

obtained by assuming *no random orientation* in the solid. The agreement is well within the possible theoretical uncertainties and therefore we do not need, on the basis of the available evidence, to make the assumption that the third law breaks down for this substance.

Further details of the measurements on the heat capacities, on the study of the vibration frequencies, and on the method of calculating thermodynamic properties for molecules containing hindered rotators will be published separately. It should be noted that the vibration frequencies used herein are still provisional so that the value 2120 cal. for the potential barrier is not final; it does, however, correlate all the data now available. It further indicates that 59.93 E. U. is the proper value of the entropy at the boiling point.

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#### A PHOTOCHEMICAL PRODUCTION OF REDUCING SUGARS FROM GLYCOSIDES BY ULTRAVIOLET LIGHT

Sir:

Ultraviolet light absorbed by fructosides and glucosides liberates reducing sugars.

A special arrangement of apparatus soon to be published in *Science* made it possible to illuminate aqueous solutions of these glycosides in thermostated quartz tubes where 11 or 12 cc. absorbed about  $10^{19}$  photons of  $\lambda$  254  $m\mu$  per minute. The light flux was measured with the uranyl oxalate actinometer. Portions of the solutions were

kept in the dark at the same temperature as the illuminated portions and analyses were made on all portions at the same time and under the same conditions. The ml. of 0.002 *M* sodium thio-sulfate entered as hypo in Table I represent the difference between Shaffer-Hartmann-Somogyi (S.-H.-S.) estimations on the dark and illuminated solutions, although the dark reaction was usually negligible. One ml. of hypo was equivalent to  $5.6 \times 10^{-5}$  g. of glucose or  $6.1 \times 10^{-5}$  g. of fructose acid which was reproduced to 0.1 ml. Professor C. B. Purves kindly supplied the glycosides as pure crystals.

Solutions were water white after these photolyses, but the solutions titrated with hypo were sometimes a light amber at the end-point as, for example, in Expts. 3 and 5. Also, strongly photolyzed solutions turned amber after a day or more in the dark at room temperature. The differences in the photochemical efficiencies of the  $\alpha$  and  $\beta$  isomers are significant.

The change in the optical activity accompanying the formation of the reducing sugar was measured for solutions of  $\beta$ -benzylfructopyranoside. Rotations of the D lines of sodium were read to  $0.02^\circ$  in a four-decimeter tube at  $21.5^\circ$ .

In a typical experiment, a molar acetate solution at pH 3.5 contained 1.8016 g. of  $\beta$ -benzylfructopyranoside in 100 cc. The initial rotation of the solution was  $-9.45^\circ$  and the change expected for complete hydrolysis was  $5.1^\circ$  to give a rotation of  $-4.35^\circ$ . Three samples illuminated at  $10^\circ$  with light of  $\lambda$  254  $m\mu$  gave observed rotations of  $-9.00$ ,  $-8.77$  and  $-8.56^\circ$ , corresponding to 9, 14 and 18% hydrolysis; and the estimations of reducing sugar gave 9, 13.5 and 18% respectively. The corresponding percentages agree within the limits of error. The calculations based on the S.-H.-S. estimations assumed the

TABLE I

Typical data on glycosides at 0.02 *M* in water; temperature,  $23^\circ$ ; volume illuminated, 11 cc.; pH of solutions not photolyzed, 6.2; light flux per minute,  $8.6 \times 10^{18}$  photons of  $\lambda$  254  $m\mu$ .

Expt.	Glucopyranosides	pH after photolysis	Minutes photolyzed	Hypo, ml.
1	$\alpha$ -Phenyl	3.5	47	6 $\times$ 11/5 = 13.2
2	$\beta$ -Phenyl	3.5	47	8.8 $\times$ 11/5 = 19.4
3	$\alpha$ -Benzyl	4.2	64	27.6 $\times$ 11/5 = 60.8
4	$\alpha$ -Benzyl	...	30	16.2 $\times$ 11/5 = 35.6
5	$\beta$ -Benzyl	3.7	64	11.2 $\times$ 11/2 = 61.5
6	$\beta$ -Benzyl	...	29	18.2 $\times$ 11/5 = 40.0
7	$\beta$ -( $\beta$ -Phenylethyl)	4.4	82	7.05 $\times$ 11/2 = 38.8
8	$\beta$ -( $\beta$ -Phenylethyl)	...	32	11.8 $\times$ 11/5 = 26.0
Fructopyranoside				
9	$\beta$ -Benzyl	4.5	40	6.4 $\times$ 11/2 = 35.0

measured product to be fructose. In the dark reaction  $\alpha$  changed to  $-9.37^\circ$ . These experiments suggest that the main reaction in the photolysis gives the same products as hydrolysis by acids, where the change in  $\alpha$  also agreed with the S.-H. S. estimation of the amount hydrolyzed.

The photochemical efficiency of the measured reaction was independent not only of the light intensity when (5 to 700) $10^{16}$  photons were absorbed per minute by 11 cc. of solution, but also of the pH—at least between 3.5 and 6.5. Gross quantum yields were independent of the initial concentration of glycoside but decreased as the liberated alcohol or phenol absorbed a larger fraction of the light incident on the solution.

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### THE STRUCTURE OF INSULIN

Sir:

As reported at the Baltimore meeting of the American Chemical Society, I have made an electron density projection of the insulin structure using Crowfoot's  $hk \cdot O$  x-ray data [D. Crowfoot, *Proc. Roy. Soc. (London)*, **A 164**, 580 (1938)] and assuming (incorrectly) that the true projection has a center of symmetry and that the structure proposed by Wrinch and Langmuir [D. M. Wrinch, *THIS JOURNAL*, **60**, 2005 (1938); *Science*, **88**, 148 (1938); *Nature*, **143**, 763 (1939); D. M. Wrinch and I. Langmuir, *THIS JOURNAL*, **60**, 2247 (1938); I. Langmuir and D. Wrinch, *Nature*,

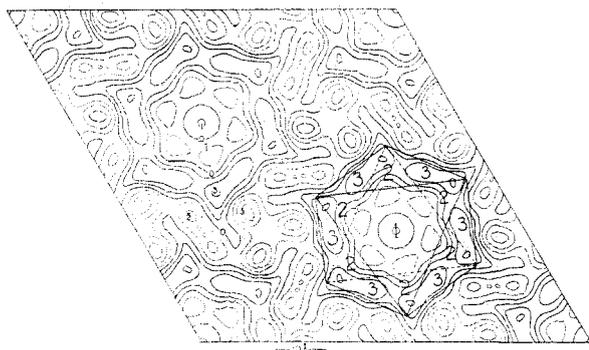


Fig. 1.—Electron density projection on (0001), assuming a center of symmetry and that the structure factor signs are as calculated for simplified  $C_2$  octahedron molecules, oriented as indicated.

**142**, 581 (1938)] is a sufficiently close approximation for the determination of the signs of the structure factors. If the latter assumption is correct, the density at each point of the projection is a sort of average of that at the same point in the true structure and that at another point the same distance on the opposite side of the origin.

This projection is here reproduced (Fig. 1), with a projection of Wrinch's " $C_2$  octahedron," oriented as she has assumed, superimposed. The numbers 1, 2 and 3 designate areas for which one would expect low, medium and high densities, respectively. With a slight change in orientation, the fit is not bad.

It would seem at first that this electron density projection lends support to the hypothesis of a cage or ring molecule or ion of about the size postulated by Wrinch. However, the chief features of the projection depend on the model assumed in deducing the signs of the structure factors. If, for this purpose, one postulates a molecule composed of six point atoms at corners of a regular octahedron, the resultant projection (Fig. 2) shows no indication of a cage structure.

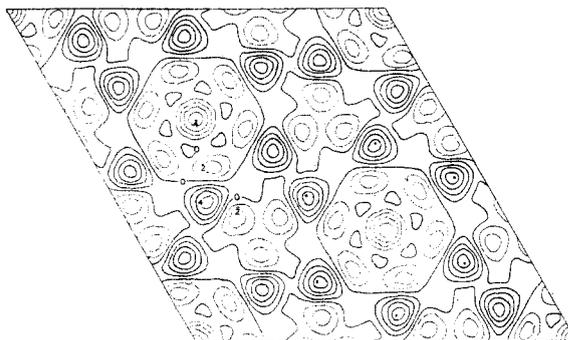


Fig. 2.—Same, except that the structure factor signs are assumed to be as calculated for molecules consisting of six point atoms, distributed as indicated by the dots.

Projections of this sort may prove useful in testing minor features of proposed structures and in suggesting modifications. For example, from Fig. 1 one can deduce that, if the structure contains cage ions even roughly resembling the  $C_2$  cyclol model, the metal ions (Zn) are not at the midpoints of the centerlines joining adjacent cages.

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