chemistry in Australia

September–November 2022

Plastics pollution: why chemistry isn't enough

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- The Chemical Weapons Convention three decades on
- The competitive streak in plant pathogens
- RACI 22 National Congress retrospective

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Rosalind Franklin

To Jenny Sharwood's comments on Rosalind Franklin in the June–August issue (p. 24), I should like to add the following. She says 'By this time [1950s], Rosalind Franklin had pioneered the technique of using X-rays to determine the position of atoms in complex organic molecules'. X-ray crystallographic determinations of organic structures began long before then. The father-and-son Nobel Laureate pair W.H. and W.L. Bragg were surely the originators of X-ray crystallography. I think that the first application to a natural product was the determination of the structure of vitamin D in 1932 by J.D. Bernal (*Nature* 1932, vol. 129, pp. 277–88), who a few years earlier had been a research student under W.H. Bragg. Dorothy Hodgkin (of whom I have written in the March–May issue (p. 5)) announced the structure of penicillin, having deduced it by X-ray crystallography, in 1945.

Jenny Sharwood informs us of the Nobel Prize awarded to James Watson and Francis Crick for their discovery of the structure of DNA. There were three recipients of that Nobel Prize – Watson, Crick and the New Zealander Maurice Wilkins.

According to the entry for Lise Meitner in the Royal Society of London Biographical Memoir, during 1939–45, 11 papers were attributed to her. In about 1939, one paper to which she had contributed was published minus her name, at her own request. As a Jew, she was fleeing from the Nazis and at that particular time for her name to be on the paper might have jeopardised her secrecy. It is not that she was 'not permitted' to put her name on the paper.

Clifford Jones FRACI CChem

Reply: Rosalind Franklin

I did not claim that Rosalind Franklin invented X-ray crystallography or that she was the only pioneer. I credited Linus Pauling with having already deduced the spiral structure of some proteins using X-ray crystallography.

I recently consulted the head of an X-ray crystallography department who studied under Professor Bruce Penfold, who was supervised by Lawrence Bragg at Cambridge and conducted research on the base pairs in DNA. He stated that while others, including Dorothy Hodgkin, had been able to find light atoms in organic molecules, Rosalind made a great breakthrough in her discovery of DNA's double helix structure.

Mindful of word limits, I did not mention that Maurice Wilkins shared that Nobel Prize with Watson and Crick. If I had, I would have also been compelled to talk about how badly he treated Rosalind. Apart from evidence of his undermining her, it is believed that he was the colleague who went behind her back and provided her work to Watson and Crick without her permission.

Lise Meitner may well have sent papers to Britain over the war period, but my sources stated that her hitherto long-time friend and research colleague Otto Hahn, with whom she conducted research in Berlin, with her being the more brilliant partner, stopped her publishing in Germany and further afield in relation to their work on nuclear reactions. He was fearful of how any evidence of him working with someone of Jewish origin might affect his safety and his career. He insisted that she communicate with him by private letter only. For this reason, he was given credit for her work as well as his, and he received the Nobel Prize that she should have shared.

The whole point of my brief stories (an extract of a presentation I gave) about Lisa Meitner, Rosalind Franklin and others was to highlight a serious issue in science. I hope that they instil a determination to bring justice and fair play to and encouragement of women in science, in contrast to undermining, fault-finding and blocking women from all they can achieve and contribute.

Jenny Sharwood OAM FRACI CChem

Apology for stolen knowledge

My thoughts after reading Jenny Sharwood's article (June–August, p. 24) are that perhaps it is now time for IUPAC and the RACI and the RSC and the ACS etc. to offer a formal apology to the women chemists and other female professionals whose work has been stolen, plagiarised, by men! I am happy to sign first a national or international Apology to the Stolen Knowledge of women scientists. I also read the article about the prejudice about women on Wikipedia and so the list goes on and on!

Congratulations to you, to the presidents and the editorial committee and all the team that brought us the new beginning of ways forward. Special thanks go to Ian Rae for his delightful article (p. 42) and my appreciation of a good bottle of red wine goes increasingly to Geoff Scollary.

Ian MacLeod FRACI CChem

New VCE Chemistry Study Design

The final edition of the VCE Chemistry Study Design for 2023–2027 has now been published online, after a very extensive consultation process.

Scroll down to find it at www.vcaa.vic.edu.au/curriculum/vce/vce-study-designs/chemistry/Pages/Index.aspx.

This Study Design will be implemented at Year 11 in 2023 and at Year 12 in 2024.

Chemistry educators will be pleased to see that the periodic table is back in, and the entire course is far more rigorous, balanced and cohesive than that outlined in the draft edition, about which concerns were raised in the December 2021 – February 2022 issue (p. 34).

While there is still a strong emphasis on sustainability, it is placed in meaningful contexts and will encourage worthwhile research. The continued emphasis on quantitative practical investigations, experimental design, and the use of analytical instruments for both chemical analysis and the elucidation of structures of organic compounds are very strong features of the Victorian Study Design.

Jenny Sharwood OAM FRACI CChem

Oh, the humanity!

With these famous words, proclaimed by a reporter as he watched the burning wreck of the *Hindenburg* airship, the burgeoning age of hydrogen was dead. Today, many chemists in RACI are wondering whether hydrogen has been re-born and if a new age of hydrogen, especially for transport, is about to begin.

In February 2018, Elon Musk's *Falcon Heavy* rocket lifted a unique payload into space. Powered (ironically) by the combustion of kerosene with liquid oxygen to make carbon dioxide, the rocket rose to a sufficient height and speed to successfully deploy in its second stage probably the most unusual cargo ever sent into space: a used battery-powered Tesla Roadster owned by Musk himself. Many RACI members might be surprised to know that Musk's Roadster was not the first car in space. It wasn't even the first *electric* car in space. However, despite the high cost of Tesla Roadsters (they sold for well over $200 000), it was by far the *cheapest* car ever sent into space.

Almost 50 years earlier, as part of the space race, *Apollo 15* landed on the Moon, carrying an electric car, a 'Lunar Roving Vehicle' (LRV). The LRV allowed the astronauts to explore further afield than the proximity of their landing site. Made by General Motors, in collaboration with Boeing and others, the LRV cost an estimated US$13 million in 1971 (about A$135 million today). It has been described as the most expensive car ever built, especially since it was only used for three days and then abandoned. At the same time in Australia, General Motors' subsidiary Holden was making its most expensive car, the Statesman de Ville, which it sold for $4800. The Australian-designed (and manufactured) General Motors Statesman had a V8 petrol engine that delivered more than 200 kW. This dwarfs the modest 0.8 kW of total power provided by the 36-volt batteries in the General Motors LRV left behind on the Moon. In contrast, Musk's Roadster has a maximum power output of 215 kW, so it would appear that he won the race for both the *cheapest* and *most powerful* electric vehicle in space.

Today we find ourselves caught up in another race, a race to find the best, most economically viable chemistries to provide clean power for our increasingly populated planet. Increasingly, the choices we make about the cars we drive will have an impact on our climate. All prospects seem expensive, and therefore unpalatable, until we remember the recent prediction by CSIRO that by 2050, without lowering CO_2 levels, weather events could cost us more than $39 billion per year. Advocates for expensive battery-powered vehicles espouse their credentials, while ignoring that they are often effectively coal powered. Advocates for petrol–electric hybrid vehicles claim they deliver a much smaller total CO_2 footprint, and point out the advantages of the smaller batteries involved. Others believe that neither approach can better the potential of fuel cell cars powered by hydrogen and claim fuel cell–battery hybrids should be our focus.

About a century ago, hydrogen featured significantly in transportation as airships plied international routes carrying passengers further and more comfortably than aeroplanes and far faster than ocean liners. Hydrogen-filled 'airships' with numbers such as R34 and ZMC-2, or names such as *Graf Zeppelin* and *Hindenburg*, circumnavigated the world, flew over the Arctic and criss-crossed the Atlantic and Pacific. Commercial flights occurred mainly between Europe and South America, but airships also stopped off in the US. The newly constructed Empire State Building had a large metal tower incorporated on its roof to which airships could 'moor'. However, with the tragic *Hindenburg* fire (and a number of other accidents, including the crash and fire that destroyed the UK's R101 on its maiden voyage), European countries largely lost interest in hydrogen-filled airships. The US, however, continued their development and its Akron class airships were large enough that they could even carry aeroplanes and so were essentially airborne aircraft carriers. The US was able to more safely pursue airship development because it was able to use helium instead of hydrogen. At that time, the US was the only source of helium and interestingly almost all of the available helium in the entire world was used to fill its first airship, the USS *Shenandoah*.

As chemists, we know that hydrogen can be synthesised by a number of approaches, but helium cannot be generated by chemical reaction. Helium is only sourced from gases trapped in deep oil and gas wells and a century ago these were all in the US. At this time, chemistries for hydrogen production by treating hot iron with sulfuric acid or by forcing steam through hot coal were established. Today, because hydrogen is seen as a green energy source that produces no CO_2, research efforts are underway to improve this ancient synthetic chemistry. One attractive approach is to generate hydrogen by breaking up methane to make elemental carbon and hydrogen gas. Chemically, methane (CH_4) is an atom-efficient source of hydrogen. Methane is also a potent greenhouse gas, so large-scale consumption (without conversion to CO_2) would be beneficial. However, expensive catalysts and high temperatures (1000°C) are still required. If new catalytic processes can be found and if the carbon could be generated in a high-value form (such as graphene), such approaches become very attractive. Clearly, good chemists are required to make the many discoveries needed to progress these ideas. Another, even greener, approach is to source hydrogen from the electrolysis of water by using solar, wind or hydro power. Australia is very well placed to be involved in such efforts and the planned Aerosmith Hydrogen Project in Western Australia, which is aiming to generate 25 000 kg/day, is one example of what the future might hold. However. large-scale electrolysis faces its own technical challenges, not the least of which is storage and

Continued on page 35

Diamonds, gold and gems of chemistry

Before I walk off into the sunset, I've accepted an invitation to reflect on my career experiences at RACI.

I can say, categorically, that my career path wasn't planned – very few careers are. I graduated with a BSc(Hons) at a time when the employment market in the UK was as dead as the dodo. During my degree program, I had been a bit adventurous and spent a year making car batteries in South Africa, so I was very aware of that resource sector. Thinking 'What the hell, let's try it', I applied to AngloAmerican/De Beers for a mineral processing job. They must have been pretty desperate because I landed a mineral processing job with De Beers. Looking back, this seems weird because I had a chemistry degree and diamond recovery used virtually no chemistry except a bit of X-ray luminescence technology. Anyway, I was off and running on the AngloAmerican training program. Six years later, I joined AngloAmerican as a gold plant manager, running a facility that milled 180 000 tons of ore per month producing around a ton of gold. I had progressed to a project manager responsible for building small plants and retro fixing existing ones by the time I left the resources sector. I left when the gold price fell from a heady $800 to $200 per ounce, putting a dampener on any building programs.

After 12 years in the resources sector, I became a tyre factory production manager. From there, I moved to factory scheduling, then to procurement and logistics, ending up as general manager logistics responsible for the procurement of all raw materials and chemicals for two tyre factories, the transport and warehousing of tyres and all imports and exports. Ten years later, a supplier headhunted me to run a heavy-duty textile company manufacturing fabrics for use in tyres and conveyor belts. There was a bit of chemistry involved because the fabrics had to be chemically treated to make sure they stuck to the rubber in the tyre and conveyor belt manufacturing process.

After five years in that job, and 28 years in South Africa living through apartheid, transition and democratic freedom, I needed to leave for my children's future. Career opportunities for youngsters were limited and the country was going through a pretty violent phase. So bags were packed and off we went to Perth, with no job to go to but confident that that wouldn't be a problem in the resources hub of the universe – wrong!! After three years looking in vain for a 'proper job' (being told I was overqualified and had no Australian experience), I joined a group of consultants providing services to small business and worked with the local TAFE system in a program of certification of small business entrepreneurs.

Now let's talk about my 12 years with RACI. When I was appointed CEO, RACI was in the throes of major organisational change. Since the turn of the century, RACI had made a $1.2 million loss, and membership had been falling steadily. At least one of my predecessors had been 'terminated'.

The introduction of GST forced the organisation to become an association, subject to normal accounting rules; this removed a lot of the financial autonomy that the Divisions, Branches and Groups had enjoyed.

The global financial crisis had decimated the finances of the organisation.

CEO's tips for starting a career journey

1. Never stop learning. When I started out, I soon found out I knew nothing about business or how companies run. As well as every in-house training course available, I did a BCom to augment my knowledge. As I moved up the hierarchy, I studied for an MBA to keep the knowledge levels where they needed to be and I did the CPA program to rectify my lack of Australian experience.
2. Join associations. This has a twofold reward: it dovetails with point 1 as associations and their members are a repository of knowledge and it helps you build networks. I've been a member of a multitude of associations related to my industry and job function. All served a useful purpose and memberships are tax deductible.
3. Don't be frightened to make a radical change of direction. If you have been doing points 1 and 2 well, then you will have laid a solid platform to do so. This opens up your opportunities!

chemistry in Australia
chemaust.raci.org.au

EDITOR
Sally Woollett
Ph 0406 321 312
wools@westnet.com.au

PRODUCTION EDITOR
Catherine Greenwood
catherine.greenwood@bigpond.com

ADVERTISING SALES
Mary Pappa
Ph/fax (03) 9328 2033/2670
mary.pappa@raci.org.au

PRODUCTION
Control Publishing
publishing@control.com.au
www.control.com.au

BOOK REVIEWS
Damien Blackwell
damo34@internode.on.net

RESEARCH HIGHLIGHTS
David Huang
david.huang@adelaide.edu.au

EDUCATION RESEARCH HIGHLIGHTS
Reyne Pullen
reyne.pullen@sydney.edu.au

GENERAL ENQUIRIES
Ph/fax (03) 9328 2033/2670
chemaust@raci.org.au

PRESIDENT
Steven Bottle

MANAGEMENT COMMITTEE
Antigone Christou-Rappos, Helmut Hügel, Melanie MacGregor, Nigel Simpson, Richard Thwaites

CONTRIBUTIONS
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The *Chemistry in Australia* magazine had a net annual cost of $160 000, which was creeping up all the time.

These factors led to a loss of trust and a huge amount of dissatisfaction among the leadership of the Divisions, Branches and Groups, with many claims that the National Office 'stole' their money. So much so, that many did not want to run events that made money.

My first two years weren't great; delivering the expansive International Year of Chemistry program increased the drain on resources in addition to all the other problems we had. The end result over the two years was a financial loss of almost $500 000, membership dropping by 700 and loss of the Cereals and Colloids Divisions. Looking back, I'm surprised they kept me on!

The main task was to address the financial situation, including:

- introducing a budgeting system (with great support from my first three Presidents – Watts, Wood and Buntine) for Branches, Groups and Divisions with the underlying proviso that no events were off the table as long as they showed a surplus over a three-year horizon
- putting in controls around event organising that required a budget to be submitted with the authorisation request
- getting control over the magazine costs, including great work by the committee chairs (David Wood and then Sam Adeloju); the magazine is now almost in a cost-neutral position
- running conferences in house again. Three in-house conferences in 2018 helped achieve a surplus of more than $200 000 for the year
- monthly reports to Branches, Groups and Divisions detailing financial performance to budget so people knew how they were tracking.

To rebuild trust levels among the membership, so they were willing to run events and provide benefits for their fellow members, we rotated Board meeting locations around the country. We started having monthly phone updates with Assembly members. A new marketing position aimed to improve relations between the RACI hierarchy and the membership.

The end result was a turnaround that began in the 2015–16 financial year with surpluses being made in five of the next six years and membership stabilising at about 4200.

What does the new CEO have to focus on?

Although membership numbers are stable overall, we have an attrition rate of 12% and we are failing to keep many of the new sign-ups for longer than three years. We have to tip members' cost–benefit analysis in favour of remaining a member. Branches, Groups and Divisions need to increase the number of events they deliver and look wider than the regular activities.

We still have a long way to go in the trust area – communication, communication and more communication is needed.

We have to provide benefits and activities for those outside the university sector; they are the 'forgotten children' of the organisation. The professional development survey we did at the end of last year identified areas we need to address.

Financial discipline must be maintained. In-house conference organising must be developed to the level that any conference size can be handled. A business development capability would find those commercial partners and available grants for our multitude of activities.

We need to find new revenue sources – this could be coupled with providing benefits such as business development programs.

I've been fortunate to work with some amazing staff. Top of the list are Mary Pappa and Robyn Taylor; Carolyn Collins, who was marooned in the UK by Covid and still managed to run our National Chemistry Quiz; Ben Fletcher, a regional coordinator for 10 years; and Pam Chantrell, who has been involved in just about everything. Of the original crew, only Pam and Mary remain but we have had a great group of new talent join us, so service delivery will continue.

Then there is the Board. These are the unsung heroes of our organisation – they are all volunteers. Many of them contribute an inordinate amount of time to RACI affairs and all of them bring a different perspective to the leadership group. I've worked with a number of Presidents – all very different yet all bringing something positive to RACI during their presidency.

Finally, I'd like to wish my successor well. I hope they get as much pleasure in being associated with RACI as I have. I'm sure you will all give them as much support (and problems) as you gave me.

Roger Stapleford MRACI (roger.stapleford@raci.org.au) is CEO of RACI.

Robyn Taylor received an award for service to RACI for her exceptional work in membership and other roles since 2008. CEO Roger Stapleford presented Robyn with her certificate and gifts of appreciation. Both Robyn and Roger retire this year and the team at *Chemistry in Australia* thanks them for their support, guidance and collegiality.

More STEM learning for remote schools

Merck ANZ Managing Directors with DeadlyScience's Corey Tutt (centre), Dr Naomi Koh Belic and Tom Gordon (far right).

Merck and DeadlyScience are partnering with Indigenous communities, Elders and Indigenous subject-matter experts to create experiments, complete with worksheets and video tutorials, that can be used in school classrooms or at home. The kits will explore chemistry, physics and biology with experiments based in Indigenous science.

DeadlyScience was founded in 2019 by proud Kamilaroi man Corey Tutt OAM, and has delivered more than 20 000 books, 500 telescopes and countless other learning tools to students in remote communities.

'We work with hundreds of remote schools, who collectively have more than 28 000 students. Over 75% are Indigenous.

'We want to get them engaged with science, help them learn with play and hands-on experience, and show them Indigenous scientists. You can't be what you can't see,' said Tutt.

The first kit, themed around chemistry, is currently under development with the Garawa and the Gunindiri peoples at Robinson River in rural Northern Territory.

'We've had the privilege of listening and learning to the acting principal of Robinsons River School, as well as two Indigenous Elders, Patsy Anne and Susan.

The students are also really keen. Right now, we're mulling over some great suggestions for chemistry experiments, including making soap and testing bush medicine for bio-active substances,' said Tutt.

Merck and DeadlyScience aim to distribute the first kit to approximately 500 children across a range of remote communities and follow the impacts on Indigenous STEM education and engagement.

'The initial project also includes an internship education program for emerging Indigenous science communicators, to join the DeadlyScience team,' said Rebecca Lee, Managing Director Life Science and Country Speaker, Merck ANZ.

'We're excited to work with Corey, who has been recognised with a Medal of the Order of Australia for service to Indigenous STEM – science, technology, engineering, and maths education,' she said.

The intern program is part of DeadlyScience's larger goal of creating long-term connections, said Corey. 'We never, under any circumstances, want to send a single kit to a student and let the relationship end there. These children deserve extended support. With Merck's partnership, we could create a meaningful and long-term program that we believe will have a memorable impact.'

Merck

New governance structure for IUPAC

On 4 June, the International Union of Pure and Applied Chemistry (IUPAC) held a Special Council Meeting that marked an important milestone in its 100-year history. National Adhering Organisations (NAOs) approved changes to the Statutes, Bylaws and Standing Orders that update the governance structure of IUPAC by 137 out of 162 votes. The changes replace the existing Bureau and Executive Committee of IUPAC by an Executive Board and a Science Board, and provide the organisation with a more agile and sustainable structure to meet the needs of the global chemistry community. The Executive and Science Boards will be instrumental in setting the agenda of the organisation and its scientific direction and will help to create a more sustainable and impactful IUPAC. The transition to the new organisational framework has already begun.

The new Organisational Structure was first presented in December 2020 after a careful and comprehensive analysis and evaluation of the entire organisation by an international review group. There followed an extensive period of consultation with IUPAC members and volunteers, including 'town hall' meetings at the General Assembly of August 2021. Another important recommendation of the Review Group was to improve communication with the NAOs belonging to IUPAC. The first NAO Forum, an informal online conversation between the IUPAC leadership team and NAOs, was held virtually in July 2022.

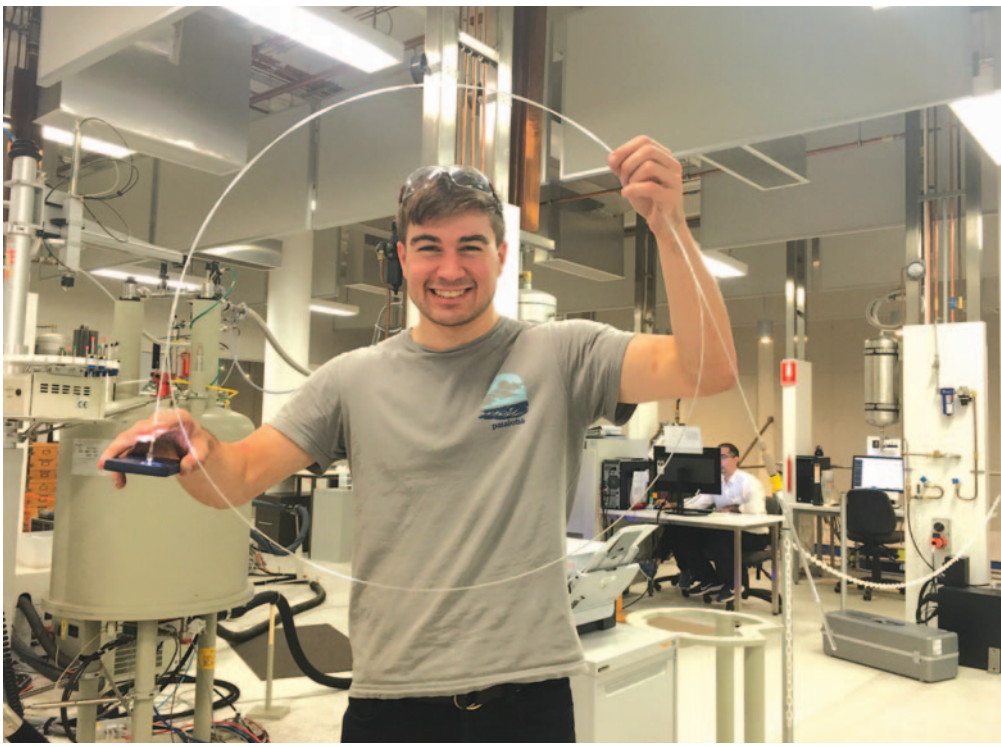
Mary Garson FRACI CChem

New hope for methane recycling

University of New South Wales chemists have engineered a new molecular 'vice' that can bind methane for hours – providing crucial evidence for an intermediate step that will inform new catalysts to store, transport or transform the gas into methanol and help to avert wastage of the gas worldwide.

The new osmium–methane complex can bind methane for hours, much longer than the current standard of microseconds, allowing for its analysis to create potential new catalysts to transform methane.

James Watson, lead author publishing in *Nature Chemistry* (doi.org/10.1038/s41557-022-00929-w), said 'We have found that methane, which is generally inert, will interact with an osmium-metal centred species to form a relatively stable osmium–methane complex. Our complex has an effective half-life of around 13 hours.' NMR spectroscopy is used to define the metal–methane complex so that catalysts might be developed for transforming the methane into methanol or other products.



James Watson holding the apparatus used to photolyse the sample in the NMR spectrometer.

'Methane is an unwanted by-product from oil production and usually, for economic reasons, is burned by "flaring",' said co-author Associate Professor Graham Ball. 'The amount of gas burned in this way is roughly equivalent to the natural gas demand of Central and South America, leading to 265 million tonnes of CO_2 emissions in 2020.'

This waste occurs because the process of converting methane (gas) into a practical fuel at the site – like methanol (a liquid) – has, historically, been economically unviable. We simply haven't been able to convert it.

'One way of converting methane to liquid fuels is through the use of catalysts that contain transition metal elements,' explained Ball.

'Liquid fuels are easier to transport and would be easily integrated into our existing fuel infrastructure – E10 petrol already has 10% ethanol. If there were efficient, commercially viable methods to convert methane to methanol for example, this would also provide incentive to retain methane for conversion, and to avoid burning it without purpose, reducing overall fossil fuel use and damaging emissions.'

'Perhaps the most pertinent use of methane as a feedstock would be its sequestration from the atmosphere, which could curb the lasting damage that is being done to the environment and help limit global warming to 1.5°C,' Watson said.

Given osmium's prime candidacy for binding methane – why did it take so long to find? And how did the team identify it?

'Before we synthesised any molecules, we used computational methods to predict which molecules would contain both a reactive metal and a "vacant site", a site that would bind methane most strongly,' said Ball.

'That's why we ended up using a rather esoteric metal, osmium in this case, with other groups of atoms around it, as the modelling predicted it should bind methane well … which it does.

'The vacant site is generated by shining UV light onto a solution of a precursor transition metal compound that is dissolved in a carefully selected hydrofluorocarbon solvent, all of which occurs in the presence of added methane. The solvent choice is crucial as common laboratory solvents all bind in preference to methane, but the hydrofluorocarbon does not.'

'[While it] is unlikely that this exact [osmium–methane] complex will be exploited for the benefit of the environment, if we could further refine the complex so that it would continue to preferentially bind methane at temperatures higher than –90°C then we may be able to perform more manipulations on the bound methane and ultimately convert methane into value added products,' said Watson.

According to the researchers, this osmium–methane complex represents an important step in the conversion of methane into other compounds.

University of New South Wales

Towards novel ammonia production

In *Nature* (doi.org/10.1038/s41586-022-05108-y), Dr Hoang-Long Du (School of Chemistry, Monash University), Dr Alexandr Simonov and Professor Doug MacFarlane report that they can achieve almost complete selectivity for the conversion of nitrogen, from the air around us, and renewable electricity into ammonia at an unprecedented rate.

The research developed a unique electrolyte that produces a high-performance layer on the operating electrode to support the reaction that converts nitrogen into ammonia.

The price of fertilisers has more than doubled in recent years in part because of increases in natural gas prices, placing many farmers under severe strain.

Simonov said a process for the carbon-free production of fertilisers using renewable energy had been known for some time, but it was not very selective.

'Typically, a significant portion, sometimes as large as half, of the electricity was used in making other unwanted compounds, making the process impractical,' Simonov said.

'Our new discovery shows how ammonia can be made with complete selectivity.'

Co-leader MacFarlane said that reaching 100% selectivity for ammonia was a vital step in making the process industrially practical.

'This discovery builds on years of work in our group understanding the fundamental chemistry underpinning the process.'

Du said another important feature of the new electrolyte was the high stability it provided to the process.

'Since the electricity is exclusively used for the nitrogen to ammonia reaction, no degradation processes can occur and the process can operate stably on a long timescale,' Du said.

Monash has spun off a company, Jupiter Ionics, which is scaling up the process discovered by the research team.

Jupiter Ionics hopes to have its first prototype devices on a farm in regional Victoria next year, according to the company's CEO Dr Charlie Day.

'This new research is opening up a novel pathway to ammonia production, over a century after Haber and Bosch first developed their eponymous process,' Day said.

'Importantly, it will enable production at a range of scales and in a range of settings, all powered by increasingly abundant and cheap renewable energy.'

Of particular interest to the agricultural sector, the technology can be installed on farms or in regional centres, producing fertilisers locally using onsite renewable energy supplies.

Monash University

Reporting negative results to improve reaction planning

Databases containing huge amounts of experimental data are available to researchers across a wide variety of chemical disciplines. However, a team of researchers has discovered that the available data is unsuccessful in predicting the yields of new syntheses using artificial intelligence (AI) and machine learning. Their study published in *Angewandte Chemie* (doi.org/10.1002/anie.202204647) suggests that this is in large part due to the tendency of scientists not to report failed experiments.

Although AI-based models have been particularly successful in predicting molecular structures and material properties, they return rather inaccurate predictions for information about product yields in synthesis, as Frank Glorius and researchers at Westfälische Wilhelms-Universität Münster, Germany, have discovered.

The researchers attribute this failure to the data used to train AI systems. 'Interestingly, the prediction of reaction yields (reactivity) is much more challenging than the prediction of molecular properties. Reactants, reagents, quantities, conditions, the experimental execution – all determine the yield, and thus the problem of yield prediction becomes very data-intensive', explained Glorius. So, despite the huge amounts of available literature and results, the researchers came to realise that the data is not fit for accurate predictions of the expected yield.

The problem is not only due to a lack of experiments. The team identified three possible causes for biased data. First, the results of chemical syntheses may be flawed because of experimental error. Second, when chemists are planning their experiments, they may, either consciously or unconsciously, introduce bias based on personal experience and reliance on well-established methods. Finally, since only reactions with a positive outcome are believed to contribute to progress, failed reactions are reported less frequently.

To find out which of these three factors had the greatest influence, the researchers altered the datasets for four commonly used (therefore data-rich) organic reactions. They artificially increased experimental error, reduced the size of the data sampling sets, or removed negative results from the data. They showed that the experimental error had the smallest influence on the model, while the contribution made by the lack of negative results was fundamental.

The group hopes that these findings will encourage scientists to always report failed experiments as well as their successes. This would improve data availability for training AI, ultimately helping to speed up planning and making experimentation more efficient. Glorius added: 'machine learning in (molecular) chemistry will increase efficiency dramatically and fewer reactions will have to be run to achieve a certain goal, for example, an optimisation. This will empower chemists and will help them to make chemical processes – and the world – more sustainable'.

Angewandte Chemie International Edition

Specialty gas, Australian made for energy security

Energy's centrality to Australia's economic growth is well recognised, and securing an uninterrupted energy supply is vital for many local businesses where hydrocarbon processing is part of their supply chain.

Specialty gases as used in the hydrocarbon process for safety, process control and compliance have historically been imported into Australia; however, global supply chain issues are now affecting Australian companies that have traditionally relied on overseas suppliers.

Coregas is the only Australian industrial gases company manufacturing locally and distributing specialty gases throughout Australia and New Zealand, including calibration gases, chemical gases, process gases, purging/inerting gases, electronic gases and instrumentation gases.

Coregas supplies a range of specialty gases and related gas control equipment used in the hydrocarbon processing industry.

Speed of delivery is often as important as quality. Coregas has standardised certain high-volume products to be made from stock and are available for despatch next day. Coregas has also tailored its production and ordering processes for calibration gases that are made to order to ensure conformance to customer bespoke requirements, to minimise the wait time for delivery.

Coregas has jumped at the challenge to meet the demands of Australian specialty gas users and encourages businesses to reduce the risks from future disruptions that are certain to occur, and mitigate global supply chain risks by buying Australian.

For more information, visit www.coregas.com.au.

Analytical solutions for safer and better batteries

Lithium-ion batteries play an increasingly crucial role in everything from handheld electronics to electric vehicles. As such, laboratory professionals need to accelerate insights and answers to achieve technology advancements and meet essential sustainability goals.

Across the battery manufacturing continuum, Thermo Fisher Scientific helps scientists make big strides towards a sustainable, zero-carbon future. Work behind the scenes includes:

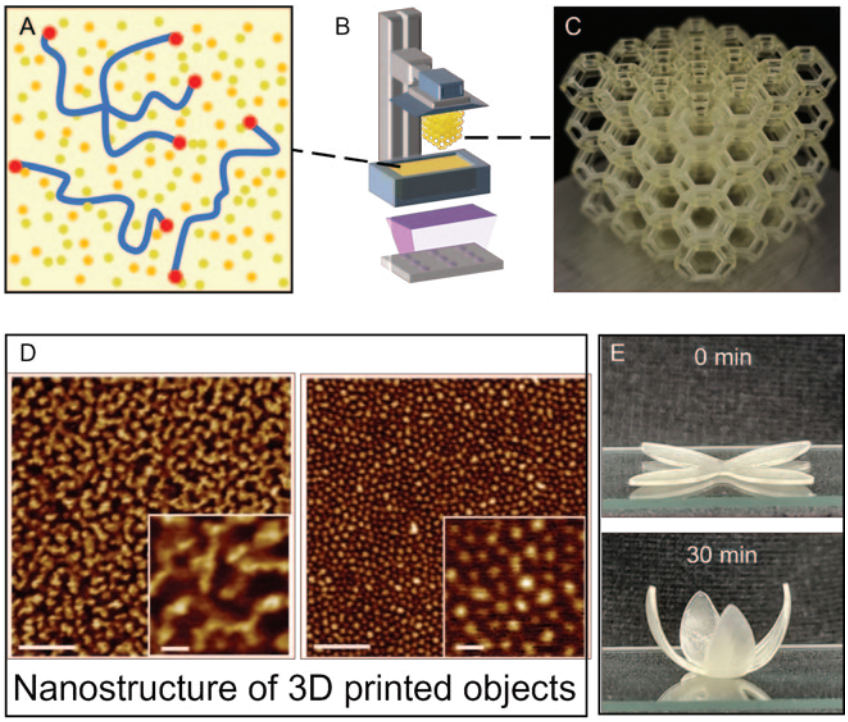
- Research – material composition and purity characterisation in the exploration of new methods, improvements of existing techniques for battery material recycling, or the development of next-generation batteries (solid state, sodium)
- Raw materials – mined material processing, refined product purity analysis, and quality assurance and control
- Cell components and assembly – ensure the quality of design, enable process control, detection and quantification of elemental impurities, and routine QA/QC measurement etc. in the making of battery cells or cell arrays and electrolyte composition confirmation
- Battery testing – analysis of degradation products in battery failure analysis and rejection, battery ageing, and environmental and electrical studies
- Battery recycling – support inspection and characterisation in processes such as battery recycling and material recovery, inspection and reuse

There are application notes and technical notes on topics such as the determination of elemental impurities in graphite powder for lithium-ion battery anodes at www.thermofisher.com/battery-solutions. Also available are case studies and a broad range of tools and instruments for the production of advanced battery technology.

To receive Analytical Solutions for Li Battery Update, subscribe at thermofisher.com/LiBatt-updates.

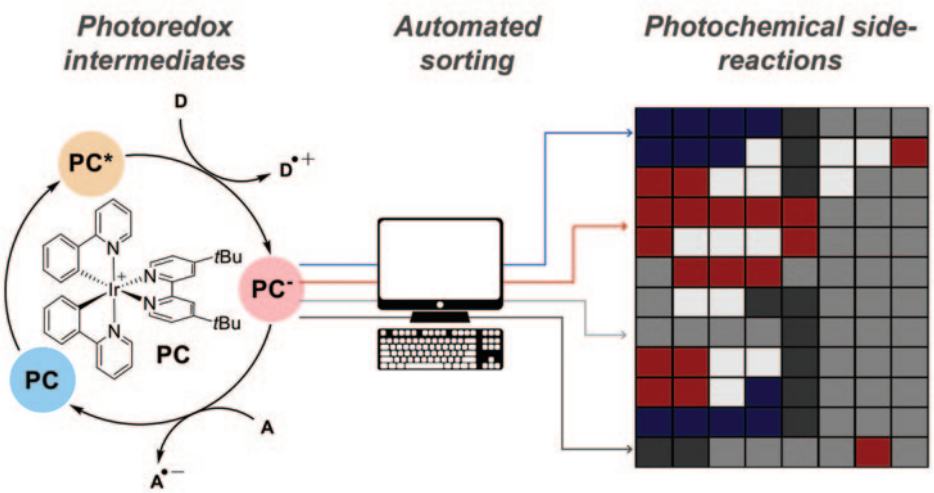
3D printing complex architectures of nanostructured polymers

Nanostructured polymeric materials play important roles in many advanced applications, but controlling the morphologies of polymeric thermosets remains a challenge. Now, researchers at the University of New South Wales Sydney have used a multi-arm macro-chain transfer agent (A) to mediate polymerisation-induced microphase separation by reversible addition-fragmentation chain transfer polymerisation to prepare nanostructured materials by photoinduced 3D printing (B) (Shi X., Bobrin V.A., Yao Y., Zhang J., Corrigan N., Boyer C. *Angew. Chem. Int. Ed.* 2022, **61**, e202206272). By using this method, objects with complex architectural features (C) and tunable nanostructures (D) were obtained using photocurable resins of varied compositions. Furthermore, the 3D-printed nanostructured objects were successfully applied for swelling-induced actuation (E), which could find application in soft robotics.



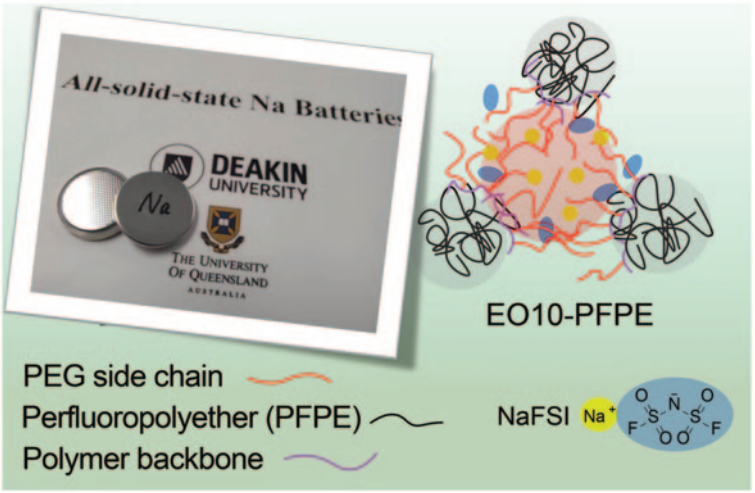
Monitoring photocatalysts everywhere, all at once

Photoredox catalysis is a versatile synthetic tool for the sustainable making and breaking of C–C and C–X bonds. The molecular photocatalysts that power this methodology are primarily selected based on their ground- and excited-state properties, although activity is also intrinsically tied to their reactive open-shell intermediates. A multi-university team led by researchers at Deakin University has explored the reactivity of iridium(III) photocatalyst intermediates by using a unique high-throughput approach (Bawden J.C., Francis P.S., DiLuzio S., Hayne D.J., Doeven E.H., Truong J., Alexander R., Henderson L.C., Gómez D.E., Massi M., Armstrong B.I., Draper F.A., Bernhard S., Connell T.U. *J. Am. Chem. Soc.*, 2022, **144**, 11 189–202). Several different chemical pathways were identified, affording either product formation or various side-reactions, ultimately governed by ligand composition. The ancillary ligand determined photochemical stability, producing an intermediate either resistant or susceptible to hydrogen atom transfer and partial saturation of the pyridyl rings. Controlling the cyclometallating ligands dictated how this chemical transformation altered the catalyst's photophysical properties and subsequent activity. The results demonstrate how high reactivity often results in reduced stability, and balancing these competing properties is the critical challenge in designing next-generation catalysts tailored for increasing synthetic demands.



Fluorinated solid electrolyte makes more reliable batteries

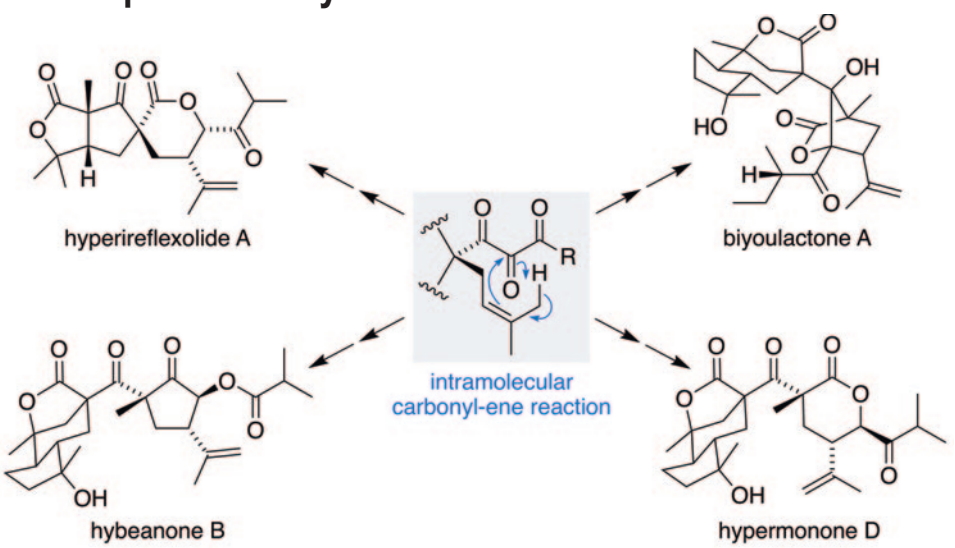
To meet its energy priorities, Australia needs new battery storage technologies that are efficient, reliable and safe. Batteries containing flammable liquid electrolytes currently dominate the energy market, but they are dangerous and prone to explosion. Researchers from Deakin University's Institute for Frontier Materials and the University of Queensland's Australian Institute for Bioengineering and Nanotechnology (AIBN) have developed an innovative technology to advance the development of safe, rechargeable all-solid-state batteries that provide reliable long-lasting energy storage (Wang X., Zhang C., Sawczyk M., Sun J., Yuan Q., Chen F., Mendes T.C., Howlett P.C., Fu C., Wang Y., Tan X., Searles D.J., Král P., Hawker C.J., Whittaker A.K., Forsyth M. *Nat. Mater.* 2022, doi.org/10.1038/s41563-022-01296-0). Featuring key contributions from Deakin's Dr Xiaoen Wang and Professor Maria Forsyth – as well as AIBN's Dr Cheng Zhang and Professor Andrew Whittaker – the team found that their newly developed fluorinated solid electrolyte transformed all-solid-state sodium batteries into a safe and more reliable power storage system. The study promises opportunities for the design of new and efficient solid electrolytes for all-solid-state sodium batteries to ensure highly reliable electricity storage and supply for Australians.



EO10 = oligo(ethylene oxide) methyl ether acrylate decamer

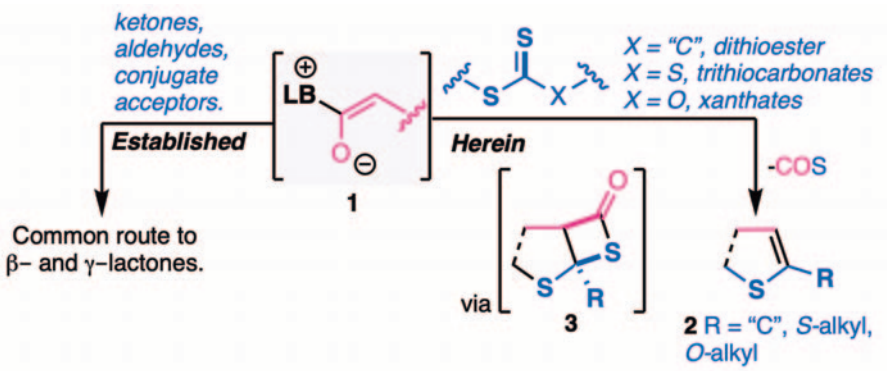
A unifying hypothesis for meroterpenoid biosynthesis

Meroterpenoids are natural products derived from mixed terpene and polyketide biosynthetic pathways. Commonly found in flowering plants of the *Hypericum* genus, their stereochemically complex structures of bewildering variety can sometimes obfuscate their precise biosynthetic origin. However, researchers at the University of Adelaide recently proposed a unifying hypothesis to explain the biosynthesis of several *Hypericum* meroterpenoids (zur Bonsen A.B., Peralta R.A., Fallon T., Huang D.M., George J.H. *Angew. Chem. Int. Ed.* 2022, **61**, e202203311). The key step in their proposal is an intramolecular carbonyl-ene reaction between a prenyl group (of terpene origin) and a 1,2,3-triketone (of polyketide origin). The resultant α-hydroxy-β-diketones can undergo further base-catalysed rearrangements to give the characteristic δ-lactones of the hyperireflexolides, hypermonones and biyoulactones, and the highly functionalised cyclopentanones of the hybeanones. Although total syntheses of these natural products remain elusive, the important biosynthetic steps were chemically mimicked in model systems under remarkably simple reaction conditions. In particular, the key intramolecular carbonyl-ene reaction occurred spontaneously at room temperature on a range of highly electrophilic 1,2,3-triketone substrates, whereas all previous examples of this transformation require either high temperature or acid catalysis. This work therefore shows that solving biosynthetic puzzles can inspire the development of predisposed organic reactions for the synthesis of complex natural product scaffolds.

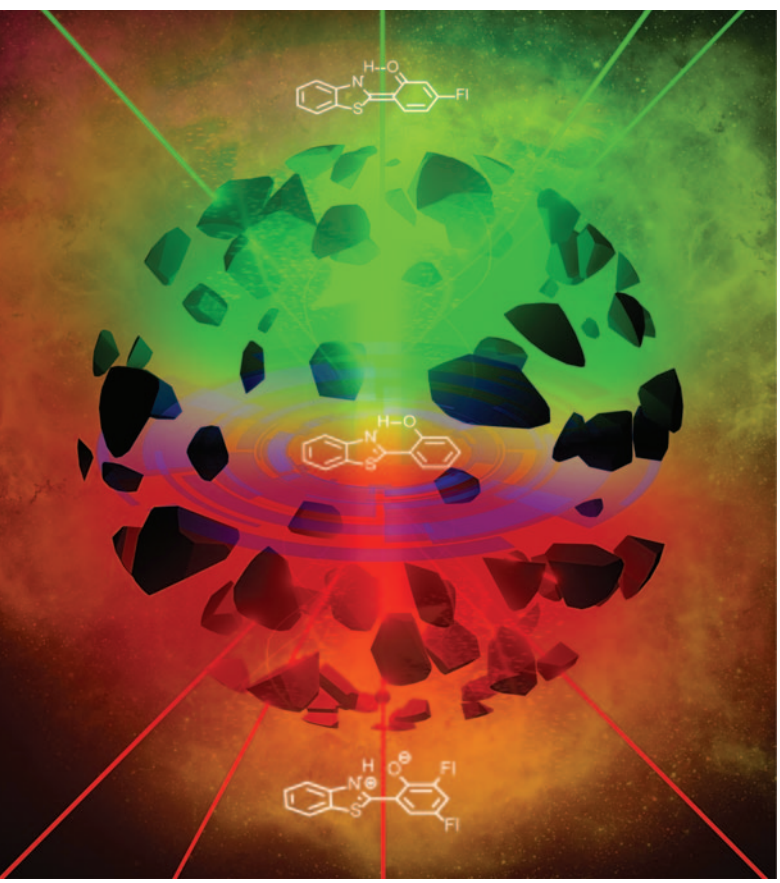


New organic catalysis approach to sulfur heterocycles

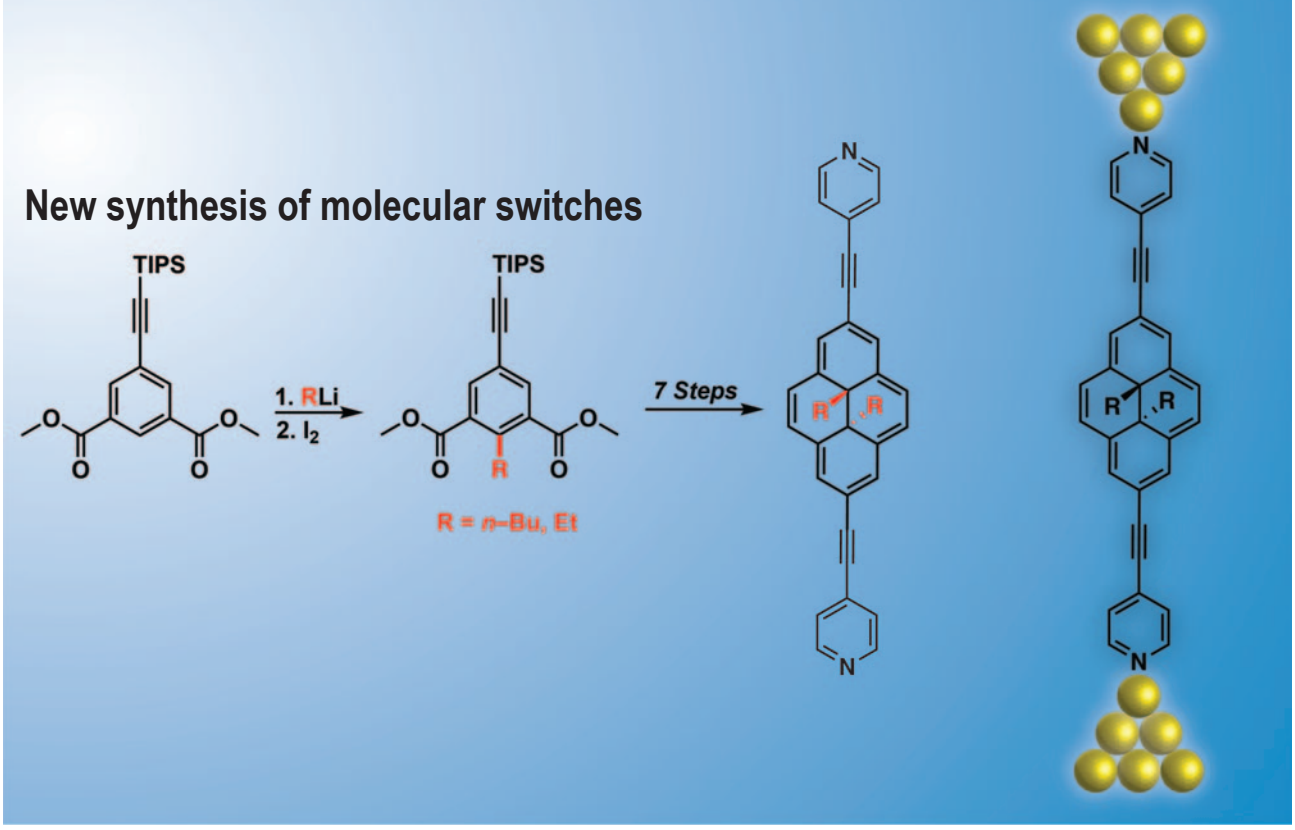
Catalytic approaches to the Lewis base (LB) enolate **1** have enabled an array of organocatalytic reactions. Although various Lewis base catalysts and enolate precursors are known, significantly less is established regarding the species to which the enolate couples. Specifically, reactions remain largely limited to additions to carbonyl compounds and conjugate acceptors, thereby producing β-lactones and δ-lactones. Recent studies led by David Lupton at Monash University in collaboration with Georgina Such at the University of Melbourne have focused on developing reactions involving reactions of the Lewis base enolate with thiocarbonyl partners, species well known in polymerisation chemistry but yet to be examined in organocatalysis. Through these studies, they demonstrated that an array of dithioesters, trithiocarbonates and xanthates can engage in annulative reactions to deliver sulfur-containing heterocycles **2** (Cromwell S., Sutio R., Zhang C., Such G.K., Lupton D.W. *Angew. Chem. Int. Ed.* 2022, **61**, e202206647). The reaction probably proceeds via β-thiolactone **3**, which loses carbonoxysulfide (COS) to give the final product. While this study demonstrates the viability of these novel coupling partners, significant possibilities remain to develop enantioselective processes and more elaborate reaction cascades.



Recharging proton transfer via zwitterion formation



The unique four-level photocycle of excited-state intramolecular proton transfer (ESIPT) materials enables large spectral separation between absorption and emission. This feature makes ESIPT materials strong contenders for many applications, including bio-imaging, sensing, molecular optoelectronics and organic lasers. Current ESIPT materials typically rely on delocalisation of the π-bonds to attain the proton-transferred tautomer. However, the achievable maximum Stokes shifts between the absorption and emission spectra for this process is limited. A research team from the University of Queensland, collaborating with researchers at CSIR-NIIST (India), has used a unconventional strategy to address this issue (Shukla A., Mai V.T.N., Divya V.V., Suresh C.H., Paul M., Karunakaran V., McGregor S.K.M., Allison I., Narayanan Unni K.N., Ajayaghosh A., Namdas E.B., Lo S.-C. *J. Am. Chem. Soc.* 2022, **144**, 13 499–510). The team demonstrated proton transfer through charge redistribution to yield a zwitterionic tautomeric form, which exhibits an extraordinary Stokes shift of 236 nm while retaining an excellent photoluminescence quantum yield. The zwitterionic ESIPT dye exhibits laser oscillation with a remarkably low threshold value (only 5.3 μJ/cm^2), one of the lowest reported for a red-emitting organic chromophore.



Switchable molecules are attractive building blocks for applications in molecular-scale electronics. Incorporated into a molecular electronic circuit, such systems allow the modulation of electrical current on the nanoscale. Researchers at the University of Western Australia have discovered a new synthetic method for synthesising 2,7-functionalised dihydropyrene (DHP) molecular switches based on the early-stage functionalisation of small organic precursors (Roemer M., Gillespie A., Jago D., Costa-Milan D., Alqahtani J., Hurtado-Gallego J., Sadeghi H., Lambert C.J., Spackman P.R., Sobolev A.N., Skelton B.W., Grosjean A., Walkey M., Kampmann S., Vezzoli A., Simpson P.V., Massi M., Planje I., Rubio-Bollinger G., Agraït N., Higgins S.J., Sangtarash S., Piggott M.J., Nichols R.J., Koutsantonis G.A. *J. Am. Chem. Soc.* 2022, **144**, 12 698–714). The critical step involves the novel nucleophilic alkylation of a dimethyl isophthalate, giving access to new DHP motifs along with more conventional DHP motifs synthesised by the team by existing methods. The hydrocarbons display electrochemical switching behaviour as measured by spectroelectrochemical experiments. Equipped with Au surface anchoring groups, they form stable single-molecule circuits, which were investigated in detail in single-molecule scanning tunnelling microscope break junction measurements. The experimental observations were supported by quantum transport calculations, in collaboration with researchers from the UK and Spain.

Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high-impact journals (e.g. *Nature, J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Sci.*) are encouraged to contribute general summaries, of no more than 200 words, and an image to David.

Plastics pollution

The role of international collaboration

This giant plastic tap was installed beside the Nairobi headquarters of UNEP, where the authority met in June. Artist and activist Benjamin Von Wong collaborated with communities in Nairobi to construct it from plastics collected in a nearby district. UNEP/Ahmed Nayim Yussuf/CC BY-NC-SA 2.0

BY **GREG SIMPSON, TOM SPURLING, JOHN WEBB** AND **ELIZABETH FERGUSON**

One hundred years ago, there were no plastics in our oceans; it is now unlikely that will ever be the case again. Solving the problem of plastics pollution will take more than innovative chemical technology.

Chemistry is at the heart of the solutions to many global challenges, including the increasingly pressing challenge of plastic pollution. However, it is how the world works together to adopt new chemical technologies that makes the difference.

We need interdisciplinary physical and social science, connected to policy and diplomatic efforts at national and international levels to achieve systemic change – this is science diplomacy.

Here, we describe the science diplomacy already occurring to address plastics pollution, and to perhaps stimulate thought as to how chemists can contribute further to this work.

The ubiquitous nature of chemistry means that chemists are often closely involved with the strategic and diplomatic interactions that go well beyond scientific research. Science and chemists have had a key role in defining and measuring problems as they arise, and connecting with communities and policymakers to build momentum for action.

If an issue is sufficiently serious, genuinely of global concern, and voluntary action has been insufficient, the solution may be to develop a multilateral treaty, which places legally

binding obligations on the countries that sign up to it. Prominent examples are the Montreal Protocol on Substances that Deplete the Ozone Layer, the Chemical Weapons Convention preventing the use of chemical weapons and the Antarctic Treaty on the protection of the Antarctic region.

To get a treaty right, science diplomacy needs to drive cross-disciplinary connections and build broad expertise. Science diplomacy is key to ensuring that:

- negotiators build policy and legal frameworks to solve problems that account accurately and effectively for technical limitations and opportunities
- scientists undertake research and develop advice that supports the development and implementation of effective legal and policy frameworks
- both negotiators and scientists build their competency in communicating with one another and other stakeholders.

This involves establishing mechanisms to drive international and cross-disciplinary collaboration, including for sharing resources and knowledge, managing compliance and measuring progress against objectives.

The plastics revolution – the commercial production of synthetic plastics – began in the early decades of the 20th century. In the post-World War II period, there was an explosion of plastic use when plastic replaced more expensive glass, paper or metal in myriad consumer items, often designed to be 'disposable'.

Plastics pollution has now become an international problem due to increasing global plastic use and production. In 2015, plastic production reached 407 million tonnes per year. By 2050, this is expected to grow to 1600 million tonnes per year. Almost all the plastic ever produced is still in existence, and much of it ends up in natural environments. About 14 million tonnes of plastics are discharged into the ocean every year. Most (80%) of the plastic in the sea originates on land, and the remainder comes from sea-based sources such as ships and debris such as fishing nets.

Once in the sea, plastics destroy habitat, and wildlife swallow plastic, mistaking it for food, or become tangled in discarded nets that continue to fish ('ghost' fishing). Marine debris (of which 92% is plastic) affects more than 800 species of fish, marine mammals and birds worldwide. On current projections, about 99% of seabirds will have ingested plastics by 2025, and plastics in the sea will outweigh all the fish by 2050.

On current projections, about 99% of seabirds will have ingested plastics by 2025, and plastics in the sea will outweigh all the fish by 2050.

Plastics pollution may also be harmful to human health. Plastics may carry toxic pollutants, and some microplastics have been shown to carry carcinogens, mutagens and reproductive toxins. Humans currently swallow up to 52 000 microplastic particles each year in their food and drink.

As well as threatening our health, wildlife and ecosystems, marine plastic litter threatens our livelihoods. Deloitte estimates that marine plastic pollution resulted in economic losses of US$6–19 billion (about AU$8–25 billion) for 87 coastal countries in 2018. This is largely due to impacts from fishing, trade and coastal tourism, which are critical to the prosperity and economic resilience of coastal states such as Australia and our Pacific Island and South-East Asian neighbours.

Plastics pollution was first noted as a problem by scientists in the 1960s and 1970s. By 2012, recognition of the problem had grown to the point that United Nations environment forums were making commitments to better understand and attempt to reduce marine debris. The United Nations Environment Assembly (UNEA) has made resolutions to address marine debris and plastic pollution at every meeting since its first meeting in 2014. Decisions through the UN are summarised in the table on page 18.

In 2017, the third session of UNEA agreed to a resolution calling for the long-term elimination of all discharge of litter and microplastics to the ocean and established an intersessional Ad Hoc Open-Ended Expert Group on Marine Litter and Microplastics (AHEG) to examine measures for combating marine plastic litter and microplastics from all sources, especially land-based sources. This group concluded in 2021 that the patchwork of binding and non-binding national and international measures was insufficient to address the problem, and presented a range of options, including establishing a new multilateral treaty.

The work of AHEG – a significant example of science diplomacy in action – was critical to building the momentum that culminated in March 2022, with the Australian Government and other Members of the United Nations Environment Assembly (UNEA) agreeing to establish an Intergovernmental Negotiating Committee (INC) to negotiate a new treaty on plastic pollution. The decision was made through the UNEA resolution 'End plastic pollution: towards an international legally binding instrument'.

During these negotiations, Australia and others successfully advocated for a comprehensive mandate to address plastic pollution in all environments,

covering the entire life cycle of plastics, and based on circular economy principles. This aligns with Australia's domestic policies to build a circular economy for plastics.

Following UNEA 5.2, there was a special session to commemorate UNEP's 50th birthday, where it was noted that in 1972 'the environment was a fringe issue'; however, now it is ever more central to global progress. A global science diplomacy process is underway – 'on track for a cure' to the plastic pollution challenge (UNEA-5 President Espen Barth Eide).

Commencing negotiations on a new treaty is vital, of course. But these will take several years to complete, and even more to implement. In the interim, industry, community groups, regional organisations, environment non-government organisations and Australian, state and territory and local governments are taking significant action to address plastic pollution. The connections between technical expertise and policy development that have resulted in action at the community and national level are a solid basis to build the science

Ten years of science diplomacy on plastics pollution

Year and city	UN event	Decision
2012, Rio de Janeiro	UN Conference on Sustainable Development	'We further commit to take action to, by 2025, based on collected scientific data, achieve significant reductions in marine debris to prevent harm to the coastal and marine environment'
2014, Nairobi	UNEP/EA.1	'… to undertake a study on marine plastic debris and marine microplastics, building on existing work and taking into account the most up-to-date studies and data'
2016, Nairobi	UNEP/EA.2	'… undertake an assessment of the effectiveness of relevant international, regional and subregional strategies and approaches to combat marine plastic litter and microplastics, taking into consideration the relevant international, regional and sub-regional cooperation and coordination, and to present the assessment to the EA at its next session'
2017, Nairobi	UNEP/EA.3	'… convene meetings of an open-ended ad hoc expert group to further examine the barriers to and options for combating marine plastic litter and microplastics from all sources, especially land-based sources'
2019, Nairobi	UNEP/EA.4	'… develop guidelines for the use and production of plastics in order to inform consumers, including about standards and labels; to incentivise businesses and retailers to commit themselves to using sustainable practises and products; and to support governments in promoting the use of information tools and incentives to foster sustainable consumption and production'
2022, Nairobi	UNEP/EA.5	'… develop an international legally binding instrument on plastic pollution, including in the marine environment, which could include both binding and voluntary approaches, based on a comprehensive approach that addresses the full lifecycle of plastic'

EA, Environment Assembly. UNEP, United Nations Environment Programme.

Applause all around the house as the resolution on plastic was passed by UNEA in March this year; 175 countries adopted 'End Plastic Pollution: Towards a legally binding instrument'.
UNEP/Cyril Villemain/CC BY-NC-SA 2.0

diplomacy that will occur through the work of the Intergovernmental Negotiating Committee negotiations.

The Australian Government has worked closely with industry and other key stakeholders to start building a circular economy for plastics, including through actions to minimise plastic waste through design, phase out unnecessary plastics and find alternatives, recover more from our waste streams, and invest in more facilities to repurpose our plastic waste.

CSIRO has established a whole-of-organisation mission to end plastic waste, with a goal of an 80% reduction in plastic waste entering the environment by 2030. Major research programs have been established across CSIRO, including for turning plastic waste into commodities, using the principles of the circular economy and supporting new industries based on what is now waste. Capability in chemistry, data science, materials and manufacturing will be employed to help build a more resilient manufacturing base in Australia.

Chemistry Australia, Australia's national body representing Australia's $40 billion chemical industry, has taken a leadership role, working with the community and governments to contribute to building a circular economy for plastics, including by establishing product stewardship initiatives.

Grassroots citizen science is also supporting innovative not-for-profit organisations to take action. Community not-for-profit groups such as Tangaroa Blue, Conservation Volunteers Australia, Keep Australia Beautiful and Clean Up Australia have been working directly on beaches and other environments around Australia, organising volunteers to clean up plastic pollution. These groups often work with Indigenous rangers in remote regions and have shown what a difference working together can make. Their work has allowed us to increase our understanding of what the waste is and where it is coming from, which is vital if we are to stop waste streams from entering the environment in the first place.

We are living through the development of a global response to plastic pollution, a response that started in the 1960s with environmental research and is now approaching the level of a global treaty. It is important that scientists and officials understand not only their part of the problem, either technical or diplomatic, but how to work with each other to develop practical, and implementable, policy and regulatory frameworks and technical solutions. It is important that our schools and universities relay these stories to inspire the next generation of committed individuals to meet the challenges of the future.

Many in RACI have contributed to solving this broad and complex problem. Often this has been by way of the many opportunities and channels that RACI provides for people to be informed and to come together. We need to continue to provide and to grasp these opportunities to contribute, personally and through our multiple organisations and networks so that we can improve our environment for all.

Further reading

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UNEA. *UNEA-5.2: Major Step Toward A Comprehensive Plastics Treaty – A New Global Treaty On Plastic Pollution*.

Greg Simpson FRACI CChem, **Tom Spurling** FRACI CChem and **John Webb** FRACI CChem are at the Centre for Transformative Innovation, Swinburne University of Technology. **Elizabeth Ferguson** is at the Department of Climate Change, Energy, the Environment and Water, Canberra.

OPCW maintains readiness if and when chemical weapons are used. There are different ways in which the OPCW can respond to the use or alleged use of chemical weapons, ranging from carrying out a formal investigation to providing emergency assistance.
OPCW/CC-NC-ND-2

Closing Pandora's box

The Chemical Weapons Convention 30 years on

BY **DAVE SAMMUT** AND **CHANTELLE CRAIG**

The Chemical Weapons Convention has seen substantial progress in three decades, but important and ongoing work remains.

In unbearable agony, men stagger blindly, choking on the chlorine fumes filling their trenches while the enemy descends swiftly towards them.

That was the horrible reality of chemical warfare during World War I. When the Germans launched the first chemical attack of the war, more than 5000 French and Algerian soldiers died. The Allies retaliated. The weapons of chemical warfare developed. Many, many more soldiers were maimed or killed. By the end of the Great War, chemical weapons had been responsible for more than one million casualties.

The chemical munitions of World War I are referred to as first-generation weapons. The World War II nerve agents are known as second generation, and Cold War agents are third generation. Now emerging, the fourth-generation 'non-traditional' agents include the binary nerve agents known as 'novichocks'. Counterterrorism investigations and a public enquiry in Britain determined

that this was used by the Russian Government in 2018 for the attempted murder of Sergei Skripal and his daughter in Salisbury, England, and the accidental murder of Dawn Sturgess, who four months later came into contact with the perfume bottle the agent had been stored in (bit.ly/3zizrOv).

These chemical agents are a terrifying reality. Choking agents, like chlorine and phosgene. Blister agents, like mustard gas. Blood agents, like hydrogen cyanide. Nerve agents. Incapacitants. Riot control agents, which have been used illegally as weapons of war, and have even killed protesters when used in high concentration. Herbicides, like Agent Orange, with long-term biological and ecological consequences.

Chemical warfare dates back nearly three millennia. As early as 600 BCE, the Athenian army poisoned the water supply of the besieged city of Kirrha with hellebore plants. A little over a century later, Peloponnesian forces used sulfur fumes against the town of Plataea. The use of chlorine for chemical warfare was proposed by both sides in the American Civil War, although neither side actually resorted to its use.

The international community quickly came to abhor the cruelties of chemical warfare. As early as 1675, the Strasbourg Agreement between France and Germany banned the use of poisoned bullets. In 1925, the Geneva Protocol made it illegal for treaty participants to employ chemical or biological weapons.

Nonetheless, between the Geneva Protocol and the later Biological and Toxin Weapons Convention of 1972, chemical agents were illegally used by Italy (Ethiopia, 1935–36), Germany (the Holocaust), Japan (Asia, World War II) and Egypt (Yemen 1960s). The use of a dioxin-containing herbicide as part of a US operation during the Vietnam War was not deemed illegal under international law at the time, but can be reasonably viewed today as being a form of chemical warfare that should not be considered acceptable. Iraq then used chemical weapons extensively against both military and civilian targets in Iran (1980–88) and within Iraq in cities such as Halabja. Numerous countries developed and accumulated vast stockpiles of chemical and biological weapons, more than enough to destroy all life on Earth.

It wasn't until 3 September 1992 that the world saw a true turning point in this dreadful race. Thirty years ago, the United Nations Conference on Disarmament adopted the Chemical Weapons Convention (CWC). The treaty came into force in April 1997, 180 days after Hungary became the 65th country to ratify the treaty.

So began the slow and laborious process of disarming the world and ratifying the destruction of these deadly materials. By March this year, 99% of the world's declared stockpiles – more than 72 000 tonnes of chemical death – had been destroyed (bit.ly/30F69FM). This has grown from 78% in 2013, and 96% in 2016.

The last to destroy its declared stockpiles, the US was hampered by its own Congress, which banned the transport of chemical munitions. It was forced to approve and construct destruction facilities in eight separate states, and has declared its plans to have the remaining stockpiles destroyed by 2023.

As the implementing body for the CWC, the Organisation for the Prohibition of Chemical Weapons (OPCW) has declared that as of March 2022, the total cost of this destruction process was nearly €72 billion (A$106 billion).

By March this year, 99% of the world's declared stockpiles – more than 72 000 tonnes of chemical death – had been destroyed.

The OPCW observes the annual Day of Remembrance for all Victims of Chemical Warfare on 30 November 2019. During the ceremony – at which representatives of the victims' associations participate as guests of honour – the OPCW Member States renew their resolve to achieve a world truly free of chemical weapons. OPCW/CC-NC-ND-2

Of 97 declared chemical weapon production facilities, 74 have now been destroyed, and 23 have been converted to peaceful purposes. Four of these sites remain 'inspectable facilities', as do another 4939 industrial facilities worldwide.

Australia was an original signatory to the CWC on 13 January 1993 and was among the first nations to ratify it in 1994. Since 1995, the Australian Safeguards and Non-Proliferation Office (ASNO) has surveyed more than 3000 companies and organisations in Australia, to identify activities to be declared to the OPCW. About 150 companies or organisations were identified as having had relevant facilities or activities.

These days, 98% of the world's population across 193 member states lives under the protection of the CWC. This is maintained by a rigorous system of inspections and verification, for which Australia plays an active role. In recognition of the incredible effort to eliminate chemical weapons, the OPCW was awarded the 2013 Nobel Prize for Peace.

As early as 1985, our government and scientists were instrumental in the establishment of the Australia Group – a voluntary and informal forum currently consisting of 42 countries and the EU – to establish and harmonise another layer of due diligence in export controls. Australia is the permanent Chair of the Australia Group.

Across five categories, the Australia Group establishes agreed 'control lists' of chemical weapons precursors; 'dual-use' biological equipment, technology and software; pathogens and toxins; and 'dual-use' chemical manufacturing facilities, equipment and technology. According to the Arms Control Association: '… the 42 member countries assert that the regime acts as an impediment to CBW [chemical and biological weapon] proliferation by working to ensure that industries in member nations do not, either inadvertently or intentionally, assist states or groups seeking to develop CBW capabilities.'

RACI member Dr Vanessa Robertson is Director of CWC Implementation within ASNO. Robertson was in Europe in July this year for the most recent Australia Group Plenary, commented to *Chemistry in Australia* that 'Participants reaffirmed their commitment to strengthening chemical and biological weapons-related counter-proliferation efforts, and agreed it was a timely opportunity to further strengthen global endeavours to rid the world of chemical and biological weapons once and for all'.

Notwithstanding these international efforts, and the outstanding successes of the CWC over the last 30 years, the use of, and threat of, chemical weapons continues to plague our world. The United Nations Security Council has condemned the use of chemical weapons by Syria since 2013 in its ongoing civil war. At the Moscow theatre in 2002, Russia accidentally killed 125 of its own people when it exposed 750 hostages to overdoses of a fentanyl derivative in a rescue operation.

Arguably even more troubling, there have been multiple instances of the use of chemical agents by non-state groups, notably including the 1994 and 1995 attacks by AUM Shinrikyo in Japan, with 13 killed and more than 6000 people sickened or injured in the Tokyo subway attack of March 1995.

How Australia implements CWC obligations

More information is available on how Australia implements obligations under the CWC and works to counter the proliferation of chemical and biological weapons.

Australian Safeguards and Non-Proliferation Office

A number of chemicals produced or used for normal industrial, medical or research activities can also have applications in the manufacture of chemical weapons. Moreover, the types of chemical processes involved in the production of chemical warfare agents are also very commonly used in the legitimate production of commercial chemicals. The Australian Safeguards and Non-Proliferation Office (dfat.gov.au/asno) regulates the import, production, processing, consumption, acquisition and transfers of CWC Scheduled chemicals, and the production of 'discrete organic chemicals'.

Defence Export Controls

Defence Export Controls (www.defence.gov.au/business-industry/export/controls) regulates the export of military and dual-use goods and technology, including CWC Scheduled chemicals, Australia Group control lists and items captured in other export control regimes.

Australia Group

The Australia Group (www.dfat.gov.au/publications/minisite/theaustraliagroupnet/site/en/index.html) is an informal forum of countries that, through the harmonisation of export controls, seeks to ensure that exports do not contribute to the development of chemical or biological weapons. Australia is the permanent Chair of the Australia Group, with the Chair and Secretariat located within the Department of Foreign Affairs and Trade.

An Al-Qaeda attack on the New York city subway was averted in 2005.

Speaking in March 2022, OPCW Director-General Ambassador Fernando Arias stated 'As we draw closer to realising the disarmament goal of the Convention, we must increase our focus on preventing the re-emergence of chemical weapons use'.

As demonstrated by Syria (with at least 336 documented cases of the small-scale use of chemical weapons) and by Russia – both acting in criminal violation of their obligations as signatories to the CWC – there is a significant challenge in the policing of violations. A key issue has been that individual instances have been small scale and not necessarily meeting the threshold for intervention (although the US did launch missile strikes on Syrian facilities in 2017 as punitive response for specific attacks), while the benefit to the aggressor states accumulate over time with each successive use. Small-scale attacks are much harder to investigate, assess and attribute.

The same issue applies to the small-scale use of chemical weapons for targeted assassinations, as conducted by North Korea (Kim Jong-nam, Malaysia, 2017) and Russia. Beyond the 2018 Skripal poisoning mentioned earlier, the ABC has reported multiple Russian poisonings dating back as far as Lenin in 1919 (https://ab.co/3PJQleo). A British investigation also held Russia responsible for the 2006 radiological murder of Alexander Litvinenko, using polonium-210. Russia continues to refuse to cooperate with the OPCW to investigate the poisoning of Alexei Navalny, who was poisoned with a novichok nerve agent by the Russians in 2020 (bit.ly/3cxAIIG).

Russia has proved persistent in using its veto power in the UN Security Council to frustrate accountability for its use of chemical weapons. Russia and Syria consistently fail to cooperate with the OPCW, but there Russia has no veto so action proceeds. North Korea remains one of only four countries yet to accede to or ratify the CWC, and is believed to have the largest active stockpile in the world.

Delegates, including Australian Ambassador to the Netherlands H.E. Matthew Neuhaus, participate at the 100th Meeting of the OPCW Executive Council. The 100th Executive Council Meeting was held at OPCW Headquarters in the Ieper Room on 5–8 July 2022.

OPCW/CC-NC-ND-2

Chemical precursors remain another key challenge. The Centre for Strategic and International Studies notes that more than 15 000 new chemical substances are developed each day – more than 100 million new chemicals since the establishment of the CWC. Three of the top ten chemical producers, Russia, China and Brazil, all fall outside the precursor control regime; that is, they are not participants of the Australia Group. The backward-synthesis of known weapons from alternative and uncontrolled precursors remains a major problem.

Australia has recently committed an extra $350 000 to support the OPCW in developing additional scientific, chemical and operating capabilities, particularly forensic and analytical capabilities, to address the new and changing threats to international safety, and for assistance and protection activities in Ukraine.

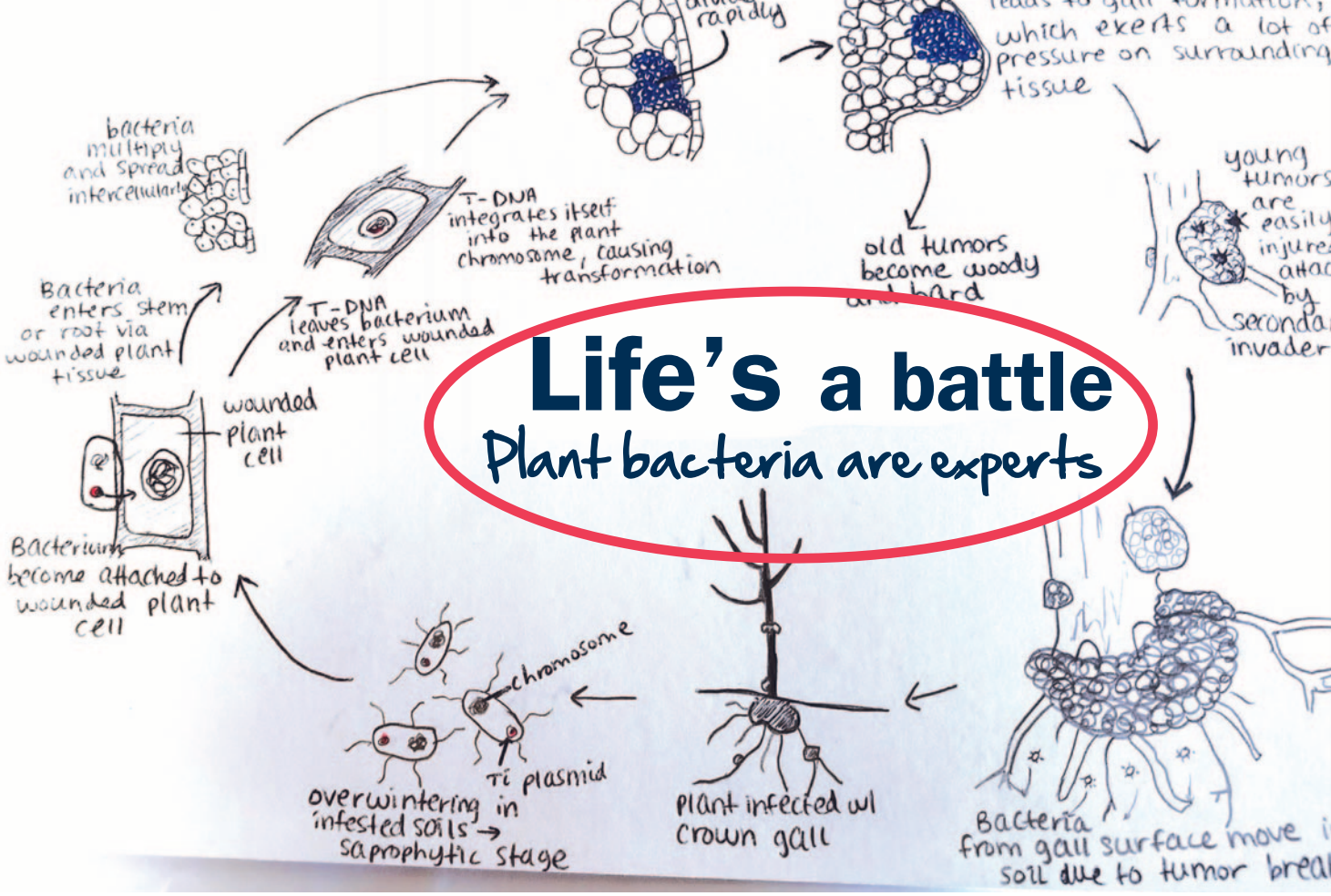
The evolving nature of the challenge is a responsibility for us all. We have the opportunity to make a positive contribution through care and compliance.

Dima Korotayev of Reuters summed this up well: 'Chemistry cannot be blamed for chemical warfare or terrorism, but the chemistry community has a duty to be aware of the danger and to act to prevent the misuse of chemicals. We must work to educate people about chemical safety, waste disposal and the responsible use of chemicals, starting at school'.

Dave Sammut FRACI CChem and **Chantelle Craig** are the principals of DCS Technical, a boutique scientific consultancy providing services to the Australian and international minerals, waste recycling and general scientific industries. The authors would like to particularly thank **Dr Vanessa Robertson** for her contributions to this article, for her services to RACI and the RACI Mentoring community, and most especially for her services to the people of Australia in making our world a safer place to be.

Life's a battle

Plant bacteria are experts



Disease cycle of *Agrobacterium tumefaciens*. Lkazen/Wiki

Publication of three papers by researchers at the University of Adelaide's School of Agriculture, Food and Wine has completed the work of the late Max Tate into bacterial antibiotics and control of plant pathogens.

More than 40 years ago, Max Tate and his co-workers at the University of Adelaide studied the compounds produced by bacteria that invade plants. At the time, important results from three students – Christopher Elvin, Anna Savage and Benjamin Lethbridge – could not be published with confidence.

Improvements in NMR spectroscopy and mass spectrometry have led to results that can be published. The studies of the three students all relate to compounds produced by bacteria that infect or colonise plants to outcompete their rivals.

Both symbiotic and pathogenic bacteria infect plants. The most important symbiotic bacteria are rhizobia, of which the genus *Rhizobium* is of most interest here. Rhizobia fix nitrogen in leguminous plants. They are attracted to plants by plant root exudates, while the plant uses lectins (non-catalytic proteins) to recognise the bacterial cell wall polysaccharides. Rhizobia commonly infect the plant through root hairs but can also enter the plant at wounds or cracks, or between cells of the intact epidermis. Once inside the plant, the bacterium forms a very close association with the plant that results in the formation of specialised nodules where the nitrogen fixation occurs. Cells of *Rhizobium* species change to a bacteroid form and colonise the nodules. The plant provides energy in the form of C4 dicarboxylic acids and in return the bacterium gives the plant nitrogen-rich compounds, which are synthesised by using nitrogen derived from the atmosphere.

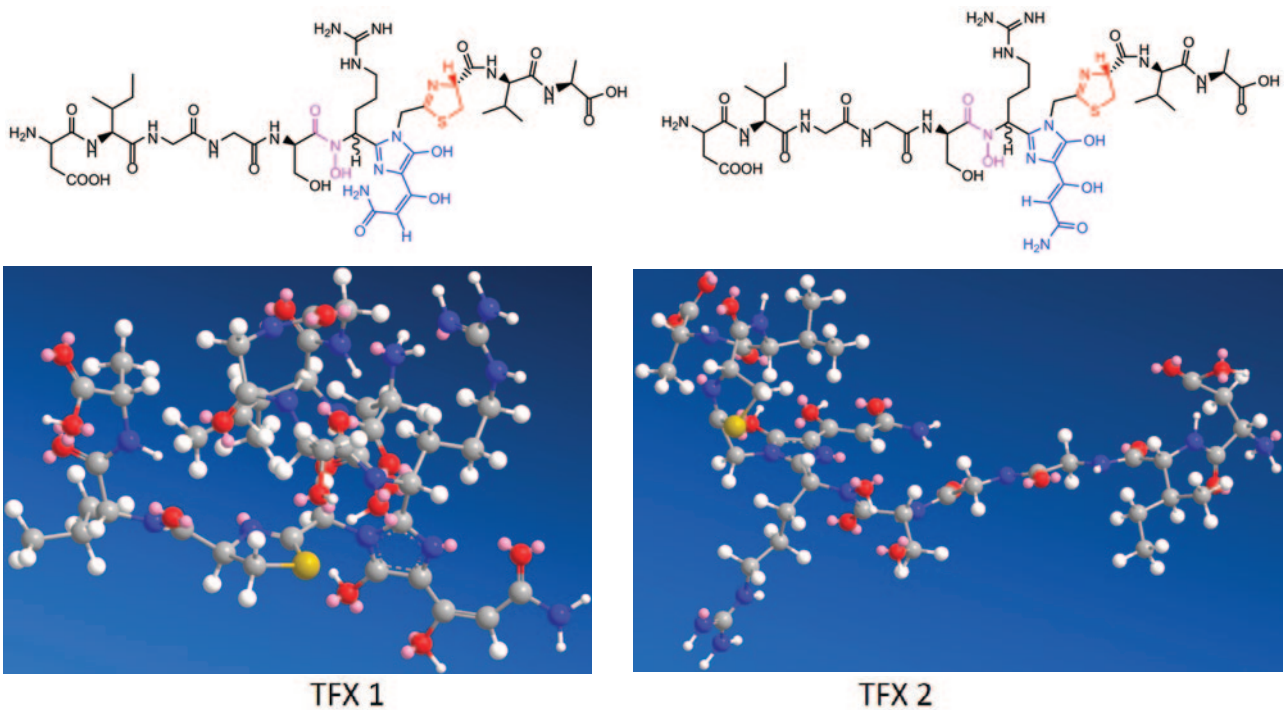
To gain an advantage over other rhizobia, some *Rhizobium* bacteria produce peptide-type bacteriocins (bacterial antibiotics). When first discovered in 1968, a bacteriocin produced by *Rhizobium leguminosarium* biovar T24, called trifolitoxin, was of great interest. This

Nodules on clover.

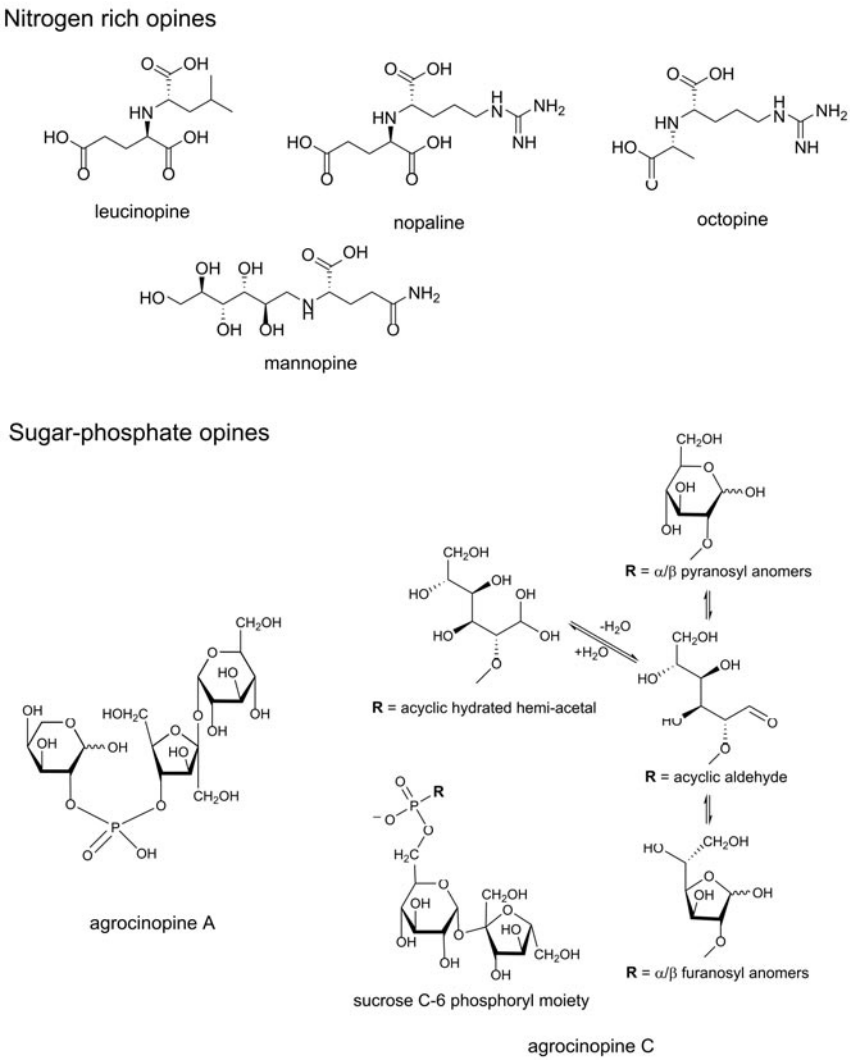
Crown gall on cherry tree roots (left) and kalancho stem (right).

bacterium is extremely aggressive in nodulation-competition experiments on clover through the production of an antibiotic that showed broad activity against fast-growing rhizobia. Ben Lethbridge devoted his PhD to the study of this bacteriocin peptide (doi.org/10.1038/s41429-021-00497-0). The bacterium has a simple strategy of producing trifolitoxin, which when released into the soil has direct action on other rhizobia.

There are more than 150 different pathogenic bacteria. Max and his colleagues were particularly interested in the tumour-inducing bacteria *Agrobacterium tumefaciens* and related species. Pathogenic *Agrobacterium* are closely related to symbiotic *Rhizobium* bacteria and are present in most agricultural soils. Crown gall is a plant disease caused by the bacterium *A. tumefaciens*. This carries a tumour-inducing plasmid (a self-replicating extrachromosomal DNA molecule) that contains pathogenicity-related genes, which enable it to cause gall formation on a range of dicotyledonous plants. Pathogenic agrobacteria are first attracted to specific chemicals leaking from plant wound sites and then firmly attach to injured plant cells. Plant wound chemicals can also activate the transfer of part of the tumour-inducing plasmid directly into the chromosomal DNA of the host plant cells. The T-DNA (transferred DNA) of the tumour-inducing plasmid, once inserted and



Trifolitoxin (TFX) is a bacteriocin peptide. It has a thiazoline ring, which is important for function. The three-dimensional shape is critical because TFX1 has little biological activity. The *cis–trans* configuration of the hydroxy-glutamine determines the three-dimensional structure of TFX.



Opines serve as *A. tumefaciens*-specific substrates synthesised by the plant after bacterial 'engineering' of the plant genome.

functional inside the plant cell, codes for the production of plant hormones, which leads to the formation of disorganised tumour tissue and opines, which are bacterium-specific nutrients. *Agrobacterium* is the only known organism capable of inter-kingdom DNA transfer.

Prior to the development of a biological control treatment that prevents crown gall (NOGALL™, based on *R. rhizogenes* (formerly *A. rhizogenes*) strain K1026; Professor A. Kerr, University of Adelaide), plant nurseries as well as almond and stone fruit orchardists lost up to 50% of seedlings to crown gall. Strain K1026 cells can colonise wounded plant tissue and block infections by the predominant crown gall-causing pathogenic agrobacteria that infect nut trees (such as almonds and walnuts), stone fruit trees (such as peach, plum, apricot and cherry), roses and many other horticultural crops. Galls are typically located on the crown of the plant at or below the soil surface but can also be found on other plant parts. Fruit trees infected with crown gall produce lower yields with variable fruit set, size and quality. In severe cases, crown gall can weaken or kill the host plant. Losses to the nursery industry can be particularly severe because plants with crown gall must be culled.

In the case of rhizobia, plants voluntarily supply the nutrients specifically required by the bacterium. In contrast, pathogenic agrobacteria 'engineer' the plant to synthesise opines required by the bacterium. Opines are produced in crown gall tissue because the pathogenic bacteria manipulate the plant's metabolic activities to force the plant to provide nutrients in a form that only the inciting bacteria can catabolise. Most of the known opines such as octopine, nopaline, leucinopine and mannopine are secondary amines and act as both a source of a nitrogen and a source of energy for the bacteria. Two carbohydrate phospho-diesters, agrocinopine A and agrocinopine C, were identified by Max Tate and his students at the University of Adelaide in the 1980s. They are a source of both phosphorus and energy for the tumour-inciting bacteria. These opines also promote the spread of the tumour-inducing plasmid in populations of *Agrobacterium*. After the identification of agrocinopine A, agrocinopine C was characterised by Anna Savage as part of an honours project. Our recent publication shows that agrocinopine C exists in solution as a mixture of five anomers (doi.org/10.1038/s41429-017-0014-y). We expect that agrocinopine A also occurs as a mixture of isomers in solution.

Agrocin 84 and agrocin 434 are two bacteriocins identified by Max and his students that are produced by different strains of *R. rhizogenes*. These non-peptide antibiotics are produced by the NOGALL bacteria (strain K1026) and form the basis of four decades of successful biological control of crown gall.

An interesting feature of the agrocins is that they have a toxic moiety and an uptake moiety. The uptake moiety allows the entry of the bacteriocin through recognition by certain membrane transporters (permeases) by deception. This uptake system has been described as a Trojan horse. For example, only

Max Tate, natural product chemist

Max Tate passed away in 2016 after a battle with melanoma and having spent the best part of 35 years working at the University of Adelaide, initially in the Faculty of Agricultural Science, later known as the School of Agriculture, Food and Wine, on the Waite campus. Max studied at the University of Sydney, did his PhD with Stephen Angyal at the University of New South Wales, and then did a postdoc in Canada before moving to the University of Adelaide in 1964, where he taught until his retirement in 1998. He continued working there as visiting scientist until his death. During this time Max trained numerous research students, with his initial research focusing on the structure and function of inositol phosphates. A very productive part of Max's research career was with his good friend Professor Allen Kerr on the internationally recognised biological control of crown gall and the study of naturally occurring antibiotics against plant pathogens. This research led to the development of a genetically modified biological control agent for crown gall, a plant tumour disease of economically important tree crops, which is still a commercial product in several countries worldwide.

Max applied chemistry to solve a diverse range of biological problems that, besides the work mentioned above, included non-wetting sands, bacterial conjugation factors, anti-helminthics and wine chemistry. Even though Max was an early adopter of thin-layer chromatography, when he discovered high-voltage paper electrophoresis, this became his method of choice. However, Max was not afraid to use a diversity of techniques to give him the independent data necessary to complete a study. Max always claimed he had a well-developed 'bullshit detector' and would not be compromised by soft arguments. To quote Professor Allen Kerr, 'Max taught his students to think of nature as chemical simplicity rather than biological complexity'. Max was a long-time member of the RACI. He told the story of how Adrien Albert thought that some of Max's work was interesting and so asked if Max would join a soon to-be-formed Division of the RACI. For this reason Max considered himself (others may disagree) the Agricultural part of the Medicinal and Agricultural Chemistry Division. These three papers essentially complete Max's studies. The only research problem remaining on which Max devoted a great amount of energy in his later years was to develop a vetch (*Vicia sativa*) without the potential neurotoxin γ-glutamyl-β-cyanoalanine. It is now time to say vale Max Edwin Tate (1932–2016).

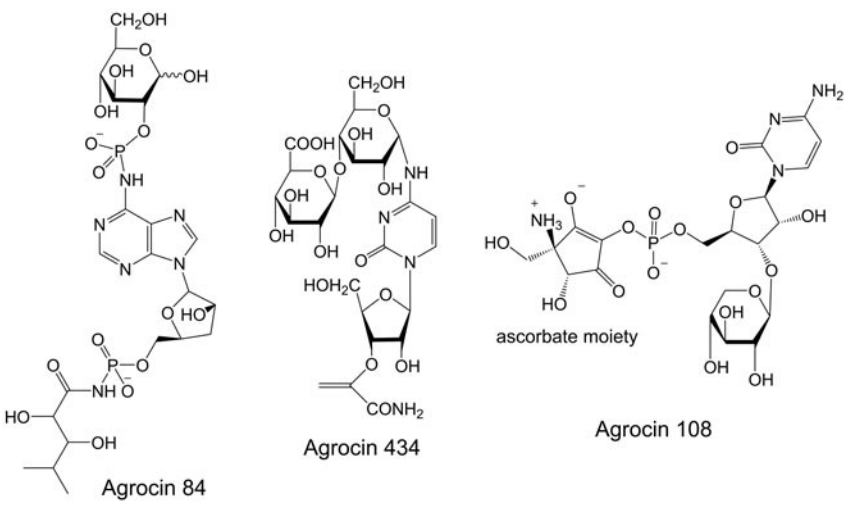
bacteria with specific agrocinopine transporters are sensitive to agrocin 84. To protect against crown gall, both agrocin 84 and agrocin 434 are delivered by the application of a live, non-pathogenic *R. rhizogenes* (strain K1026) to the roots, cuttings or seeds of susceptible plants before planting.

Chris Elvin studied another bacteriocin, agrocin 108 (doi.org/10.1038/s41429-017-0014-y). This was isolated from *R. rhizogenes* strain K108 and is another low-molecular weight nucleotide bacteriocin that could be used in conjunction with both agrocin 84 and agrocin 434 to give greater protection against crown gall.

It is interesting that two closely related bacteria have quite different strategies in their battle for supremacy. Ben Lethbridge's peptide antibiotic, synthesised by certain strains of *R. leguminosarum*, acts directly on the competition, while strains of *R. rhizogenes*, studied by Max and his co-workers (including Chris Elvin), not only produce non-peptide antibacterial compounds to attack competitors but also have the strategy of forcing the plant to produce opines, including Anna Savage's agrocinopine C, which neither the plant nor competing bacteria can utilise.

It has taken 40 years of improvement in instrumental chemistry, some ancient samples, a few 'naughty' bacteria and a very dedicated scientist (R.E. Asenstorfer) to be able to finalise these three publications for Max Tate.

Robert Asenstorfer MRACI CChem, **Maarten Ryder**, **Scott Donner**, **Benjamin Lethbridge** and **Graham Jones** MRACI CChem are at the School of Agriculture Food and Wine, the University of Adelaide. This paper is dedicated to the memory of Max Tate.



Agrocins are bacteriocins that have a toxic moiety and an uptake moiety. Certain bacterial membrane transporter proteins for specific nutrients allow the entry of the bacteriocin. Agrocin 84 contains a fraudulent adenosine, agrocin 434 has a fraudulent cytidine and agrocin 108 has a fraudulent ascorbate at the toxin moiety. These groups are coupled to sugars to help them pass through the membrane via a transporter (permease).

Catalysing solutions at 2022 National Congress

'Chemistry: Catalysing Solutions to Global Challenges' was the theme of RACI2022 National Congress, held in July in Brisbane. The attendance of more than 1200 delegates in person over the five days made it clear that this had been an anticipated event, both for professional development and for meeting and reuniting with others.

The Welcome to Country was given by Yuggera Elder Steve C. Coghill Snr. Speaking with *Chemistry in Australia* about his perspective for a better future and how chemistry/science can play a role to address global challenges such as climate change and energy shortages, he said, 'First and Traditional Owners are primary knowledge holders and carers of the Land, Sea, Waterways and Sky. The FTOs' participation, support and advocacy, from the outset, will contribute to, among other things, practical perspectives in social and cultural recognition and integrity.'

Steven Bekue, a Bundjalung, Yuggera and Bidjara man, created his piece *The First Scientists* (pictured) for the Congress. He was asked to paint his vision of First Nations peoples' integral relationship with the land and natural sciences.

Speaking with the RACI, Steven said, 'Our Ancestors and people have amazing scientific knowledge that has developed over thousands of years.' In relation to chemistry, he described the making and use of new substances as bush medicines, glues, paints and food sources. 'We have survived by using these scientific practices and will continue to utilise them for all generations,' he said. Steven's art was greatly admired on the wall, as well as on the t-shirts and cushions at the RACI stand. After its return to Melbourne, it will have pride of place in the National Office.

Several generations of chemistry professionals came to the Congress to share, mentor, learn and network. Although the subdisciplines represented were diverse, there were overlapping goals to solve global and interconnected problems related to climate change, sustainability, pollution, health and safety, energy/fuels, disease and medicines, defence, biosecurity and food security. Thanks to the hard work of the RACI, Congress chair Debra Bernhardt, the organising committee, PCO – Expert Events, the sponsors and the presenters themselves, more than 500 plenary, keynote, invited and contributed presentations were delivered across more than 10 streams. Here's a sample of what was on offer.

Rachel Caruso from RMIT University spoke about energy challenges as an opportunity for chemistry. 'We have to throw everything at this problem,' she said. She described the tension between some of the Sustainable Development Goals and the conundrum of needing to help people out of poverty while also needing to reduce carbon dioxide emissions. As part of her work in photocatalysis, photovoltaics, batteries and radionuclide sequestration, she has seen that manipulation of composition and morphology can enhance performance of materials. Rachel and other researchers in these fields have been using the machine learning approach to investigate which materials will make the best candidates to help meet the global energy challenge.

To help tackle rising antimicrobial resistance, James Chapman, also at RMIT, is combining machine learning and chemometrics with established benchtop systems such as spectroscopy as an alternative to often-outdated microbial assays. Using these new approaches, his team have been able to extract much more nuanced data, such as when a microbe is consuming nutrients and when it dies. Machine learning was also described at other sessions, where it is aiding design in carbon nanomaterials and fabrication of 2D heterostructures.

Several sessions in the industrial chemistry stream focused on packaging and the progress being made towards a circular economy. Leslie Fox, Partnership and Development Officer for not-for-profit organisation The Australian Packaging Covenant Organisation, explained the Australian Packaging Covenant's aim to keep packaging out of landfill and what is being done to reach the 2025 National Packaging Targets. Change is happening, but there are barriers to investment and issues with access to infrastructure – which means that a lot of package that is recyclable is not being recycled. We must ensure, she said, that there are markets for the reused and repurposed products.

Alisa Becker, Manager, Innovation and Engagement Services at CSIRO, in her 'Research to Value' presentation, described researchers as 'purpose-driven people who want to solve real-world problems,' and hence they are best placed to facilitate the move from research to impact, rather than seeing their work as separate from the commercialisation process. Many new enterprises can fail because the end use has not been clearly identified. She emphasised the importance of understanding the people behind a problem, and a mindful approach.

Ben Long reported on the successful Bush Medicine Project at Federation University, which gives students opportunities to engage outside their discipline and in Indigenous culture. Chemistry students collaborate with students studying Australian flora, microbiology and toxicology/pharmacology, and across year levels, to collect and identify plants of interest, and prepare extracts and a chemical fingerprint, and they screen extracts for antimicrobial activity and toxicity. Participating students reported liking the 'real-ness' of this project.

Stephanie Schweiker of Bond University's Faculty of Health Sciences and Medicine took session attendees on a tour of virtual laboratories and experiments developed as part of a multimodal (hybrid) model for remote students. Based on student feedback, some gamified chemistry experiments have been developed (freely available at thevirtualscientist.com).

According to Stanford University physicist and educationist Carl Wieman, 'science education has remained largely medieval', largely due to tradition and dogma, and research-based

Steven Bekue's *The First Scientists*, commissioned by the RACI for the 2022 National Congress.

teaching is 'setting the stage for a new approach to teaching'. Speaking at one of the final plenaries, he explained the importance to learning of practising expert reasoning. A surprisingly small set of decisions (just 29, he said) is common to all science and engineering disciplines – for example deciding what concepts and information are relevant, which approximations are appropriate and which solution methods to pursue. The intense thinking that happens when choosing paths and making decisions (rather than passively listening to lectures) forms and strengthens neural connections, which is evidenced by changes on brain imaging.

Tristan Casey, Chief Scientist at Work Science, shared results from a frontline supervisor safety leadership program for the explosives industry. He described the tensions of limited resources, multiple viewpoints and shifting priorities that safety leaders face. He said that often a combination of standard models (behavioural, values-based, charismatic and vision-based) is needed, as well as mindful awareness of the intent of safety measures (deep compliance) rather than surface compliance.

The HSE Division hosted a mock laboratory incident, where an expert panel delved into the planning, risk assessment, investigations and legal framework for managers and lab leaders. This was one example of the many extra events running during lunchtimes and evenings. Several meetings and symposia ran parallel to the Congress, and there was a social program that catered for partners and families.

'Flash' poster sessions (one-minute summaries) demanded that presenters deliver the 'bare bones' of their research, honing skills important for collaboration, outreach and grant applications. After a flurry of nerves in the lead-up to the event, the researchers rose to the challenge.

Other topics over the week included drug discovery, Australia's fledgling graphene industry, catalysis as an enabler of climate change mitigation and electrochemical sensor development. There was plenty of fodder for future articles, so stay tuned.

RACI CEO Roger Stapleford was particularly pleased to see the enthusiastic mingling during breaks and an excellent attendance by students. The enjoyment of meeting face-to-face again was evident. The 2021 awards were finally able to be presented, and it was wonderful to see both emerging and established chemistry professionals take to the stage.

In the same spirit as the conference theme, RACI member Qin Li and others launched the Green and Sustainable Chemistry National Group, 'to lead the research, training and debate' in addressing global issues such as climate change, resource shortages and the decline in biodiversity to enable and accelerate the societal transformation that will be needed in Australia. This group will join 14 divisions, which include many of the bright and determined minds that made the Congress such a vibrant one.

Sally Woollett is Editor of *Chemistry in Australia*.

Vale Jacob (Jack) Shemuel Shapiro (1937–2022)

Polymer chemist

Dr Jack Shapiro, formerly a senior lecturer in the (then) School of Chemistry at Macquarie University, passed away on 22 April 2022. Jack was a polymer chemist who, in the 1990s, contributed to many aspects of the conducting polymer polypyrrole. At the time, this was a competitive field of research – one that subsequently led to the development of organic light-emitting diodes.

Jack was born on 26 November 1937 in Israel. He left Israel in 1952 and spent 18 months in the US before arriving in Australia. He achieved his leaving certificate at a private college in Mosman in 1955, completing his fourth and fifth high school years in a single year. While working at a company called Chemical Materials at Glebe Point, he completed his BSc at the University of New South Wales. Resigning from the job at Chemical Materials, he undertook his honours course, graduating with first class honours in applied chemistry. He then won a postgraduate scholarship from Imperial Chemical Industries (ICI; now known as Orica Limited) and undertook PhD studies, successfully completing these in 1965. He was awarded a two-year National Research Council Fellowship by the Canadian Government and following this he undertook research work at Brookhaven Laboratories in the US. Upon returning to Sydney in 1969, he accepted a lecturing position at the College of Advanced Education (now the University of Technology, Sydney) for six months, then moved back to the US to take up a position in the Polymer Division at Amoco Oil in Naperville, Illinois.

In February 1973, Jack secured a lecturing position in the (then) School of Chemistry at Macquarie University, where he remained for the next 25 years until his retirement in 1998. Jack had fond memories of the small group teaching in that School of Chemistry when Macquarie University was in its infancy. He described those early years as 'a good time'. Jack played a major role in teaching polymer science and was also particularly fond of teaching the introductory chemistry courses offered externally to students with little or no high school chemistry background. During his years at Macquarie University, he had several periods of leave at British institutions, including Bristol University, Queen Mary College, London, and Durham University.

Jack had always had a keen interest in gardening and bird life and these became his hobbies in his retirement. While for several years he enthusiastically attended talks on native Australian plants at Ku-ring-gai Wildflower Garden, it was birdlife that became his real passion. This is evident from one of his remarks, 'My bird count of Australian birds now stands at 635, still a long way from the legendary 775 mark. 700 is a number many bird watchers in Australia strive to. One Englishman who lives in Melbourne holds the record of 803 bird species in Australia!'

Jack was admitted as a member of RACI in 1975.

Jack Shapiro in 2018.

Danny Wong FRACI CChem, FRSN and **Robert Failes**

Charles Sturt University Port Macquarie campus
Charles Sturt University

Charles Sturt University now RACI accredited

RACI congratulates Charles Sturt University on becoming the latest university to have its chemical science program officially RACI Accredited. You can find out more information on the RACI accreditation process at www.raci.org.au/web/Schools/Accreditation_Program.

Chemical Engineering lecture theatre renamed in honour of former Dean David Wood

The contribution of an 'international statesman of the chemical engineering profession', Professor David Wood AM FRACI CChem, has been officially recognised by the University of Melbourne.

The main lecture theatre within the Chemical Engineering Department has been officially renamed the David Wood Lecture Theatre, in honour of its former Head of Department and later Faculty Dean.

Professor Wood served as Head of Department for 14 years, from 1982 to 1996, before serving as Dean of the Faculty of Engineering until his retirement in 2002. He passed away in October last year.

Over 100 people attended the renaming event in July, including Professor Wood's family, former colleagues and students.

Professor Amanda Ellis, Head of the Chemical Engineering Department, said the Department had built on Professor Wood's vision and continued to thrive in recent years, with strong student numbers and contributions to many important research areas such as carbon capture, soil remediation, innovative corneal (eye) treatments, next-generation batteries, machine learning and many innovations that would provide 'clean energy solutions needed for our complex future'.

Also speaking at the event, a former student of Professor Wood's, Professor Sandra Kentish, Head of the School of Chemical and Biomedical Engineering, said two attributes stood out to her.

'He understood "diversity and inclusion" before it was invented, and he was a great leader, particularly in building links with Asia and in instilling leadership in others.'

Professor Wood joined the Department in 1964 after completing his PhD at the University of London. He was one of five academics in the department at the time and taught across the entire chemical engineering program.

Left to right: Sue and Mike Wood (David's son), Elene Wood (David's widow), Alison George (David's daughter) and Con Koumis (David's brother-in-law) at the renamed lecture theatre.
Cesar Nicolas

He was a passionate teacher and an inspiration for many students. He developed and taught the subject Process Engineering, in which students were given vague, poorly defined problems that replicated the types of real-life problems they would encounter in industry. Not all students loved the subject, but all agreed it helped to prepare them better for their roles as engineers.

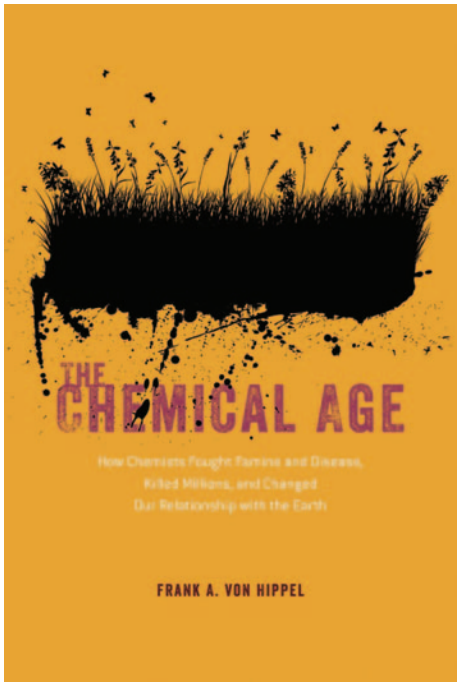
Professor Wood was a strong advocate for women to study in the field of engineering. During his tenure as Dean, he created the position of Assistant Dean (Equity and Diversity). He helped build the Department into one of the strongest in the country and established international ties with Asian institutions that led to a significant increase in the number of international students in the faculty.

He was journal editor, committee member and later Chair of IChemE, the professional qualifying body for chemical, biochemical and process engineers.

Along with his wife, Elene, he established a scholarship to provide financial support to disadvantaged and rural students. Among his many achievements, he was a chief architect of the Unisuper scheme.

After his retirement, Professor Wood continued as an emeritus professor of the university and a professorial fellow, serving the chemical engineering profession in many capacities. He chaired the Sixth World Congress of Chemical Engineering, held in Melbourne in 2001, where the Melbourne Declaration for Sustainable Development was adopted by many of the world's leading chemical engineering societies. He served as the President of RACI from 2010 to 2012 and was the first President of the World Chemical Engineering Council. During his long career, he was awarded several medals and accolades for his exemplary work and service in the field of chemical engineering in Australia and internationally.

University of Melbourne



The chemical age

von Hippel F.A., University of Chicago Press, 2020, hardback, ISBN 9780226697246, ebook ISBN 9780226-697383, 368 pp., $44.30

Frank von Hippel's *The chemical age* is sobering reading, at times exhilarating and at other times quite saddening. This is evident from the subtitle 'How chemists fought famine and disease, killed millions, and changed our relationship with the Earth'. The last century or so has really been a 'grand age' for chemistry. Significant progressions based on chemistry have advanced human civilisation in very many ways, lifting people from lives of poverty, drudgery and life-threatening disease to improved longevity and living standards. As chemists, we can feel some pride and satisfaction. If you can put Rachel Carson to one side for a moment, then there must be enormous pride in the discovery of DDT, which has saved untold millions of people from the scourge of malaria. However, equally, it is utterly not possible to ignore the ecological effects described in Carson's *Silent spring*. As with many great chemical innovations, there are benefits and there are costs, causes and consequences, swings and roundabouts. A lot depends on where you stand. Raining weapons of war on your enemies is nowhere near as evil as the converse!

The book begins with the Irish potato famine in the 1840s, which led scientists to direct effort into developing pesticides as a way to safeguard against insect infestation and enhance crop yields. Chemists got better and better at killing perceived pests right up until the 1960s when broader ecological consequences and concerns emerged (largely due to Rachel Carson). The author explores themes of famine, plague and warfare through to the modern chemical age. With warfare, again, application of chemistry has ensured nations have got much much better at the processes of mass and, indeed, individual slaughter. Yes, chemistry has done great things over the last century or so, but there have also been some nasty unexpected consequences too. The final section of the book, Ecology, traces the rise in concern for our planet from 1945 onwards. After feeling somewhat 'hang-dog' for most of the book, there is hope to be found here.

Author Frank von Hippel is professor of ecotoxicology at Northern Arizona University. His research background has encompassed the Americas, Africa and Australia and he has taught ecology field courses in more than 20 countries.

When I read this book, it enhanced my understanding of why quite a lot of young people turn away from chemistry. After all, there have been some colossal, out-loud stuff-ups that can be sheeted home to chemistry. Fortunately, or fortuitously, the world is continuously changing, and chemists are changing (or being changed?) with it. We are now much more aware of ecological systems and their role on Earth and much more aware of our need to act in harmony with them. Green chemistry is here to stay. If chemistry is to thrive into the future, we all need to start singing lustily from the same hymn sheet about all the good things chemistry has done and is doing; apologise for our past (professional!) sins; and explain how we are better now. (And, for heaven's sake, do not mention leopards!)

I found the book both enlightening and interesting. I recommend it to anybody interested in the recent history of chemistry as well as to readers interested in the ecological and societal impacts of large-scale chemical developments over the modern chemical age.

R.J. Casey FRACI CChem

Eureka! Making copper that comes out green

Science is, for most of us I hope, as much a passion as a career.

Once every few years, there comes for me a moment when all of the data, all of the literature, all of the experiments – ones that have worked and ones that have failed – fall together. This moment hits me like the chime of a perfect note. The ideas crystallise in my mind in perfect formation, and for one fleeting instant it feels as if I could almost understand the universe.

That feeling slips away again pretty rapidly, but those few moments of unalloyed intellectual joy sustain me through the long hours of all the other hard work and discipline that being a scientist demands.

In late 2021, I got to experience that thrill again. While working a problem with my colleagues, taking their ideas and adding them to the collective, I was struck by an idea so revolutionary (in my little specialist field), so utterly perfect, that I instantly *knew*. I knew that the idea was right. I knew that it would work. I knew that it would solve a challenge that I had been idly pondering on since the beginning of my career – in other words, for nearly the last 30 years of my life.

I started my career at a small industrial research lab in Sydney. We were trying to develop and commercialise an entirely new way of producing copper and other base metals from mineral concentrates.

Putting that into context, copper typically comes out of the ground at about 5% concentration, in various forms of copper sulfide mineral: most commonly $CuFeS_2$, but also CuS, Cu_2S, Cu_5FeS_4 and occasionally more exotic minerals such as Cu_3AsS_4. The host rocks are crushed and the target minerals extracted by froth flotation to yield a 'concentrate' of 20–25% copper grade.

There are various processes to make metal, but the most common route is (by train, truck or ship) to a matte smelter, which separates metal sulfides from gangue to produce copper matte – an enriched mineral sulfide mixture at about 60–65% copper grade. The matte is transported to a 'converting' smelter to make 'blister copper' metal at 98–99% purity. Then the blister copper is transported yet again, to a refinery that finally produces 99.99% purity metal by anodic dissolution and cathodic reprecipitation in a (sulfate-based) electrowinning tankhouse.

It *is* possible to leach the minerals directly into solution by using sulfuric acid, then to purify the mixture by solvent extraction, and then to electrowin the copper back directly from the 'pregnant' leach liquor. Rather than smelting (pyrometallurgy), this is called hydrometallurgy, and it's a growing alternative in global copper production. The problem is that sulfate is a very poor chelating agent, so all of the existing processes are slow (and therefore costly) or require high temperatures and pressures (which is *really* costly).

The idea that we were working on was a single process to use the extremely strong chelating effects of halides for much more efficient mineral leaching. In theory, we could take copper concentrate directly through to high-purity metal *at the mine site*. Leach, purify, electrowin. Fast, flexible and cheap. Doing so would have massive environmental and cost advantages: no gaseous emissions, no liquid effluents, safe rejected iron and sulfur solids that never leave the mine site. It could also more fully utilise existing resources, and safely process contaminated resources, such as those containing arsenic.

Critically, copper forms Cu^{2+} in sulfate, but in the halide system it can also form Cu^{+}. Needing only one electron per atom to recover the metal from solution, and with key electrical advantages, the electricity requirement would be more than halved, with all the cost and greenhouse advantages that arise from that.

That approach in itself wasn't new. The first papers on the topic appeared in the early 19th century. Until the 1980s, materials of construction made it impossible. However, unlike sulfate systems (which form neat, flat-plate cathodes), the direct electrowinning from halide forms dendritic crystal structures – effectively 'little trees'. These make electrowinning incredibly challenging, and none of the previous designs worked very well – not well enough for commercial application.

That latter problem is what has kept halide hydrometallurgy to being just a niche industrial application for the last 40 years. You could either get copper into solution easily (for which halide is best) or get it back out easily (for which sulfate has until now been the best), but not both.

I'm delighted to report that this easy-in easy-out problem is what my colleagues and I at DCS Technical have finally cracked. We've designed a completely novel electrowinning cell to produce and recover the dendrites in a controlled fashion, at a fraction of the cost of existing technologies.

That means that we can have all the advantages that halide leaching has promised for so long, but now with an effective and efficient way of directly electrowinning the copper metal from that halide solution. With all the resulting economic and environmental advantages, we're calling it 'copper that comes out green'.

With just 6–8 years of further effort in commercialising this breakthrough, my team and I could become an overnight success!

In the meantime, let's all celebrate that special element, 'enthusiasum', that brings us all together as scientists. Your Eureka moment is out there, just waiting for you. I wish each and every one of you that joy.

Science for life!

Dave Sammut FRACI CChem is the principal of DCS Technical, a boutique scientific consultancy providing services to the Australian and international minerals, waste recycling and general scientific industries.

Chris Ryan/iStockphoto

Innovation: joint technology planning

The most important value in building successful research partnerships between a researcher and a business executive is trust. Therefore, having a clear common purpose is critical. Building trust can be complicated by different expectations of the researcher and the executive involved in developing a partnership. A top researcher expects to be operating at the edge of new knowledge, whereas a business executive seeks a secure innovative opportunity to grow the business. A novel material recently developed in a laboratory may provide a solution to a problem that is not the central problem for the company. This is the difference between the two factors, science-push and industry-pull. Research innovation is at its best and most productive when there is an optimum balance between these two factors.

Research innovation itself has many variations, all of which are valuable. Choosing the form for best results depends largely on context. First, a single researcher or small group may develop a novel product that is able to be commercialised and they then engage with a company to manufacture and market the product under contract. Second, a company may identify and engage a single researcher with special expertise to develop a product that the company knows will have a strong market. Third, a company and a research team may conduct joint technology planning together where the intellectual contributions to innovations come from both parties operating as a unified team. Joint technology planning (JTP) works best when there is a high level of shared but complementary technology knowledge, a shared commitment to innovation, and trust between the company and the research team.

The JTP approach emulates to some extent corporate R&D planning around an important new product. For example, in the case of Du Pont developing a new coating for golf balls (a very large global market!), the company probably established an interdisciplinary project group drawn from several of its divisions, including polymer chemists, mathematicians (modellers), fluid dynamics engineers, manufacturers and marketers.

During 2008–20, I initiated and convened JTP meetings with many New Zealand companies as an important aspect of several large research contracts. The JTP process was progressively refined over that interval. The JTP process always started with the convenor, usually me, and one other senior researcher meeting informally with the CEO and/or CTO of the company to explore and confirm if there was a genuine interest in joint research and a shared culture of innovation. The senior executive also outlined for us briefly the core business of the company. Then as convenor of the JTP, I selected and then invited a team of several senior researchers with different capabilities from across the fields of science, engineering and medicine to cover the main dimensions of the core business of the company. With major NZ Government-funded research, we were strongly encouraged to establish a 'NZ best team' and so some members of the team would be from other provider organisations, including other universities and NZ Crown

Research Institutes (government laboratories). I recommended to the senior executive the names and range of research capabilities in the interdisciplinary research team for their agreement.

We then convened a JTP meeting with non-disclosure agreements signed prior to the meeting. The JTP meeting was limited to not more than 12 members because smaller groups encouraged genuine exchange, discussion and debate by individuals. The senior company executive began by explaining the core business and the technology aspirations of the company (in confidence) and the future product options that the research team might be able to help the company develop. Each researcher then briefly described how their research capability related to the technology aspirations of the company. At this point, the senior executive nominated the top priority new product concept and the team of researchers brainstormed ideas for achieving success with the future product. The company executive then critiqued or elaborated the product development suggestions. This was done for all prioritised future product projects. These joint product development plans were written up as a confidential JTP plan for the partnership and this plan was submitted to the company for agreement or amendment. The plan then became the basis of a terms sheet and then a formal agreement between the research organisation and the company.

The key to our JTP success over the interval 2008–20 was a high level of mutual understanding of each other's needs and capabilities. The advantage to the company as a result of JTP is that they get a complete product development plan rather than just a single product development or modification or single problem solved. The advantage to the researcher is that they get a bespoke partnership with the company in their primary capability area, which may lead to other future joint projects. With my retirement in 2020, the JTP strategy is certain to be continued and refined further by researchers and executives in other new research programs. Of course, the international corporate world that inspired the JTP approach will continue to deploy its original version of interdisciplinary product development strategy.

The JTP protocols outlined here were employed by NZ Ministry of Business Innovation and Employment (MBIE)-funded research projects and programs: the Biocide Toolbox, Hybrid Polymers, Materials Accelerator etc. As the founding director of these MBIE programs and Pro Vice Chancellor of the Innovation Campus, I introduced the JTP process to help achieve contracted levels of industry engagement. These were large national network programs involving interdisciplinary teams. The JTP method was initially developed and employed at the University of Auckland Tamaki Innovation Campus but also continued strongly on other campuses during 2008–20. The Innovation Campus was developed as a mainly postgraduate campus based on international foresighting themes that involved research partnerships between the universities, Crown Research Institutes (government laboratories) and NZ companies.

Ralph Cooney ONZM, FRSNZ, FRACI CChem has had a science and innovation career bridging New Zealand and Australia. He was former University of Auckland Pro Vice Chancellor of the Tamaki Innovation Campus, Dean of Science, Head of Chemistry and Science Leader of several major national research programs.

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transport from the remote locations contemplated. Again, new chemistries are being explored to solve these problems.

It is interesting to note that the general public are becoming increasingly aware of the various chemistries and technologies needed to transition to cleaner, lower-CO_2 energy. Just as the pandemic drove everyone to become amateur epidemiologists and experts on vaccines, the impact of global warming now drives the public to judgement on the merits of the chemistries contemplated to solve this looming crisis. Election outcomes are being decided on a candidate's advocacy for technical solutions, which focuses governmental attention. The internet amplifies the voices of nouveau experts on many topics, including the merits of various hydrogen production chemistries, which influences voter behaviour. As professionals in the discipline of chemistry, it is important that RACI members inject rationality where we can into this debate, especially when simple answers are sought for complex questions. Electric vehicles are broadly considered by the public to be the solution to our global greenhouse emission problems. Engineers worry that we are short of the infrastructure needed to deliver this level of power. Geologists wonder if we have enough copper in the world for all the electric motors envisaged. As chemists, we recognise we must move away from simple combustion to power our society, but we also understand the challenges involved and that potential solutions are nuanced. Thermodynamics makes high-temperature oxidation hard to beat, but smart solutions can still be delivered by good chemistry.

Like some of the methods for the synthesis of hydrogen, the RACI is also over 100 years old. This doesn't mean that new ideas and approaches aren't being generated in our organisation. At the July RACI Congress, chemists came together to consider the creation of a new Division, provisionally entitled Green and Sustainable Chemistry. Perhaps in the future, 'GASC' Chemistry members may discover and deliver the new environmentally sustainable energy chemistries we all need for a viable future.

How prominently hydrogen will feature in that future is yet to be determined, but it is clear that chemists and chemistry certainly will.

Steven Bottle FRACI CChem (president@raci.org.au) is RACI President. This is his final column as President.

Mugil cephalis **(flathead grey mullet)** Paolo Gamba/Flickr/CC-BY-2.0

Natural products – mainstream but not always natural

It is generally accepted that advances in natural products chemistry early last century inspired much of what is modern organic chemistry. Each year, peer-reviewed scientific journals publish thousands of articles, and legions of researchers, educators and students attend conferences and seminars showcasing the latest discoveries in basic and applied natural products science, spanning such topics as detection, isolation, characterisation and structure elucidation, biosynthesis and synthesis, chemical ecology and pharmacology, molecular targets and mechanism of action, and much more. Knowledge of natural products has informed our understanding of life, inspired many of the world's most successful drugs, agrochemicals and biomaterials, and fuelled a revolution in industry, commerce, health care and agriculture.

No longer exclusive to science, awareness of natural products has moved mainstream. Public encounters with natural products as antibiotics (penicillins, tetracyclines), antilipidemics (statins), analgesics (aspirin, opioids), antiparasitics (avermectins), insecticides (pyrethroids, spinosads), herbicides (glufosinate – forerunner to glyphosate) or stimulants (caffeine in coffee, tea and various soft and energy drinks) has had a lasting and profound impact. Natural products make our lives better! As a result, we all know what natural products are – but do we really? Within the world of natural products science lies an inconvenient truth – *natural products are not always natural!* Before elaborating, consider what we mean by the term 'natural product'.

It is surprisingly difficult to pin down a working definition of a natural product. Without going down the historical rabbit hole of who said what, when and why, for a large part of the last century natural products were viewed through the binary delimiters of primary versus secondary metabolites, with the former being essential and the latter non-essential to normal growth, development and reproduction. For some, this provided a satisfactory albeit naive circular logic that defined natural products as secondary metabolites, and secondary metabolites as natural products. Equally out of touch with modern thinking, as an undergraduate in the 70s I remember a very senior biochemistry professor advising me that much like non-protein-coding DNA, natural products were nuisance chemistry with no particular purpose – so if I wanted a career in science, it would be best to avoid such molecular detritus. Fortunately, my organic chemistry professors were more enlightened, and the rest is history. Putting aside the primary versus secondary dichotomy, perhaps a safer definition of a natural product is 'any chemical isolated from a living organism'. But is it really safer? Let me illustrate with an example from my lab.

For several decades, my research team has studied Australian natural products, with a bias towards those of marine origin. One particularly fun project started with a visiting Brazilian student purchasing three fresh mullet (*Mugil* species) from the local fish shop, from which she excised gastrointestinal tracts and isolated more than 500 chemically distinct fungi. An array of technologies was used to prioritise these fungi in favour of those most likely to produce natural products new to science, with subsequent studies yielding many noteworthy discoveries, including unprecedented Schiff bases such as **1**–**3** (*Org. Lett.* 2018, vol. 20, pp. 377–80). Of note, although the dimer **1** and trimer **2** were isolated from a solvent extract of the fungal

culture, the monomer **3** was not. We speculated that **3** *should* be a precursor of **1** and **2**, so carefully chemically analysed fresh extracts and *proved* that **3** was in fact a natural product. Furthermore, during handling and purification, **3** underwent rapid and quantitative acid-mediated transformation to **1** and **2**, requiring that the latter be reclassified as artifacts.

While artifacts are not uncommon in the natural products literature, they are often mis-identified as natural products (see *Nat. Prod. Rep*. 2020, vol. 37, pp. 55–79), so we were pleased with ourselves not to have been fooled (as so many are), or so we thought. In a follow-up study (*Marine Drugs* 2021, vol. 19, p. 151), we determined that the fungus did not biosynthesise any of the Schiff bases **1**–**3**! Instead, the fungus produced the unprecedented, chemically reactive cryptic natural product *N*-amino-L-proline methyl ester **4**, which it retained in the mycelia. On solvent extraction, **4** was released from the fungal mycelia to encounter 5-hydroxymethylfurfural **5** (produced during autoclave-mediated thermolysis of media carbohydrates) and undergo rapid transformation to the Schiff base **3**. These observations also explained why the Schiff bases were only detected in certain culture media – those that were carbohydrate rich and which after autoclaving had high levels of the furan aldehyde **5**.

This experience reaffirmed:

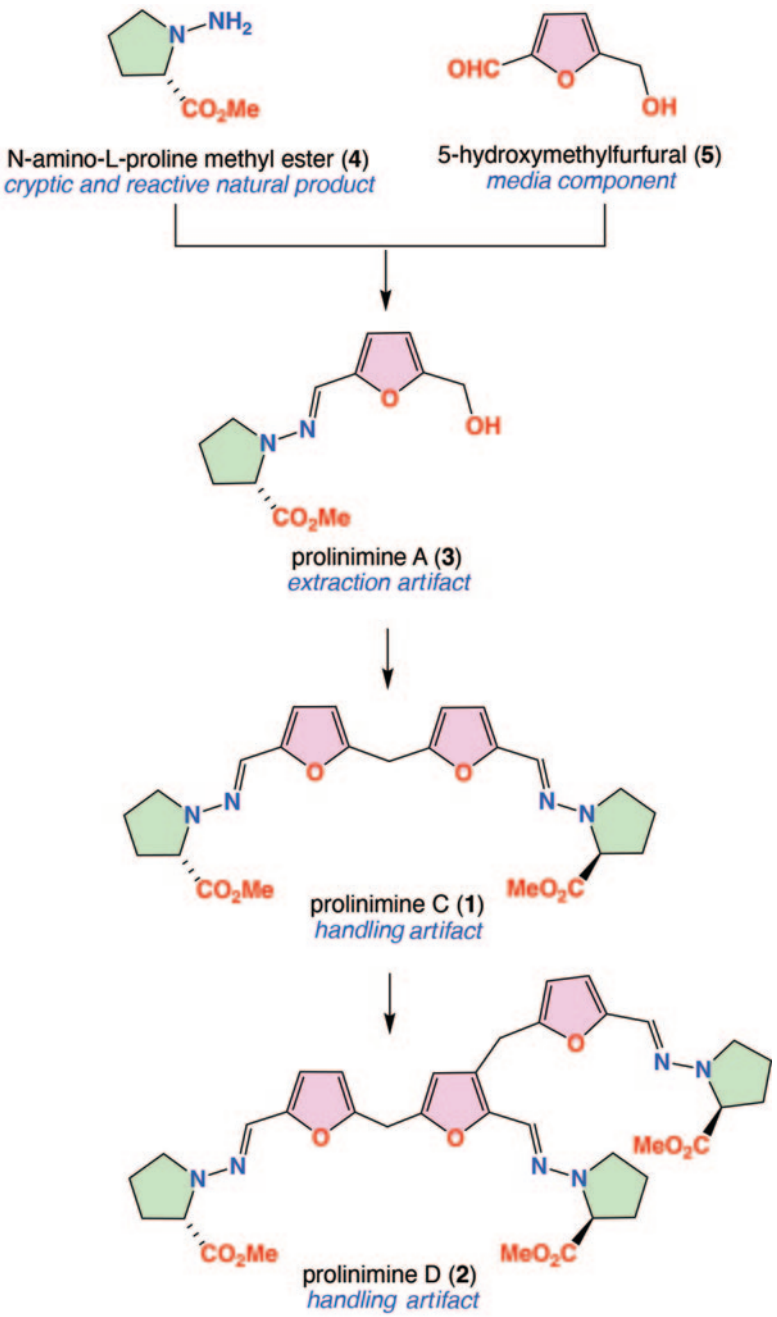
- natural products can be chemically reactive
- natural products can be cryptic
- culture media can be a source of reactive chemicals
- fungi have the option to retain and/or secrete natural products
- artifacts can form under even the mildest conditions
- just because a chemical is isolated from an extract doesn't mean it is natural.

It also prompted the following more inclusive definitions:

- 'A natural product is a chemical that originates from, and can be detected in, a fresh extract of a source organism, provided the process of extraction and/or detection does not initiate a chemical transformation that is solely responsible for producing the chemical.'
- 'An artifact is a natural product that has undergone a chemical transformation during extraction, handling, storage and/or analysis.'

Notwithstanding, in the eyes of many, a natural product will always be 'any chemical isolated from a living organism' – which as definitions go has the appeal of simplicity (even if it sidesteps an inconvenient truth).

Rob Capon FRACI CChem is Professorial Research Fellow and Group Leader in the University of Queensland, Institute for Molecular Bioscience, and Program Leader in the Marine Bioproducts CRC.



A gateway to the history of chemistry in Australia

We need your help in continuing to document the contribution chemists have made to the social and economic development of Australia through contributions to the *Encyclopedia of Australian Science and Innovation*.

The Encyclopedia is a gateway to the history and archives of science, technology and innovation in Australia and is built from data systematically collected and progressively published in various forms (print and online) since 1985. The Encyclopedia contains quite a lot of information and references to the history of chemistry in Australia, but there are many gaps. It is a community-driven enterprise that relies on volunteers to propose new entries and help amend existing entries. The Encyclopedia includes the *Bibliography of the History of Australian Science*, which had been published annually since 1981 (see www.publish.csiro.au/HR/HR22901 and www.eoas.info). From 1985 to 2020, the enterprise was housed at the University of Melbourne. It was relocated to Swinburne University of Technology in 2021. The first edition published by Swinburne was in March 2022.

Of the nearly 10 000 entities registered in the Encyclopedia, more than half are individuals and many of the those are chemists of some form or another (552 – as at March 2022). Following the model of the *Australian Dictionary of Biography*, each entry is tagged with one or more occupations (or functions). By scrolling down, you will find 'Cereal chemist' (2), 'Chemical analyst' (8), 'Chemical engineer' (45), 'Chemical physicist' (7) and 'Chemist', but on other browse pages you can find 'Agricultural chemist' (12), 'Analytical chemist' (52), 'Applied chemist' (21), 'Industrial chemist' (88), 'Inorganic chemist' (18), 'Manufacturing chemist' (6), 'Medical chemist' (3), 'Medicinal chemist' (1), 'Mineral chemist' (9), 'Mining chemist' (2), 'Organic chemist', 'Pharmaceutical chemist' (1), 'Physical chemist' (25), 'Polymer chemist' (5), and 'Quantum chemist' (2). Biochemists and geochemists have been treated as separate groups. Organisations with a chemical focus have been tagged under 'Chemical industries'.

Of the nearly 10 000 entities registered in the Encyclopedia, more than half are individuals and many of the those are chemists of some form or another (552 – as at March 2022).

For example, there is an entry for Ezio Rizzardo (1943–), an organic chemist who became a leading expert in the chemistry of polymerisation. During his time at CSIRO (1974–2016), he led projects on free radical polymerisation, polymeric biomaterials and engineering polymers. He contributed to the development of nitroxide-mediated living radical polymerisation and invented reversible addition-fragmentation chain transfer (RAFT) polymerisation. His entry in the Encyclopedia is rich in career events and links to entries for related organisations as well as links to entries for prizes and awards. However, apart from a link to *CSIROpedia*, there are no other references to historical publications and archival collections that tell the story of his life. This is where we need help.

As an expert or practitioner in your field of chemistry, you can let us know of people or organisations who should be, but are not yet, in the Encyclopedia. You can let us know about publications and other sources of evidence (archival resources) that we could register (and link to). If you can supply copies of images, video, audio, publications and documents that will help us build an entry, then that will be useful to students, scholars and researchers now and in the future.

A notable chemical researcher, who does not yet have an entry in the Encyclopedia, is Matthew Hill (PhD 2006), who is working towards the usage of ultra-porous metal–organic frameworks (MOFs) for gas storage and separation. He has a particular interest in carbon dioxide, having discovered a material with a record capacity for its capture, and through simulations predicted materials that could have outstanding potential for separating CO_2 from other gases. With useful background information provided by colleagues, Hill is now high on the list for the next edition.

The bibliography also includes the work of David Collins (Monash University and on the backlog list for a personal entry in the Encyclopedia) in Chemistry in 19th Century Australia – Select Bibliography. (See the 2005 Exhibition: www.eoas.info/exhibitions/ciab/ciab.html). An illustrative entry is Bosisto, J., 'Is the Eucalyptus a Fever-Destroying Tree?', *Pharmaceutical Journal and Transactions* (1874–1875), 270. By following the 'Details' link, you get to the full entry for the article, including the keywords added by Collins. The link to the personal entry for Joseph Bosisto (1824–1989) takes you to a rich entry with links to archival collections and publications (see eoas.info/biogs/P000082b.htm).

We hope that you will search the Encyclopedia for people who you think should be included and, if they are not, contact us to remedy the situation. Contact us as well if you wish to update or amend existing entries. We would love to hear from you at gavanmccarthy@swin.edu.au or tspurling@swin.edu.au.

Tom Spurling FRACI CChem and **Gavan McCarthy**

Knowing your onions

The dictionary meaning of the expression 'to know your onions' is 'to be experienced in or knowledgeable about a subject'.

There were two people with the family name of Onions who made a name for themselves in 19th-century England. One was S.G. Onions, who in 1843 introduced sets of coins as teaching aids for school children, to help them to learn their pounds, shillings and pence.

The other was C.T. Onions, a grammarian and lexicographer, who in 1895 became the fourth editor of the *Oxford English Dictionary* and wrote other scholarly works.

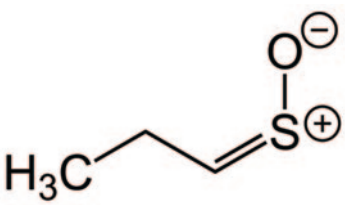
But the expression 'knowing your onions' did not appear in print until the 1920s, strongly suggesting that neither S.G. nor C.T. was responsible for the expression. It is now generally accepted that it originated in the United States, appearing first in *Harper's Magazine* in March 1922.

No tears here!

Heat the whole onions before wielding the knife – this destroys the enzymes, short circuiting the cascade of reactions.

On 26 January 2022, there were short articles in *The Times* (London) and other UK newspapers arising out of a national survey in the previous year that identified some endangered expressions in the English language. Of those surveyed, 68% said they would never use the expression 'know your onions'.

Often, chemistry writers treat the chemistry of onions in a perfunctory manner. Please forgive me, but it is clear that these writers do not *know their onions* about the chemistry of onions. It is more complex than might be imagined.



***syn*-Propanethial *S*-oxide**

Jü/wikicommons

The chemical agent that causes people to 'cry' when cutting onions is *syn*-propanethial *S*-oxide. But it is not waiting in whole onions for some unsuspecting person to plunge a knife into the onion, to wreak its teary effect. Two more chemical steps are required.

Among the chemical compounds that give onions their characteristic flavour are amino acid sulfoxides, the most abundant being derived from arginine and glutamine. The act of cutting an onion breaks open onion cells, releasing enzymes called allinases, which generate sulfenic acids. But it doesn't stop there. 1-Propenesulfenic acid itself is rapidly rearranged by a second enzyme, the lachrymatory factor synthase, yielding *syn*-propanethial *S*-oxide. This volatile compound diffuses through the air and, on contact with the eye, stimulates sensory neurons, producing a painful, stinging sensation. The eye responds by releasing tears to dilute and flush out the irritant.

Can onions be sliced and diced without the discomfort of tears?

Numerous solutions have been proposed. Heat the whole onions before wielding the knife – this destroys the enzymes, short circuiting the cascade of reactions. Cool the onions first in the freezer or in ice water – the low temperature reduces the rates of reaction in the cascade. Insert a screen between the onions and the person cutting them up.

Children are known to be naturally innovative. The photo shows my then five-year-old London granddaughter's simple solution – wear your swimming goggles!

But there is a new solution at hand. For some years, plant breeders at Bayer in the US (since taken over by BASF) have been working to breed onions that do not cause tears. These are called 'Sonions' and went on sale at Waitrose supermarkets in the UK in January this year, although they have been available in the US for two years.

Peter G. Lehman FRACI CChem joined RACI as a student member in 1963, subsequently pursuing a career in academia and industry, the latter in Australia and the US. In his retirement, he has been writing occasionally for *Chemistry in Australia*.

Wine sulfites: reactions of consumers and chemistry

There are two chemical forms of sulfur dioxide: 'free' and 'bound'. The free form is the pH-dependent balance of molecular SO_2 and bisulfite. This is the critical form from a winemaking perspective because molecular SO_2 is the antimicrobial or preservative form. The bound form consists of bisulfite attached to aldehydes and ketones. Acetaldehyde is a common binding compound. Together, the free and bound forms give the 'total sulfur dioxide' concentration: this is the legislative value in winemaking countries around the world.

From a consumer perspective, the issue with SO_2 is its perceived allergic reaction. This requires mandatory labelling indicating that 'sulphites' have been added in excess of 10 mg/kg. The 'added' is important here because some sulfite may be produced during the fermentation. The wine industry seems reluctant to move from the use of 'sulphites', despite the IUPAC nomenclature rule change and the 1999 decision of the Australian Therapeutic Goods Administration approved terminology of 'sulfites' for medicines. Well, wine is sometimes regarded as medicine!

Whether the reaction to sulfite in wine is an allergic response or not is still not certain. In 2021, the 'Food Safety Experts' of the International Organisation of Vine and Wine (OIV) published a detailed review on the safety assessment of sulfite in wine (bit.ly/3vxG2SJ). The report authors concluded that 'Most sulfite sensitivities are not true allergic reactions'. There is a lack of clarity about what causes sulfite intolerance. It would appear that the intolerance is not just to sulfite itself, and the OIV review concludes that it is 'likely due to various biological reactions, depending on the individual genetic background'.

A replacement for SO_2 needs to address its dual role of antimicrobial and antioxidant activity. Lysozyme has been extensively studied (*Compr. Rev. Food Sci. Food Saf.* 2014, vol. 13, pp. 1062–73), although it has several limitations. Its common source is egg white and in some jurisdictions its use requires allergen labelling. It is most effective against Gram-positive organisms but has a very limited half-life in wine. Professor Leigh Schmidtke of Charles Sturt University advised that 'I'm not immediately aware of any winemakers using it regularly – maybe this reflects changes in the wine production syllabus over the past 15 or so years, ensuring good wine conservation measures are emphasised so there is not the need'.

Recently, chitooligosaccharide has been proposed as a possible replacement for SO_2 (*Appl. Sci.* 2020, vol. 10(2), p. 578). This oligosaccharide is claimed to show antibacterial, antifungal and antioxidant behaviour, among other things. Approval for its use has not been obtained.

Ascorbic acid is used as an antioxidant in white wine. However, because the oxidation of ascorbic acid produces hydrogen peroxide, some SO_2 is required to scavenge the peroxide. In addition, some ascorbic acid degradation products can react with wine phenolic compounds, leading to a brown coloration, an unattractive aspect of white wine (*Aust. J. Grape Wine Res.* vol. 22, pp. 169–81). Ascorbic acid is not effective in red wine.

Glutathione is found in small amounts in juice or must after grape processing and in wine post-fermentation. It is known to scavenge some phenolic compounds and it is capable of protecting aroma compounds through its antioxidant behaviour. It is thus a potential replacement for SO_2, but it is not an approved additive. Some yeasts release glutathione and this might be a potential source.

A detailed review on glutathione identified several deficiencies in our knowledge of its behaviour in wine (*J. Agric. Food Chem.* 2013, vol. 61, pp. 269–77). One major deficiency was the lack of experiments carried out under wine-like conditions, especially longer-term storage. Glutathione is known to contribute to hydrogen sulfide production and this would detract from the wine's acceptance.

The Australian Wine Research Institute has recently reported the outcomes of a longer-term glutathione trial using small-scale wine production trials (bit.ly/3oOF6FO). The results questioned the value of adding glutathione because low added concentrations showed little effect, while higher concentrations led to 'undesirable sensory outcomes'.

Finding replacements to reduce the amount of SO_2 remains a challenge. The 2021 OIV review suggested a need to perform winemaking with a lower SO_2 concentration than is presently common practice. The OIV published in 2020 a 'Review of practices for the reduction of SO_2 used in winemaking' (bit.ly/3PQmQrr) that sets out management principles for each winemaking step from the vineyard through to the finished wine in bottle.

Using less SO_2 is now increasingly common here in Australia and elsewhere. In France, where I am more familiar with the practice, many wines are now available that have no added sulfite at any stage of the winemaking process. This is sometimes a deliberate decision due to sulfite sensitivity: Drappier sans soufre champagne is a classic example. Or it may be a response to producing so-called natural wines, where no or minimal additions are made. This has been driven by the 'Raw Wine' movement. Check out Isabelle Legeron's book *Natural wine* (3rd edn), for a detailed discussion. In France, two optional labels for natural wines are available – one for zero sulfite addition and another for a maximum of 30 mg/L sulfite addition.

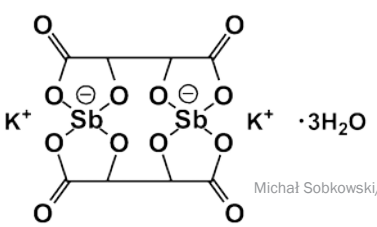
Geoffrey R. Scollary FRACI CChem (scollary45@gmail.com) has been associated with the wine industry in production, teaching and research for the last 40 years. He now continues his wine research and writing at the University of Melbourne and Charles Sturt University.

An antimony mystery solved

Like a household or a business, a chemistry department needs to review its holdings from time to time, focusing on certain possessions and asking whether to keep them, move them to new homes or ultimately see to their destruction. So it was that I learned a few months ago that the Chemistry School at the University of Melbourne was asking if anyone had a use for a large bottle of antimony potassium tartrate. I recognised right away that this substance was also known as tartar emetic and that my family had used it as an ant poison.

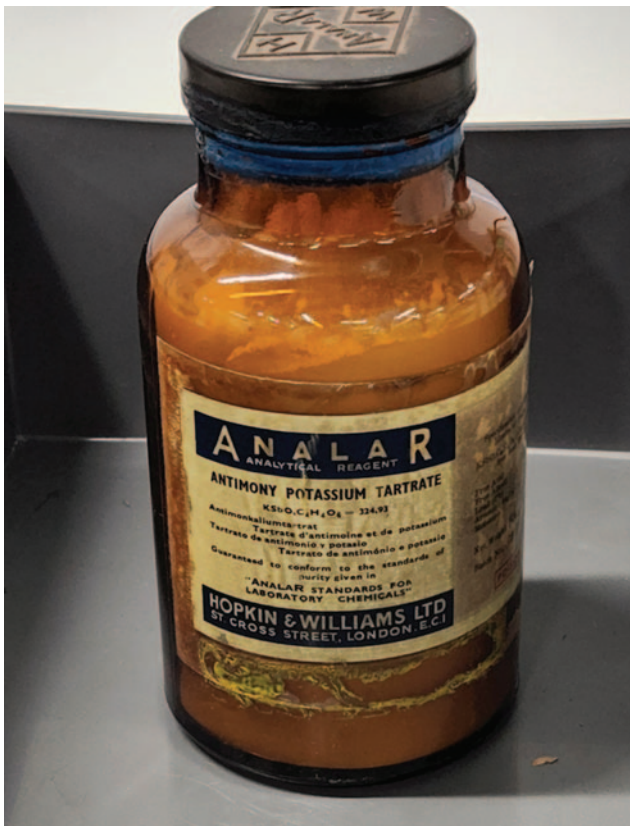
When I was growing up in Melbourne, we were plagued by the small brown Argentine ant (*Linepithema humile*) that roamed the kitchen looking for sugar. Departments of agriculture recommended poison baits based on borate or arsenic. I'm not sure if my parents knew about those but they somehow knew that poisoning was the way to reduce the ant populations (now I know that you should use talcum powder, which they don't like because it sticks to their feet). So my mother asked a local pharmacist to help; he recommended tartar emetic and sold her a small amount, which we mixed with honey and placed in shallow containers such as bottle tops in places that the ants frequented. It was a family pharmacy and I know the current owner, who possesses the 'poisons book' of those days. He confirmed that tartar emetic was sold for that purpose, but for privacy reasons, he said, he would not tell me whether my mother was among the customers who purchased it. The baits certainly worked and, as a budding chemist, I stored away this little piece of chemical toxicology.

The bottle of this chemical had been at the university for many years, and no record of its purchase was available. Was there an ant problem in that old building in the early 1950s, I wondered? I rather doubted it, and so I turned to the internet to see what other uses were recorded for antimony potassium tartrate. Tucked away at the end of the Wikipedia entry (first stop for any chemical search these days) was a 1960 reference to its use in the resolution of *cis*-dinitrobis(ethylenediamine) cobalt ion, by Francis Dwyer and F.L. Garvan at the University of Sydney. This cobalt complex had been resolved by Werner, using



Michał Sobkowski/wikicommons

... antimony potassium tartrate has a very unusual chemical structure, with four chiral centres ...



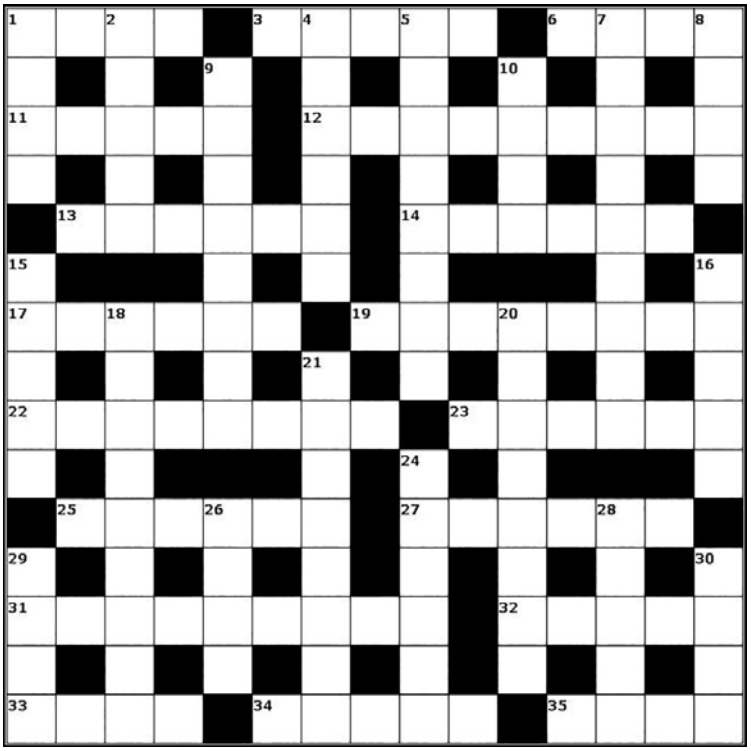
D-camphorsulfonate, but achieving good yields of both optical antipodes was quicker and cheaper with antimony potassium tartrate. This was not the first time that Dwyer and his students had used this unusual resolving agent: the first was in 1949 with tris-*o*-phenanthroline ruthenium(III) and some ruthenium(II) complexes; then with the analogous osmium(II) and iron(III) species in 1950; and with a number of tris-2,2′-dipyridyl metal complexes in 1951.

So, is this why the Melbourne chemistry store had a bottle of antimony potassium tartrate? It didn't take me long to guess which member of staff had been interested in metal coordination chemistry, and to zero in on Professor Don Stranks. Sure enough, I found a paper with Geoff Lawrance, published in 1978 (after Stranks had moved to South Australia), on enantiomers of tris-(1,10-phenanthroline) complexes of nickel(II) and iron(II), prepared using the antimony complex and used for racemisation studies. Peter Tregloan confirmed my guess and thought there might have been an undergraduate laboratory exercise based on this chemistry but ... it was a long time ago and no laboratory manuals seem to have survived. As you can see, antimony potassium tartrate has a very unusual chemical structure, with four chiral centres, so no wonder it's a great counter ion for effecting optical resolutions.

Ian D. Rae FRACI CChem (idrae@unimelb.edu.au) is a veteran columnist, having begun his Letters in 1984. When he is not compiling columns, he writes on the history of chemistry and is an editor of *Historical Records of Australian Science*.

Anticipating Global Women's Breakfast 2023

President of IUPAC, Professor Javier Martinez Garcia (Spain), and Professor Nicole Moreau (France; President of IUPAC 2010–11) promoting the Global Women's Breakfast for 2023 at the launch of the International Year of Basic Science and Sustainable Development held at UNESCO headquarters in Paris in July.



Across

1 Pony up one element over two others. (4)
3 Primitive hydrogen. (5)
6 Celebrated heavenly body. (4)
11 CH_2=CH–CH_2– held in an artificially layered structure. (5)
12 Damp rag with hydrogen iodide cleaned up the partition. (9)
13 Lead? Or carbon? List it tentatively. (6)
14 Pastry language. (6)
17 More than one 34 Across nights out. (6)
19 Treading on dangerous ground slope. (8)
22 Explanation often too cryptic. (8)
23 Five elements all together. (6)
25 It links five radical papers with germanium. (6)
27 Stay about the open ocean. (6)
31 Intellectual property knock off on the money. (9)
32 Got through multi agency panel ending sulfenyl. (5)
33 Two elements compete. (4)
34 Object obsession. (5)
35 42 way in the majority. (4)

Down

1 Two element attire. (4)
2 See 5 Down.
4 C_8H_7N in allowance. (6)
5 and 2 Down Lava tar sudden movement from reference point. (8,5)
7 Signs over and passes on. (9)
8 Element representative slope. (4)
9 Stores energy in intriguingly cogenerative process. (8)
10 Two elements lean. (4)
15 Junk jam. (5)
16 Base stance ... (5)
18 ... or is topic turning out to be the same no matter the direction? (9)
20 Propane-1,2,3-triyl trinitrate + sorbent + stabiliser made tiny product! (8)
21 Ability to withstand start and finish of significant ribosome navigating through. (8)
24 The Carnot or pressure-volume cycle diagram shows up something positive. (6)
26 Aphotic caliginosity!! (4)
28 The group discovered in Weilheim in Oberbayern. (5)
29 Two element mark. (4)
30 Graph first principal law of thermodynamics. (4)

Graham Mulroney FRACI CChem is Emeritus Professor of Industry Education at RMIT University.
Solution available online at chemaust.raci.org.au, Other resources.

Chocolate and science

On 1 July 2022, the Her Research Matters group at Monash University in collaboration with the RACI Women in Chemistry VIC group held a 'Chocolate and Science' event at the Monash Institute of Pharmaceutical Sciences.

The goal of this event was to promote awareness of the cutting-edge science being conducted by early career researchers to the public in a fun and relaxed environment. The event was hosted by Lara Mollé (PhD student) and commenced with a presentation by Ashleigh Gould (PhD student), who shared her research on the immune system that lives inside your gut.

A highlight of the event was a guided chocolate tasting by Debbie Makin, the founder of bean to bar chocolate manufacturer Ratio Cocoa Roasters. Debbie has a background in science and is now applying her knowledge to the development of sustainable and high-quality chocolate. Each attendee received a tasting plate consisting of six different chocolates and a chocolate bar to take home. The first tasting was some cocoa nibs from Vanuatu, followed by a single-origin 58% milk chocolate from the Dominican Republic. Next, there was Ratio's own Melbourne blend of 63% dark chocolate. Finally, attendees sampled three single-origin chocolates from Trinidad and Tobago (66%), Solomon Islands (76%) and Ecuador (88%). All participants enjoyed identifying the different flavour notes in each chocolate, and Debbie discussed how cocoa percentage does not directly correlate with perceived bitterness. Debbie also highlighted the importance of fair trade and sustainable practices in the chocolate industry and how many confectionary companies do not use ethical practices.

The chocolate tasting was followed by Dr Enyuan Cao (early career researcher), who presented her work on how the lymphatic system is involved in the transport of fats from the chocolate everyone just ate. Finally, Michael Mah (PhD student) discussed the role lipids play in health and disease and how his research aims to understand the implications of lipid imbalance in different disease states.

Chocolate tasting and bars to take home. Karen Gregory

The Chocolate and Science event was a fun and tasty way to learn more about cutting-edge research and network with like-minded people. This event was made possible by our generous sponsors, Monash University Faculty of Pharmacy and Pharmaceutical Sciences, and the RACI Women in Chemistry VIC group, who are supported by Agilent Technologies, BASF, CSIRO and Phillips Ormonde Fitzpatrick.

Anita D'Angelo (Chair, Women in Chemistry VIC) and **Angus Johnston** (Ally, Her Research Matters)

The speakers and event host. Left to right: Michael Mah, Ashleigh Gould, Enyuan Cao and Lara Mollé. Lauren May

About the organisers

Her Research Matters: The mission of Her Research Matters is to promote, sponsor and foster women's academic careers (www.monash.edu/pharm/about/people/hrm, @HRM_MIPS).
Women in Chemistry (VIC): The Women in Chemistry (VIC) group supports chemists in all stages and types of careers across Victoria. The group aims to increase the visibility of women in STEM, and do this by running a range of social, professional, networking and scientific events. The events are not exclusively for women or chemists, and are open to all interested parties (@WinC_RACI_VIC)
Ratio Cocoa Roasters: 186 Sydney Rd, Brunswick, Victoria 3056 (ratiococoa.com.au)

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