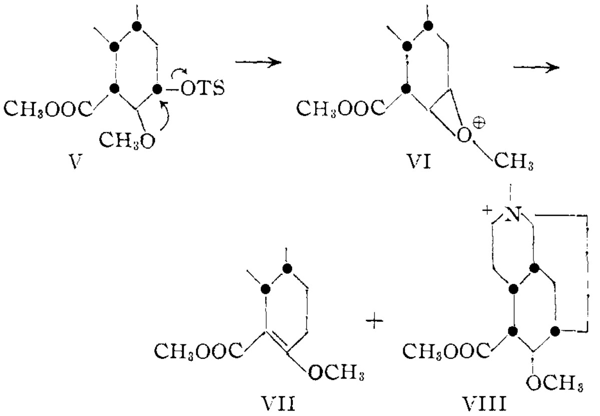
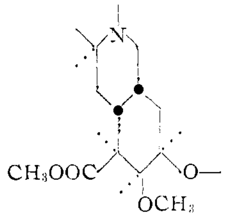
quaternization of methyl reserpate tosylate (V) can be most readily accommodated by neighboring group participation of a C-17 methoxyl placed *trans* to the groups at C-16 and C-18, proceeding through an intermediate oxonium salt (VI),[8] followed on the one hand by loss of a proton to yield VII and on the other hand by a *second* displacement at C-18 through backside attack by N-4, affording the quaternary salt VIII. Justification for this interpretation is offered by our observation that *trans*-2-methoxycyclohexylbenzenesulfonate, on being refluxed in collidine, is converted in significant yield to—among other products—cyclohexanone enol methyl ether, identified by hydrolysis to cyclohexanone.

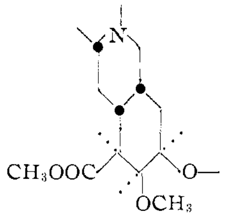


V VI VII VIII

The stereochemical expression IV stands in contrast to the two previously proposed for reserpine: IX by Schlittler, *et al.*,[3] and supported by Wintersteiner, *et al.*,[4] and more recently X, by Janot, Goutarel, Prelog, *et al.*[9] The internal quaternization of V, presumed to occur by simple displacement with inversion at C-18,[4] was taken to indicate a *cis* relationship of the C-18 substituent and the C-15 and C-20 hydrogens, as expressed in both IX and X. This reaction, however, can be considered to proceed, as shown above, by *double-inversion with over-all retention of configuration* at C-18, consistent with the *cis* assignment to hydrogens at C-18 and C-20 (structure IV). The rotational evidence bearing on the relative configuration at C-3 and C-16 which led to the modification[9] of IX to X is automatically accommodated by the expression IV, which also places the C-16 hydrogen *trans* to that at C-3.



IX



X

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(8) Elimination of V leading to VI requires in V a diaxial-type conformation at C-17 and C-18, which can result from IV through appropriate rotations in the ring system.

(9) M. M. Janot, R. Goutarel, A. LeHir, G. Tsatsas and V. Prelog, *Helv. Chim. Acta*, **38**, 1073 (1955).

BOOK REVIEWS

Monographien zu Angewandte Chemie und Chemie-Ingenieur-Technik. Nr. 67. Verteilungsverfahren im Laboratorium. By ERICH HECKER, Max Planck Insitut für Biochemie, Tübingen, and ADOLF BUTENANDT, Max Planck Institut für Biochemie und Physiol.-Chem. Institut der Universität, Tübingen, Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, Germany. 1955. 229 pp. 15.5 × 23 cm. Price, $4.75.

While such laboratory methods of laboratory separation and purification as fractional distillation and chromatography have been well treated in monographs, there has been no whole book devoted to a comprehensive account of the theory and practice of liquid–liquid extraction. The need is now filled. This newest member of an important German series is authoritative, well-documented (525 references), and up to date (through 1953).

The book begins with the Nernst distribution law and a definition of multiplicative partition. Batchwise application of the latter is considered in detail, with descriptions of extraction batteries, the computation of theoretical partition curves, and the several recycling and withdrawal procedures, which are critically evaluated. Attention is centered on the fractionation of mixed solutes rather than on the mere transfer of a solute from one phase to another. The number of extraction stages is shown to depend on the separation factor, determined by the composition of the solute and the two solvent phases; the volume factor, determined by the relative volumes of the phases; the initial concentration of impurities; and the degree of purity desired in the product. Laboratory-scale continuous extraction also is treated, along with some aspects of partition chromatography.

The special part is essentially a review of the partition behavior of organic compounds classified according to structure, and metal ions classified as their neutral or anionic complexes. A kind of appendix gives mathematical derivations and pertinent numerical tables.

Quantitative relationships between partition behavior and constitution of solutes and solvents are mostly lacking, but the lack is also in present knowledge. A more serious possible flaw is the incompleteness of literature coverage. In spite of its extensive bibliography, the book cannot be trusted to supply all references to individual studies of apparatus or materials. It is the reviewer's impression that analytical separations and those dealing with natural organic products fare better than those verging on industrial processes and those developed in research on the production of atomic energy. However, an attempt to include *every* pertinent citation would have lowered the ratio of usefulness to price of the book.

The German style is clear and straight-forward, and the mathematics limited to algebra. The book is very well manufactured; only three trivial misprints have been noted. It is heartily recommended.

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Elsevier's Encyclopaedia of Organic Chemistry. Series III. Carboisocyclic Condensed Compounds. Volume 14—Supplement. Nor-Steroids. Steroids. Hydrocarbons. Halogen, Nitrogen, and Unsubstituted Monohydroxyl Compounds. Edited by F. RADT. Elsevier Publishing Company, 2330 Holcombe Blvd., Houston 25, Texas. 1954. xxxix + pages 1347 S–1868 S. 18.5 × 25.5 cm. Price, $36.00 for set subscribers, $42.00 for subscribers to Series III, $48.00 per single copy.

It is difficult to add anything complimentary about this new supplement in the "Elsevier" series, which has not been said already about earlier volumes. The physical appearance, the organization and the general approach are superb and in so far as coverage of steroids or triterpenes is concerned, there simply does not exist anything comparable in the chemical literature.

The original volume 14 covered steroids and triterpenes up to 1936, but in view of the enormous research effort expended in those fields since that time, it has been impossible to cover the next period (1937–1946) in one single supplement. The section on triterpenes has appeared already and the present supplement represents the first of several which will cover the steroid literature up to 1946.

The present volume is concerned chiefly with sterols and some of their halogenated derivatives; sterols containing amino and nitro groups also are included. The portion on "nor-steroids" does not deal with the physiologically important 19-norhormones but rather with sterols in which rings A or B are five-membered. Finally, both aromatic (1,2-cyclopentenophenanthrene and analogs) and perhydro steroidal (androstane, cholane, etc.) hydrocarbons are covered.

A particularly impressive feature is that while the coverage concerning compounds ends in 1946, almost every section includes references from the 1947–1954 literature, where this pertains to recent changes in the structure or stereochemistry of the particular compound under discussion. A few striking examples of this up-to-dateness follow.

Most of the 1953–1954 references to the absolute configuration of steroids are listed in the nomenclature and stereochemistry section in the beginning of this volume. The section on cholestan-1-ol and cholestan-2-ol contains two references from 1944, one each from 1949 and 1952 and two from the 1954 literature. The structures of the dienone–phenol rearrangement products in the cholestane series all have been corrected in the light of latest structural revisions (1951) in spite of the fact that this subject presumably will be covered again in a future 1947–1956 supplement.

The section on cholesterol is particularly impressive, covering as it does over 100 pages and over 1000 references. This material represents for all practical purposes a monograph on cholesterol and is concerned with the physical constants, occurrence, chemistry and biological effects of this substance. The other sterols (*e.g.*, ergosterol, stigmasterol, sitosterols) are discussed in an equally complete manner. It is interesting to note that of the 1000 references dealing with cholesterol, nearly 300 refer to literature citations prior to 1936 in spite of the fact that cholesterol already has been reviewed up to 1936 in the original volume 14.

The system of nomenclature is outlined in the introduction and the wisdom of some of the editorial decisions appears open to question. While the Fieser system is used generally, some of the more recent recommendations of the Ciba Foundation Conference on Steroid Nomenclature are not employed, principally because these terms are not found in the 1937–1946 literature with which this volume is concerned. While this is not regrettable for names such as "gonane" which have never received general acceptance, the *i*-steroids surely could have been named according to the "cyclo" system and similarly ring scission should have been indicated by the prefix "seco" rather than by following the antiquated (1938) Sobotka proposals. Admittedly, these are minor objections but since the present nomenclature may constitute a precedent for future supplementary volumes, it might be pertinent to reconsider some of the editorial decisions along those lines.

Possibly the most commendable practice in the preparation of the "Elsevier" volumes has been to cover first of all fields (such as steroids) of current interest which for all practical purposes are not even mentioned in other compendia such as Beilstein. Consequently, it is somewhat surprising that this first supplementary volume on steroids should concern itself chiefly with sterols rather than with steroid hormones, which certainly have received and are receiving the main emphasis in current steroid research and where a more recent coverage is extremely desirable. Similarly, the section on steroidal sapogenins in the original volume 14 is completely out of date since the structural formulas have been revised since that time (1936) and indeed the majority of sapogenins only were isolated in the period 1937–1946; a supplement of this subject is sorely needed.

"Elsevier" has become so indispensable to the steroid chemist that it is hoped that the remaining supplements to volume 14 will be issued shortly.

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July 10, 1955—August 10, 1955

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RICHARD T. COX. "Statistical Mechanics of Irreversible Change." The Johns Hopkins Press, Homewood, Baltimore 18, Maryland. 1955. 130 pp. $5.00.

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