water in exchange with sodium dichromate.

3. The excess density due to air oxygen is 7.65 ± 0.2 γd if Madison city water is regarded as normal in isotopic composition, or 7.1 ± 0.2 γd if Lake Mendota water is normal.

MADISON, WISCONSIN RECEIVED JULY 12, 1940

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XIII. The Heat Capacities and Entropies of Creatine Hydrate, *dl*-Citrulline, *dl*-Ornithine, *l*-Proline and Taurine

BY HUGH M. HUFFMAN AND SIDNEY W. FOX

In continuation of our program[1] involving the study of thermal properties of organic compounds of physiological interest, we have determined the heat capacities of creatine hydrate, *dl*-citrulline, *dl*-ornithine, *l*-proline and taurine in the temperature range 90 to 298°K. These data have been used in conjunction with the extrapolation formula of Parks, Kelley and Huffman[2] to calculate the entropies of these compounds at 25°.

Experimental

In principal the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[3] so that only a brief account need be given. In brief it consists in supplying, electrically, a measured amount of energy to a gold calorimeter containing the substance under investigation. To ensure rapid attainment of thermal equilibrium, the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer by the proper use of accurately calibrated resistances. Time measurements are made by means of a calibrated stop watch. The temperature measurements are made by means of the White potentiometer in conjunction with a single junction copper–constantan thermocouple. This couple is periodically standardized against one of the couples calibrated in the investigation of Giauque, Johnston and Kelley.[4]

Materials.—Creatine hydrate from Eastman Kodak Company was once crystallized from water. Nitrogen determinations by macro-Kjeldahl indicated a purity of 99 to 100%.

dl-Citrulline was prepared by the alkaline hydrolysis of arginine.[5] The material thus obtained was crystallized from a hot aqueous solution by the addition of several volumes of ethyl alcohol. Determination of amino nitrogen by formol titration gave 99% of the theoretical.

dl-Ornithine was synthesized from arginine flavianate as the starting material by a method the details of which will be published in a separate communication. Determination of C, H and N indicated a purity between 96 and 100%. This material is extremely hygroscopic, thus causing considerable uncertainty in the analytical data.

TABLE I

HEAT CAPACITY PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		Creatine Hydrate			
87.3	0.1326	155.5	0.2051	258.8	0.3052
92.0	.1380	172.8	.2222	273.6	.3189
97.2	.1435	190.1	.2402	279.9	.3259
103.1	.1507	210.0	.2600	285.6	.3306
109.7	.1576	226.3	.2749	297.2	.3366
116.5	.1649	242.9	.2909	298.4	.3423
136.3	.1852				
		dl-Citrulline			
89.4	0.1261	157.3	0.1889	264.8	0.2844
95.7	.1324	177.3	.2069	277.5	.2957
101.7	.1383	181.5	.2222	283.9	.3022
110.1	.1463	207.9	.2335	290.5	.3076
125.5	.1608	223.5	.2483	300.8	.3176
140.7	.1740	239.4	.2622		
		dl-Ornithine			
88.6	0.1237	178.6	0.2131	277.1	0.3096
94.6	.1298	193.7	.2276	283.3	.3175
100.0	.1364	209.1	.2423	288.5	.3274
109.5	.1464	223.8	.2563	290.8	.3324
126.0	.1633	237.0	.2681	298.0	.3441
144.1	.1821	263.8	.2951	298.1	.3460
156.3	.1933	277.0	.3087		
		l-Proline			
87.7	0.1223	154.2	0.1811	247.0	0.2630
94.8	.1286	171.8	.1969	257.5	.2724
101.3	.1348	189.1	.2119	276.8	.2892
108.3	.1411	204.0	.2257	283.2	.2947
116.5	.1478	219.2	.2390	291.8	.3027
125.1	.1555	237.3	.2549	300.4	.3096
		Taurine			
87.3	0.1039	159.7	0.1663	249.9	0.2326
92.8	.1089	178.1	.1806	263.7	.2425
97.9	.1138	183.4	.1926	276.3	.2508
112.6	.1274	208.0	.2037	281.8	.2547
123.9	.1373	221.9	.2136	293.0	.2630
140.7	.1516	236.4	.2236	300.3	.2684

(1) Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).
(2) Parks, Kelley and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).
(3) Parks, THIS JOURNAL, **47**, 338 (1925).
(4) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).
(5) Fox, *J. Biol. Chem.*, **125**, 687 (1938).

l-Proline was prepared by the method of Bergmann.[6] Determination of C, H and N indicated a purity of 97 to 100%. This material is also very hygroscopic.

Taurine was prepared by the method of Cortese.[7] Determination of sulfur indicated a purity of 99%. The material was halide free.

The heat capacity data, in terms of the defined conventional calorie, are given in Table I. The purity of the citrulline and ornithine was not very high, nevertheless since these compounds are crystalline over the temperature range covered, we believe that the data are reasonably reliable.

The entropies of these compounds have been calculated by a graphical integration of a plot of C_p against ln T over the experimental range and by the extrapolation method of Parks, Kelley and Huffman[2] from 0 to 90°K. The molal entropies of these compounds are given in Table II.

(6) Bergmann, *J. Biol. Chem.*, **110**, 471 (1935).

(7) Cortese, THIS JOURNAL, **58**, 191 (1936).

TABLE II

ENTROPIES OF THE COMPOUNDS IN CAL. DEGREE^{-1} MOLE^{-1}

Substance	S_{90}	$\Delta S_{90-298.1}$	$S_{298.1}$
Creatine hydrate	16.39	39.62	56.0
dl-Citrulline	18.15	42.65	60.8
dl-Ornithine	13.16	33.08	46.2
l-Proline	13.40	27.38	40.8
Taurine	10.56	26.19	36.8

Summary

1. The experimentally determined heat capacities of creatine hydrate, *dl*-citrulline, *dl*-ornithine, *l*-proline and taurine are given over the range 90 to 298°K.

2. The entropies of the above compounds have been calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Acyclic Derivatives of *d*-Lyxose

BY M. L. WOLFROM AND F. B. MOODY

To our knowledge, the only open-chain or acyclic derivative of *d*-lyxose is the *d*-lyxose diacetamide prepared by Wohl and List.[1] In the course of the past year we had in hand a small amount of this rare sugar and we have applied to it several of the reactions leading to acyclic products. The sugar formed a crystalline diethyl mercaptal which was water-soluble and which was isolated according to the general procedures established[2] previously in this Laboratory for the isolation of water-soluble sugar mercaptals. The crystalline diethyl mercaptals of *d*-xylose,[2] *d*-fructose[3] and *d*-lyxose are water-soluble. All the other known crystalline sugar mercaptals possess a low water solubility. From the diethyl mercaptal of *d*-lyxose its tetraacetate was obtained readily.

Demercaptalation of *d*-lyxose diethyl mercaptal tetraacetate failed to yield a crystalline *aldehydo*-tetraacetate but acetylation of the sirupy reaction product led to the crystallization of its 1,1-diacetate derivative, designated *aldehydo-d*-lyxose hexaacetate. This substance also was obtainable by the acetolysis of the acetylated mercaptal according to the general procedure of Pirie.[4]

We have thus obtained three new crystalline acyclic derivatives of this rare sugar. Several other reactions leading to acyclic products were attempted but this sugar structure, in common with most of the sugars possessing the *cis*-configuration on carbons two and three, showed a decided tendency to produce only sirups when submitted to such procedures.

Experimental

***d*-Lyxose Diethyl Mercaptal.**—A solution of *d*-lyxose (10 g.) in 12 cc. of concentrated hydrochloric acid (d. 1.19) was treated, at 0° and under mechanical stirring, with ethyl mercaptan (12 cc.). After thirty minutes of stirring at 0°, the mixture was diluted with 50 cc. of water and lead carbonate was added until the solution was neutral to congo red. The lead salts were removed by filtration and washed with water. The filtrate was treated with hydrogen sulfide until no further precipitation occurred, aerated and filtered. The filtrate was shaken with an excess of silver carbonate, filtered and again treated with hydrogen sulfide. The colloidal silver sulfide precipitate was removed by adding Super-Cel (Johns Manville) and filtering through a bed of Super-Cel. The resultant solution was concentrated under reduced pressure (40°) until crystallization ensued at a

(1) A. Wohl and E. List, *Ber.*, **30**, 3101 (1897).

(2) M. L. Wolfrom, Mildred R. Newlin and E. E. Stahly, THIS JOURNAL, **53**, 4379 (1931).

(3) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 880 (1934).

(4) N. W. Pirie, *Biochem. J.*, **30**, 374 (1936).