

Book Reviews *

Advances in Enzymology. Volume 72. Amino Acid Metabolism.

Part A. Edited by Daniel L. Purich (University of Florida). John Wiley: New York. 1998. 448 pp. \$125.00. ISBN 0-471-24643-3.

This volume marks only the second "changing of the guard" in the nearly 70-year history of the venerable *Advances in Enzymology* series. About half of the preceding volumes were edited by the founding editor, F. F. Nord, with Alton Meister taking over for the last 35 volumes. Now, following Meister's untimely death in 1995, Daniel Purich steps in as editor and continues the tradition of providing comprehensive, up-to-date reviews of enzyme expression, characterization, mechanism, kinetics and regulation, while introducing a number of notable innovations. For example, short abstracts have been added upfront to give the reader a sense of the major issues to be covered. Perhaps most importantly, each *Advances in Enzymology* volume is to have a theme that ties the chapters together as best possible.

In Volume 72, Purich succeeds in establishing a theme threaded through Chapters 1 (glutamine synthetase, Purich), 3 (glutamine usage via amidotransferases, Zalkin and Smith), 4 (asparagine synthetase, Richards and Schuster), and 6 (γ -glutamyl transpeptidase, Tanikuchi and Ikeda). All of these chapters revolve around the chemistry of the ω -carboxamide functionality, primarily in glutamine, i.e.: (i) How does Nature activate an ω -carboxyl group for amide bond formation? (Chapters 1 and 4; acyl phosphate vs acyl adenylate formation) (ii) How is the notoriously non-nucleophilic amide nitrogen transformed into a nucleophilic nitrogen? (All four chapters).

The physically oriented bioorganic chemist will particularly appreciate the careful analyses provided by Purich of glutamine synthetase chemistry (Chapter 1), and by Nigel Richards and Sheldon Schuster of the related asparagine synthetase reaction (Chapter 4). Purich does a superlative job of providing a historical context for the study of the mechanism of this latter enzyme. The volume opens with a second printing of Meister's classic 1960 *Journal of Biological Chemistry* paper, in which he provides the first suggestive evidence for the intermediacy of a mixed anhydride intermediate in the Gln synthetase reaction. Purich then builds the mechanistic picture from there, showing, for example, how with time more sophisticated techniques such as trapping experiments and positional isotope exchange came to confirm Meister's early prediction. He then shows how, even in the absence of structural information, one could begin to build a three-dimensional picture of the bound substrate in the active site from the clever design and evaluation of stereochemically defined inhibitors.

For their part, on Asn synthetase, Richards and Schuster do a masterful job of carefully laying out several mechanistic alternatives for glutamine nitrogen activation and allowing the experimental evidence (from kinetic isotope effects to pK_a 's, electrostatics, sterics, and semiempirical heats of formation of postulated intermediates) to weigh in as best it might at this early stage (X-ray structural information is still wanting for the asparagine synthetases). Just to whet the prospective reader's appetite, mechanisms examined for amide nitrogen activation include (i) amide cleavage/ammonia channeling, (ii) thiolate attack at the glutamate γ -carboxyl to interrupt conjugation and thereby produce an orthoamide type nitrogen nucleophile, and (iii) acid/base activation of the amide nitrogen (tautomerization in the extreme), followed by imide formation.

Chapter 2 adds a more biological dimension to the overriding theme, taking the reader to the organismal level for a look at hepatic glutamine transport and metabolism. The remaining three chapters deal with unrelated issues in the general area of amino acid metabolism. To be sure, there is a curious link between Chapters 5 and 6. Namely, each illustrates a step in one mechanism for the metabolism of glutathione S-conjugates, first transamidation at the Glu γ -carboxyl (Chapter 5), then PLP-promoted β -thiolate elimination along the side chain of the central Cys residue. But the "central unifying theme" ends there.

Nonetheless, good reading follows, particularly in the penultimate chapter on L-lysine biosynthesis. Therein, Scapin and Blanchard efficiently chart the mechanistic and biochemical logic whereby bacteria synthesize some five amino acids from L-aspartate, among them L-lysine. The lysine biosynthetic pathway itself has several variants, and, in this one chapter, all nine enzymatic players are concisely

described. For each enzyme, the authors outline the most essential information on characterization and structure, while referring the reader to the most recent references for details. Nice ribbon diagrams are used to illustrate the three-dimensional structure of those proteins whose X-ray structures have been solved (Protein Data Bank filenames direct the reader to the actual coordinates).

The reader will sense Blanchard's mechanistic bent. The chapter is densely packed with mechanistic schemes that do not leave an arrow unturned. Blanchard provides an insightful chemical logic for the sometimes seemingly arbitrary, or even "steppy" biosynthetic pathway. Thus, N-acylation is seen as a temporary protecting group strategy to block intramolecular imine formation and thereby allow for transamination at a flanking keto center. The intervention of an epimerization step between L,L-diaminopimelate synthesis and decarboxylation is proposed to enforce mono-decarboxylation by equipping the substrate with "enantiomeric" and hence readily distinguishable ends.

In the final chapter, Kivirikko and Pihlajaniemi provide a thorough taxonomy of the family of Fe^{2+} -dependent collagen hydroxylases. This account focuses on recent (1990s) literature and includes particularly useful discussions of the current understanding of collagen hydroxylase structure (multiple sequence alignments are presented), domain function, and how mutations (in lysine 5-hydroxylase) lead to the various forms of Ehlers-Danlos syndrome. This review also nicely sets the stage for the elegant work that has appeared more recently from Tadhg Begley's laboratory on the mechanism-based inactivation of 4-proxyl hydroxylase by 5-oxaproline-containing peptides (*J. Am. Chem. Soc.* **1999**, *121*, 587–588).

Overall, this volume belongs on the shelf of every chemistry or biochemistry library, beside the previous 71 volumes of this classic series. In taking the baton from the late Alton Meister, Dan Purich succeeds both in providing a fitting tribute to Meister the scientist and in giving his inaugural volume a flavor of its own. The chemist will especially enjoy the mechanistic depth in which many of the chapters are written, particularly those by Purich, Richards and Schuster, and Scapin and Blanchard. As a stand-alone volume, *Advances in Enzymology, Volume 72*, works well as a review of the issue of the biological "sequestration" and controlled activation of nucleophilic nitrogen...in the form of glutamine. Those chemists particularly fascinated by this long-standing question should also consider adding this volume to their own personal collections.

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Chemical Fungal Taxonomy. Edited by Jens C. Frisvad (Technical University of Denmark), Paul D. Bridge (International Mycological Institute), and Dilip K. Arora (Banaras Hindu University). Marcel-Dekker: New York. 1998. viii + 398 pp. \$175.00. ISBN 0-8247-0069-4.

"It is therefore timely and important to present a broad range of information on these techniques, and their application in systematic mycology, in a single volume. We have asked the authors of individual chapters to give a full and critical account of the use of particular methods in fungal systematics and hope that this volume will then serve as a valuable reference source." These two sentences, taken from the Preface (p iv), serve well to characterize the aim and scope of this volume.

This collection of reviews covers a specialty, or subspecialty depending upon one's own viewpoint, which is either in its infancy (DNA, RNA, immunology, enzymes, monoclonal antibodies, volatiles) or adolescence (proteins, polysaccharides), according to the chemical class being considered. As described by the authors, fungal chemotaxonomists divide mainly into the DNA/RNA/protein or the secondary metabolite arenas.

The international flavor of the effort and the product is most impressive. That is, there are 24 contributors, 20 of which are at the Ph.D. level, representing 16 institutions in 11 countries. Even the

*Unsigned book reviews are by the Book Review Editor.

editorship reflects this comprehensive input; 3 editors/3 institutions/3 countries. To me, this is a most striking and appreciated feature of the book.

One fault with the book, from the point of view of a non-mycologist, is the lack of a classic and annotated phylogeny in the lead chapter by the editors; that is, granted that the largest audience for this work will and should be the mycologist/lichenologist. However, the addition of a classic taxonomic table and/or tree would have eased placement of each chemotaxonomic argument into a more generalized overview of the topic and made it easier following for the pure chemist, natural product scientist, or organic geochemist *inter alia*. For the specialist, there should be no trouble in keeping track of the various phylogenetic positions under discussion. Certain assistance along these lines was gained within Chapter 4 (Proteins in Fungal Taxonomy) by Drs. Hennebert and Vancanneyt. Additionally, treatises such as *Ainsworth & Bisby's Dictionary of the Fungi* (8th ed.; CAB International: Wallingford, Oxon, UK, 1995) are extremely helpful and should be kept handy.

There are 14 chapters in this monograph. The chapters (parenthesized value is the percentage of references dated 1990+) cover the following annotated topics: Chapter 1 (62%), editorial overview; Chapter 2 (24%), numerical analysis methodologies; Chapter 3 (76%), PCR (polymerase chain reaction) and RFLP (restriction fragment length polymorphism) analyses of DNA; Chapter 4 (17%), protein analyses using NP- (native protein), SDS- (sodium dodecyl sulfate), IEF- (isoelectric focusing), and 2D-PAGE (polyacrylamide gel electrophoresis) methods of protein identification; Chapter 5 (61%), use of isozyme to study microevolution patterns; Chapter 6 (40%), immunotaxonomy using polysaccharides, especially extracellular forms (i.e., exoantigens) as analyzed with ELISA (enzyme linked immunosorbent assay) methodologies to the species level; Chapter 7 (17%), analysis, including high-field NMR, and subdivisions of cell wall (skeletal) polysaccharides; Chapter 8 (61%), utility of the "unsaponifiable" lipids (=solubility and acetate derivation definition) including ubiquinones, steroids, and a bit on the carotenoids; Chapter 9 (23%), discussion of the fatty acids as tools for rapid identification of spoilage agents and as alternative "fats" for human consumption; Chapter 10 (19%), polysaccharides as differential characters, especially using polyol patterns for the differentiation of pytopathogenic taxa; Chapter 11 (43%), exposé of the study and use of volatiles, mainly the terpenes, long known to impart "odors", in attempts to rapidly identify aflatoxin/nonaflatoxin producing strains; Chapter 12 (43%), role and use of secondary metabolites (includes many odor, color, and allelopathic substances); Chapter 13 (7%), consideration of growth condition influences on the quality and quantity of "special" (=secondary) metabolites; and Chapter 14 (30%), use of fungal chemotaxonomy in unraveling lichen community structure.

Not only must a "review" cover the most modern state-of-the-art literature, but it must also pay homage to the past and do so in a way that allows the reader to avoid reinventing the wheel by keeping the older, often "classic", works from slipping into obscurity. *Chemical Fungal Taxonomy* contains chapters with post-1990 references ranging from a low of 7% (Chapter 13) to a high of 76% (Chapter 3), with an overall mean of 37.4%. If one examines the topics of the chapters, comparing the corresponding reference age distributions in each, then, I feel, that this monograph did, indeed, succeed in doing a good-to-excellent job in covering the literature base. That is, we expect nearly all post-1990 references in Chapter 3 (PCR and RFLP) and more "classic" references in chapters on proteins (Chapter 4), polysaccharides (Chapter 7), and carbohydrates (Chapter 10), all of which have huge older literature banks. Regarding shortcomings in the reference list, only Chapter 13 leaves one wanting for more "modern" data, and it must exist. However, this very same chapter is the one which I personally found most thought provoking. For example, "The morphological characters of classical taxonomy are phenotypic and influenced by the conditions of growth." So too, Dr. Frank goes on to explain, are the chemicals which we wish to employ as taxonomic tools. Nearly all chapters reflected upon this theme—environment influencing

specific metabolism in both qualitative and quantitative ways. This then becomes a caveat for chemotaxonomy—one must consider growth stage, growth conditions, allelopathy, build up of exogenous substances, and the like, as they likely all influence the phenotypic taxonomic chemicals.

Understandably, much of the data covered and directions suggested stem from the industrial applications of fungi (cheese, spirits, antibiotics, spoilage, etc.). However, one soon sees that underlying patterns of genetics and its encoded biochemistries are becoming more and more understood. This is of benefit not only to all dealing with the activities, products, and influences of fungi but to the biochemical generalist as well.

As detailed in this text, one of the basic tenets of chemotaxonomy is the unbiased assessment of the quality and quantity of specific biochemicals, be they direct genotypic (DNA, RNA) codes or resultant phenotypic expressions (polysaccharides, secondary metabolites), to remove uncertainty and to hopefully present a more scientifically detailed picture of each taxon. Each chapter does cover the present "state-of-the-art", and most chapters offer directions for further study. Many informative tables of taxa versus substance (+/−) are given and allow the reader to draw his or her own conclusions and directions for additional study.

In closing, I return to my lead quotation and conclude that, yes, this book does accomplish its stated purpose. I found this book to be well rounded and comprehensive. That is, it has both breadth and depth. It will, indeed, serve well those who require a source book on fungal chemotaxonomy and natural products as well. Again, the international flavor of the authorship speaks well of global cooperation. I gladly add this monograph to my reference collection.

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Advances in Photochemistry, Vol. 25. Edited by Douglas C. Neckers, David H. Volman, and Gunther Von Bunau. J. Wiley & Sons Inc.: New York, NY. 1999. 223 pp. \$110.00. ISBN 0-471-32708-5.

The stated purpose of this series of books is "to explore the frontiers of photochemistry through the medium of chapters written by pioneers who are experts". Volume 25 in the series covers four topics: Flash Photolysis with Time-Resolved Mass Spectrometry, Velocity Mapping of UV Multiphoton Excited Molecules, Catalysis of Photoinduced Electron Transfer Reactions, and Laser Trapping-Spectroscopy-Electrochemistry of Individual Microdroplets in Solution.

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Tailored Polymeric Materials for Controlled Delivery Systems. Edited by Iain McCulloch and Shalaby W. Shalaby. Oxford University Press: New York, NY. 1999. 336 pp. \$115.00. ISBN 0-8412-3585-6.

This ACS Symposium Series 709 examines a range of polymer materials that facilitate the controlled delivery of active moieties for medical, dental, agricultural, and industrial applications. Both fundamental and applied research are covered. Although a wide range of applications are discussed, those pertinent to the pharmaceutical industry dominate.

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