same value. Birch xylan, compared viscometrically with barley xylan, had a degree of polymerization of 35. Optical rotational measurements indicate a 1,4′,β-linkage. This is based on the rotational shift method of Reeves and comparisons with Haworth's esparto xylan.

Mannan "A" of ivory nut readily forms supersaturated solutions of 1% concentration. Such a solution crystallizes if heated to 60–70° for several days. The crystals initially are rods and gradually become dumb-bell shaped as growth continues. Slight double refraction is evident. A mannan-rich fraction from slash pine gave similar crystals. Repeated recrystallization did not alter the facility or habit of crystallization. The crystals assayed only 50% mannan and had a light tan color.

This work will be published in full at a later date.

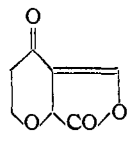
THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN ALBERT P. YUNDT

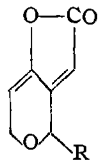
RECEIVED JANUARY 15, 1949

THE STRUCTURE OF PATULIN

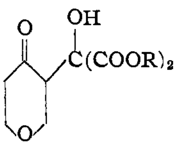
Sir:

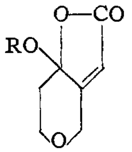
We are reporting elsewhere in detail the considerations which led us to reject the accepted structure[1] (I, *and/or* tautomers) for the well-known mold metabolite and antibiotic, patulin, in favor of a new expression (II, R = OH). Here we record the synthesis of (II, R = H), which we designate as *desoxypatulin*, since its relevant physical properties resemble those of patulin so closely as to provide very strong support for our structural views.


I


II

Condensation of tetrahydro-γ-pyrone with ethyl mesoxalate gave the ketol (III, R = Et), m. p. 58.5–60° (Calcd. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.57. Found: C, 52.73; H, 6.67). When the corresponding acid (III, R = H) was heated with acetic anhydride and acetic acid, among the products obtained were: (i) the *cis*-acid (IV, R = H), m. p. 122–123° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.77; H, 5.18), (ii) the lactol acetate (IV, R = Ac), m. p. 121.5–123° (Calcd. for $C_9H_{10}O_5$: C, 54.55; H, 5.05. Found: C, 54.64; H, 5.02), (iii) the *trans*-acid (V), m. p. 153° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.89; H, 5.25). Treatment of (IV, R = Ac) with warm acetic anhydride–acetic acid–sulfuric acid[2] gave desoxypatulin (II, R = H), m. p. 46–48° (Calcd. for $C_7H_6O_3$: C, 60.80; H, 4.35. Found: C, 60.62; H, 4.37), whose ultraviolet spectrum possessed a single maximum at 273 mμ (log ε, 4.17) (patulin: $\lambda_{max.}$, *276 mμ (log ε, 4.22)*), and whose infrared spectrum in the double bond region reproduced in detail the very characteristic spectrum of patulin in the same region (Fig. 1).


III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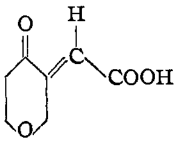
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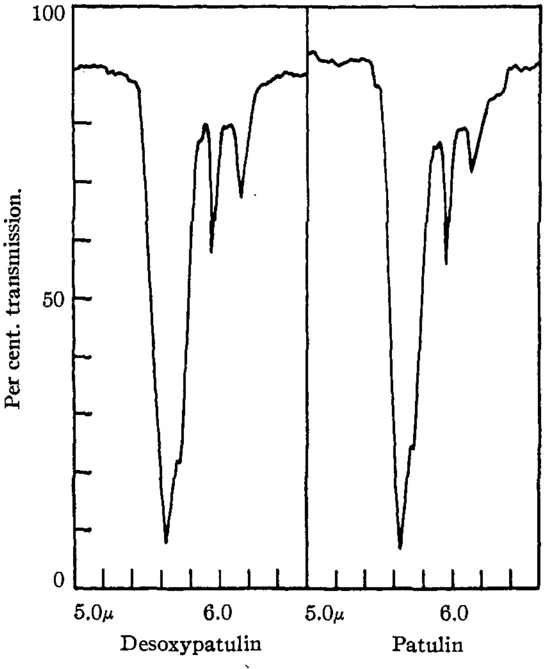
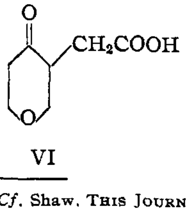
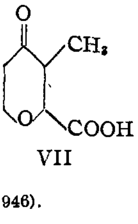


Fig. 1.—Spectra in CH_2Cl_2.

Further support for the structure (II, R = OH) was forthcoming when the oily acid (VI), obtained by the hydrogenation either of the *cis*-acid (IV, R = H) or the *trans*-acid (V), was shown to be identical, through comparison of the methyl ester 2,4-dinitrophenylhydrazones, m. p. 149–150°, with the acid $C_7H_{10}O_4$ originally obtained by Ber-


VI


VII

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[1] For references *cf. Quart. Reviews Chem. Soc.*, **2**, 53 (1948).

[2] *Cf.* Shaw, THIS JOURNAL, **68**, 2510 (1946).

gel, *et al.*,[3] from patulin, and assigned by them the structure (VII).[4]

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(3) Bergel, Morrison, Moss and Rinderknecht, *J. Chem. Soc.*, 415 (1944).

(4) A reduction of our *trans*-acid and the first comparison of (VI) with Bergel's acid was carried out by Professor Pl. A. Plattner and Dr. Engel (Zürich). We thank Professor Plattner warmly for his co-operation, and for samples of derivatives of Bergel's acid which enabled us to carry out the similar correlation with the *cis*-acid (IV, R = H).

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GURBAKHSH SINGH

RECEIVED JANUARY 17, 1949

NEW BOOK

Carotinoide. By PAUL KARRER AND ERNST JUCKER, Chemical Institute of the University of Zurich. (Lehrbücher und Monographien aus dem Gebiete der Exakten Wissenschaften, 17. Chemische Reihe, Band III.) Verlag Birkhäuser, Basel, Switzerland, 1948. 388 pp. 17 × 24.5 cm. Price, 39.-Swiss francs (paper binding); 43.-Swiss francs (linen binding).

With the rapid expansion of chemical research in the past twenty-five years, the organization and correlation of diverse observations in complex fields has become a great problem to all specialists, research workers, teachers and students. Although *Chemical Abstracts* and the numerous review journals provide leads to many isolated facts, there is as yet no satisfactory substitute for the comprehensive monograph written by an authority in the field. For this reason, there are widespread benefits when so productive research workers as Professor Karrer and his collaborator, Dr. Jucker, summarize the studies of the carotenoids, a highly specialized field in which they have made many significant contributions over a long period.

If a technical book is to be more than a handbook, the authors must select their material carefully, omitting the extraneous observations and including and emphasizing the pertinent facts that lead to progress in the field. The choice of material will of necessity reflect the aims, the interest and the experience of the writers. The readers, on the other hand, will examine the book from their particular points of view seeking new information often with a view toward further application in their own fields.

This new monograph on the carotenoids is divided into two parts; a general section of 100 pages and a special section of 231 pages. The general part contains rather brief descriptions of the state or condition of the carotenoids in plants and animals (4 pp.); the origin and physiological significance of the carotenoids in plants and animals (10 pp.); the isolation of the carotenoids (9 pp.); the chemical constitution of the carotenoids, represented by 31 formulas (8 pp.); *cis–trans* isomerization of the carotenoids (5 pp.); methods for determination of the chemical structure (10 pp.); relationship between constitution and color of the carotenoids (7 pp.); and partial syntheses of carotenoids (5 pp.). The last 35 pages of this general section are devoted to tables showing the occurrence of carotenoids in various species of plants and animals classified according to families. For these tables alone, 434 publications are cited. Here is a mass of information not readily available elsewhere.

The second part of this monograph describes the individual carotenoid pigments; particularly, their occurrence, with tables illustrating sources; methods for their preparation; their chemical constitution; their properties such as absorption maxima, solubility, optical activity, adsorbability, etc.; *cis–trans* isomers; and various derivatives of the pigments. Some 28 pigments of known structure and 37 pigments of unknown structure as well as numerous derivatives of these substances are described. Finally, there are 12 colored pictures of carotenoid crystals and 28 figures of spectral absorption curves determined in various solvents. Two indexes provide references to the plants and animals in which the pigments occur and to the usual subject matter.

All this diverse material has been brought together according to a carefully arranged outline, so that the included facts are readily found by readers with different points of view. As a result, this book provides a service to everyone interested in the carotenoid pigments, although at the price quoted ($13.50) it is rather expensive. Unfortunately, there are some omissions of important data; hence, this monograph cannot be relied upon as an impartial source of information.

All chemists, especially those in the food and fodder industries where determinations of the carotenoid pigments have contributed so much to the improvement of our food supply, will be amazed to find few if any references to the careful spectral absorption work carried out in the United States during the past fifteen years. Most of the American results, which have been obtained with different instruments calibrated in different ways and which are in remarkably good agreement, differ significantly from many of those presented in the monograph. As one example, Figure 28 showing lycopene with smaller absorption coefficients than carotenes is contrary to all this uncited experience and to the theories concerning the spectral absorption capacity of unsaturated compounds.

In view of Professor Karrer's contributions, chemists interested in the chromatographic adsorption method will not be surprised that so much emphasis has been placed upon the use of zinc carbonate as an adsorbent. They will be astonished, however, to find that so little attention has been devoted to other adsorbents which have been widely used and which occasionally have made possible separations and identifications not included in this monograph, specifically the separation of neoxanthin and violaxanthin and the confirmation of the identity of violaxanthin from leaves with violaxanthin from pansies. Variation of the adsorption sequence with variation of the solvent and adsorbent is not reported. For the one adsorption sequence of the carotenoids that is summarized in the form of a table, there is no record of the solvent and the adsorbent.

The universal occurrence of carotenoid pigments in the photosynthetic apparatus of green plants and the possible role of these pigments in the utilization of solar energy have stimulated a great deal of biological, physiological and chemical investigation in the past decade, but none of these publications are cited in the present monograph. This work on chloroplast pigments has led to the discovery of many new carotenoids that are not included in this book. Examples are: neoxanthin from leaves, dinoxanthin from dinoflagellates, diadinoxantin from diatoms and dinoflagellates, etc. The fact that fucoxanthin is the principal xanthophyll of diatoms is omitted as is also the universal occurrence of zeaxanthin in green leaves. No mention