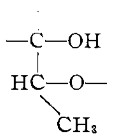
230 mμ, ε 8,000 (*trans*) was consistent with the ethyl β-formylcrotonate structure.[6] The 2,4-dinitrophenylhydrazone melted at 199–200° [Calcd. for $C_{13}H_{14}N_4O_6$: C, 48.45; H, 4.38; N, 17.37; C_2H_5O (1), 13.9. Found: C, 48.38; H, 4.67; N, 17.03; C_2H_5O, 12.4]. Hydrolysis of this ester with 6 *N* hydrochloric acid gave β-formylcrotonic acid[7] (IV), 2,4-dinitrophenylhydrazone, m.p. 251° dec. [Calcd. for $C_{11}H_{10}N_4O_6$: C, 44.90; H, 3.43; N, 19.03. Found: C, 45.06; H, 3.55; N, 18.89]. This 2,4-dinitrophenylhydrazone did not depress the melting point of the same derivative obtained from the periodate oxidation product of base-treated II. The infrared spectra of the two 2,4-dinitrophenylhydrazones were identical.

The periodate oxidation of base-treated II with formation of acetaldehyde in conjunction with previous information indicated the presence of the grouping



The position of the other hydroxyl on C_1 has already been shown. The isolation of acetaldehyde and β-formylcrotonic acid by degradation of II is proof of a six carbon chain in cladinose. The appearance of α,β-unsaturation in II after base treatment indicates the β-position of the methoxyl group (C_3 in cladinose). The position of the second C–CH_3 group in II (C_3 in cladinose) is shown by formation of IV, and this fragment also indicates that base treatment of II eliminates the methoxyl group. These facts are consistent only with structure I for cladinose.

[6] T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 1772 (1950).

[7] This compound has been reported from a natural product, but it was evidently not identical with the one isolated here: see I. J. Rinkes, *Rec. trav. chim.*, **48**, 1093 (1929).

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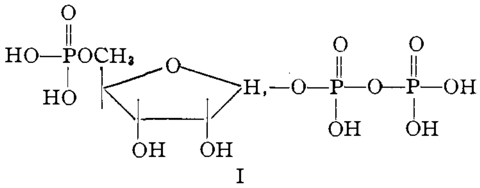
A SYNTHESIS OF β-D-RIBOFURANOSE-1-PHOSPHATE

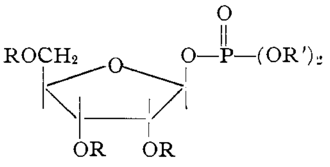
Sir:

Since the isolation by Kalckar[1] of ribose-1-phosphate as a product of the enzymatic "phosphorolysis" of certain nucleosides, two other related ribose derivatives have been discovered. Ribose-1,5-diphosphate[2] has been shown to be the coenzyme in the phosphoribomutase-catalyzed isomerization of ribose-1-phosphate to ribose-5-phosphate and 5-phosphoribose-1-pyrophosphate[3] (I) has been demonstrated to be a precursor in the enzymatic synthesis of nucleoside-5′-phosphates. Although the available evidence would appear to be conclusive as regards the location of the phosphate groups in these substances, the configurations at C_1 of the ribose moiety remain unknown. As part of our work aimed at the chemical synthesis of these compounds, we wish to report a synthesis of D-ribofuranose-1-phosphate. Also, evidence is presented which indicates that the configuration of the phosphate residue at C_1 in the synthetic sample is β, in contrast with the α configuration of a sample of ribose-1-phosphate prepared by the action of the fish muscle riboside phosphorylase[4] on guanosine.

2,3,5-tri-O-benzoyl D-ribofuranosyl-1-bromide, prepared according to Ness, *et al.*,[5] was treated in benzene solution at 5–8° with one equivalent of triethylammonium dibenzyl phosphate. Triethylamine hydrobromide which separated was removed by centrifugation and the sirup, presumably II, obtained after evaporation of benzene, was hydrogenated at 0° in anhydrous methyl alcohol, using freshly prepared 15% palladium–carbon catalyst. The methanolic solution of III was diluted with water and brought to and maintained at *p*H 10.5.



I



II, R = benzoyl, R′ = benzyl
III, R = benzoyl, R′ = H

Debenzoylation was complete after *ca.* 3 hours and ribose-1-phosphate was isolated as the barium salt and purified by the method of Kalckar[1]; yield on a 2-g. scale, 20%. *Anal.* Calcd. for $C_5H_9O_8PBa\cdot 1H_2O$: ribose, 39.1; P, 8.07. Found: ribose,[6] 38.8; P,[7] 7.9. The sample was non-reducing[8] and was free from inorganic phosphate.[9] Paper chromatography in several solvent systems showed the product to be homogeneous and identical with the enzymatically prepared sample of ribose-1-phosphate.[4] Furthermore, the two samples showed identical rates of hydrolysis in 0.1 *M* perchloric acid at room temperature. They were found to be much more labile than the following isomeric phosphates: D-ribopyranose-1-phosphate, synthesized as the crystalline barium salt from 2,3,4-tri-O-acetyl-ribopyranosyl-1-bromide, ribose-2-phosphate,[10] ribose-3-phosphate[10] and ribose-5-phosphate. Enzymatic tests on the natural and the synthetic samples of ribose-1-phosphate were carried out as follows: Each sample (7.35 μM./cc.) was incubated at 37° with the fish muscle riboside phosphorylase in the presence of excess of hypoxanthine. After 3 hours, whereas *ca.* 90% of the natural sample had disappeared, with the concomitant liberation of an

[1] H. M. Kalckar, *J. Biol. Chem.*, **167**, 477 (1947).

[2] H. Klenow, *Arch. Biochem. Biophys.*, **46**, 186 (1953).

[3] A. Kornberg, I. Lieberman and E. S. Simms, This Journal, **76**, 2027 (1954); I. Lieberman, A. Kornberg and E. S. Simms, *ibid.*, **76**, 2844 (1954).

[4] H. L. A. Tarr, *Fed. Proc.*, **14**, 291 (1955).

[5] R. K. Ness, D. W. Diehl and H. G. Fletcher, Jr., This Journal, **76**, 763 (1954).

[6] A. H. Brown, *Arch. Biochem. Biophys.*, **11**, 269 (1946).

[7] R. A. Bonar and E. L. Duggan, *J. Biol. Chem.*, **212**, 697 (1955).

[8] M. Macleod and R. Robinson, *Biochem. J.*, **23**, 517 (1929).

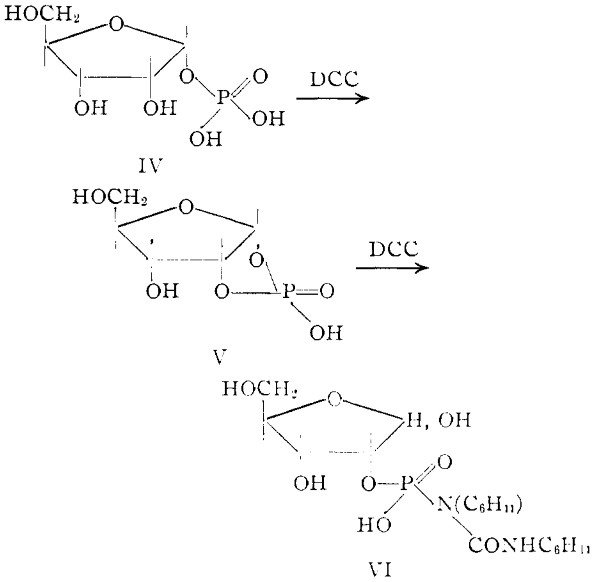
[9] Determined by the method of O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946).

[10] We are grateful to Dr. Waldo E. Cohn of Oak Ridge National Laboratory for gifts of these substances.

equivalent amount of orthophosphate,[9] the synthetic sample remained unchanged. It may therefore be concluded that the two samples have opposite configurations.

It has previously been established[11] that phosphate esters bearing an adjacent *cis*-hydroxyl function react with dicyclohexylcarbodiimide (DCC) in aqueous pyridine to form first the cyclic phosphates (*e.g.*, V), the latter reacting further to give the N-phosphorylureas (*e.g.*, VI). This reaction sequence may be readily followed by paper chromatography in suitable solvent systems,[12] the mobilities of the reaction products following the order VI > V > IV. A study of the reaction time-course of the pyridine salts of the natural and synthetic samples of ribose-1-phosphate showed the formation of V and VI[13] from the natural material only, thus showing that the latter has the α-configuration. Further work to confirm this assignment is in progress.

We wish to thank Dr. H. L. A. Tarr for generous supplies of the enzymatically prepared samples of ribose-1-phosphate and for carrying out the enzymatic tests. This work was carried out under a Consolidated Grant from the National Research Council of Canada, Ottawa.



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[11] C. A. Dekker and H. G. Khorana, THIS JOURNAL, **76**, 3522 (1954); G. M. Tener and H. G. Khorana, *ibid.*, in press.

[12] For example, 7.5 vol. of 95% ethyl alcohol plus 3 vol. of 1 *M* ammonium acetate solution, A. C. Paladini and L. F. Leloir, *Biochem. J.*, **51**, 426 (1952).

[13] This relatively stable phosphate was the major product after a reaction period of 19 hours.

BOOK REVIEWS

Metal Physics and Physical Metallurgy. Volume II. The Theory of Cohesion. An Outline of the Cohesive Properties of Electrons in Atoms, Molecules and Crystals. By M. A. JASWON, M.A., Ph.D., Dept. of Mathematics, Imperial College of Science and Technology, London. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1954. viii + 245 pp. 14.5 × 22 cm. Price, $5.75.

This book is primarily a discussion of the quantum mechanical theory of cohesion in systems for which quantum mechanical effects are of predominant importance. It begins with a presentation of the Schroedinger theory of quantum mechanics and the theories of the hydrogen and helium atoms. The author then proceeds to a detailed study of the hydrogen molecule and the hydrogen molecule ion, and a less detailed discussion of the treatment of more complicated molecules. A long section on the cohesion of metals is followed by a shorter section on covalent structures which ends the book. No discussion is given of the cohesion of ionic solids, possibly because, although this is the one class of solids for which cohesion theory is relatively satisfactory, it is just the one for which quantum mechanical effects are least important.

It is clear from the outline above that Dr. Jaswon's book traverses a very wide area of subject matter. Nevertheless, the book is by no means the ponderous tome which might be suggested by the table of contents. As a consequence he has had to limit himself to thorough treatments of some few subjects and cursory treatments of others. In a general way he has done this deliberately and with a proper balance between the amounts of detailed and cursory considerations.

The material of which this book is constituted gives every appearance of being well thought out, but the book as a whole does not. It is never clear, for instance, to what kind of reader the book is addressed. Thus the entire first third of the book consists of an elementary introduction to quantum mechanics. The reader to whom this material is useful would doubtlessly be too inexperienced in the use of quantum mechanics to benefit very much from the rest of the book.

The discussion of molecular binding is probably the best section of the book for the reader who is well acquainted with the use of quantum mechanics but knows little about its application to molecular systems. In this section there seems to be the happiest blend of qualitative exposition with quantitative discussion of important simple cases. However, the writer substantially ignores the contributions of Lowdin to the subject and, as elsewhere in the book, seems almost completely unaware of a large amount of the American work.

The section on metallic cohesion is poorer. The material is somewhat disorganized, and the whole section apparently suffers from the lack of a point of view. The final section on covalency struck the reviewer as being well written, but out of place, in that it should have preceded the section on metals, since metallic systems are the only ones treated from the loose binding viewpoint.

The reviewer enjoyed several sections of the book. In reading it he was struck by the singular difficulty involved in trying to write an advanced textbook of this sort. It seems in retrospect that it would have been better to somewhat more formally separate the book into two treatises on molecular cohesion and metallic cohesion, respectively. While to the purist there may be no sharp distinction of this kind, the working theorists often make a methodological distinction. In this book the better parts seem to be those which would belong in the first treatise.

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