Two additional repetitions of this methanol purification procedure yielded 8.2 g. of a product melting at 149° (uncor.) and having a rotation $[\alpha]^{20}D$ +107° (*c* 1.6, $CHCl_3$).

α-Lactose-1-phosphate.—To 15 ml. of dry benzene in a flask containing a magnetic stirring bar was added 1.0 g. of bromoacetyllactose. To the clear solution was added 0.52 g. of pure silver diphenyl phosphate[9] and the mixture refluxed with stirring for 30 minutes. After the addition of 0.1 g. of silver diphenyl phosphate the reaction mixture was refluxed again for 30 minutes. After filtration the benzene solution was evaporated. The resultant sticky mass was taken up in 10 ml. of absolute ethyl acetate and the excess silver diphenyl phosphate which crystallized was removed by filtration. The product, diphenylphosphonoheptaacetyllactose, could not be crystallized but was obtained only as a brittle glass.

Anal. Calcd. for $C_{38}H_{45}O_{21}P$ (868): P, 3.57. Found: P, 3.36.

The phenyl groups were removed by catalytic hydrogenation (Adams catalyst) in absolute ethyl acetate at room temperature and 2–6 cm. pressure. The volumes of hydrogen used were those calculated. The product, heptaacetyllactose-1-phosphoric acid, could not be crystallized and was impure.

Anal. Calcd. for $C_{26}H_{37}O_{21}P$ (716): P, 4.33. Found: P, 3.6.

In order to deacetylate, the product was dissolved in the smallest quantity of ethyl acetate permissible, 3 ml. of ice-water added, and titrated to the phenolphthalein end-point with 0.5 *N* sodium hydroxide at 0°. The emulsion was broken by centrifugation and the ethyl acetate removed. A small amount of barium phosphate was removed after the addition of 4 ml. of 10% barium acetate. The aqueous solution was evaporated *in vacuo* to dryness and the residue extracted with 95% ethanol. Addition of a catalytic amount of potassium methylate caused deacetylation and precipitation of barium lactose-1-phosphate. The reaction was allowed to proceed to completion at 0° overnight. The precipitate was centrifuged, drained, and extracted with small portions of 0.01 *N* acetic acid. The aqueous extract was adjusted to *p*H 8.2 with sodium hydroxide and two volumes of 95% ethanol, adjusted to *p*H 8.2, were added. This extraction–precipitation procedure was repeated until a product was obtained which dissolved completely in water. The pure barium salt was washed, by centrifugation, with ethanol and ether and dried *in vacuo* over P_2O_5 for five days. The yield was 0.26 g.

Anal. Calcd. for $C_{12}H_{21}O_{14}PBa\cdot 5H_2O$: C, 22.2; H, 4.78; P, 4.8. Found: C, 22.6; H, 4.5; total P, 4.85.

The compound did not reduce alkaline copper reagents. The phosphate linkage was completely hydrolyzed by normal sulfuric acid at 100° in seven minutes. The rotation of the anhydrous lactose-1-phosphoric acid was calculated to be $[\alpha]^{23}D$ +99.5° (*c* 0.4, H_2O) from measurements on the pentahydrate barium salt. Failure attended all attempts to prepare brucine, strychnine or cyclohexylamine derivatives.

β-Lactose-1-phosphate.—Monosilver phosphate was prepared by adding 0.18 ml. of 90% phosphoric acid to 0.6 g. of freshly prepared, pure, dry trisilver phosphate in a round bottom centrifuge tube containing a stirring magnet. Three milliliters of dry ether was added and the tube and contents were cooled to 0°. Dropwise 3.0 g. of bromoacetyllactose in 8 ml. of dry chloroform was added with efficient stirring and the mixture allowed to react for 30 minutes at 0°. The precipitate was removed. To the supernatant liquid was added 10 ml. of water and normal sodium hydroxide until *p*H 8.0 resulted. After removing the chloroform layer, 2 g. of barium acetate in 10 ml. of water was added and the *p*H adjusted to 9. The precipitate was removed and the aqueous solution evaporated to dryness *in vacuo*. The residue was dissolved in 95% ethanol and deacetylated with catalytic amounts of potassium methylate. The resultant barium salt of the β-isomer of lactose-1-phosphate was then purified and dried as described above for the α isomer. This procedure yielded 0.57 g. of a compound whose specific rotation, calculated for the anhydrous acid form, was $[\alpha]^{23}D$ +31.5° (*c* 0.5, H_2O).

Anal. Calcd. for $C_{12}H_{21}O_{14}PBa\cdot 5H_2O$: C, 22.2; H, 4.78; P, 4.8. Found: C, 22.54; H, 4.5; P, 4.75.

(9) M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 3079 (1949).

The compound did not reduce alkaline copper reagents. The phosphate linkage was completely hydrolyzed by normal sulfuric acid at 100° in seven minutes.

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Concerning Hydrogen Transfer in a Reaction Sensitized by Chlorophyll[1]

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While it is known that chlorophyll is capable of sensitizing a variety of oxidation–reduction reactions in solution,[2] the primary act has not been established unambiguously for any of these reactions. It has been postulated that either the energy of excitation is transferred, in all or in part, to one or both of the reactants, or else that the excited chlorophyll is oxidized or reduced to an unstable intermediate by one of the reactants. If the chlorophyll were first reduced, the intermediate could react rapidly with the oxidizing agent to regenerate the chlorophyll. Conversely, if the primary reaction were one in which the excited chlorophyll gave up a hydrogen atom to the oxidizing agent, the intermediate could be rapidly hydrogenated by the reductant. Only in the latter case, would the sensitized reaction result in a transfer of hydrogen from the reductant to the sensitizer.

The experiments described in this note were performed to determine whether a proton–deuteron exchange between chlorophyll and the reductant accompanied a sensitized oxidation–reduction reaction. The reaction studied was the chlorophyll-sensitized reduction of an azo dye, butter yellow, by deuterated ascorbic acid. When this reaction occurs in methanol, its limiting quantum yield is about one-half and its products are aniline, dimethylphenylenediamine and (presumably) dehydroascorbic acid.[3] To avoid the possibility of exchange between chlorophyll and the solvent, dry dioxane was substituted for methanol in the present experiments. Unfortunately, the yield in dioxane is 20- to 100-fold less than it is in methanol; accordingly, there can be no certainty that the reaction proceeds by the same mechanism in the two solvents.

The reaction mixtures contained approximately $2.0 \times 10^{-4}m$ chlorophyll-a, $2.0 \times 10^{-3}m$ butter yellow and $2.7 \times 10^{-2}m$ deuterated ascorbic acid. The solution, at a temperature of 45°, was illuminated with red light for 5 to 7 hours, until about 75% of the butter yellow was reduced. This corresponded to an average of 4–7 butter yellow molecules reacted per molecule of sensitizer present. The chlorophyll was then separated from the reactants and products by chromatography on a paper pulp column. The deuterium content of the chlorophyll was determined with a mass spectrograph. In no case was the amount of deuterium found more than 4% of that which would be ex-

(1) This work was made possible by the support of the Office of Naval Research (NR 059,028, Contract N6ori-212, T.O. 1) to which the authors are indebted.

(2) E. I. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, New York, N. Y., 1945, pp. 510–512.

(3) R. Pariser, Ph.D. Thesis, University of Minnesota, 1950.

pected, if one hydrogen were fixed for each dye molecule reduced and if the chlorophyll molecule contained one transferrable hydrogen. The small amounts of deuterium found in the chlorophyll samples could easily be accounted for as due to traces of deuterated impurities.

To test whether deuterium gained in the reaction might have been lost during the process of separation, an experiment was performed with deuterated *o*-nitrophenol. Most of its deuterium was lost when the compound was passed through the paper column under conditions similar to those prevailing in the chlorophyll separations. However, subsequent to the completion of these experiments, it was demonstrated[4] that chlorophyll does not exchange with D_2O in either homogeneous or heterogeneous liquid systems. Therefore, if deuterium had been introduced photochemically into the chlorophyll molecule, it would have replaced a non-labile hydrogen and presumably would not have been lost during the separation.

These results indicate that, under the experimental conditions used, the mechanism of the sensitized reaction does not involve a primary removal of a hydrogen atom from the chlorophyll. However, it is not justifiable to conclude that this primary step is excluded from the mechanisms of other chlorophyll-sensitized reactions or of this same reaction occurring in other solvents (*e.g.*, methanol). The slowness of dark exchange between chlorophyll and deuterium oxide suggests that it would be feasible to repeat the present experiments using deuterated methanol as a solvent.

These results are similar to those of Ruben and co-workers[5] and of Calvin and Aronoff,[6] who were unable to demonstrate significant uptake of tracer hydrogen in the chlorophyll of *Chlorella* photosynthesizing in heavy water. It may also be remarked that Krasnovsky and his co-workers[7] have presented evidence for the reversible reduction of chlorophyll by ascorbic acid in pyridine. They have also demonstrated that, in the same solvent, chlorophyll sensitizes the oxidation of ascorbic acid by riboflavin and by certain dyes.

Experimental

Ascorbic acid containing about 40% D/(D + H) was prepared by exchange of normal U.S.P. acid with excess heavy water and was analyzed with a mass spectrometer. Butter yellow was purified by repeated chromatography and recrystallization (m.p. 116.5°). Other reagents and solvents have been described elsewhere.[4]

Since oxygen inhibits the reaction under study, the mixture was boiled vigorously and sealed under a vacuum prior to illumination. The light source was a 1000-watt water-jacketed tungsten lamp, covered by a Corning H.R. 3480 filter.

After illumination, the reaction mixture was transferred to petroleum ether by methods already described[4] and adsorbed at the top of a 2 × 30 cm. chromatography column. (The adsorbent, Whatman Ashless Filter Paper Pulp, had been packed under suction from aqueous suspension, then washed with over 500 ml. each of solvent grade acetone and petroleum ether.) Residual butter yellow, occasional traces of pheophytin and the product amines were completely removed by petroleum ether and benzene, whereupon the chlorophyll was eluted with ether. Only the leading 50-75% of the band was collected; it exhibited the normal absorption spectrum and fluorescence of chlorophyll-a.

Partial infrared spectra of chlorophyll from four of the runs showed no bands due to deuterium or to decomposition products. All samples were burned and analyzed for deuterium by methods previously described.[4]

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Some Substituted 5-Benzalhydantoins and 5-Benzylhydantoins[1]

BY HENRY P. WARD

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A significant feature of the new hydantoins reported in this paper is their physiologically active[2] phenethylamine skeleton structure. They were made as precursors to phenylalanines which yield on decarboxylation phenethylamines related to mescaline.

The benzalhydantoins reported here were made by condensing the following aldehydes with hydantoin: 2,4-dichlorobenzaldehyde, 2-ethoxybenzaldehyde, 3,4-diethoxybenzaldehyde, 4-hydroxy-3-ethoxybenzaldehyde and 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde). The condensations were usually effected in glacial acetic acid and acetic anhydride in the presence of fused sodium acetate after the method first used by Wheeler and Hoffman.[3] It was found more satisfactory to convert the phenolic aldehydes to hydantoins by using diethylamine as the condensing agent in pyridine solution.[4]

The benzylhydantoins were made from the benzalhydantoins by several reduction methods in addition to those cited. The 2,4-dichlorobenzalhydantoin was most readily reduced to the corresponding hydantoin with hydriodic acid in acetic acid. The alkoxy substituted benzalhydantoins were reduced in 1 *N* NaOH solution with Raney nickel and hydrogen.

Table I summarizes data for the hydantoins.

Experimental

The following procedures are representative examples by which the benzalhydantoins, $ArCH{=}C(CO{-}NH)(CO{-}NH)$, and the benzylhydantoins, $ArCH_2{-}CH(CO{-}NH)(CO{-}NH)$, in Table I were prepared.

5-(2,4-Dichlorobenzal)-hydantoin.—A mixture of 10 g. of hydantoin, 15 g. of 2,4-dichlorobenzaldehyde, 9 g. of fused sodium acetate, 58 ml. of glacial acetic acid and 2 ml. of

(1) The author is grateful to the Research Corporation for a grant toward the support of this work.
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