

to room temperature, isopropyl iodide (680 mg, 4 mmol) was added to the murky green-colored solution, and the mixture was stirred under argon for 30 min. The mixture was poured into H₂O and then extracted with Et₂O (3 times), and the combined ether layers were washed with H₂O (3 times), dried over anhydrous Na₂SO₄, and then evaporated under argon to give 363 mg (71%) of diisopropyl diselenide (1) as a yellow-colored, foul-smelling oil. The diselenide 1 was dissolved in 25 mL of a C₆H₆/MeOH mixture (2:3) and reduced with excess NaBH₄ under argon until a colorless solution of sodium isopropylselenol (2) was obtained. Following the addition of 80 mg of NaOH, the 3β-acetoxy-24-bromochol-5-ene substrate (3; 229 mg, 0.5 mmol) was added, and the mixture was refluxed for 1 h. The mixture was poured into H₂O, and the crude product was obtained by Et₂O extraction as described above. The product was dissolved in C₆H₆ and chromatographed on a SiO₂ column (1 × 20 cm) by elution (30-mL fractions) with petroleum ether, fractions 1–5, and the following increasing concentrations of Et₂O in petroleum ether: fractions 6–10, 2%; fractions 11–15, 5%; fractions 16–20, 10%; fractions 21–15, 25%; and fractions 26–30, 50%. The desired 24-(isopropylseleno)chol-5-en-3β-ol (4) was eluted in fractions 25–27, which were combined, and evaporated, and the residue was crystallized from MeOH–H₂O to give 92 mg (40): mp 91–93 °C; TLC (CHCl₃) *R*_f (CHCl₃) 0.09, *R*_f (4% MeOH–CHCl₃) 0.55; low-resolution MS (150 °C probe temperature), *m/z* 466 (M, 82), 448 (M – H₂O, 29), 433 (M – H₂O – CH₃, 12), 423 (M – C₃H₇, 41), 405 (M – H₂O – C₃H₇, 53), 271 (23), 255 (M – side chain – H₂O, 33), 231 (23), 213 (45); high-resolution MS calcd for C₂₇H₄₆O³⁰Se, *m/z* 466.2713; found, 466.2720; IR (KBr) 3495 (OH) cm⁻¹; NMR (200 MHz, CDCl₃) δ 0.61 (s, 3 H, C-18 CH₃), 0.86 (t, 3 H, C-21 CH₃, *J* ≈ 6 Hz), 0.94 (s, 3 H, C-19 CH₃), 1.34 (d, 6 H, C-26 and C-27 CH₃'s, *J* ≈ 7–8 Hz), 2.49 (2 H, m, C-24 CH₂), 3.10 (m, 1 H, C-25 H, *J* ≈ 6 Hz), 3.48 (m, 1 H, C-3α H), 5.29 (m, 1 H, C-5 olefinic proton). Anal. Calcd for C₂₇H₄₆OSe: C, 69.63; H, 9.96. Found: C, 69.42; H, 9.82.

24-(Isopropyl)[⁷⁵Se]seleno)chol-5-en-3β-ol. The synthesis of sodium [⁷⁵Se]diselenide ([⁷⁵Se]I) was conducted on a 1-mmol scale. The Se-75 (25.13 mCi) was combined with carrier to give 80 mg of Se (1 mmol), which was stirred with Na (25 mg, 1.1 mmol) under argon in 20 mL of liquid NH₃. The mixture proceeded through the typical color change: blue to green to reddish-brown.

After 2 h, isopropyl iodide (240 mg, 1 mmol) was added with a syringe, and the mixture was stirred for an additional 2 h. Following evaporation of the NH₃, the light yellow gum was extracted with small portions of C₆H₆ (15 mL total volume), the extract was filtered through a short bed of SiO₂, and the filtrate was diluted to 25 mL with MeOH. The yellow-colored solution contained 8.39 mCi (33%) of diisopropyl [⁷⁵Se]diselenide (1), which was reduced under argon with NaBH₄ to a colorless solution of sodium isopropyl[⁷⁵Se]selenol (2). After the addition of NaOH (~80 mg, 2 mmol), 3β-acetoxy-24-bromochol-5-ene (3; 45 mg, 0.10 mmol) was added in a small volume of C₆H₆, and the mixture was refluxed. After 30 min, TLC analysis (CHCl₃) indicated the coupling reaction to be complete (1, *R*_f 0.80; 3, *R*_f 0.70; 4, *R*_f 0.10). The mixture was cooled and then poured into H₂O, and the aqueous layer was extracted three times with C₆H₆. The combined organic extracts were washed with H₂O (3 times), dried over anhydrous Na₂SO₄, and evaporated under argon to a volume of 1–2 mL. This solution was applied to a SiO₂ column packed in C₆H₆. A nonpolar radioactive peak was eluted with C₆H₆ (fractions 1–10, 25 mL in volume). Further elution with 5% Et₂O–C₆H₆ removed the [⁷⁵Se]4 in fractions 12–15, which were combined to give 1.05 mCi [42% from 3β-acetoxy-24-bromochol-5-ene (3)]. TLC analysis using two solvent systems indicated a single radioactive component (>98%), which cochromatographed with authentic 24-(isopropylseleno)chol-5-en-3β-ol: *R*_f (CHCl₃) 0.25, *R*_f (10% EtOAc in CHCl₃) 0.75.

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Book Reviews

Concise Encyclopedia of Biochemistry. By Mary Brewer and Thomas Scott. W. de Gruyter, Berlin and New York. 1983. 518 pp. 14.5 × 22 cm. ISBN 3-11-007860-0. \$29.90.

An amazing amount of useful information is packed into this small volume. What's more, the definitions are readable, up-to-date, and accurate. The many structural formulas and metabolic pathways shown are clear and well-chosen. Also included are abbreviations, Enzyme Commission numbers, and extensive cross-references. Terms used in molecular biology (for example, attenuator), immunology (for example, IGM), and natural-product studies (for example, miraculin) are included. Miraculin is a taste-modifying glycoprotein derived from the berry of *Synsepalum dulcificum* native to West Africa. It causes sour substances to taste sweet. This encyclopedia should find wide use among all those interested in biological science, students, teachers, and researchers alike. At its modest price it is an outstanding bargain.

The work is an English translation as well as a revision of "Brockhaus ABC Biochemie" edited by H. D. Jakubke and H. Jeschkeit, the second edition of which was published in 1981. Congratulations all!

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New Comprehensive Biochemistry. Volume 3. Stereochemistry. Edited by C. Tamm. Elsevier Biomedical Press, Amsterdam, The Netherlands (distributed in the U.S. and Canada by Elsevier Publishing Co., Inc., New York). 1982. x + 342 pp. 17 × 24.5 cm. ISBN 0-444-80389-0. \$65.00.

This book is highly recommended to all scientists with an interest in stereochemistry, and, in particular, it should be in the libraries of all those interested in modern biochemistry. This volume contains seven chapters, each written by an expert in the particular area. Each chapter is of approximately equal length, and each contains an extensive list of references, many to work published in the late 1970's and up until 1981. Figures are freely used, are informative, and are well done.

There are two introductory chapters; the first by B. Testa, "The Geometry of Molecules: Basic Principles and Nomenclatures", defines "dissymmetric", "enantiotopic", and "diastereotopic" groups, faces, symmetry planes and rotation-reflection axes, chiral planes and axes, etc. and thus should serve as a valuable reference. The second introductory chapter, "Chemical Methods for the Investigation of Stereochemical Problems in Biology", by R. Bentley, is particularly well written and provides an interesting description of the historical development of this field. The classification of reaction types and selectivities should be useful to teachers and researchers concerned about the precise de-

scription of processes. The recommendation that biological processes be referred to as stereoselective, with qualifiers added when appropriate, is particularly timely.

In Chapter 3, "Stereochemistry of Dehydrogenases", J. Jeffrey discusses what the enzymes do, how the stereospecificity (stereoselectivity?) arises, the relationship between structural features and functions, and the relationship between structures. Chapter 4, "Stereochemistry of Pyridoxal Phosphate-Catalyzed Reactions", by H. G. Floss and J. C. Vederas, gives a comprehensive review of the experimental evidence for the stereoselectivities of each class of reactions mediated by pyridoxal phosphate. A final section describes the common stereochemical features of pyridoxal phosphate enzymes. In Chapter 5, "Stereochemistry of Enzymatic Substitution at Phosphorous", P. A. Frey describes the methods used in the stereospecific syntheses and stereochemical analyses of substrates with chiral phosphates groups. The stereoselectivities of the enzymes are presented and the results are discussed in terms of various possible mechanisms. J. Retey in Chapter 6, "Vitamin B₁₂: Stereochemical Aspects of its Biological Functions and of its Biosynthesis", reviews the stereochemical course of the coenzyme B₁₂ catalyzed rearrangement and the stereospecificity (stereoselectivity?) of some enzymes in the biosynthesis of the corrin nucleus. The final chapter, Chapter 7, "The Stereochemistry of Vision", by V. Balogh-Nair and K. Nakanishi, has a long introduction followed by sections on in vitro regeneration of visual pigments, the primary event, conformation of the chromophore, visual pigment analogues, models proposed to account for molecular changes in the primary event, and finally models to account for the color and wavelength regulation in visual pigments.

The one criticism of this otherwise excellent book is to be found in the inconsistencies in nomenclature among the various contributors, in spite of the superb two introductory chapters detailing the most acceptable nomenclature.

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Biochemical and Clinical Aspects of Pteridines. Volume 1. Edited by H. Wachter, H. Ch. Curtius, and W. Pfeleiderer. Walter de Gruyter, Berlin. 1982. xv + 373 pp. 17 × 24.5 cm. ISBN 3-11-008984-X. \$68.20.

The ubiquity of pteridines in nature has long been recognized as a striking feature of these important natural products, although their precise biological function still remains unknown in many instances. Their role in the metabolism of mammals, however, has been increasingly unraveled during the past few decades, and the malfunction of this role is now seen to be an important factor in several diseases. Therefore, in recent years, medicinal aspects of pteridine research have been receiving more and more attention, and the volume presently under review is an account of the proceedings of the First Winter Workshop on Pteridines, which was held at St. Christoph, Arlberg, Austria, in 1982. The workshop focussed attention specifically on clinical applications of pteridines, and its stated purpose was to bring together scientists in the fields of biochemistry, clinical biochemistry, analytical chemistry, and immunology, as well as clinicians working in the pteridine field. In the event, 31 participants came together, representing a variety of interests, and their endeavors are published in this book in the form of 25 research reports, grouped under the following six main headings: "Fundamental Chemistry for Analysis and the Biochemistry of Naturally Occurring Pteridines", "Quantitative Chemical Analysis of Pteridines", "Pteridines in Cancer Detection and Monitoring", "Pteridines in Immunology", "Pteridines in Proliferation and Differentiation", and "Pteridines in Metabolic Diseases". In their preface, the editors express the hope that this book will serve not only as a source of reference for factual information, but will also afford any interested investigator an easy access to clinical research on pteridines, and it is fair to say that this hope has been realized. The first chapter gives an extremely useful overview by W. Pfeleiderer on the value of UV spectroscopy in the structural elucidation of pteridines, and this should be of

great help to chemists working in the pteridine field. A substantial part of the book is then taken up with methods of detection and analysis of pteridines, and here it is evident, as in so many other areas, that HPLC has established itself as one of the main analytical tools. Seventeen of the twenty-five papers, in fact, make use of HPLC and offer a state of the art survey for anyone interested in using HPLC with pteridines. All in all, it can be confidently asserted that this volume is one that most "pteridinologists" will want to include on their bookshelves. It is well produced in hardback cover and is well served by both author and subject indexes.

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XI International Congress of Clinical Chemistry. Edited by E. Kaiser, F. Gabl, M. M. Muller, and P. M. Bayer. Walter de Gruyter, Berlin and New York. 1982. 1575 pp. 17.5 × 24.5 cm. ISBN 311-008447-3. \$145 (DM 320).

This volume contains the proceedings of the International Congress held in Vienna, August 30 to September 5, 1981. The editors are to be congratulated on successfully compiling the articles from such a large number of authors from so many different countries. In general, the material is topical with the listed references being up-to-date.

The great diversity of activity in the field of clinical chemistry is reflected in the division of the proceedings into five major sections: (I) General Aspects, (II) Clinical Aspects, (III) Biochemical Aspects, (IV) Methodological Aspects, and (V) Aspects of Laboratory Organization. Section I examines the historical development of the discipline, including ethical and education considerations. While of general interest, this section does not appear to add much to what has already appeared in the literature during the past decade. Similarly, section V, which deals with laboratory planning and organization as well as computers in clinical chemistry, was somewhat disappointing in that much of the material and many of the problems addressed were successfully resolved in the U.S. during the mid-1970's. Herein lies what is probably a significant deficiency in the structure of this Congress, that is, certain sections of the proceedings would have been improved by an increased U.S. representation.

Sections II-IV are most comprehensive and, in general, attain a very high standard. There are excellent subsections on nutrition, hormone receptors, inborn errors of metabolism, corrective tissue, membrane proteins, drugs, luminescence, trace elements, as well as the techniques of immunoassay, fluoroimmunoassay, and dry reagent chemistries, among others. Since these sections represent the bulk of the proceedings, the book is well worth its price, since it contains a wealth of information for both the group of individuals who are actively working within specific areas and for the group of individuals particularly interested in gaining a rapid, comprehensive, and timely review of specific subject material.

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Biomedical Aspects of Fluorine Chemistry. Edited by R. Filler and Y. Kobayashi. Kodansha Ltd., Tokyo, and Elsevier Biomedical Press, Amsterdam, New York, and Oxford. 1982. x + 246 pp. 16 × 23 cm. \$74.50.

The book "Biomedical Aspects of Fluorine Chemistry" is, in the words of the editor, "an outgrowth of the proceedings at a Symposium on Fluorine in Biomedical Applications" held in April 1979 in Honolulu. The literature of the individual articles (11 altogether) is updated to 1981-1982.

In the first chapter, R. Filler and S. M. Naqvi outline the main directions of research in fluorinated drugs: anticancer, antiviral, and antiinflammatory drugs, central nervous system agents, en-

zyme inhibitors, fluorine-containing isoprenyl derivatives, fluorinated prostaglandins, and use of fluoro derivatives in medical diagnosis. The chapter on "Fluorinated Vitamin D₃ Analogs" (Y. Kobayashi and T. Taguchi) describes synthesis of fluorinated derivatives used for the study of the metabolism of vitamin D₃. In the next chapter, A. J. Elliott surveys fluorinated compounds used as central nervous system agents: neuroleptics, anxiolytics, antidepressants, analgesics, anorectics, and sedatives. The chapter "Synthesis and Biological Properties of Ring-Fluorinated Biogenic Amines" (K. L. Kirk, D. Cantacuzène, and C. R. Creveling) is a discussion of the metabolism and mechanism of action of fluorinated norepinephrines and dopamines. In the chapter on "Suicide Substrate Enzyme Inactivators", J. Kollonitsch shows syntheses of β -fluorinated amino acids and β -fluoro amines and their specific irreversible deactivation of some enzymes. The cytotoxic activity of 5-fluorouracil and its analogues and derivatives is discussed by D. V. Santi, A. L. Pogolotti, Jr., E. M. Newman, and Y. Wataya.

The importance of radioactive fluorine (¹⁸F) is a topic of the chapter on "Biochemical Applications of Radioactive Fluorine". The authors (T. Ido, K. Fukushi, and T. Irie) show new applications of ¹⁸F-labeled compounds in diagnosis by means of tomography or autoradiography. Because of characteristic NMR spectra, fluorinated biological materials can be easily identified by means of NMR spectroscopy. The chapter on "Applications of Fluorine NMR in Biochemistry" (J. T. Gerig) describes how labeling with fluorine is used for investigation of biochemical pathways. Two chapters, one written by K. Yokoyama, T. Suyama, and R. Naito and the other by L. C. Clark, Jr., and R. E. Moore, deal with emulsions of perfluorinated compounds as oxygen-transport agents used as blood substitutes. The final chapter (H. Matsumoto) is devoted to the technique of using expanded (porous) poly(tetrafluoroethylene) as artificial veins.

The monograph has a very high standard. The main emphasis is on biochemical and medicinal aspects, while synthetic chemistry of fluorinated compounds is kept to a minimum. Some of the topics, such as fluorinated drugs and blood substitutes, have been surveyed recently in Banks' series, "Organofluorine Chemicals and Their Industrial Applications" (1979) and "Preparation, Properties and Industrial Applications of Organofluorine Compounds" (1982) (Ellis Horwood, Chichester), but the overlap is only partial. Most of the topics have their premières. The book is certainly an important contribution to the monographs on fluorine chemistry and is especially desirable for researchers in biochemical and medicinal fields.

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Organic Syntheses with Carbon-14. By Richard R. Muccino. Wiley, New York. 1983. xi + 676 pp. 17 × 24 cm. \$52.50.

Carbon-14 labeled organic compounds have become exceedingly useful tools in the hands of organic and medicinal chemists and biochemists to probe such issues as reaction mechanism and the biosynthesis and metabolic fate of interesting organic substances. Although established procedures for the preparation of simple to complex organic compounds abound, they are scattered throughout the literature in numerous journals. This volume successfully addresses the need for a comprehensive survey of the literature dealing with ¹⁴C-labeling methods to facilitate information retrieval.

Covering the literature from 1965 to 1979, the author utilized the *Journal of Labelled Compounds and Radiopharmaceuticals*, *Chemical Abstracts*, and *Chemicus Index* as a source of references. The book contains 15 chapters, including carboxylic acids, organic nitrogen compounds, hydrocarbons, heterocyclic compounds, and organic sulfur compounds. Each chapter is further subdivided into separate functional groups, and examples of specific compounds appear in increasing order of structural complexity. Although nonradiolabeled chemistry is not included, structural

formulas, reagents, and useful yield data for the radiolabeled steps are given. The inclusion of both a comprehensive formula and subject index expedites the location of specific compounds. Although the author does not disclose the exact number, this literature survey easily includes over a thousand references. Technically, the book is well put together and I found no typographical errors.

Succeeding in its advertised purpose, this volume represents a convenient entry into the literature of synthetic ¹⁴C chemistry. As pointed out by the author in the Preface, this survey should also represent a valuable resource to synthetic chemists involved with other isotopes of carbon.

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Advances in Chromatography. Volume 20. Edited by J. C. Giddings, E. Grushka, J. Cazes, and P. R. Brown. Marcel Dekker, New York. 1982. xv + 286 pp. 15.5 × 23.5 cm. \$45.00.

The editors of *Advances in Chromatography* have once again assembled a distinguished list of contributors for this 20th volume of the series. The book essentially consists of two parts. The first three chapters describe practical applications of chromatography, while the latter three are either hardware oriented or theoretical in nature.

Probably the most useful chapter to the practicing chromatographer is M. T. W. Hearn's excellent review of the use of HPLC in protein chemistry. Protein, peptide, and amino acid derivative and free amino acid separations are described. The main emphasis is on the use of reversed-phase columns, the workhorse in the field, but size exclusion and ion exchange are also included. The extensive reference list alone makes this a worthy chapter. The only significant deficiency is the short treatment given ion-exchange protein separations, an unfortunate consequence of the rapid growth in this technique in the 2 years since this chapter was written.

The second chapter, a discussion of vitamin D₃ and metabolite chromatography by K. T. Koshy, is less ambitious in scope, but no less thorough in depth. After a brief introduction to vitamin D biochemistry, analysis of vitamin D₃ by a variety of chromatographic techniques is described. These include open column chromatography, TLC, GC, and HPLC. The numerous examples, including the analysis of vitamin D₃ in food products, are very informative.

Much less satisfying is the chapter on clinical uses of HPLC in a children's hospital. Few details are provided with nearly all of the references on therapeutic drug monitoring from the author's own work. This seems somewhat self-serving, and the reader would have benefited more if a more thorough review were provided. However, a description of catecholamine analysis, which is treated in more detail, saves the chapter from being a total waste.

The last three chapters are probably less useful to medicinal chemists. A section by R. P. W. Scott has useful information on the properties of silica gel and the nature of its interactions with solvents and solutes, but most of the data are not pertinent to the practicing chromatographer. W. G. Jennings describes recent innovations in capillary GC column technology, although the newest bonded vitreous silica columns which have been shown useful for difficult polar compounds, such as steroids, are probably too recent to be included. The final chapter by Editor J. C. Giddings is a lucid, theoretical discussion of the problems encountered in size exclusion chromatography of very large polymers. Although again this topic is not of much interest to medicinal chemists, it is a very timely discussion for polymer chromatographers.

In summary, this volume would be a fine library addition for anyone with a strong interest in chromatography from either an applied or theoretical viewpoint.

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Free Radicals and Cancer. Edited by Robert A. Floyd. Marcel Dekker, New York. 1982. xii + 541 pp. 16 × 23.5 cm. \$69.75.

This volume presents a substantial amount of information from diverse points of view concerning the relationship between free radicals and cancer development. Perhaps predictably, the majority of chapters focus on the production and detection of free radicals produced during the activation of chemical carcinogens, but the book also includes such areas as the use of radiation sensitizers in cancer therapy. In fact, two such included chapters are strangely separated by 100 pages of unrelated information. Surprisingly, the book does not contain any chapters discussing the production of superoxide radicals from cell membranes during the process of tumor promotion or the role of tumor promoters in their formation and that of superoxide dismutase as an inhibitor of tumor promotion. Since the study of tumor promotion is a very active area in cancer biology, this omission seriously weakens the value of this book to cell biologists. It is also apparent from scanning the references in each chapter that at least some of the contents of this volume do not present the most current ideas on a subject, i.e., chapter 4 does not list any references beyond 1978, and many other chapters have few references from years beyond this. Nevertheless, this volume does provide a reasonably adequate exposition of the possible molecular mechanisms

whereby free radical formation is associated with cancer development and should be useful to medicinal chemists interested in mechanisms of carcinogenesis.

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Books of Interest

Encyclopedia of Emulsions Technology. Volume 1. Basic Theory. Edited by Paul Becher. Marcel Dekker, New York. 1983. xiv + 725 pp. 18 × 26 cm. ISBN 0-8247-1876-3. \$95.00.

Current Topics in Reproductive Endocrinology. Volume 1. Androgens and Antiandrogen Therapy. Edited by S. L. Jeffcoate. Wiley, New York. 1982. ix + 188 pp. 15.5 × 23.5 cm. ISBN 0471-10154-0. \$43.95.

Advances in Chromatography. Volume 21. Edited by J. Calvin Giddings, Eli Grushka, Jack Cazes, and Phyllis R. Brown. Marcel Dekker, New York. 1983. 360 pp. 15.5 × 23.5 cm. ISBN 0-8247-1679-5. \$49.75.