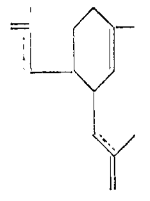
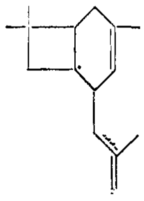
sequent chromatography on alumina employing *n*-heptane as developer and tetranitromethane as a streak indicator. Similar methods yielded a pure β-caryophyllene, $[\alpha]^{20}_{D}$ −8.8°, n^{20}_{D} 1.4994, from clove oil. Application of these chromatographic procedures to the dehydrogenation (with benzene and a palladium catalyst[1]) products of α- and β-caryophyllene yielded naphthalenic and benzenic fractions identical in their ultraviolet and infrared spectra. Oxidation of the naphthalenic fraction from β-caryophyllene with alkaline permanganate produced 1,2,4-benzenetricarboxylic acid anhydride, identified by melting point (158°), mixed melting point and X-ray diffraction pattern. Similar dehydrogenation of an impure β-caryophyllene, n^{20}_{D} 1.4980, from clove oil, led to the isolation of a blue and a purple azulenic fraction.

Ruzicka[2] has presented excellent evidence for the structure shown below for β-caryophyllene (from clove oil). Later[3] a seven-membered ring structure was favored on the basis of the isolation, in low yield, of degradation products indicating the presence of such a ring system. Our demonstration of azulenic fractions as impurities in a dehydrogenation mixture from clove oil points to a probable similar origin for the seven-membered ring degradation products reported by Ruzicka and associates. Accepting then the original formulation of Ruzicka, shown below, for β-caryophyllene, and accepting the demonstration (verified in our laboratory) of Sŏrm and coworkers[4] that α- and β-caryophyllene contain three and two double bonds, respectively, then our dehydrogenation results suggest the formula shown below for α-caryophyllene (from hop oil).


α-Caryophyllene


β-Carophyllene

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[1] H. Adkins and D. C. England, THIS JOURNAL, **71**, 2958 (1949); H. Adkins and G. F. Hager, *ibid.*, 2962.

[2] L. Ruzicka, *Chemistry & Industry*, **13**, 509 (1935).

[3] L. Ruzicka, K. Huber, P. A. Plattner, S. S. Deshapande and S. Studer, *Helv. Chim. Acta*, **22**, 716 (1939).

[4] F. Sŏrm, J. Mleziva, Z. Arnold and J. Plíva, *Collection Czechoslov. Chem. Commun.*, **14**, 699 (1949).

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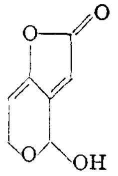
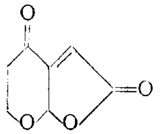
RECEIVED SEPTEMBER 1, 1950

*Allo*PATULIN

Sir:

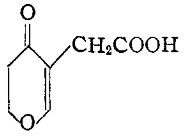
The structure (I) for patulin has now been established beyond question by degradative and synthetic studies.[1,2,3,4,5] None the less, much interest still attaches to the closely related structure (II), which has been suggested[6] as an alternative to (I) for patulin, and whose reactions may be

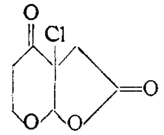

I


II

expected to simulate those of the mold metabolite in many respects. We wish to record the synthesis of (II), which we designate here as *allo*patulin.

Desoxypatulinic acid[3] (III) was smoothly transformed by chlorine in dry chloroform to the **chlorolactone (IV)**, m. p. 124.0–125.5° (calcd. for $C_7H_7O_4Cl$: C, 44.09; H, 3.67. Found: C, 43.99; H, 3.82). When the lactone was treated with an equivalent of potassium acetate


III


IV

in anhydrous methanol, ***allo*patulin (II)**, m. p. 116–117° (calcd. for $C_7H_6O_4$: C, 54.54; H, 3.90. Found: C, 54.56; H, 4.00) was formed. The lactone gave a normal **phenylhydrazone,** m. p. 195° (calcd. for $C_{13}H_{12}O_3N_2$: C, 63.93; H, 4.92; N, 11.48. Found: C, 63.75; H, 5.04; N, 11.32) and **semicarbazone,** m. p. >270° (calcd. for $C_8H_9O_4N_3$: C, 45.49; H, 4.26; N, 19.91. Found: C, 45.08; H, 4.47; N, 19.77).

Like patulin, *allo*patulin was converted to desoxypatulinic acid (III) on hydrogenation. On the other hand, while patulin reacts with hydrogen chloride to give chlorodesoxypatulinic acid (V, X = Cl),[3] *allo*patulin reacted with that reagent to form **isochlorodesoxypatulinic** acid (VI, X = Cl), m. p. 133–135° (*dec.*) (calcd. for $C_7H_7O_4Cl$: C, 44.09; H, 3.67. Found: C, 43.52; H, 3.71). Treatment of the chloro acid with diazomethane, followed by Brady's reagent (methanol) gave **methyl *iso*methoxydesoxypatulinate dinitrophenylhydrazone,** m. p. 194–195° (*dec.*) (calcd. for $C_{15}H_{16}O_8N_4$: C, 47.37; H, 4.21; N, 14.73. Found: C, 47.53; H, 4.42; N, 14.77). With acetic acid, *allo*patulin gave ***iso*acetoxydesoxypatulinic acid** (VI, X = OAc), m. p. 139–140° (calcd. for $C_9H_{10}O_6$: C, 50.47; H, 4.67. Found: C, 50.90; H, 5.04), which reverted to its progenitor when it was pyrolyzed.

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[1] Woodward and Singh, THIS JOURNAL, **71**, 758 (1949).

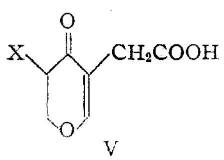
[2] Woodward and Singh, *Experientia*, **6**, 238 (1950).

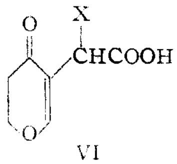
[3] Woodward and Singh, *Nature*, **165**, 928 (1950).

[4] Woodward and Singh, THIS JOURNAL, **72**, 1428 (1950).

[5] Dauben and Weisenborn, *ibid.*, **71**, 3853 (1949).

[6] Engel, Brzeski and Plattner, *Helv. Chim. Acta*, **32**, 1166 (1949); **32**, 1752 (1949).


V


VI

Bromination of desoxypatulinic acid in dry chloroform led, not to a bromolactone, but to **bromodesoxypatulinic acid** (V, X = Br), m. p. 136–137.5° (calcd. for $C_7H_7O_4Br$: C, 35.47; H, 2.98. Found: C, 35.96; H, 3.25). The bromo acid was transformed by excess hot aqueous potassium chloride to **chlorodesoxypatulinic** acid (m. p. 130.5–131.5°, methyl ester dinitrophenylhydrazone, m. p. 188.5–190°; mixture melting points with authentic samples undepressed). Since the chloro acid was earlier[3] converted into patulin acetate, the new transformations provide the hitherto missing stages of a second complete synthesis of patulin.[4]

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RECEIVED AUGUST 11, 1950

BOOK REVIEWS

A German-English Dictionary for Chemists. By AUSTIN M. PATTERSON, Professor Emeritus of Chemistry, Antioch College. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1950. xviii + 541 pp. 13.5 × 17.5 cm. Price, $5.00.

For more than 30 years Dr. Patterson's dictionary has been a vademecum for both academic and industrial chemists. The second edition went to press sixteen years ago, and now an expanded third edition has appeared, containing a vocabulary of 59,000 terms. The number of words has thus increased by 40%, and most of the additions are drawn from technical fields in which rapid development has been accompanied by a corresponding flood of new *termini technici,* as, for instance, in high-polymer technology, or military chemistry. After an examination of entries concerning fields with which this reviewer can claim a certain familiarity, it appears that the words newly included were well and wisely chosen.

A part of the purpose of this review is to acquaint chemists with the fact that this valuable library tool has been re-edited; although its widespread use speaks, by itself, for the merits of the work, a brief restatement of its special features at this time may not be amiss. Those possessing a rudimentary knowledge of German will welcome the excellent introduction (reproduced as in the second edition), where common pitfalls in German word and sentence constructions are discussed; the listing of suffixes and prefixes with their various meanings is useful. The vocabulary includes a fair selection of nontechnical words which, nonetheless, are commonly encountered in scientific writing. Particular attention is devoted to terms stemming from arts and crafts, some of them archaic or even obsolete, the meaning of which cannot be guessed at or otherwise deduced.

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Technique of Organic Chemistry. Volume III. Editor: ARNOLD WEISSBERGER, Research Laboratory, Eastman Kodak Company, Rochester, N. Y. Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y., 1950. ix + 661 pp. 16 × 23.5 cm. Price, $10.00.

Two excellent chapters: IV (140 pp.) on Extraction and Distribution by Lyman C. Craig and David Craig, and VI (121 pp.) on Crystallization and Recrystallization by R. Stuart Tipson make this book worthwhile. The former is a clear and scholarly treatment of an important subject by outstanding experts in the field. It includes the most recent developments from the senior author's laboratory on the new glass apparatus for multiple extractions in countercurrent distribution. Chapter VI is the best exposition on the subject of crystallization and recrystallization known to the reviewer. It is extremely well written by a man who is obviously thoroughly familiar with the art, and should be required reading for all students of organic chemistry.

The remaining six chapters suffer by comparison, but this is due in part to the nature of the subject matter. Chapter V on Dialysis and Electrodialysis by R. Eliot Stauffer, and Chapter VII on Filtration by Arthur B. Cummins are well written and quite comprehensive. Chapters I on Heating and Cooling by Richard S. Egly, II on Mixing by J. H. Rushton and III on Centrifuging by Harold B. Golding consist largely of detailed descriptions of pieces of apparatus (with drawings) reminiscent of an apparatus catalog, coupled with theoretical sections including mathematical treatment. The main criticism of these chapters is their inadequate treatment of the subjects with respect to the practice of organic chemistry. In Chapter II, for example, a variety of stirring techniques are described without particular consideration of specific uses. For example, in describing the wire stirrer, in addition to the general remarks, it would be helpful to give directions for its construction, to cite specific cases where it is particularly useful, as in heterogeneous Friedel–Crafts reactions, to point out disadvantages as in the formation of Grignard reagents where nichrome wire, particularly if etched by acid, may promote extensive coupling, and to indicate how the difficulty can be eradicated by use of tantalum or platinum wire. It is also unfortunate that the problem of stirring motors, which is a very real one to the laboratory chemist, is dismissed with the statement that "these appliances are commercially available and do not warrant further discussion at this place." Actually very few really satisfactory motors are available which provide all of the virtues of good control of speed, power at low speeds and sparkless features. Suggestions as to the use and availability of the more powerful utility air driven motors would also be appreciated by the reader.

Chapter VIII on Solvent Removal, Evaporation, and Drying, by Geoffrey Broughton is somewhat disappointing since it does not give very much practical information. The subject of drying solvents, for example, is treated mostly in generalities, whereas it could well include a section with directions for or references to preferred procedures and