highly unlikely that the nudibranch is preying on the two sea hares. However, many opisthobranch species are known to transfer their defensive metabolites into egg ribbons that they deposit on algae and other hard substrata. The nudibranch *C. amoena* may have foraged on chemically defended egg ribbons and thus sequestered allolaurinterol into its own tissues. At present this unusual trophic cascade seems the most likely pathway for the acquisition of a red algal metabolite in *C. amoena.*

The secondary metabolite chemistry of two other local nudibranch species, *Tambja verconis* and *T. morosa*, was studied as part of an ecological investigation of the genus *Tambja* carried out in collaboration with Haagh and Babcock at the Leigh Marine Lab.[14] *Tambja* nudibranchs are known for their ability to sequester a range of alkaloids, known as tambjamines, from their bryozoan prey *Bugula dentata*.[15] The present study found a range of related tambjamine metabolites in the two nudibranchs, but not all of the compounds were present in the bryozoan. Therefore, the two nudibranch species are not only sequestering secondary metabolites from their invertebrate prey but also structurally modifying these compounds and expanding their defensive arsenal.

## Anatomical distribution of costatone and cinnamolide

Tissue localization of a secondary metabolite is an important ecological feature. Tissues which are directly exposed to predators, such as skin and mantle, should have a higher concentration of a defensive metabolite compared to the internal organs.[16] Two organisms, a sea hare *Aplysia parvula* and the nudibranch *Dendrodoris denisoni* and their major metabolites costatone and cinnamolide, respectively, were chosen for a metabolite localisation and quantification study. The digestive gland, a large enzyme-producing organ where digestion and absorption of food takes place, was taken as the internal organ, and skin and mantle as the external organs. The metabolites were quantified by $^1$H NMR spectroscopy.

Costatone was found primarily in the digestive gland of the sea hare *A. parvula* (Fig. 2), but having close to 95% of the total metabolite content in an internal organ that is not in direct contact with a predator does not suggest a predator deterrence role for costatone. Concentrating algal secondary metabolites in the digestive gland might represent a simple detoxification mechanism by the sea hare. However, on many occasions during collection dives, we have observed that when large predatory fish such as snapper are offered live *A. parvula* initially they are taken in but then rapidly rejected, suggesting that there is a form of chemical deterrence associated with this organism. In contrast, *D. denisoni* stores cinnamolide both in the internal and external organs (Fig. 3). Our study showed that the relative concentration of cinnamolide in the external organs (skin and mantle) is significantly higher than that in the digestive gland consistent with previous investigations into secondary metabolite chemistry of the genus *Dendrodoris*. This strongly suggests that the organism utilises cinnamolide as a defensive, predator deterrent metabolite, but feeding deterrence studies with ecologically realistic predators need to be conducted in the field before any definite conclusions can be reached.

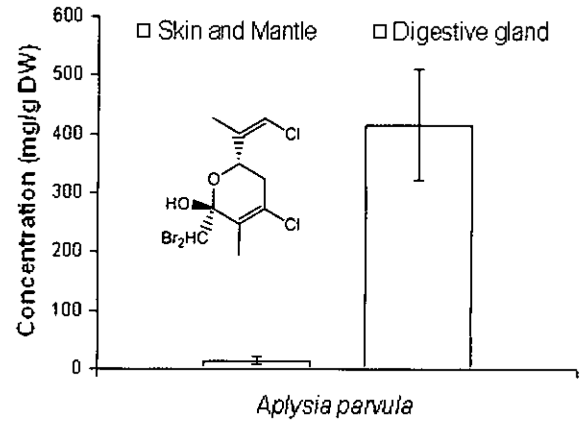


Fig. 2. Concentration of costatone in *Aplysia parvula* tissues; values quantified by $^1$H NMR and presented as means ±SD, n=4.

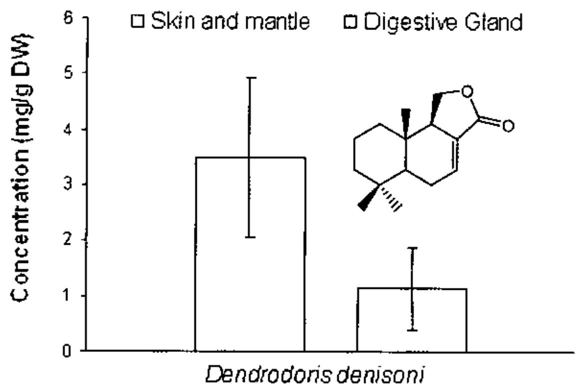


Fig. 3. Concentration of cinnamolide in *Dendrodoris denisoni* tissues; values quantified by $^1$H NMR and presented as means ±SD, n=5.

## Why study opisthobranch molluscs?

Chemical studies of opisthobranch molluscs provide a diverse source of new isoprenoid and amino acid-derived natural products. The evolution of chemical defences also represents an interesting ecological study of these organisms. It has been suggested that the shift from a hard-shell physical defence to a soft-bodied chemical one has been facilitated by a newly acquired ability to sequester, safely store and modify secondary metabolites by a hard-shelled ancestral species.[17] Sea hares display a diet-dependant acquisition of chemical defences. Their dietary algae are the primary source of their own secondary metabolites. Many studies have shown that purified sea hare secondary metabolites act as effective feeding deterrents, but their anatomical distribution suggests otherwise. It is not yet clear whether sea hares are a true example of chemically-defended organisms. On the other hand, nudibranchs display complex methods of secondary metabolite acquisition and their optimized anatomical distribution. Some, such as the genus *Tambja*, sequester the secondary metabolites of their prey, while *Dendrodoris* spp. nudibranchs are able to biosynthesize their own.

Our ongoing studies of soft bodied opisthobranchs have yielded several novel natural products including malyngamide S, and dactylamides A and B. Other compounds such as costatone, cinnamolide and isolaurenisol have been fully characterized for the first time. Our studies focus not only on finding new sources of bioactive natural products, but also on understanding the dietary relationship, anatomical distribution, and quantification of secondary metabolites, thus giving insight into the chemical ecology of selected species of New Zealand opisthobranch molluscs.

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## NEW ZEALAND INSTITUTE OF CHEMISTRY CONFERENCE 2006

2-6 December 2006
at
The Royal Lakeside Novotel, Rotorua

*Invited Speakers:*

***Inorganic-Organometallic Chemistry:* - Warren Roper (Auckland)**

***Organic-Medicinal Chemistry:* - David Mcmillan (Caltech)**

***Materials Chemistry:* Mark Barteau (Delaware)**

***Physical and Theoretical Chemistry:* Richard Zare (Stanford)**

***Biochemistry and Molecular Biology:* Harry Gray (Caltech)**

**Registration:** $NZ550.00 NZIC members
(concessions for NZIC student and retired members to be advised)

Chemistry in New Zealand December 2005

# Virtual Institute for Metrology in Chemistry: Cost Effective Traceability in Chemical and Biological Measurement

John Love and Laly Samuel*

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PO Box 20-028, Christchurch (E-mail: l.samuel@irl.cri.nz).

## Introduction

Traceability to common references is one of the foundations of good measurement with results that are consistent between laboratories, countries, and regions. It is a concept well developed in physical measurement but, until recently, had been developed relatively poorly in its support for analytical chemistry. The Measurements Standards Laboratory [MSL - as the NZ National Metrology Institute (NMI)] is developing a Virtual Institute for Metrology in Chemistry (VIMT) as a cost effective approach to make the best use of existing analytical expertise in NZ. It will allow us to join with developing metrological initiatives to support better chemical measurement and maintain the acceptability of local chemical measurements in their role of supporting trade and commerce.

Good measurement requires a system of traceability to link the measured result to both the true result represented as an internationally accepted and defined reference value for the analyte being quantified and an estimation of the uncertainty of this link. Without traceability to a common reference, no-one can have confidence that measurements made on the same sample in different laboratories, different countries, or different regions are consistent. ISO/IEC 17025 is the standard for competence of calibration and testing laboratories and ISO 15189 is that for competence of medical testing laboratories; both require procedures that show traceability of their measurements to these defined references and procedures to estimate the associated uncertainty.

Traceability and uncertainty are well established concepts in physical testing but less well established in chemical and quantitative biological measurement. Analytical chemists and microbiologists are well aware that all measurements have inherent variability with a need for systems to demonstrate consistency in results between laboratories, countries and regions. Resolution 10 of the 21st General Conference on Weights and Measures (1999) recognises a continuing need for improvement in the traceability of chemical measurement because of the importance these measurements have in the facilitating trade. It recommended that NMIs increase their support for this type of testing.

Metrology and the NMIs depend on traceability and uncertainty to provide the link between an individual measurement and the defined international reference. Both are well defined and quantifiable concepts that interpret measurement variability into a form that shows the consistency expected between laboratories and countries when results are reported on equivalent samples.

Traceability in chemical measurement normally depends on the quality of the calibration standard and the appropriateness of any matrix Certified (Standard) Reference Material used during validation, and used as part of any on-going quality control protocol. It may include proficiency testing if the target value and its uncertainty have been estimated in an appropriate manner. In recent years the international community of NMIs, *e.g.* NIST (USA), NARL (Australia), the NMIs in Europe, and NMIJ (Japan), have spent considerable effort in developing a more complete set of certified reference and other materials that better cover the traceability links that apply to chemistry.

NZ has made less progress in developing chemical metrology and a national system of traceability to support chemical measurement. However, this is a development that cannot be ignored if the international community is to maintain full confidence in the national measurement infrastructure for chemical analysis, for its accreditation system, and for trade and commerce. The NZ NMI has little expertise in chemical measurement but it has a legislative mandate to address the development.

In NZ, expertise in chemical measurement is spread between government owned commercial laboratories and research institutes. The economy is too small for the NMI to set up a separate group of experts with skills across all areas of analytical chemistry important to it within the MSL. Thus the MSL has spent time and effort in devising a workable system to unite the existing nationally-dispersed experts with its chemical metrology responsibilities. Discussions have involved input from stakeholders who support a measurement infrastructure and interested laboratory staff through workshops. As a result the NZ Virtual Institute for Metrology in Chemistry has been formed as a cost effective solution. MoRST, as the Government arm responsible for the national measurement standards, has agreed that this is appropriate for traceability in chemical measurement.

## The Virtual Institute for Metrology in Chemistry

The VIMC is a model designed to unite the dispersed NZ experts (and sometimes users) into a single web-centred organisation. It will link our expert laboratories to the international measurement infrastructure of the NMIs, to working chemical testing laboratories, and to users of chemical measurement as shown in Fig. 1. This will ensure traceability of the measurements from the working laboratories to the VIMC experts, to other NMIs, and the international measurement system.

In developing the VIMC it has been noted that many of

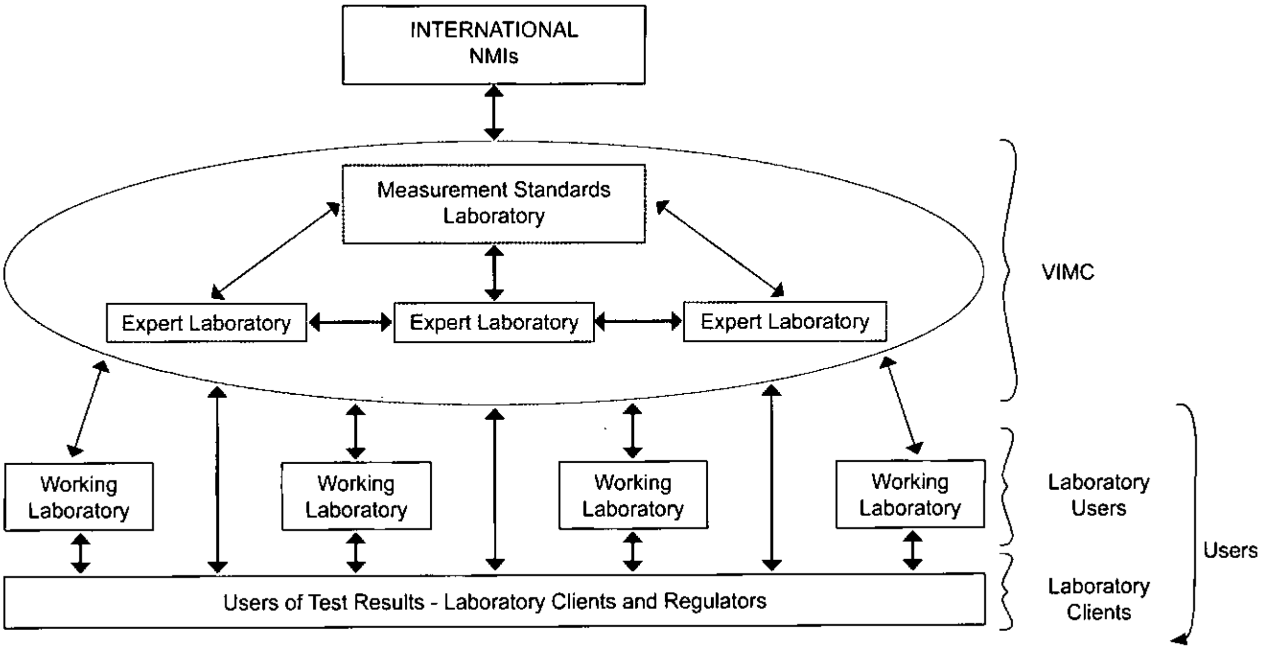


**Fig. 1.** Relationships of the VIMC to NMIs and NZ user groups

the newer methods of biological measurement, and many of the methods being used in medical testing laboratories, are based on processes that are essentially chemical in nature. These methods require a similar support infrastructure to that needed for chemical measurements; ultimately they will be included within and supported by the VIMC.

## The VIMC Web Page

The development of the VIMC in NZ is being led by the Measurement Standards Laboratory with an introductory web page at: http://www.irl.cri.nz/msl/VIMC/index.html.

Laboratory, trade, and regulatory users can use this to join the VIMC as members of an awareness group with an interest in the production and appropriate use of high quality and traceable analytical results. The VIMC web page is to be central to the Institute and provide a communication channel for laboratory users of the Institute, NZ experts in chemical and biological measurement, trade and commercial users of laboratory results, and regulators. When fully developed, it will be structured in two levels. Open access will maintain an awareness group of individuals, laboratories, and users of laboratory results interested in chemical and biological measurement, and to whom the VIMC will circulate information on laboratory best practice and use of analytical reports. A secure level will be accessible by VIMC members only.

The MSL has already made contact with staff in a number of laboratories and with a number of users of chemical measurement. From these, it has identified many laboratories and users of chemical measurements who are interested in being involved in the awareness group to assist in the development and application of metrology to chemical and biological measurement. This group comprises contacts from CRIs, industrial research organisations, city and regional councils, manufacturers, testing laboratories, universities, and hospitals.

VIMCs key challenge is to develop this awareness group and be attractive to industry and trade users from the outset. Ultimately, everyone must recognise that the VIMC offers a unique and high value service that could not otherwise easily or economically be obtained. Those interested are encouraged to join the VIMC as members and to contribute to the national good by supporting better measurement.

**Acknowledgement:** *This work is funded by NZ Government as part of a contract to provide national measurement standards.*

# The 2005 Nobel Prize in Chemistry

**PhotoCaption:** 2005 Chemistry Laureates (L-to-R) Grubbs, Schrock and Chauvin

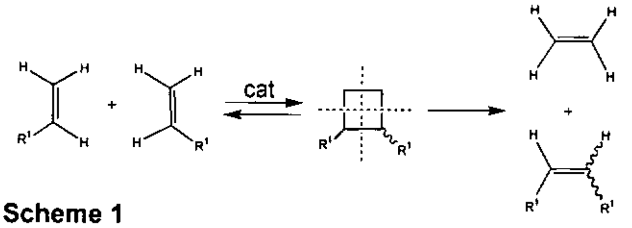
## Synopsis

This year's Nobel Prize in Chemistry has much more connection with NZ than many might imagine. This is because one of the laureates, Prof. Bob Grubbs, was at Canterbury University on an Erskine Fellowship when the prize was announced on October 5. More coincidental is the fact that his first publication in the chemical literature is co-authored by Prof. Halton (Victoria University) from time at the University of Florida where Grubbs completed an MSc degree under the supervision of Prof. Merle Battiste, a former Erskine Fellow and visitor at Canterbury. It is even more coincidental that an original off-print of the communication was jointly signed in Wellington some hours ahead of the announcement being made.

The Prize for 2005 is shared by Americans Robert H. Grubbs and Richard R. Schrock, and Frenchman Yves Chauvin who are cited *for the development of the metathesis method in organic synthesis*. Their contributions have assumed major significance in the chemicals industry, opening up new opportunities for synthesising molecules that will streamline the development and industrial production of pharmaceuticals, plastics, and other materials. Production will become cheaper and more environmentally friendly.

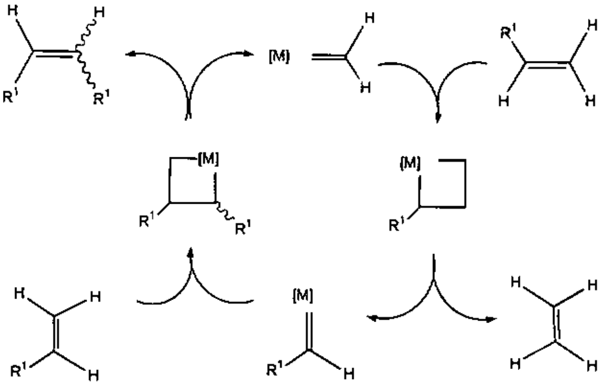
## Metathesis – a change-your-partners dance!

The reaction at the focus of this year's Nobel Prize in Chemistry is ***metathesis***. Derived from the Greek *meta* (change) and *thesis* (position), metathesis is the exchange of parts of two substances, e.g. in the reaction, AB + CD → AC + BD, B has changed position with C, while Scheme 1 shows olefin (alkene) metathesis they key reaction of this year's award. Formally, two alkenes can come together in one direction and separate in the opposite one whereby one alkene exchanges its $CHR^1$ moiety for the $CH_2$ group in the other – hence the concept of *a change your partners dance*. However, for the reaction to proceed a catalyst is needed. While it has long been possible to produce new molecules this way, it was in 1970 that Chauvin proposed the first mechanism showing that the catalyst functions as a metal carbene. His experimental results tallied with the new mechanism and could not be explained by anything previously proposed.



**Scheme 1**

Scheme 2 shows how a metal methylene catalyses the exchange of alkylidene units between two different alkenes giving two entirely new alkenes ([M] designates binding of the metal to other groups). This is also shown in Fig. 1 where it may be viewed as a dance in which the *catalyst pair* and the *alkene pair* dance round and change partners with one another. The metal and its partner hold hands with both hands and when they meet the *alkene pair* (a dancing pair consisting of two alkylides) the two pairs unite in a ring. After a while they let go of each other's hands, leave their old partners and dance on with their new ones. The new *catalyst pair* is now ready to catch another dancing *alkene pair* for a new ring dance – continuation of catalyst activity in metathesis. Thus researchers were given a new challenge to grapple with, namely to construct new efficient catalysts. Here Grubbs' and Schrock's fundamental research enters the picture as they have provided catalysts that are so useful today.



**Scheme 2.** Chauvin's mechanism for olefin metathesis involving matalacyclobutanes.

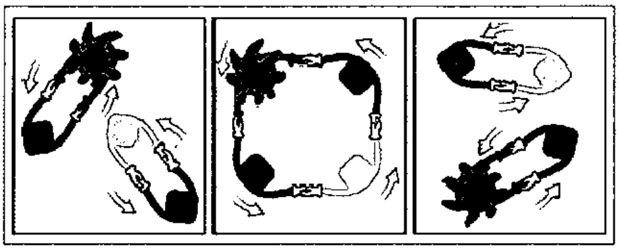
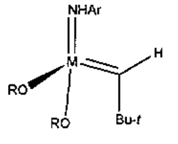


**Fig. 1.** Chauvins' mechanism viewed as a dance in which the catalyst pair and the alkene pair meet, dance round, and exchange partners.

## Schrock's creation of the first well-defined useful catalysts

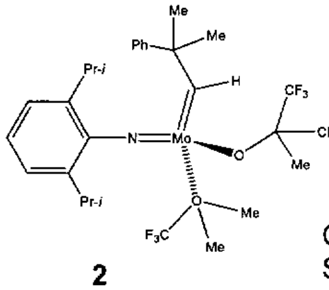
Chemists began to realise that metathesis could assume great importance for organic synthesis if reliable and effective catalysts could be found. Early studies used undefined catalysts, sensitive to air and moisture with relatively short life-time. The need was for stable and well-defined catalysts with reactivity that could be adjusted depending on the purpose. In addition, they had to be selective reacting only with double bonds and leaving other parts of the molecules intact. A number of chemists made major contributions to the development of metathesis catalysts and their applications; but the crucial progress in this area was made by Grubbs and Schrock.

Richard Schrock started research on new alkylidene complexes in the early 1970s trying catalysts containing different metals such as tantalum, tungsten, and molybdenum. He gradually developed an understanding of what metals could be used in the catalysts and how they functioned. For Schrock, molybdenum and tungsten soon appeared to be the most suitable metals and catalysts were produced with those metals, but there was still uncertainty as to what groups would bind to the metal to give stable yet active alkylidene complexes. A breakthrough came in 1990 when Schrock and co-workers reported the construction of a group of very active, well-defined catalysts shown generically by **1** and specifically by a commercial example (Scheme 3). With this discovery chemists began to realise that olefin metathesis could be used for general purposes in organic synthesis and it gained increasing attention among researchers active in synthetic chemistry. It turned out that it can replace a number of traditional synthesis methods while, at the same time, permits entirely new approaches to the synthesis of organic molecules. Molybdenum catalysts, such as **2**, are sensitive to *e.g.* oxygen and moisture but, with the right treatment, are very powerful tools in organic synthesis.



**1**

General formula of Schrock's catalyst; M = Mo or W, R and Ar are bulky groups



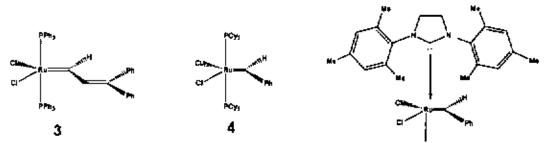
**2**

Commercially available Schrock catalyst

**Scheme 3**

## Grubbs discovery of practical catalysts

Yet another breakthrough in the development of metathesis catalysts came in 1992 when Grubbs and his co-workers published their discovery of a ruthenium catalyst, stable in air and with higher selectivity but lower reactivity than Schrock's catalysts. The new catalyst **3** also had the ability to initiate metathesis in the presence of alcohols, water, and carboxyl acids. Grubbs subsequently improved his catalysts with the compound **4** (Scheme 4). This now commercial compound is the first well-defined catalysts for general metathesis applications in ordinary laboratories, is generally named Grubbs' catalyst, and has become the standard with which all new catalysts are compared.



3
Grubbs' 1992 catalyst

4
Grubbs: 1995
1st generation
commercial catalyst;
Cy = cyclohexyl

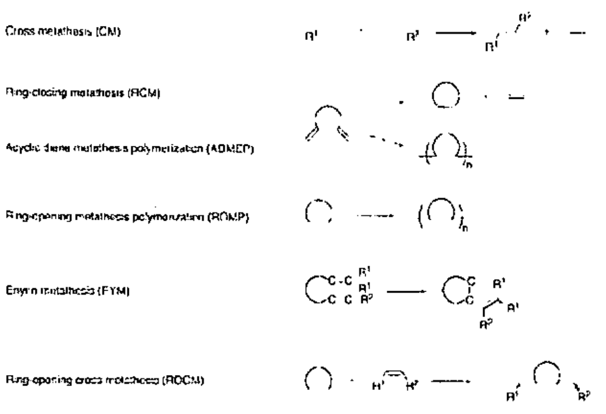
5
Grubbs: 1995
2nd generation
commercial catalyst;
Cy = cyclohexyl

**Scheme 4**

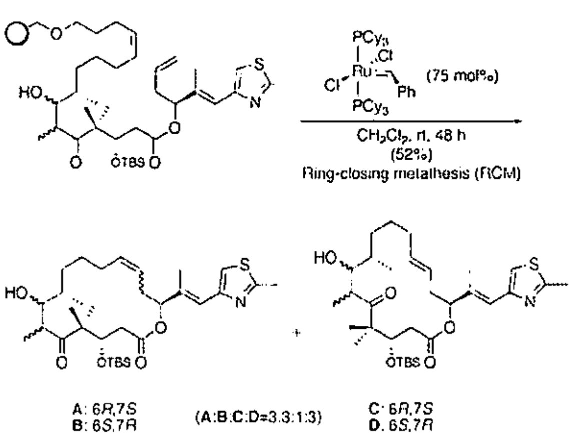
Grubbs bases his catalyst design on detailed mechanical studies. He has continued development of Ru-based metathesis catalysts into yet more powerful tools for synthesis, including that of polymers with special properties. In a number of difficult ring-closing reactions, the lifetime of the catalyst was insufficient to give high yields of products with reasonable catalyst loadings - catalysts with improved properties were needed. Detailed mechanistic studies led Grubbs' group to conclude that the reaction first involved the dissociation of one of the phosphine ligands to generate the reactive ruthenium intermediate. By replacing just one of the phosphines with a cyclic bis-amino carbene ligand Grubbs found the dissociation to be accelerated and the dissociation rate of the remaining phosphine increased, thus increasing metathesis activity. The new, more reactive, catalyst **5**, termed a second generation Grubbs'catalyst, is currently the most used catalyst for efficient cross-metathesis reactions and it is available commercially. The general applicability of Grubbs' catalyst has given rise to future prospects of the possibilities of organic synthesis.

## The multitude of applications

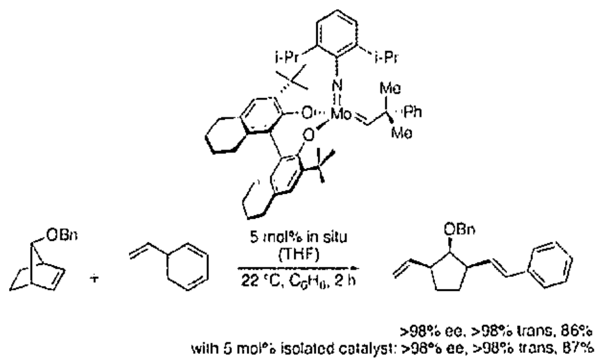
The Grubbs and Schrock catalysts offer synthetic chemists widespread opportunities. Their extensive use in organic chemistry is due to their tolerance of a large variety of functional groups, combined with their efficiency and, for Grubbs' catalysts, their ease of handling in air. Scheme 5 shows the different types of olefin metathesis reactions that can take place with the examples of Schemes 6-8 serving to illustrate the power of the novel catalysts.



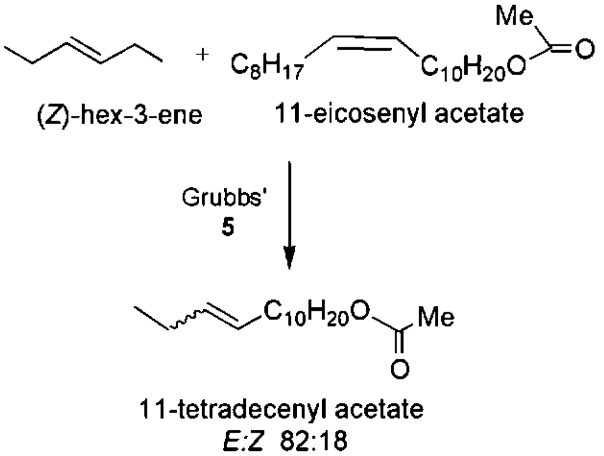
**Scheme 5.** Use of olefin metatheis in synthesis.



**Scheme 6.** A solid phase synthesis used by Nicolaou in the syntheses epothilone A and its various derivatives using a ring-closing metathesis (RCM) cyclization/cleavage strategy; see Fürstner, A, and Thiel, O.R., *J. Org. Chem.*, **2000**, *65*, 1738.



**Scheme 7.** An efficient stereoselective cross metathesis (CM) using *in situ* prepared and isolated chiral catalyst, respectively, see: Teng, X., Cefalo, D., Schrock, R.R., and Hoveyda, A.H., *J. Am. Chem. Soc.*, **2002**, *124*, 10079.



**Scheme 8.** The omnivorous leafroler (OLR) is a pest of apples, pears, peaches, and nectarines. The OLR pheromone is an 82:18 ratio of *E* to *Z*-tetradecenyl acetate isomers. The synthesis of OLR pheromone is a particularly attractive target for metathesis because this CM reaction, using the second generation Grubbs'catalyst, produces the desired isomeric ratio; see: Pederson, R.L., Fellows, I.M. Ung, T.A. Ishihara, H., and Hajela, S.P., *Adv. Synthesis Cat.*, **2002**, *344*, 728.

## Further catalyst development

Catalyst design (or redesign in some cases) remains vibrant, and seldom a month passes without the disclosure of a new catalyst for metathesis applications. Many of these novel systems are inspired by, or derived from, efforts to facilitate the construction of highly functionalized, complex molecules. Given the established ability of metathesis to effect transformations otherwise difficult to achieve, this trend is likely to continue.

## Consequences and applications

It is important to emphasize the great significance of the laureates' discoveries and improvements for both academic research and industry for the development of commercially viable compounds. Considering the short time during which Grubbs' and Schrock's catalysts have been available, the breadth of applications is truly remarkable. We have witnessed the synthesis of polymers with special properties, additives to polymers and fuels, and biologically active compounds such as insect pheromones, herbicides and drugs. Importantly, catalytic metathesis uses shorter synthetic routes to products that are formed in higher yields than previously, thereby offering major possibilities for a *greener* chemistry.

*This article was compiled by Brian Halton (Editor) from material freely available on the Nobel Foundation web site, see: www.nobel.se.*

# President's Report 2005 - Synopsis

Full version available at www.nzic.org.nz

### Actions:

- NZIC by-line ***Supporting Chemical Sciences*** (Kate McGrath, VUW) is in place.
- Council meeting times amended for improved planning with Executive teleconferences between times.
- All Councillors are allocated specific portfolios.
- New member recruitment reversed subscription income decline but more must be done.
- Professional Secretariat successfully moved to Christchurch; database almost completely updated. Members financially in arrears have amnesty for renewal in 2006
- ***Chemistry in New Zealand*** Managing Editor/Publication moved to Christchurch.
- Financial uncertainty followed the Secretariat to Christchurch resulting in late payment of Branch Grants.
- 2004 Audited Accounts (available 20 Nov - see web site) show improved position.
- Financial situation in 2006 will remain constrained.
- Elections to Fellowship (see elsewhere in this issue; Feb. P.15; Sept., P.20).
- Annual Prizes – see elsewhere in this issue.
- NZIC Representatives:
- Pacifichem – Prof. Rob Smith (Otago)
- IUPAC:
    - Union Advisory Committee (and Div. V Analytical): Prof. Kip Powell (Canterbury).
    - National Contacts: Div. I (Physical & Biophysical): A/Prof. Jim McQuillan; Div. II (Inorganic): A/Prof. Lyall Hanton; Div. III (Organic& Biomolecular): A/Prof. Carol Taylor; Div. IV (Macromolecular): Dr. Greg Russell; Div. VI (Chemistry and Environment): Dr. Pat Holland Div. VII (Clinical/Human Health): Dr. Paul Fawcett; Div. VIII (Nomenclature& Struct. Representation): Dr. Richard Hartshorn.
- Asia-Pacific Association of Catalysis Societies (APACS): A/Prof. Hicham Idriss.
- RSNZ Council: Prof. Andrew Brodie (also representing NZIP).

**Chemical Education Trust** - The 2005 distribution has yet to be finalized; Leon Phillips' term ends and Andrew Brodie joins Pat Holland and Andrew MacGibbon.

**Specialist Groups** – Activities vary markedly; Dr. Suzanne Boniface is reactivating ChemEd and Branch representatives are appointed to assist.

**Presidential Visits** All Branches were visited, addressed (*Shedding Light on Molecular Structure: Applications of Spectroscopy in Structural and Materials Chemistry*), and discussions on NZIC affairs and activities held.

**Representations** – The President represented NZIC at:

- *The Halton Retirement Symposium* (Sept issue pp.14-15. 20);
- *13th General Assembly of FACS/11th Asian Chemical Congress, Seoul.* As National Representative of the NZIC (a FACS member) I was invited to attend these meetings and reports appear elsewhere in this issue.
- *Pacifichem 2005.* Pacifichem is held every 5 years *to disseminate recent research results in the chemical sciences among chemists of the Pacific Rim countries, thereby fostering industrial development, improving local and global environments and the material well-being of their peoples.* NZIC is an organizing society, and I will be representing it as one of my last Presidential duties.

### Future NZIC Conferences

- *National Conference: Rotorua, 2-6 December 2006* (See advertisement elsewhere in this issue and web site).
- *RACI/NZIC/NZASE Chemical Education Conference, Auckland, July 2007.* The Chairman of the local organizing committee is **Dr. David Salter** and it will provide a focus for the rejuvenated NZIC Chemical Education Specialist Group under Suzanne Boniface.

### Editorials

Editorials for *Chemistry in New Zealand* and *CHEM NZ* and an item for *RSC News* on the sponsored NZ lecture tour of Professor Bob Grubbs at the time of the announcement of the 2005 Nobel prize (see elsewhere in this issue) met requests.

### Response to RACI Survey

The RACI undertook a study to gather information on the state of chemistry in Australia and, especially, to explore the anecdotal view that they have a *disconnect* between the strengthening demand for quality graduate chemists and a decline in numbers and their quality. It achieved this through a desktop review of the Australian secondary school sector, collating information from a university survey of Chemistry Heads and also a university student questionnaire, as well as analysing data collected from people employing chemists (employer survey) designed by the RACI. Information from the Australian Bureau of Statistics, the Graduate Careers Council of Australia and the RACI database was analysed. Where applicable, international benchmarks were used and discussed. Following release of *Future of Chemistry - Interim Report* (Mar. '05), NZIC was invited to submit feedback. Following discussion at Branches level during my visits, a formal NZIC response was submitted. I recommend the final report (available on the RACI web site www.raci.org.au) as worthwhile reading for all NZIC members.

### Valedictories

I thank Council for their work and support, and particularly: *Colin Freeman* (Treasurer) and *Richard Rendle* (Hon. Gen. Sec.) who have given generously of their time and have done a magnificent job in managing the 2005 changeover; *Brian Halton* in editing *CiNZ* to a high standard, and for providing invaluable assistance to the new Managing Editor/Publisher; the Canterbury-based *CHEM NZ* editorial team for their ongoing work on this popular education publication; *Rebecca Hurrell* as web manager.

Finally, I thank all NZIC members for their support. If you are not actively involved in the affairs of the NZIC consider becoming more involved, for example as a Branch committee member. As Brian Halton said at his retirement symposium in reply to comments about his long involvement with NZIC *Whatever effort you put in will be rewarded one-hundredfold.* This kind of attitude guarantees the future of the Institute - it depends much more on the support and enthusiasm of its members than on the actions of its President or Council!

**Graham Bowmaker, President** (15 Nov '05)

# NZIC - supporting chemical sciences

December News

## **STOP PRESS**

## 2005 NZAS Awards

**Dr. Kevin Tate** (Landcare Research, Palmerston North) is the 2005 recipient of the NZAS Marsden Medal for his contribution to, and leadership of, research into ecosystem processes and climate change. The award was presented at the RSNZ Awards dinner in Wellington in November.

The Marsden Medal is awarded for outstanding service to science and in recognition of services rendered to the cause or profession of science.

## NZIC Awards 2005

Council is pleased to announce that its 2005 awards are made as per:

**Easterfield Award** (including a UK lecture tour): **Dr. Emily Parker** (Massey University)

**HortRes Prize: Prof. Margaret Brimble** (Auckland University)

**NuPharm Prize: Selwyn Yorke** (NZ Pharmaceuticals, PN)

**Chem Education Award: Dr. Trevor Kitson** (Massey University)

## Election to Fellowship

Council is pleased to advise that the following members have been elected to Fellowship (FNZIC):

**R.T. Anderson,** A/Prof. and Director, Pulse Radiolysis Facility, University of Auckland;

**B. Copp** Senior Lecturer in Medicinal Chemistry, University of Auckland;

**H. Idriss**, A/Prof. in Physical & Materials Chemistry, University of Auckland;

**A. Easteal**, A/Prof. in Materials Chemistry,University of Auckland;

**N. Edmonds**, Director, Polymers and Coatings Science (University of Auckland);

**L. Main**, A/Prof. in Organic and Mechanistic Chemistry, University of Waikato,

**A. Limmer**, Vintner and Winemaker, Stonecroft Wines, Hawkes Bay;

**C. Taylor**, A/Prof. in organic synthesis of biomaterials, Massey University;

**H. Kjaergaard**, A/Prof., Spectroscopy and Computational Chemistry, University of Otago.

The **2005 RSC** lecturer, **Prof. Allan Canty** (University of Tasmania) toured the Branches in October delivering his lecture *Organopalladium and Platinum Chemistry Related to Potential Roles for Palladium(IV) in Organic Synthesis and Catalysis.* Allan described some of the roles for Pd catalysts in organic synthesis, mainly for C-C and C-O bond formation, and the fundamental organometallic chemistry relevant to the processes was discussed. Emphasis was given to proposed roles for $Pd^{IV}$ in contrast to the established role for $Pd^{II}$, and an exploration of reactions at Pd and Pt centres that could model the proposed steps in synthetic applications were discussed.

**NZIC President Graham Bowmaker** attended the (biennial) **11th Asian Chemical Congress:** *For the Quantum Leap of Asian Chemistry* in Seoul in August. Organized by FACS (now comprising 22 societies in the Asian region including NZIC), it followed FACS 13th General Assembly. The quantum leap was very much evident, *e.g.* with *ca.* 1300 participants over the 250 participants previously. The program covered a wide range of topics with the plenary lecturers including Nobel laureates Alan J Heeger, Yuan Lee and Ryoji Noyori. It was clear that the Asian Societies wish to increase the standing of their meetings to compare to ACS, and to make the FACS the *third axis* of world chemistry. The meeting was attended by representatives of the IUPAC, ACS, RSC, and recently renamed (European) EuCheMS that plans to hold its 1st European-wide congress in Budapest next August.

The 11ACC meeting was very well organized and if the current upward trend in the size and quality continues, it has the potential to become a major event on the world chemistry calendar. The organizers made it clear that they are keen to see more involvement of NZIC members in these meetings.

## BRANCH NEWS

### *AUCKLAND*

The Branch has had a relatively eventful programme recently with two interesting speakers at Branch meetings. **Prof. Allan Canty** gave the 2005 RSC Australasian Lecture (see above) and **Prof. Bob Grubbs** (CIT), a 2005 Nobel laureate (see elsewhere) spoke on *Metathesis catalysts for the synthesis of large and small molecules.*

NZIC members will be saddened to hear of the recent death of **Dr. Allan Aspell** after a period of illness. Allan was NZ's foremost analyst of environmental water and air samples. Until his untimely retirement he ran the highly regarded consulting analytical firm Allan Aspell and Associates on Auckland's North Shore. Allan was prepared to tackle awkward and technically demanding jobs and will be greatly missed.

Congratulations to Committee member **Dr. Jadranka Travis Sejdic** on her appointment to a Senior Lectureship in Macromolecular Chemistry at the University of Auckland.

### *Chemistry Department UA*

Congratulations go to **Prof. Margaret Brimble** (*Turning metabolites from microorganisms into medicines using molecular chess*) and **Dr. Peter Boyd** (*Photoactive fullerence-porphyrin constructs*) who each secured $745,000 in the 2005 Marsden funding round, and to glass-blower **Mike Wadsworth** who won the Art Glass Competition at the recent Australasian Symposium on Scientific Glassblowing (Perth) with a beautiful and highly distinctive wine glass design. **Dr. Rudolf Kiefer** (Freiburg, Germany) has joined the Polymer

Electronics Research Centre as a post-doctoral researcher to work on polymer actuators.

## *CANTERBURY*

Recent Branch events have included a series of talks by truly excellent speakers. In August **A/Prof. Juliet Gerrard** (Biological Sciences) spoke on her research into the *Evolution of quaternary structure in an antibiotic target – dihydrodipicolinate synthase*. In September **Prof. Robert H. Grubbs** (an Erskine visitor from Caltech) gave a talk entitled *Ruthenium-based olefin metathesis catalysts: design, mechanisms and applications* about his work which earned him the 2005 Nobel Prize (see elsewhere). A week later the visiting RSC Australasian lecturer **Prof. Allan Canty** continued the catalyst theme with his nation-wide NZIC lecture (see above).

We welcome three new members to the Canterbury Branch committee: **Sarah Lundy**, a student in the Chemistry Department, **Alisa Roddick-Lanzillotta** from Canesis, and **Darren Saunders** from ESR.

Bob Grubbs holding Rutherford's Nobel medal

Helen and Bob Grubbs cutting a celebratory cake

L-R: Peter Steel, Bob Grubbs and Martin Banwell

### *Chemistry Department UC*

The Department recently hosted **Profs. Martin Banwell** (ANU) and **Robert H. Grubbs** (CIT) as Erskine visitors. Having a visiting lecturer win the Nobel Prize while in our Department has been quite an experience and our heartiest congratulations go to Bob. Unfortunately as a result of this award his stay was cut short. **Prof. Chris Pursell** (Trinity University, Texas) has commenced a sabbatical year working with **Leon Phillips**. **Rebekah Pawley** has joined **Ward Robinson** for 6 months as an undergraduate exchange student from the University of Bath.

In August, **Richard Hartshorn, Laurie Anderson** and **Jan Wikaira** hosted the Canterbury Branch of the Institute of Fire Engineers to provide an overview of the safety procedures in the teaching and research laboratories, and the chemical store of the Department. The fire fighters were surprised to find much less danger than they had anticipated.

Congratulations go to a number of people in the Department: **Andrew Abell** and co-workers won a Marsden Fund grant for their *To beta or not to beta, that is the question?* Project; the review by **Peter Steel** in *Accounts of Chemical Research* has been listed as its fifth most accessed article this year, and **Jan Wikaira** has been awarded a 2005 UC Teaching Medals for 2005. PhD degrees have been completed by **Glen Fern** (Owen Curnow supervisor), and **Barbara Thomson** (part-time candidate with Andrew Abell and Ian Shaw while continuing to work at ESR). PhD student **Kelly Anderson** was one of three to be awarded an *IUPAC Best Poster Prize* at the recent 40th IUPAC Congress in Beijing. **Anna McConnell** is the recipient of a prestigious Woolf-Fisher prize that is to support her PhD studies at Oxford University. **Sam Edwards**, a PhD student with Colin Freeman and Murray McEwan has been selected as a Top Achiever Doctoral Scholar in the 2005 round. **James Bull**, a 300-level student, has been awarded a UC summer scholarship to work with Peter Harland and Bryce Williamson. **Emelyn Tan** and **Andre Pinkert** were members of the team that won the inaugural *College of Science Quiz*.

Department Prizes have been awarded to **Annabel Murphy** (Ralph Earle Jr Prize for best 2nd year PhD review seminar) and **Alan Downward** and **Anna McConnell** (Fenwick Prize for the best 400-level demonstrator in 1st-year labs – shared). **Jenni Gadd, Michelle Hamilton** and **Ben Perston** have received support for research and conference travel from the Evans Fund.

## *MANAWATU*

**Lucy Meagher** has moved from Agresearch's Food and Health Group to Fonterra Innovation, PN. She joins the Analytical Development Team working with **Steve Holroyd** on the development and implementation of analytical chemistry methods related to the dairy industry. **Benny Theng** attended the 13th International Clay Conference at Waseda University in Tokyo where the majority of the ca. 300 attendees were Japanese, many young; this reflects the healthy state of clay science and the relatively stable funding system there. The oral sessions covered a variety of topics from the crystal chemistry and reactivity of clay minerals to industrial and environmental applications and there were five special symposia. It was at the *Clays and Polymers* symposium that Benny gave his invited paper. The organizers included a few novel themes, such as *Clays and Human Health* and *The Clay-Biology Interface*. A post-conference tour to the Hojun bentonite mine and factory in Gunma Prefecture was enjoyed by Benny and his wife. He also visited **Hideo Hashizume** (National Institute for Materials Science, Tsukuba) to assess the thermal stability of some organoclays using a specially equipped X-ray diffractometer.

### *Massey University*

**Emily Parker** has been awarded the Easterfield medal (see above) donated by the Royal Society of Chemistry in honour of the late Sir Thomas Hill Easterfield. **Mark Waterland** was presented with the Massey University Early Career Research Medal by the **Hon. Steve Maharey** at an awards dinner held at Parliament. Mark's major research focuses on Raman spectroscopy, the study of light spectra to determine the chemical composition of substances, and the physical properties of molecules, ions and atoms.

**Photo Credit:** Mark Waterland, Massey University Early Career Research Medal recipient.

**Bill Williams** has received a Marsden grant to investigate the nanomechanical structure-function relationships in nature's structural biopolymers with single molecule stretching; **Paul Plieger** has been awarded a Fast Start grant related to his work using supramolecular chemistry in the design of anion drug delivery; Postdoctoral funding has been awarded to **Eric Ainscough** and **Andrew Brodie** for their projects involving novel phosphazene molecules; **Carol Taylor** is overseas on sabbatical leave at the Harvard University until early next year; **Trevor Kitson** has been awarded the NZIC Chemical Education Prize, and **Gavin Hedwig** and **Carol Taylor** have been made fellows of the NZIC.

**Amy Ballantyne** recently summarised her research in a seminar that followed the successful defence of her thesis. Amy examined terthiophenes polymerization and polymer characterisations. Part of her research was carried out at Wollongong University where she investigated the possible applications of the polymers in devices such as actuators and batteries.

## *OTAGO*

**Henrik Kjaergaard** gave an invited addresses at the *Water Dimers and Weakly Interacting Species in Atmospheric Modeling* workshop at the European Centre for Molecular and Atomic Calculation in Lyon and the IUPAC workshop *Hydrogen Bonding and other Molecular Interactions* in Pisa. He has joined the IUPAC sponsored task group *Defining the hydrogen bond* and gave a seminar at Caltech on his way to Pisa.

Other members from the Chemistry Department have also been out and about. **Penny Walsh, Natasha Lundin** and **Keith Gordon** attended the International Symposium on Photochemistry and Photophysics of Coordination Compounds (ISPPCC) in Monterey (CA), a meeting that brought about 70 scientists together to discuss excited state properties of metal complexes. Talks ranged from solar cells to chemosensors and there was significant emphasis on theoretical studies – **A/Prof. Keith Gordon's** talk was in such a session. A lot of interest was shown in the theoretical work showcased by the Otago group. Keith also attended a meeting in Dallas hosted by Noble laureate **Prof. Alan MacDiarmid**, in which a new class of electronic polymers based on azanes was described; by using a modification of the well-known preparation of polyaniline it is now possible to create a new series of polymers possessing an N-N backbone. Keith's group are now involved in examining spectroscopically and modelling theoretically these materials.

**A/Prof. Keith Gordon** and **Prof. David Officer** visited Prof. Leslie Dutton's lab at the University of Pennsylvania to establish details for objectives associated with Marsden grant *Artificial Photosynthesis: Mimicking Light Harvesting*. Prof. Dutton is an expert in maquette synthesis and handling and as these house porphyrin species they are a critical part of the programme. Keith also visited Korea as part of the FoRST Science Mission in which an MoU was signed with KOSEF (a major science funding agency in Korea). Visits were made to a number of Korean research facilities and Keith also hosted a breakfast meeting with scientists from Seoul National University in his role as Focal Point Coordinator for interfacing the Advanced Materials and Nanotechnology areas. The visit provided an opportunity for information transfer between the two nations in a number of science areas.

**Tracey Clarke, Cushla McGoverin, Penny Walsh,** and **Keith Gordon** recently attended the Australasian Conference on Vibrational Spectroscopy at the University of Sydney. A wide range of vibrational spectroscopists gathered with the Otago participants presenting their studies: *chemometrics in drug formulation* (Cushla), *theoretical and spectroscopic studies of modified porphyrins* (Penny), *electronic materials* (thiophene oligomers) (Tracey), and *metal polypyridyl complexes* (Keith). **Tracey Clarke** took out the student oral presentation prize. Cushla and Penny also attended a workshop on advanced chemometric techniques.

The Biochemistry staff had **Dr. Eng Tan** give a seminar on bifunctional inhibitors of catechol-o-methyltransferase. They also look forward to two exciting arrivals this summer: the arrival of newly appointed **Prof. Kurt Krause** and installation of a new system for macromolecular X-ray crystallography. Krause's research interests lie in the structure of virulence factors, drug targets and related enzymes from pathogenic micro-organisms. Currently at the University of Houston, he will hold the second chair of Biochemistry. The X-ray machine, which includes copper and chromium anodes to allow collection of anomalous dispersion data from crystals of seleno-methionine protein, is also a Texan - a MicroMax007HF with R-Axis image plate detector from MSC/Rigaku. The appointment and purchase reinforce Otago's commitment to structural molecular biology and complement last year's acquisition of a CD spectrophotometer.

Protein chemistry at Otago has also received a lift from the purchase of a new ABI 4800 MALDI-TOF-TOF. The upgrade package also includes a Dionex nanoLC for LC/MS, offers a significant increase in capability for ultra low volume LC sample preparation, and represents a campus-wide initiative from **Drs. Vernon Ward** (Microbiology/Immunology) and **Catherine Day** (Biochemistry), **A/Prof. Richard Cannon** (Oral Sciences), and **Profs. Warren Tate** (Biochemistry) and **Stephen Robinson** (Paediatrics and Child Health).

Congratulations are extended to Biochemists, **Dr. Catherine Day** and **A/Prof. Iain Lamont**, and chemist **Prof. Keith Hunter** for their successes in the recent Marsden round. Finally we congratulate **Prof. Tony Reeve** (Biochemistry) for receiving the 2005 University of Otago Distinguished Research Medal.

## *WAIKATO*

### *University of Waikato*

**Michèle Prinsep** was one of the NZ group at the 4th Euroconference on Marine Natural Products (ECMNP) in Paris and presented a paper entitled *Further Chemical & Biological Studies of the Pterocellins, Alkaloids from the Marine Bryozoan* Pterocella vesiculosa. She then spent two weeks at the National University of Singapore in Singapore meeting with colleagues and giving a series of graduate workshops entitled *The Chemical Ecology and Pharmaceutical Potential of Natural Products.*

### *NIWA*

**Michael Ellwood** has returned from a successful trip to the University of Canberra to use Prof. Bill Maher's inductively coupled plasma mass spectrometer for measurements of germanium speciation in sponge and diatom samples. Such measurements aid in understanding the cycling of germanium in the ocean. Michael was able also to catch up with Prof. Patrick De Deckker at the ANU. Bill, Patrick and Michael have formed a collaboration to see whether the germanium signature of fossil siliceous organisms can be used to track changes in ocean during the past.

### *WINTEC*

The Waikato Institute of Technology (Wintec) is again running its Basic (Nov. 29 – Dec. 2) and Advanced (6-9 Dec.) Gas Chromatography courses later in the year. Anyone interested should contact Denise Martin: denise.martin@wintec.ac.nz.

## *WELLINGTON*

September saw **Dr. Tony Clemens** (Research Manager, CRL Energy Ltd.) tell us about the *Designing, Building and Commissioning a Coal to Fuel Cell Grade Hydrogen Production Plant.* The evening involved his talk and then a site-visit. As government has invested in a six-year research project *Hydrogen Energy for the Future of NZ* to create the technological platform required for us to transition to a hydrogen energy economy and realise its benefits, Tony was able to describe the major component that focuses on the production of high purity hydrogen from NZ coal. The likely role of coal-based hydrogen production technologies in the development of a hydrogen economy in NZ (given that NZ has sufficient recoverable coal reserves to last for centuries, dwindling gas supplies and insufficient economically viable renewable resources to meet likely future demand) was discussed recognising that a transitional period of several decades will be needed during which hydrogen production from coal will play a major role. Several applications of coal to hydrogen technologies were considered including large-scale plant for production of the hydrogen required to meet the needs of a future, hydrogen fuel cell powered transport fleet.

October provided two meetings. First was RSC Australasian Lecturer **Prof. Allan Canty** (see above) while in mid-month **Sean Bearsley** (Product Development Manager, Higgins Contractors Ltd.) spoke on *Bitumen: A Chemical Solution to Civil Engineering Problems.* Bitumen is one of the oldest construction materials known to man and Sean described the considerable challenge to civil engineers that still exists in predicting its physical properties despite its 10,000 year pedigree. It is an extremely complex, naturally occurring material that varies by source and from refinery. Although it behaves like an oil, it is not an oil; it has polymeric properties, yet is not a polymer; is resinous, yet is not a resin. This confusing behaviour and the rheological attributes of bitumen were very nicely described in a lecture that provided the audience with far more insight than they had expected.

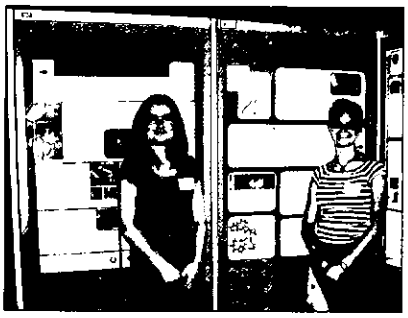
### *Victoria University*

Congratulation go to **Drs. Kate McGrath** and **Peter Northcote** who were promoted to A/Prof. in the 2005 exercise.

Recent visitors to the School have included **Profs. Allan Canty** (on his RSC Australasian tour) and **Bob Grubbs** (Caltech) who spoke on *Metathesis catalysts for the synthesis of large and small molecules* a few hours ahead of the announcement of his Nobel Prize (see elsewhere in this issue).

**Peter Northcote** and his Branch-sponsored students **Wendy Popplewell** and **Joanna Wojnar** attended the 4th European conference of Marine Natural Products in Paris in September. The venue, the Muséum National d'Histoire Naturelle, provided for lectures in the same auditorium that many of the great French chemists, including Lavoisier, had lectured in. The conference attracted 210 participants from 22 countries and, though largely from Europe, it had a strong Australasian contingent, highlighted by Canterbury's **Prof. Murray Munro** giving the opening plenary lecture; three other New Zealanders including Peter addressed the conference.

The poster sessions were well attended with many leaders in the field offering helpful suggestions to those presenting. Joanna and Wendy gave posters detailing *The Chemical Characteristics of Selected New Zealand Nudibranchs*, and *Novel Compounds from the New Zealand Marine Red Alga* Phacelocarpus labillardieri.



### *IRL*

**Gary Evans, Richard Furneaux**, and **Peter Tyler** attended the fall ACS Meeting in Washington DC. A highlight was the Tetrahedron Symposium honouring Prof. Koji Nakanishi (Tetrahedron Prize for Creativity awardee). Nobel laureate Barry Sharpless was fashionably late for his presentation having been flown down to Mexico to observe Hurricane Katrina from above *by an old Airforce buddy;* he was forced to land in Mexico and this delayed his return flight somewhat! The *Iminosugars: Therapeutic Potential* symposium highlighted (among others) the IRL work. Following the ACS national meeting the trio flew into hurricane-lashed Birmingham (Alabama) to visit Biocryst Pharmaceuticals to review progress on the Immucillin compounds Fodosine™ and BCX-4208 currently in phase-II trials for a variety of cancers and phase-I trials for psoriasis. A special protocol assessment for Fodosine™, in the treatment of relapsed or refractory T-Cell Leukemia has now been filed with the FDA and is a significant step in this compound making it to market. They also visited the Albert Einstein College of Medicine in the Bronx, NYC to present their latest results on *Transition State Design and Synthesis*.

**Graeme Gainsford** attended the 20th International Union of Crystallography Congress in Florence in August as one of ca. 2800 attendees, ¼ of whom were students and 450 bursary-supported. Graeme also represented NZ at the Assembly Meeting. Florence (and the Fortezza da Basso) was an excellent venue, with some outstanding meeting presentations and functions. Graeme also attended an *Acta Crystallographica* Editorial Board meeting at Montecatini; NZ representation at this meeting far outweighed our relative numerical size!

**Ruth Falshaw** and **Susie Carnachan** (with NIWA assistance), have succeeded in growing the NZ red seaweed Gigartina atropurpurea, starting with bare Korean string. They have achieved spore settlement, outgrowth from microscopic spores to plantlets of ~1 mm in length, and then outgrowth of the gametophytic life stage (male and female plants) on a mussel farm in the Marlborough Sounds. This remarkable scientific achievement required multi-disciplinary skills but a crucial chemistry input. This seaweed contains a κ-II carrageenan that IRL has shown to be excellent at stabilizing cocoa suspensions in milk, *viz*. chocolate milk drinks.

## 2005 RSNZ Fellowships Awards

The following were elected at the RSNZ Academy AGM on Nov. 16:

**To Honorary Fellowship – Professor Paul J. CLARKE** - Professor of Geography, Bristol, UK

**To Fellowship**

**Jacob BERCOVITCH** – Political Science, Canterbury University

**Roger J. BOWDEN** – Economics and Finance, Victoria University

**John S. BUCKLETON** – Principal Scientist (Forensic) ESR Auckland

**Roberta L. FARRELL** – Biological Sciences, Waikato

**Bakhadyr M. KHOUSSAINOV**– Computer Science, Auckland

**Graham S. LE GROS** – Director Malaghan Institute, Wellington

**Neil E. PEARCE** – Public Health (Massey University, Wellington)

**D. Norman SHARPE** – Medical Director, National Heart Foundation, Auckland

**A. James SNEYD** – Applied Mathematics, Auckland

## NZAS Awards

New Zealand Association of Scientists (NZAS) Marsden Medal recipient is Dr Kevin Tate of Landcare Research, Palmerston North, for his contribution to, and leadership of, research into ecosystem processes and climate change.

New Zealand Association of Scientists Shorland Medal is awarded to Dr. Adya Singh, of Scion (New Zealand Forest Research Institute, Ltd), Rotorua, for an outstanding contribution to basic and applied plant and wood sciences.

New Zealand Association of Scientists Research Medal is awarded to Dr Fiona McDonald of the Department of Physiology, University of Otago for her outstanding physiological research over the last 3 years.

The Association's Science Communicator Award is presented to practising scientists for excellence in communicating to the general public in any area of science or technology. The 2005 winners are Alison Campbell and Penny Cooke of the School of Science and Engineering at Waikato University for their adaptation of the idea of Café Scientifique to provide opportunities for the public to listen and contribute to discussions and debates on scientific issues, and to learn about the methods and significance of science.

## RACI INORGANIC CHEMISTRY DIVISION

### Alan Sargeson Lectureship Award

The Division has established a prestige Award open to early career researchers who have made a significant and innovative individual contribution to Inorganic Chemistry predominantly in Australia or New Zealand. The Award is open to any Australian or New Zealander, or a Permanent Resident of either country, who is within ten years of the award of their PhD on the closing date for applications; nominees must be financial members of the RACI or NZIC at the time of nomination.

The Award comprises a lecture tour of Australian and NZ University Chemistry Departments and/or other research institutions. Applications for the inaugural 2006 Award are to be made by nomination only. A detailed CV (with publications and/or other research output), names and addresses of three referees, and the title and abstract of the intended lecture are required; see:

www.raci.org.au/division/inorganic/awards.html

Nominations close with the Divisional Secretary [Dr. Peter Junk, School of Chemistry, Box 23, Monash University, Clayton, Vic. 3800] on 27 January 2006.

# New Zealand Science Scene

## Coconut provides alternative fuel

Two engineering students from the University of Auckland have found another use for the humble coconut.

The coconut palm is considered one of the most versatile plants in the world. The leaves can be used to thatch roofs, the wrapper of the palm can be used as toilet paper and the shells made into many forms of containers.

Samoan, Dominic Schwalger and Fijian, Penaia Rogoiumari have been investigating the use of pure coconut oil as a fuel to run diesel engines.

For the first time in New Zealand they have had the engine running on the pure oil as well as in a blend with traditional diesel.

Some biodiesels require complex processing before use but Mr Schwalger said producing coconut oil for use in standard engines is a simple process. "What we have shown is that without any modification to either the pure oil or the engine you can use it as an alternative fuel." He said.

The ease of processing, along with a ready supply of coconuts could make coconut oil a viable option to run equipment like generators and boat engines Mr Rogoiumari said.

## Top Achievers rewarded with Scholarships

Two Chemistry students were successful in winning Top Achiever Doctoral Scholarships in the latest round.

Samuel Edwards, a Physical Chemistry student at the University of Canterbury and Kim Meyer, an Inorganic Chemistry student from the University of Auckland were awarded scholarships along with 38 other students.

The scholarships are fully funded by the Government. They provide the PhD student with $28,000 per year for three years as well as paying for the student's university fees.

The aim of the scholarships is to help increase the number of highly trained researchers and graduates as well as signal the value of intellectual skills and abilities and their importance to New Zealand.

The next round closes on December 14.

## Biotech Company of the year winner

This year Neuren Pharmaceuticals has won the NZBio Biotechnology Company of the Year Award.

Neuren's lead compound, Glypromate©, has been shown to provide potent protection for multiple types of cells and areas of the brain against cell death and its consequences. Tests on this naturally occurring compound have progressed through Phase I trials and Neuren is currently conducting Phase II pharmacokinetics and safety trials at a number of New Zealand and Australian institutions.

Neuren Pharmaceuticals was formed from the merger of NeuronZ Limited and EndocrinZ Limited, two University of Auckland 'spin-off' businesses.

Highly commended was Living Cell Technologies Ltd, who has their research and technology department based in Auckland.

The award is sponsored by NZBio, New Zealand's biotechnology industry organisation. It is open to biotechnology and life sciences companies at any stage of business development. Entries are judged on aspects of demonstrated skill and success in proprietary technology, business development, and entrepreneurial strategy.

Winners in previous years have been Proacta Therapeutics Limited (2004) and Protemix Corporation Ltd (2003)

## Update on Chem-E-Car Competition

For those wondering how the cars powered by a chemical reaction went in the Grand Final mentioned in the September journal, the results are in.

Two teams from the University of Canterbury were placed first and second in the poster section of the Grand Final held in Brisbane during the Chemeca Conference.

An Auckland team won the performance section while the Canterbury team with the aluminium-air cell powering an electric motor came in third.

The Canterbury teams' success lead to them being approached by the chairman of the Asian and Pacific Confederation of Chemical Engineering (APCChE) conference. He invited them to take part in a Chem-E-Car challenge at their conference in Kuala Lumpur next year.

## NZ discovered drug yielding positive results

A drug discovered in New Zealand is showing promising results in reducing the risk of cancer progression in lung cancer

The drug is AS1404 and preliminary results from a Phase II clinical trial show the addition of the vascular disrupting agent, AS1404 to standard chemotherapy reduces the risk of cancer progression more effectively than chemotherapy alone in patients with lung cancer. AS1404 works by attacking blood vessels that transport nutrients to cancer cells.

The Phase II trials are being conducted in hospitals in France, Germany, Australia and New Zealand.

Over a decade ago AS1404, chemical name DMXAA, was discovered by Professors Bruce Baguley and William Denny and their teams at the Auckland Cancer Society Research Centre, University of Auckland. It was acquired with exclusive worldwide rights in 2001 by Antisoma, a biopharmaceutical company based in the United Kingdom. In 2002, Antisoma formed an alliance agreement with Roche to develop and commercialise products including AS1404.

## Chemistry Olympiad

The training group selection examination for the 2006 Chemistry Olympiad was held on 3 November. 174 entries were received from 55 schools. This was the highest ever number of entries. 18 schools entered students for the first time. Offers have been made to 37 students from 18 schools to join the training group. Students from 3 schools who had not put forward students before, received offers, including the student with the highest mark in the selection exam. The 2006 International Chemistry Olympiad will be held 2-11 July, 2006 in Gyeongsan, Korea.

## Pacifichem 2005 Update

15-20 December 2005

Registration & Accommodation Available via the Web

*www.pacifichem.org*

The Technical Symposia programme is set, the Program Schedule is available for inspection, and a Pacifichem 2005 Itinerary Planner can help you with decisions on which of the symposia and sessions/ presentations that you wish to attend - all via the web site. There are some 11,501 presentations in the 168 symposia many in the numerous poster sessions. The contribution from NZ is also at an all time record with some 67 papers accepted for presentation. Registration can be completed and accommodation booked via the secure web site but NZ participants are reminded again of the potential difficulties of getting to and from Hawaii in December; if you have not secured rtravel reservations you are advised to attend to this as a matter of urgency. Pacifichem 2005 promises to be the biggest and best yet!

## Conferences and Seminars

***57th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy***
***March 12-17, 2006, Orlando, Florida USA***

The world's most comprehensive coverage of the latest developments in the traditional and emerging disciplines of analytical chemistry and applied spectroscopy. The programme will be both broad in scope and well balanced. Major focus areas of the programme will include bioanalytical chemistry (proteomics, genomics, and metabolomics), pharmaceutical chemistry, nanotechnology, environmental chemistry, forensic analysis, food analysis, applied molecular spectroscopy, mass spectrometry, and chemical separations.

**http://www.pittcon.org**

***4th ISE Spring Meeting 17-20 April 2006, Singapore***

The theme is Electrochemical Materials Science: Fabrications, Characterisation and Applications with the following sub-themes: hybrid and composite materials, molecular tailoring and engineering, supramolecular chemistry, MEMS/ NEMS, scanning probe microscopy, nanoelectronics/nanodevices and nanobiotechnology.

**www.ise2006.org**

***International Conference on Organometallic Chemistry, Zaragoza, Spain 23-28 July 2006***

All modern advances and trends in organometallic chemistry will be discussed. This will be a special occasion as it is the first time since its inception in 1963 that this important international scientific event will take place in Spain. Organometallic chemistry is one of the more active areas of Spanish chemistry.

Zaragoza is a lively, animated city with more than two thousand years of history, offering many cultural and tourist attractions.

***http://wzar.unizar.es/icomc2006/***

***19th International Conference on Chemical Education 12-17 August 2006, Seoul, Korea***

The 19th ICCE has adopted a theme of "Chemistry and Chemical Education for Humanity". Accordingly, this conference will provide an ideal opportunity for chemistry-related professionals to gather together to share and exchange their experiences and expertise related to such subjects as recent trends in chemistry and chemical-related education, dissemination of chemistry/chemicals information, innovative instrumental methods, the latest research findings, and the benefits of the chemistry/chemicals for humanity and society.

**www.19icce.org**

***1st European Chemistry Congress, 27-31 August 2006 Budapest, Hungary***

This Congress aims to be a showcase for chemical sciences in Europe and will bring together chemical and molecular scientists from industry, academia and government institutions across Europe and from around the world. Keynote lectures will highlight important areas of chemistry and invited lectures will be part of a coordinated series of symposia focusing on the latest developments in a wide variety of topics.

**http://www.euchems-budapest2006.hu/**

***INTERACT 2006 September 24-28, 2006, Perth, Western Australia***

Incorporating the 13th Australasian Electrochemistry Conference (13AEC), and meetings of the RACI Analytical Chemistry and Environment Divisions, and the Australasian Society for Ecotoxicology.

**www.promaco.com.au/conference/2006/raci/**

# Changes Afoot for US Patent Law

By John Landells and Helen Palmer

A bill currently before the US congress proposes some sweeping changes to the US patent system that would bring US patent law more into line with other first world countries. US patent law has undergone regular amendments in recent times, however, Congressman Lamar Smith, who introduced the bill, has said that the changes proposed will be the most comprehensive seen in the last 50 years.

The Patent Reform Act of 2005 (bill HR 2795) was introduced on 8 June 2005 but has since undergone some significant modifications as it has moved through congress. Presently, some of the proposed changes are:

- Move from "first to invent" to "first to file"
- Introduction of post-grant opposition proceedings
- A revision of the provisions that presently provide for treble damages in cases of willful patent infringement
- Introduction of a system to allow third parties to challenge a patent application by introducing new information to the USPTO up to six months after the date of publication of the patent application
- A "duty of candor and good faith" imposed on persons associated with the filing and prosecution of a patent application and on third parties who are involved in proceedings against a patent or patent application before the USPTO
- Removal of the "best mode" or "best method" requirement in patent specifications

For some time the US has differed from other jurisdictions in that the winner of the race for patent rights is the party that can show it was the "first to invent" the subject matter of a patent application. Essentially the rest of the world has relied on the more pragmatic system of providing patent rights to the applicant who was "first to file" a patent application. In other words, the person who first applies for the patent will win the race for the patent rights. Although the present US system of "first to invent" may be considered fairer, it can be complex, difficult to administer and can result in expensive litigation over who was the first applicant to invent. However, one of the most compelling reasons for the US to change from "first to invent to "first to file" is simply to provide harmonization of global patent laws. This change would bring the US more into line with other countries. The move from the present US system of "first to invent" to a "first to file" system is certainly one of the most interesting changes that has been proposed.

Another area in which the Act would bring the US patent system closer to other counties is the proposed implementation of a post-grant opposition procedure. The post-grant opposition procedure is an internal procedure through the USPTO and would provide a cheaper and more expedient means for any member of the public to challenge the validity of a patent. The opposition period is proposed to run for nine months from the grant of a patent with an extension of a further six months possible if good cause exists.

Another amendment to the US patent law includes the removal of the "best mode" or "best method" requirement in patent specifications. Presently, one of the requirements for patent specifications in the US is to disclose the best method of performing the invention that is known to that applicant at the time of filing. One of the arguments in support for the omission of the "best method" requirement is that the subjectivity within this requirement can provide the basis for much litigation.

It will be very interesting to see the final shape of the Act once it has been passed. It is hoped that the recently proposed legislation will provide for not only better harmonization of global patent laws but also greater certainty for all parties involved in the prosecution, issuance and enforcement of US patents.

A reminder: if you have any queries regarding patents, or indeed any form of intellectual property, please direct them to:

Patent Proze
Baldwins
PO Box 852, Wellington
Email: email@baldwins.com

*Helen Palmer and John Landells of Baldwins specialise in chemistry and biotechnology patents. Helen joined Baldwins in 2000. She has a PhD in chemistry from The University of Auckland and postdoctoral research experience. John joined Baldwins in 2003. He has a PhD in chemistry from the University of Otago and is in the final stages of completing an LLB at Victoria University of Wellington.*

# Edwin (Ted) Percy White BSc MSc DSc [1915-2005]

Ted White was born in Auckland, educated at Mt. Albert Grammar and at Victoria University gaining his BSc in 1936 and MSc in 1938. He worked in the Chemistry Department at Victoria until 1940 when he joined the Department of Agriculture transferring to the Ruakura Research station in Hamilton in 1944. His main area of interest was in plant chemistry. In 1951 the NZIC awarded him the ICI Prize and Medal for outstanding achievement in chemical research. By 1959 he had published 28 papers on the chemistry of legumes for which he was awarded a DSc degree by Victoria University.

Ted was best known for his isolation, purification and structural analysis of sporidesmin, the toxin causing facial eczema in sheep and cattle. Lack of identification of the toxin, even the source of this toxin - was it bacterial, fungal, or a plant metabolite - had been a major barrier to understanding the disease and to finding a solution. A *breakthrough* in facial eczema research was the outcome of Ted's experiments which had concentrated the toxic material to about 1/200,000 the weight of the dried toxic grass. This material, suggestive of a fungal origin, was subsequently confirmed as such from isolation by staff at Ruakura (later identified as *Pithomyces chartarum*) from toxic grass and growing the pathogen in culture. Shortly after this discovery, Dr. Dick Synge, a Nobel Laureate from the Rowett Research Institute in Scotland, arrived to collaborate with Ted to isolate the toxin. Combining Synge's knowledge of chromatography and Ted's experience in processing plant extracts, the toxin was isolated in a crystalline form and its empirical formula established. These milestones in agricultural research were key steps in understanding facial eczema and provided the opportunity to understand the epidemiology of the disease and the biochemistry of the toxin.

As well as his central role in facial eczema research, Ted contributed to research in other animal disorders such as ryegrass staggers, fescue foot, and ergot tremors. During his long career in animal research he published over 80 research papers. He retired in 1980.

Ted's interests were diverse and included a passion for unusual plants and roses. He had an extensive garden at his rural property at Gordonton. It was based not on garden design but on the biology of his precious plants that included more than 200 old fashioned roses. A quiet, unassuming man, he was very well liked and respected by his many colleagues. Always willing to provide knowledge and advice to his peers and especially young scientists; he is to be regarded as one of this country's high achievers in chemistry.

Doug Wright, October 2005.

# Peter P. Williams FNZIC [1932-2005]

Peter Williams passed away on September 10 shortly after his 73rd birthday. Peter joined the Chemistry Division of DSIR as a bursar student in March 1950, graduating from Auckland University with an MSc in 1954 returning to the Physical Chemistry Section in 1955 to apply IR spectroscopy to the study of clay minerals. In 1957 the X-ray diffraction equipment was upgraded with a new generator and X-ray crystallography then became Peter's main area of expertise. However, he was the operator of choice for the early $^1$H NMR equipment and demonstrated a wide understanding of spectroscopic techniques. With DSIR support, he gained a crystallography-based PhD degree at King's College (Cambridge) in 1962.

Peter was into drugs well before they became known to general public! Actually, he was *into* their structures and chemistry. He focused particularly on barbituric acids and their derivatives and was associated with Dr. Rob McKeown in this work; the studies were designed to support drug identification problems in the toxicology and forensic work of the Division. Peter used diffraction studies wherever they were required so that quantitative X-ray diffraction was developed under his tutelage for the estimation of mineral phases in cement and rocks. One of his fellow-workers noted that Peter was one of the quiet achievers of the lab; his publications included a 1959 *Nature* article.

He served as Section Leader and Manager, Special Projects. In the latter part of his career, he became a computer-coding specialist, playing a major role in the use of small computers in implementation of blood alcohol analysis automation systems. He was justifiably proud of how much information he could store and manipulate in 16-bit (computer) words. He worked with the late Dr. John Bailey, and was the perfect collaborator as he handled the early days of the system as it was tested through the NZ Courts. Peter was a strong supporter of the Institute editing the 50th jubilee book *Chemistry in a Young Country*. He retired in 1991 just before the demise and restructure of DSIR.

## Personal reminiscences

Peter hired me in 1974 as a computing support person to enable interactions with the remote DSIR and Ministry of Works mainframe computers. However, Peter knew my first love was X-ray crystallography and he allowed me and other members of Physical Chemistry considerable latitude in developing our own style and research contacts. This was one of his strengths; one of the others was his ability to craft words. I remember the masterly way he would assess and place the crystal structures I was studying into one of the major high-level goals of the government of the day; I am grateful for his continued interest and support throughout my career.

Peter was a quiet and unassuming member of staff, fondly mentioned as parts per Williams when ppm became common measure! He was approachable, using a leadership style that was thoughtful and *hands-off*: qualities that retain their virtue. There was something of the English gentleman in Peter that stood him out from other managers: somewhat private and considerate.

Science in New Zealand is poorer for his passing.

Graeme Gainsford, September 2005.

# How to Poison Your Spouse The Natural Way, A Kiwi Guide to Safer Food

By Jay D Mann Ph.D

With a title that catches the eye of any visitor, this book makes a great addition to your coffee table or book shelf.

It is a fascinating read about the many foods and food additives we eat regularly and whether or not they are hazardous. It is written with a broad readership in mind as the author states; "by making this book less technically imposing, it might get the message over to a broader public."

Jay Mann is a plant biochemist, who retired from Crop and Food in 1993. He has written over one hundred papers including a paper for Chemistry in New Zealand in 1995 entitled "Dietary Hazards, Real and Imagined". Dr Mann says that paper was part of the process, which led to the book.

The subject of food is a very topical one. There are a large number of books on the subject of safe foods but this book takes an interesting perspective from the biochemistry of nature. Dr Mann presents "a guide to avoiding non-trivial risk. My criterion for including any particular food is that there is somewhere a headstone or a hospital record confirming human harm."

Dr Mann has in most cases achieved the admirable goal of providing enough scientific evidence to reference his statements and opinions while keeping the book extremely readable. His frequent use of brief case studies keeps this book away from being just a presentation of the facts and research findings.

It also has some interesting stories about the introduction of new foods in human history including the potato. "In most of Europe, potatoes were rejected as food because they were thought to carry leprosy." His account of the acceptance of new foods culminates in a rational solution to the labelling of genetically modified foods.

The book discusses at length natural plant toxins that can affect humans. It also includes details on shellfish toxins, fungi both beneficial and harmful, herbal medicines and a brief section on food-borne infections. The book corrects commonly held views on some perceived hazardous foods including MSG and food preservatives. The final part of the book covers the more technical aspects of evaluating information presented on food risks as well as chapters on cancer and diet and how to prolong life.

The book is written in a very casual, friendly but passionate manner that makes for lively reading. The topics are broken down with clear headings thus it is an ideal book to dip into and peruse a section as well as reading from cover to cover.

The book could be improved with a little more editing because there are several typographical errors and some sections are not clear on a first reading.

Dr Mann writes "most of the facts in this book are well known to food professionals" however if food biochemistry is not your area of expertise this is an informative and useful book to own. For those who are convinced all natural foods are safe, this book will be a startling read.

The book will make ideal Christmas holiday reading, it is up to you if you decide to read it before or after you consume your Christmas lunch.

The book is published by JDM & Associates and distributed in New Zealand by Nationwide Book Distributors, retailing for $24.99. You can find further information on the website www.saferfood.co.nz

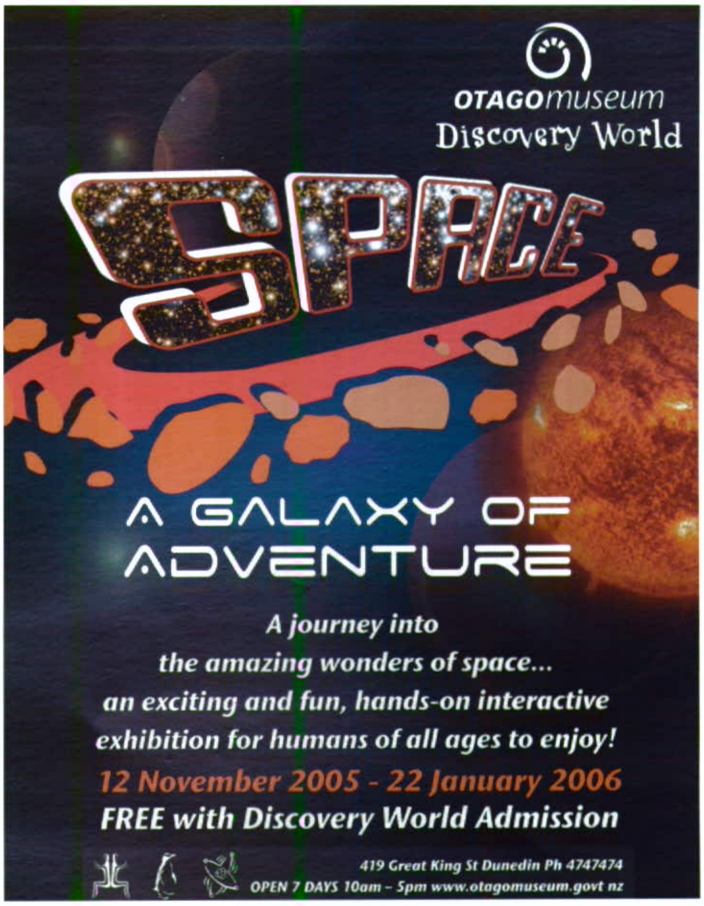
Reviewed by Fiona Summerfield

## New Exhibition at Otago Museum

The Otago Museum is proud to host a new exhibition this holiday season. *Space – A Galaxy of Adventure* will be on display in Discovery World from 12 November 2005 until 22 January 2006. Explore the outer reaches of space with this highly interactive and entertaining exhibition. See the spectacular photographs of Saturn, sent back by the Cassini spacecraft, take a guided tour of our summer night sky, or test your skills in the space shuttle flight simulator.

This exhibition was developed by SciTech Discovery Centre in Perth, Western Australia.

Please phone (03) 474 7474 or visit www.otagomuseum.govt.nz for more information.



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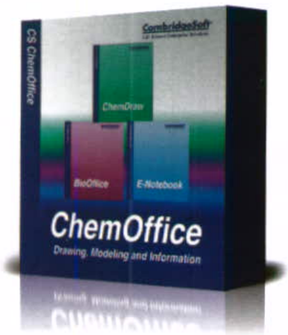
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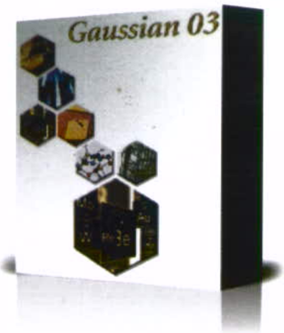
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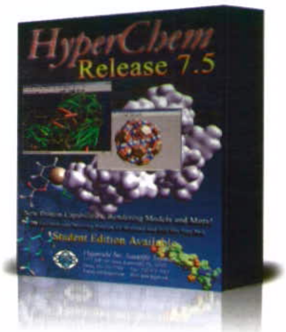
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