Warburg[8] showed that the temperature coefficient had dropped to unity at intensities as high as 6 or 7 × 10^3 ergs/sq. cm./second. (Warburg's data permit only an approximate estimate of the absolute values of the light intensities used in his work.) This is in accord with the results for Hormidium obtained by Van den Honert and for Elodea obtained by Ruttner.[9]

The photosynthetic rate at fourteen meters shown in Fig. 2 was about twice the rate of respiration at the same depth. In the quantum efficiency measurements of Warburg and Negelein,[1] the respiratory rate exceeded the photosynthetic rate, doubtless because their suspensions were so concentrated that a large fraction of the cells received almost no light.

The quantum efficiency value of 0.05 is in fair agreement with the maximum of 0.04 to 0.06 found for measurements with the same species of algae made at low light intensities in the laboratory at the University of Wisconsin.[2]

Summary

Measurements have been made of the rate of photosynthesis in *Chlorella pyrenoidosa* at various depths in a fresh water lake. Using light intensity measurements made at these depths, the approximate quantum efficiency of photosynthesis at various intensities has been calculated. The value approached for low light intensities is approximately 0.05.

MADISON, WISCONSIN RECEIVED NOVEMBER 4, 1937

(8) Warburg, *Biochem. Z.*, **100**, 230 (1919).

(9) Van den Honert, *Rec. trav. bot. neerland.*, **27**, 149 (1930); Ruttner, *Planta*, **2**, 588 (1926).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 163, AND FROM THE INSTITUTO DE FISIOLOGIA, FACULTAD DE MEDICINA, BUENOS AIRES]

The Chemistry of the Tetrose Sugars. III. *l*-Threose and Certain of its Derivatives. *d*-Lyxose Diacetamide and *d*-Arabinose Diacetamide Tetraacetate[1]

BY R. C. HOCKETT, V. DEULOFEU, A. L. SEDOFF AND J. R. MENDIVE

The two previous papers of this series[2] described the preparation of *d*-threose by modifications of the degradation procedures of Ruff[3] and of Wohl,[4] respectively, and announced a specific rotation[5] for this sugar at equilibrium in water or in dilute sulfuric acid of −12.5°. This figure deviated both numerically and in sign from that reported by Freudenberg[6] for a compound thought to be *d*-threose, and from the value to be expected from measurements previously made[7] upon what was considered to be pure *l*-threose. The conclusion drawn in these two papers to the effect that the earlier figures for both *d*- and *l*-threose were erroneous, was confirmed in later work.[8] It was therefore agreed that the study of *l*-threose should be repeated as a joint project. This undertaking was facilitated by two methods for preparing *l*-xylose which were described as plans were being laid.[9] Both methods were employed with success, that of von Vargha being employed in Buenos Aires and that of Appel in Cambridge. An early communication will report further observations upon *l*-xylose and certain of its derivatives.

The results obtained in the two laboratories with degradation of *l*-xylose by the way of *l*-xylose oxime, tetraacetyl-*l*-xylonic nitrile and *l*-threose diacetamide, are in close agreement and are wholly in accord with the predictions of the two previous papers in this series. Hydrolysis of the last named substance with 0.1 *N* sulfuric acid and titration of the sugar released by Cajori's method,[10] along with polarimetric observations, permitted determination of the equilibrium specific rotation of *l*-threose in 0.1 *N* acid as +13.2°.

Iwadare, Fukunaga and Kubota, using precisely the procedure described in the second paper of this series,[2] also have prepared *l*-threose and have determined its specific rotation as +13.1°. Their recent paper[11] anticipates our own an-

(1) A report of this investigation was delivered before the Harvard–Technology Chemical Club in Cambridge, Mass., in January, 1937, and before the Organic Division of the American Chemical Society in Chapel Hill, North Carolina, April, 1937.

(2) Hockett, THIS JOURNAL, **57**, 2260, 2265 (1935).

(3) Ruff, Meusser and Kohn, *Ber.*, **34**, 1362 (1901).

(4) Wohl, *ibid.*, **32**, 3666 (1899); Maquenne, *Compt. rend.*, **130**, 1402 (1900).

(5) All the rotations stated in this paper are specific rotations for the D line of sodium at 20°.

(6) W. Freudenberg, *Ber.*, **65**, 168 (1932).

(7) Deulofeu, *J. Chem. Soc.*, 225, 2458 (1929).

(8) Deulofeu, THIS JOURNAL, **58**, 855 (1936).

(9) Von Vargha, *Ber.*, **68**, 18 (1935); Appel, *J. Chem. Soc.*, 425 (1935).

(10) Cajori, *J. Biol. Chem.*, **54**, 622 (1922).

(11) Iwadare, Fukunaga and Kubota, *Bull. Chem. Soc. Japan*, **12**, 116 (1937).

nouncement of this value. We include, however, the report of several new derivatives of both *d*- and *l*-threose as well as new derivatives of *d*-lyxose and *d*-arabinose.

Since one of us (V. D.), in the earliest effort to prepare *l*-threose,[7] actually isolated an osazone of correct properties for erythrosazone from his hydrolyzates, it appears likely that the sugar was obtained but that the sign of its rotation and that of its diacetamide derivative were incorrectly noted.

For the removal of the elements of prussic acid from acetylated aldonic nitriles, Wohl originally employed ammoniacal silver solutions. In our experience the use of strong aqua ammonia alone (28%) invariably has produced much larger yields of the corresponding diacetamide sugar. This procedure has been extended to the preparation of *d*-lyxose diacetamide and *d*-arabinose diacetamide from the appropriate acetylated hexonic nitriles and has proved equally valuable in those cases. The study of other sugars is in progress.

A sample of *d*-arabinose diacetamide has been subjected to partial hydrolysis and the proportion of free sugar determined by titration.[10] From these data and the observed rotation of the solution, the equilibrium specific rotation of *d*-arabinose has been calculated as −103.8°. The excellent agreement of this figure with the directly determined rotation of −104.5° is considered an important check on the validity of the method we have used with non-crystalline tetroses.

We thank Mr. Robert L. Carlisle for the preparation of pentaacetyl-*d*-gluconic nitrile.

Experimental

Tetraacetyl-*l*-xylonic Nitrile.[12]—The procedure described for preparation of the *d*-isomer[2] was followed precisely. The substance, white plates, yield 48%, shows m. p. 81–82° (corr.) and rotates[5] −50.4° (*C*, 2.5595; $CHCl_3$).

Anal. Calcd. for $C_{13}H_{17}O_8N$: N, 4.44. Found: N, 4.30.

***l*-Threose Diacetamide.**—The procedure was exactly as described in the *d*- series.[2] The substance obtained in 70% yield forms white needles, melting 165–167° (corr.) and rotating[5] +10.2° (*C*, 2.5960; H_2O).

Triacetyl-*l*-threose Diacetamide.—Prepared exactly as described in the case of the *d*-substance,[2] a nearly quantitative yield was obtained of white needles melting 178–179° (corr.) and rotating[5] −74.0° (*C*, 2.5205; $CHCl_3$) and −38.1° (*C*, 2.8725; H_2O).

Anal. Calcd. for $C_{14}H_{22}O_8N_2$: N, 8.09. Found: N, 8.02.

Tribenzoyl-*d*-threose Diacetamide.—One and one-half grams of *d*-threose diacetamide was suspended in 10 cc. of pyridine and 3.0 cc. of benzoyl chloride was added slowly. Slow solution occurred with evolution of heat. After twenty-four hours the mixture was triturated with cold water until the sirup solidified. The substance crystallized from alcohol as white prisms, insoluble in water and petroleum ether but soluble in ethyl acetate, ether and acetone, melting 155–156° (corr.) and showing a specific rotation[5] of +109.7° (*C*, 2.1870; $CHCl_3$).

Anal. Calcd. for $C_{29}H_{23}O_8N_2$: N, 5.26. Found: N, 5.09.

Tribenzoyl-*l*-threose Diacetamide.—Prepared in precisely the same manner as the *d*-isomer, this substance melted at 155–156° (corr.) and rotated[5] −110.1° (*C*, 1.6670; $CHCl_3$).

Anal. Calcd. for $C_{29}H_{23}O_8N_2$: N, 5.26. Found: N, 5.47.

Benzylidene-*d*-threose Diacetamide.—One and a half grams of *d*-threose diacetamide was dissolved in 2 cc. of water and shaken for eight hours with 2 cc. benzaldehyde and 0.3 cc. of concentrated hydrochloric acid. A crystalline product formed. The needles, filtered and washed with water, are very little soluble in alcohol, acetone, benzene, chloroform, or water. Recrystallization was effected from a hot 50:50 mixture of chloroform and alcohol. The substance sinters at 261°, and melts at 265° (corr.). It is dextrorotatory but quantitative measurements are of little value owing to the low solubility of the substance.

Anal. Calcd. for $C_{15}H_{20}O_5N_2$: N, 9.09. Found: N, 8.87.

Benzylidene-*l*-threose Diacetamide.—Prepared in identical manner, the substance melts 265–266° (corr.) with sintering from 260° and is levorotatory.

Anal. Calcd. for $C_{15}H_{20}O_5N_2$: N, 9.09. Found: N, 9.12.

***d*-Lyxose Diacetamide.**—Twenty-five grams of pentaacetyl-*d*-galactonic nitrile was treated with strong aqua ammonia exactly as described in the case of tetraacetyl *d*-xylonic nitrile.[2] *d*-Lyxose diacetamide crystallized during concentration of the solution, yield 72%. Repeated recrystallization from 60% alcohol gave white needles melting at 230–231° (235–236° corr.) and rotating[5] −9.2° (*C*, 3.0540; H_2O).

Tetraacetyl-*d*-arabinose Diacetamide.—Ten grams of pentaacetyl-*d*-gluconic nitrile was treated with 200 cc. of 28% aqua ammonia overnight at room temperature; on concentration the solution yielded *d*-arabinose diacetamide in 65% yield. By warming with a six-fold quantity of 50:50 pyridine and acetic anhydride mixture, acetylation was effected, the products separating directly. Purification from alcohol gave white needles, somewhat soluble in water, very soluble in chloroform, slightly soluble in ether and moderately soluble in alcohol, m. p. 218–219° (222–223° corr.) and rotation[5] +72.5° (*C*, 1.3470; $CHCl_3$).

Anal. Calcd. for $C_{17}H_{26}O_{10}N_2$: N, 6.69. Found: N, 6.55.

Hydrolysis of *d*-Arabinose Diacetamide.—A sample of 0.7441 g. of substance was diluted to 50.0 cc. with 1.000

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(12) *Cf.* Helferich and Peters, *Ber.*, **70**, 465 (1937).

N sulfuric acid. This solution was poured into a 100-cc. flask which had reached the temperature of a water-bath at 100–101°. At the end of fifteen minutes, the cooled solution showed a rotation in a 4-dm. tube of −3.34°. A titration by the method of Cajori[10] showed a concentration of free arabinose equivalent to 0.365 g. in 50.0 cc. of solution indicating 81.7% hydrolysis and 0.1362 g. of unchanged arabinose diacetamide (specific rotation −8.9°). The rotation due to unchanged arabinose diacetamide is (8.9 × 4 × 0.1362)/50 or −0.11°. The 0.365 g. of free arabinose therefore contributes −(3.34−0.11°) or −3.23° to the rotation of the mixture, corresponding to a specific rotation of −103.8° at 29°, a figure agreeing closely with the recorded equilibrium rotation of −104 to −105° for this sugar.

Hydrolysis of *l*-Threose Diacetamide.—A sample of 1.0519 g. of *l*-threose diacetamide was made up to 50 cc. with 0.100 *N* sulfuric acid at 20°. The solution was poured into a flask previously heated to 100° in a boiling water-bath. At intervals samples were taken and cooled to 20°; 5-cc. portions were measured out at that temperature and titrated by Cajori's method.[10,3]

The Equilibrium Rotation of *l*-Threose.—At the end of one hundred forty-four minutes of hydrolysis, the solution rotated +0.33° in a 2-dm. tube. The titration showed 0.453 g. of free tetrose per 50 cc. leaving 0.2216 g. of unchanged threose diacetamide. The rotation contributed by the latter is (10.3 × 2 × 0.2216)/50 or +0.09°, leaving −0.24° as the contribution of the free sugar. The specific rotation of the latter is (−0.24 × 50)/(2 × 0.453) or +13.2°. This is considered to be in satisfactory agreement with the value of −12.5° obtained for *d*-threose.[2]

***l*-Threose Phenylosazone.**—The hydrolyzate when treated with phenylhydrazine reagent,[2] deposited an osazone melting at 162° (corr.).

Summary

1. *l*-Xylose has been prepared by the oxidation of monobenzylidene *d*-sorbitol and diethylidene *d*-sorbitol with lead tetraacetate.

2. *l*-Xylose has been degraded by way of *l*-xylose oxime and tetraacetyl *l*-xylonic nitrile to *l*-threose diacetamide.

3. *l*-Threose diacetamide has been found to show a melting point of 165–167° (corr.) and a specific rotation in water of +10.3°, the latter value agreeing in magnitude with the rotation reported in the second paper of this series for *d*-threose diacetamide.

4. Partial hydrolysis of *l*-threose diacetamide with 0.1 *N* sulfuric acid and analysis of the resulting mixture of free sugar and diacetamide compound, along with polarimetric measurements, have permitted determination of the equilibrium specific rotation of *l*-threose in dilute acid solution as +13.2°. This value is in agreement with that announced for *d*-threose in the second paper of this series.

5. The foregoing method of determining the rotation of a sugar from its diacetamide derivative has been found accurate when applied to *d*-arabinose diacetamide.

6. Certain previously published rotations for *d*- and *l*-threose are considered to be erroneous.

7. Several new derivatives of *d*-threose, *l*-threose, *d*-lyxose and *d*-arabinose are reported.

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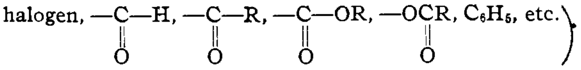
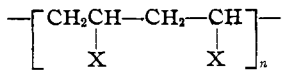
RECEIVED NOVEMBER 8, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Structure of Vinyl Polymers: the Polymer from Methyl Vinyl Ketone

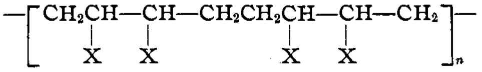
BY C. S. MARVEL AND CHARLES L. LEVESQUE[1]

The structures of the products obtained by the peroxide catalyzed polymerization of various vinyl compounds of the type $CH_2{=}CHX$ (X= halogen,  $-\underset{\underset{O}{\|}}{C}-H,\ -\underset{\underset{O}{\|}}{C}-R,\ -\underset{\underset{O}{\|}}{C}-OR,\ -O\underset{\underset{O}{\|}}{C}R,\ C_6H_5$, etc.) have been considered by many investigators. Obviously there are three ways in which units of the vinyl type may combine to form a long chain molecule. The units may join in a "head to tail" fashion to produce a linear polymer of type I;



$$-\left[CH_2\underset{X}{CH}-CH_2-\underset{X}{CH}\right]_n-$$

I



$$-\left[CH_2\underset{X}{CH}-\underset{X}{CH}-CH_2CH_2\underset{X}{CH}-\underset{X}{CH}-CH_2\right]_n-$$

II

in a "head to head, tail to tail" fashion to give a linear polymer of type II; or in a random fashion to give a linear polymer in which some of the substituents are on adjacent carbons and some are in the 1,3-positions with respect to each other.

In some of the earlier work on this type of polymer Ostromysslenski[2] presented evidence which he felt proved that polyvinyl bromide was identical with the perbromide of polybutadiene

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[1] Cramer Foundation Fellow from Dartmouth College.

[2] Ostromysslenski, *J. Russ. Phys. Chem. Soc.*, **44**, 240 (1912); *Chem. Zent.*, **83**, I, 1982 (1912).