

This issue honours the career of Lew Mander on the occasion of his 65th birthday. Possibly best known for his synthesis of gibberellic acid, his research has centred around designing synthetic strategies for complex organic molecules.

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

www.publish.csiro.au/journals/ajc

Foreword

Lewis N. Mander

Alan Battersby

Aust. J. Chem. 2004, 57, 611-617.

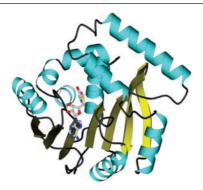
Alan Battersby, a long-time friend and colleague of Lew Mander since his 1972 sabbatical year at Cambridge University, names Mander's 'scientific courage and adventurous spirit' as being the characteristic traits of his research career. Mander has received international acclaim marked by many awards, as well as 240 original research papers and four patents.

Current Chemistry

Integrating Structural and Functional Genomics

Lisa Parsons, Fang Liu, Deok Cheon Yeh, Nese Sari, John Orban

Aust. J. Chem. 2004, 57, 619-623.



Efficient determination of the biochemical functions of poorly understood proteins requires integration of three-dimensional structural studies (such as high-throughput X-ray crystallography and NMR spectroscopy) with functional studies (such as ligand screening and enzymatic methods), and use of the many genomic databases now available. Such an approach is provided with HI0319 (shown).

Rapid Communications

Unexpected Formation of the Arcyriacyanin System by Condensation of a 3-Bromo-4-(indol-3-yl)maleimide with (2-Nitrophenyl)acetates

Guido Mayer, Claudia Hinze, Kurt Polborn, Wolfgang Steglich

Aust. J. Chem. 2004, 57, 625-628.

The slime mould alkaloid arcyriacyanin A, a member of the bisindolylmaleimide group of alkaloids, shows unique antitumour properties and inhibits protein kinase C and protein tyrosine kinase. A novel and highly convergent method of attaining the arcyriacyanin system through cyclization of suitable nitrophenyl precursors (shown) is reported.

Highly Diastereoselective Radical Reactions of Substituted Methylideneimidazolidinones and Related Systems

George A. Adamson, Athelstan L. J. Beckwith, Christina L. L. Chai

Aust. J. Chem. 2004, 57, 629-633.

Organic free-radical reactions that generally proceed with high chemo-, regio-, and diastereoselectivity may have important synthetic utility. The authors explore the factors that determine the high selectivity of stannane-mediated radical additions to imidazolidinones, such as the one depicted, and find that the stereochemical outcome is highly dependent on the nature of the N1 substituent.

Efficient Synthesis of an Enantiopure Thiasteroid by a Double Heck Reaction

Lutz F. Tietze, Lars P. Lücke, Felix Major, Peter Müller

Aust. J. Chem. 2004, 57, 635-640.

A novel enantiopure thiaestrane was synthesized by a double Heck reaction of a thiophene and a hydrindene derivative.

$$\begin{array}{c} \mathsf{Br} \\ \mathsf{S} \end{array} + \begin{array}{c} \mathsf{OBu}^t \\ \vdots \\ \mathsf{H} \end{array} \begin{array}{c} \mathsf{Pd}(\mathsf{0}) \\ \vdots \\ \mathsf{H} \end{array} \begin{array}{c} \mathsf{H} \\ \vdots \\ \mathsf{H} \end{array}$$

A Chemoenzymatic Synthesis of the *cis*-Decalin Core Associated with the Novel Anti-Mitotic Agent Phomopsidin: Some Observations Concerning a High-Pressure-Promoted Diels—Alder Cycloaddition Reaction of (1*S*,2*R*)-3-Methyl-*cis*-1,2-dihydrocatechol and the Anionic Oxy—Cope Rearrangement of Compounds Derived from the Adduct

Martin G. Banwell, Alison J. Edwards, Malcolm D. McLeod, Scott G. Stewart

Aust. J. Chem. 2004, 57, 641-644.

Chiron 1, readily obtained through a whole-cell biotransformation of toluene, has been converted, via a nine-step reaction sequence, into a product (see central structure) incorporating the *cis*-decalin core of the potent anti-mitotic agent phomopsidin.

Two Approaches to the Synthesis of the Macrodiolide Colletotriene

Dulce M. Muñoz, Stephen C. Passey, Thomas J. Simpson, Christine L. Willis, John B. Campbell, Richard Rosser

Aust. J. Chem. 2004, 57, 645-649.

Colletotriene

Two convergent approaches to the synthesis of colletotriene (pictured), a proposed intermediate in the biosynthesis of the 14-membered ring dilactone, colletodiol, have been developed. These methods may be readily adapted for the selective incorporation of deuterium at various sites on the macrocycle, giving access to substrates required for biosynthetic studies.

Anchimeric Assistance in Hydrogen- Atom Transfer to Bromine

Anna K. Croft, Christopher J. Easton

Aust. J. Chem. 2004, 57, 651-654.

$$Br^{\delta^{-}}$$

H

PhtthN

H

 Ar

NHBu

The free-radical benzylic brominations of series of phenylalanine derivatives, *O*-phenylalkyl benzoates, and *N*-phenylalkylamides with *N*-bromosuccinimide exhibit anchimeric assistance by neighbouring ester and amido groups. Rate enhancement occurs through electron donation to the electropositive carbon centre that develops in the transition state of the hydrogen-atom transfer to bromine.

Yb(OTf)₃-TMSCl, a Novel Catalytic System in Cross-Aldol Reactions

Natsuko Kagawa, Masahiro Toyota, Masataka Ihara

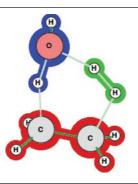
Aust. J. Chem. 2004, 57, 655-657.

A significant problem in natural product synthesis concerns the generation of silyl enol ethers from highly functionalized ketones in aldol reactions. This paper reports the first example of a Yb(OTf)₃-catalyzed cross-aldol reaction through a silyl enol ether intermediate.

Understanding Metal-Free Catalytic Hydrogenation: A Systematic Theoretical Study of the Hydrogenation of Ethene

Bun Chan, Leo Radom

Aust. J. Chem. 2004, 57, 659-663.

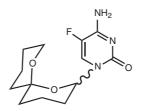


Hydrogenation reactions are of widespread industrial importance, and the determination of methods for facilitating such reactions is therefore of interest. High-level [G3(MP2)-RAD] ab initio molecular orbital calculations on the acid/base-catalyzed hydrogenation of ethene show that the catalyst (Z–X–H) becomes more effective as the atom X becomes more acidic (for X = O, F, S, Cl) or more basic (for X = N, P).

Synthesis of a Novel Nucleoside Based on a Spiroacetal Framework

Margaret A. Brimble, James E. Robinson, Ka Wai Choi, Paul D. Woodgate

Aust. J. Chem. 2004, 57, 665-668.



The prospect of developing therapeutic analogues of naturally occurring nucleosides and nucleic acids has made their synthesis of much importance to chemists. Described here is the first synthesis of the nucleoside mimic shown using a spiroacetal framework as a pseudosugar.

Asymmetric Synthesis of (-)-Swainsonine

Karl B. Lindsay, Stephen G. Pyne

Aust. J. Chem. 2004, 57, 669-672.

A new synthesis of (-)-swainsonine via the ring-closing metathesis reaction of a substituted 3-allyl-4-vinyl-2-oxazolindinone and subsequent diastereoselective syn-dihydroxylation of the resulting pyrrolo[1,2-c]-oxazol-3-one is described.

Concerning the Proposed Structure of (+)-Laurobtusol: Spectral Discrepancies with Synthetic, Racemic Stereoisomers

Joanne T. Blanchfield, Sharon Chow, Paul V. Bernhardt, Colin H. L. Kennard, William Kitching

Aust. J. Chem. 2004, 57, 673-676.

Laurobtusol, a minor metabolite isolated from *Laurencia obtusa*, contains an unprecedented carbocyclic skeleton with a relative stereochemistry as depicted. Subsequent syntheses and high-field two-dimensional NMR studies have raised doubts as to the previously proposed stereochemistry for this compound.

Cyclization of Acetylenic Amides Using a Cationic Rhodium(1) Complex

Suzanne Burling, Leslie D. Field, Hsiu L. Li, Barbara A. Messerle, Adelle Shasha

Aust. J. Chem. 2004, 57, 677-680.

The formation of C–N bonds by the addition of N–H to C–C double and triple bonds (hydroamination) is of fundamental importance in organic synthesis. Here, the intramolecular cyclization of amido alkynes to form heterocyclic compounds, using the dicarbonyl complex $[\{Rh(bim)(CO)_2\}^+BPh_4^-]$ as a catalyst, is described.

$$H \xrightarrow{C} C \xrightarrow{\text{[Rh(bim)(CO)_2]}^+} \bigcirc N \xrightarrow{\text{I}} C$$

Pigmentosin A, a New Naphthopyrone from the Lichen *Hypotrachyna* immaculata

John A. Elix, Judith H. Wardlaw

Aust. J. Chem. 2004, 57, 681-683.

Lichen-derived metabolites are of considerable interest due to their potential powerful pharmacological activities. The authors describe the isolation of the title compound and its structural elucidation using two-dimensional NMR techniques and mass spectrometry. This compound is the first lichen metabolite known to contain a bisnaphthopyran moiety.

Some Synthetic Approaches to Glutamate AMPA Receptor Agonists Based on Isoxazolones

Matthew Cox, Saba Jahangiri, Michael V. Perkins, Rolf H. Prager

Aust. J. Chem. 2004, 57, 685-688.

(S)-glutamate, the predominant excitatory neurotransmitter in the mammalian CNS, has two types of CNS receptors, one of which is activated by both AMPA 1 and TAN-950A 2, an antifungal antibiotic. Analogues of TAN-950A could be prepared as a racemic mixture by reaction of isoxazolone Mannich bases with acetylaminomalonate or addition of β -ketoester anions to dehydroalanines. To prepare enantiomerically pure analogues, acylation of pyroglutamates followed by reaction with hydroxylamine was required.

The Preparation of 1,2-Bis(2,2':6',2"-Terpyridin-4'yl)Ethanone: The First Example of 4'-Terpyridyls Unsymmetrically Linked by a Functionalized Two-Carbon Chain

Zhi-Long Chen, Ronald N. Warrener, Douglas N. Butler

Aust. J. Chem. 2004, 57, 689-692.

The use of tpy as a tridentate complexing agent has found wide use, however relatively little has been reported on the complexes from linked di(tpy) reagents. In the presence of HCl, the leftmost compounds undergo an unprecedented homo-coupling reaction.

R = CN,
$$CO_2Me$$

Full Paper

Host Defence Peptides from the Skin Glands of Australian Amphibians. Caerulein Neuropeptides and Antimicrobial, Anticancer, and nNOS Inhibiting Citropins from the Glandular Frog *Litoria subglandulosa*

Craig S. Brinkworth, Tara L. Pukala, John H. Bowie, Michael J. Tyler

Aust. J. Chem. 2004, 57, 693-701.



Amphibians have rich chemical arsenals in their skin glands that play an integral part in their defence systems. The unusual, large submental glands on the throat of *Litoria subglandulosa* (pictured) contain citrophin 1.2, which was found to be a wide-spectrum antibiotic and anticancer agent at the micromolar concentration.

Author Index

Adamson, G. A. 629 Banwell, M. G. 641 Battersby, A. 611 Beckwith, A. L. J. 629 Bernhardt, P. V. 673 Blanchfield, J. T. 673 Bowie, J. H. 695 Brimble, M. A. 665 Brinkworth, C. S. 695 Burling, S. 677 Butler, D. N. 691 Campbell, J. B. 645 Chai, C. L. L. 629 Chan, B. 659 Chen, Z.-L. 691 Choi, K. W. 665 Chow, S. 673 Cox, M. 685 Croft, A. K. 651 Easton, C. J. 651 Edwards, A. J. 641

Elix, J. A. 681 Field, L. D. 677 Hinze, C. 625 Ihara, M. 655 Jahangiri, S. 685 Kagawa, N. 655 Kennard, C. H. L. 673 Kitching, W. 673 Li, H. L. 677 Lindsay, K. B. 669 Liu, F. 619 Lücke, L. P. 635 Major, F. 635 Mayer, G. 625 McLeod, M. D. 641 Messerle, B. A. Müller, P. 635 Muñoz, D. M. 645 Orban, J. 619 Parsons, L. 619 Passey, S. C. 645

Perkins, M. V. 685 Polborn, K. 625 Prager, R. H. 685 Pukala, T. L. 695 Pyne, S. G. 669 Radom, L. 659 Robinson, J. E. 665 Rosser, R. 645 Sari, N. 619 Shasha, A. 677 Simpson, T. J. 645 Steglich, W. 625 Stewart, S. G. 641 Tietze, L. F. 635 Toyota, M. 655 Tyler, M. J. 695 Wardlaw, J. H. 681 Warrener, R. N. 691 Willis, C. L. 645 Woodgate, P. D. 665 Yeh, D. C. 619