yield, showed m.p. 240–241° after recrystallization from water.

Anal. Calcd. for $C_{12}H_{14}O_3N_2$: C, 61.5; H, 6.02. Found: C, 61.3; H, 6.00.

Since "α"-D-glucosaccharinic acid is believed to have the D-*ribo* configuration,[2] and since the anhydrobenzimidazoles normally possess the hydrofuran ring with unchanged configuration,[18] the product may be assigned the tentative structure shown above. In agreement with this assignment, the derivative was observed to consume 1.0 molecular equivalent of periodate in 30 minutes (1.2 molecular equivalents in 70 hours) with no production of formaldehyde.

The anhydrobenzimidazole derivative was oxidized to benzimidazole-2-carboxylic acid, and the latter was decarboxylated to benzimidazole, as described above for 2-(D-*xylo*-1,3,4,5-tetrahydroxypentyl)-benzimidazole.

Radioassay data for "α"-D-glucosaccharinic lactone and its degradation products are recorded in Table I.

Formic, Acetic and Lactic Acids from the Isomerization Reaction.—A sample (4.1 meq.) of the volatile acids from the preparation of "α"-D-glucosaccharinic lactone was chromatographed on silicic acid, as described above, to yield fractions of pure formic (1.46 meq.) and acetic (0.90 meq.) acids. A sample (5.74 meq.) of the crude lactic acid, obtained by ether extraction during the preparation of "α"-D-glucosaccharinic lactone, was chromatographed similarly to yield a fraction (2.98 meq., peak volume 600 ml.) of pure lactic acid.

The formic and acetic acids were further treated exactly as described above for the formic and acetic acids from the periodate oxidation of "α"-D-glucosaccharinic lactone. The lactic acid was degraded by way of 2-(α-hydroxyethyl)-benzimidazole and benzimidazole-2-carboxylic acid to benzimidazole as described by Roseman.[26] Radioassay data for the various products are given in Table II.

Acetonation of "α"-D-Glucosaccharinic Lactone.—Treatment of 1 g. of the lactone in 50 ml. of dry acetone with 0.5 ml. of sulfuric acid for 3 hours at room temperature, followed by removal of acid (ion-exchange) and concentration, gave the monoacetone derivative[12] in 83% yield. After recrystallization from benzene–petroleum ether, the product showed m.p. 62–63° and $[\alpha]^{25}D$ −38.4° in chloroform, *c* 3.4.

TABLE II

DISTRIBUTION OF RADIOACTIVITY IN THE FORMIC, ACETIC AND LACTIC ACIDS FROM THE ACTION OF LIME WATER ON D-MANNOSE-1-C^{14}

Sample	Carbon atoms	Radioactivity, cts./min./mM × 10^{-3}
Formic acid		
Sodium formate	...	21.9
Benzimidazole	...	23.7
Acetic acid		
Sodium acetate	1,2	46.8
2-Methylbenzimidazole	1,2	48.3
Benzimidazole	1	32.5
Lactic acid		
2-(α-Hydroxyethyl)-benzimidazole	1,2,3	57.0
Benzimidazole-2-carboxylic acid dihydrate	1,2	40.5
Benzimidazole	1	13.5

Titration of the acetonated lactone with sodium hydroxide, followed by oxidation with sodium metaperiodate, resulted in the consumption of 1.0 molecular equivalent of the oxidant (30 minutes or 20 hours). Formaldehyde dimedon (0.6 mol. equiv., m.p. 189–190°) was isolated in the usual manner from the oxidation mixture. Thus, the product may be assigned the structure 2,3-*O*-isopropylidene-2-*C*-methyl-D-*ribo*(?)-pentonic lactone.

Acknowledgment.—The authors are pleased to acknowledge the generous support of the Corn Industries Research Foundation, the Sugar Research Foundation and Anheuser-Busch, Inc., during the course of this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

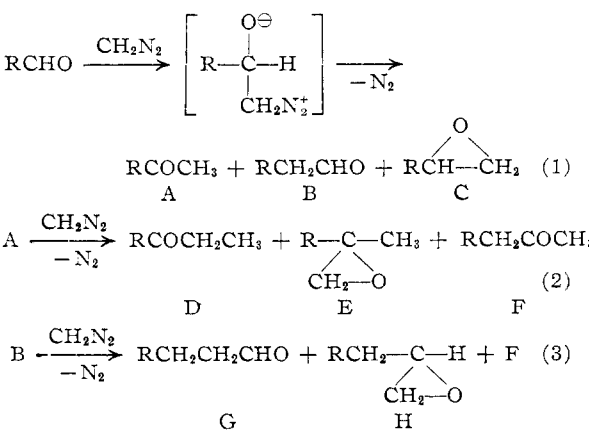
The Action of Diazomethane on the Pentaacetates of *aldehydo*-D-Glucose and *aldehydo*-D-Galactose[1]

BY M. L. WOLFROM, D. I. WEISBLAT, EVAN F. EVANS AND J. B. MILLER[2]

RECEIVED JULY 26, 1957

The action of diazomethane on the pentaacetates of *aldehydo*-D-glucose and *aldehydo*-D-galactose has given the corresponding 1,2-dideoxy-3-*keto*-octulose pentaacetates. These structures have been established by functional group tests and by syntheses from the penta-*O*-acetylaldonyl chlorides and diazoethane. The intermediate 1-deoxy-*keto*-D-heptulose pentaacetate was isolated in the D-glucose structure and its nature was proved by group tests and by synthesis through reduction of the diazomethyl ketone.

The action of diazomethane on aldehydes and ketones is known to yield homologous epoxides or carbonyl compounds.[3,4] If the initial product is itself an aldehyde or ketone, then further reaction may occur as indicated below for the aldehydes. It is well known that electronegative substituents promote epoxide formation in this reaction.[3,4] Thus, the reaction of diazomethane with CH_3-



(1) Paper No. 17 in the series entitled "The Action of Diazomethane upon Acyclic Sugar Derivatives"; previous communication: M. L. Wolfrom, J. B. Miller, D. I. Weisblat and A. R. Hanze, THIS JOURNAL, **79**, 6299 (1957).

(2) Du Pont Postdoctoral Fellow, 1957.

(3) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).

(4) B. Eistert, *Angew. Chem.*, **54**, 99, 124 (1941); translated and revised by F. W. Spangler in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 513–570.

$COCH_3$, $CH_2ClCOCH_3$ and CCl_3COCH_3 gives about 40, 65 and 90% yields of the corresponding epoxides C, respectively.[5] Similarly, diazomethane reacts with CH_3CHO and $CHCl_2CHO$ to give the corresponding epoxides C in 28 and 72% yields, respectively.[6] This promotion of epoxide formation by electronegative groups may differ in degree. Thus, in the examples given above, the electronegative group not only resists migration itself but also largely prohibits the migration of the methyl group, in the case of the acetone derivatives, and the aldehydic hydrogen, in the case of chloroacetaldehyde. We might, however, expect to find weakly electronegative groups which, although they do not themselves migrate, also do not prohibit the migration of the other group. An electronegative group of this type will eliminate B as a product of reaction 1, will therefore eliminate reaction 3, and will eliminate product F of reaction 2. Two such groups flanking a ketonic carbonyl group would ensure an epoxide as the product. The weakly electronegative –CHOAc– group appears to be of this type.

Treatment of cyclohexanone with diazomethane gives only 15% of the epoxide[7] whereas *scyllo*-inosose pentaacetate gives the epoxide in 90% yield.[8] Similarly, treatment of *keto*-D-fructose pentaacetate and *keto*-L-sorbose pentaacetate gave the epoxides in 88 and 85% yields, respectively.[1] These results indicate the failure of the –CHOAc– group to migrate and the formation in 62% yield of 1-deoxy-*keto*-D(and L)-fructose tetraacetate from *aldehydo*-D(and L)-arabinose tetraacetate on treatment with diazomethane[9,10] is consistent with considering the –CHOAc– group as one with no migratory tendency but no tendency to exclude the migration of the other candidate group. The further results reported herein substantiate this view.

In the present work we find that *aldehydo*-D-galactose and *aldehydo*-D-glucose pentaacetates give the corresponding crystalline 1,2-dideoxy-3-*keto*-octulose pentaacetates (D, eq. 2). These compounds require the methyl ketones (A, eq. 1) as precursors and this compound has, in fact, been obtained from treatment of *aldehydo*-D-glucose pentaacetate with diazomethane. These conclusions were reached in the following manner.

Analysis having indicated the addition of two methylene groups, a choice between the various possibilities D, E, F, G and H was made on the basis of a few simple tests. Ultraviolet absorption in the 2800 Å. region[11] and oxime formation (in the case of the D-galactose derivative) eliminated the epoxides E and H from consideration. Reduction of Fehling solution also eliminates the epoxides as well as F. A negative Schiff aldehyde test eliminates G and leaves D as the most probable structure.

This structural assignment was then confirmed by synthesis as indicated below.

$$RCOCl + 2CH_3CHN_2 \longrightarrow RCOCN_2CH_3 + CH_3CH_2Cl + N_2 \quad (4)$$

$$RCOCN_2CH_3 + 2HI \longrightarrow RCOCH_2CH_3 + I_2 + N_2 \quad (5)$$

We find the action of diazoethane in reaction 4 to be considerably less straightforward than the action of diazomethane, as was the experience of Wilds and Meader.[12] Employing the low temperature technique recommended by these authors, we still failed to obtain the diazo products in crystalline form. The sirupy diazo compounds effervesced on acidification and showed the expected pronounced absorptions in the 4.75 and 6.1 μ regions.[13] Hydriodic acid reduction of these sirupy diazo compounds, which gives high yields in the case of the analogous diazomethyl ketones,[10,14,15] proceeded poorly in the present case and crystalline material could be obtained only after chromatography.

The action of diazomethane on *aldehydo*-D-glucose pentaacetate also has given the methyl ketone, 1-deoxy-*keto*-D-*gluco*-heptulose pentaacetate, in analogy with the results obtained with *aldehydo*-D(and L)-arabinose pentaacetate.[9] Analysis indicated either compound A, B or C. Reduction of Fehling solution eliminated C and a positive iodoform test indicated the methyl ketone A. A compound of this structure was then synthesized unequivocally from the diazomethyl ketone by reduction with hydrogen iodide. The crystalline preparations from the two sources (eq. 6) exhibited identical X-ray powder diffraction patterns. The structure of this reaction product can therefore be considered to be established as 1-deoxy-*keto*-D-*gluco*-heptulose pentaacetate.

$$RCOCHN_2 \xrightarrow[-N_2]{HI} RCOCH_3 \xleftarrow[-N_2]{CH_2N_2} RCHO \quad (6)$$

Experimental

1,2-Dideoxy-3-*keto*-D-*gala*-octulose Pentaacetate. (a) **From *aldehydo*-D-Galactose Pentaacetate.**—A cold solution of 8 g. of *aldehydo*-D-galactose pentaacetate[16] in abs. chloroform was treated with an ethereal solution of diazomethane (about 2.2 moles), prepared by the action of methanolic potassium hydroxide on ethyl N-methyl-N-nitrosocarbamate according to the procedure of von Pechmann.[17] After standing overnight at room temperature, the solution was filtered and the solvent was removed to yield a sirup which crystallized on scratching; yield 7.0 g., m.p. 97–100°. Pure material, in the form of thick diamond-like plates, was obtained after four recrystallizations from six parts of 50% ethanol; yield 5.4 g., m.p. 99–100°, $[\alpha]^{25}D$ –10° (*c* 4, abs. $CHCl_3$), a pronounced absorption maximum at 2800 Å.[11] in U.S.P.[18] chloroform; X-ray powder diffraction data[19]:

(5) Reference 4, p. 528.
(6) Reference 3, p. 404.
(7) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).
(8) T. Posternak, *Helv. Chim. Acta*, **27**, 457 (1944).
(9) M. L. Wolfrom, D. I. Weisblat, W. H. Zophy and S. W. Waisbrot, THIS JOURNAL, **63**, 201 (1941).
(10) M. L. Wolfrom, R. L. Brown (and E. F. Evans), *ibid.*, **65**, 1516 (1943).
(11) W. C. G. Baldwin, M. L. Wolfrom and T. M. Lowry, *J. Chem. Soc.*, 696 (1935); Yvonne Khouvine and G. Arragon, *Bull. soc. chim.*, [5] **5**, 1404 (1938).
(12) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).
(13) M. L. Wolfrom and H. B. Wood, Jr., THIS JOURNAL, **77**, 3096 (1955).
(14) M. L. Wolfrom, S. M. Olin and E. F. Evans, *ibid.*, **66**, 204 (1944).
(15) M. L. Wolfrom, A. Thompson and E. F. Evans, *ibid.*, **67**, 1793 (1945).
(16) M. L. Wolfrom, *ibid.*, **52**, 2464 (1930).
(17) H. von Pechmann, *Ber.*, **27**, 1888 (1894).
(18) United States Pharmacopoeia; contains ethanol.
(19) Measurements by Mr. D. L. Fields of this Laboratory.

8.37[20] vw,[21] 7.86 vw, 7.29vs(1,1), 6.11m, 5.09vs(1,1), 4.60w, 4.32w, 4.03w, 3.93w, 3.79w, 3.60m, 3.48s(3), 3.37w, 3.17vw, 3.08m, 2.97w, 2.70w, 2.65w, 2.58vw, 2.51w. The compound showed no mutarotation in U.S.P. chloroform, gave a negative Schiff aldehyde test, reduced Fehling solution and exhibited the usual solubility properties of a sugar acetate.

Anal. Calcd. for $C_8H_{11}O_6(CH_3CO)_5$: C, 51.67; H, 6.26; CH_3CO, 11.96 ml. of 0.1 *N* NaOH per 100 mg. Found: C, 51.78; H, 6.27; CH_3CO,[22] 12.42 ml.

(b) **From Penta-*O*-acetyl-D-galactonyl Chloride and Diazoethane.**—N-Ethyl-N-nitrosourea was prepared from ethylamine hydrochloride and urea according to the procedure for the preparation of the homologous N-methyl-N-nitrosourea.[23] An ethereal solution of the urea derivative gave diazoethane on treatment[24] with a solution of potassium hydroxide in 2-(2-ethoxyethoxy)-ethanol (8% yield), in 1-propanol (21% yield, contaminated with 1-propanol) and in water (17% yield). In all cases the procedure followed was that recommended for diazomethane,[25] except for the changes noted above, and the ethereal diazoethane solutions were dried with potassium hydroxide followed by sodium.

A solution of 920 mg. of diazoethane in 77 ml. of ether was cooled in an alcohol–carbon dioxide-bath. To this was added, dropwise, a solution of 3.2 g. of penta-*O*-acetyl-D-galactonyl chloride[26] in 40 ml. of ether. The addition was carried out over 15 min. and the solution was allowed to stand an additional 15 min. It was then evaporated under freeze-drying conditions. The resultant bright yellow sirup was dissolved in 20 ml. of benzene and chromatographed in 10-ml. portions on two Magnesol[27]–Celite[28] (5:1 by wt.) columns (4.4 × 21.5 cm.) using 600 ml. of benzene: *t*-butyl alcohol (100:1 by vol.) as developer. Alkaline permanganate streaking[29] revealed a zone located 5–9 cm. from the column top. The sectioned zones from the two columns were combined, eluted with acetone and the eluate was evaporated to yield a bright yellow sirup which effervesced on acidification and which showed absorption at 4.77 and 6.1 μ.[13]

This sirupy 1,2-dideoxy-2-diazo-3-*keto*-D-*gala*-octulose pentaacetate was dissolved in 30 ml. of U.S.P. chloroform and 10 ml. of 47% hydriodic acid was added. The mixture was shaken until nitrogen evolution ceased (about 5 min.). The dark red chloroform solution was washed with water, sodium thiosulfate solution, and again with water. The bright yellow chloroform solution was then dried with sodium sulfate and the solvent removed under reduced pressure to yield a bright yellow sirup. The sirup was dissolved in 20 ml. of benzene, the benzene solution divided in half, and each half chromatographed on Magnesol[27]:Celite[28] (5:1 by wt.) columns (4.4 × 20.5 cm.) using 500 ml. of benzene:*t*-butyl alcohol (100:1 by vol.) as developer. On streaking with alkaline permanganate,[29] three zones were observed at 0–4 cm. (bright yellow), 9–12.5 cm., and 15–16 cm. (discarded) from the column top.

The middle zones from both columns were combined, eluted with acetone, and the eluate evaporated under reduced pressure to yield a light yellow sirup which crystallized on scratching. This material was recrystallized from ether–petroleum ether (b.p. 30–60°); yield 180 mg., m.p. 95–100°. Recrystallization was effected from ether–petroleum ether (b.p. 30–60°), $[\alpha]^{20}D$ −8.4° (*c* 3.02, U.S.P. $CHCl_3$), m.p. 97–99.5° unchanged on admixture with 1,2-dideoxy-3-*keto*-D-*gala*-octulose pentaacetate prepared in part (a), X-ray powder diffraction pattern identical with that reported in part (a) above.

(20) Interplanar spacing, Å., camera diameter 114 mm.

(21) Relative intensity, estimated visually; s, strong; m, medium; w, weak; v, very. First three strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

(22) A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1982 (1926).

(23) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 461.

(24) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

(25) Reference 23, p. 165.

(26) M. L. Wolfrom, R. L. Brown and E. F. Evans, THIS JOURNAL, **65**, 1021 (1943); M. L. Wolfrom, J. M. Berkebile and A. Thompson, *ibid.*, **71**, 2360 (1949).

(27) Westvaco Chemical Division of Food Machinery and Chemical Corp., South Charleston, W. Va.

(28) No. 535, Johns-Manville Co., New York, N. Y.

(29) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-3-*keto*-D-*gala*-octulose Oxime.—To a solution of 2.0 g. of 1,2-dideoxy-3-*keto*-D-*gala*-octulose pentaacetate (prepared from *aldehydo*-D-galactose pentaacetate) in 20 ml. of absolute ethanol was added a solution of 630 mg. of hydroxylamine hydrochloride and 1.2 g. of freshly fused potassium acetate in 20 ml. of 50% ethanol. The mixture was allowed to stand at room temperature for 2 hr. and the solvent was then evaporated in a stream of dry air. The solids obtained were extracted with several portions of warm methanol (total vol., 25 ml.). The methanol solution was concentrated to 15 ml. and 90 ml. of water was added. Upon standing at 15°, the oxime crystallized; yield 1.7 g., m.p. 123–126°. Pure material was obtained by recrystallization from ether–petroleum ether; m.p. 151–152°, $[\alpha]^{27}D$ +23° (*c* 2.6, abs. $CHCl_3$).

Anal. Calcd. for $C_{18}H_{27}O_{11}N$: C, 49.85; H, 6.28. Found: C, 49.83; H, 6.23.

1,2-Dideoxy-3-*keto*-D-*gluco*-octulose Pentaacetate. (a) **From *aldehydo*-D-Glucose Pentaacetate.**—An amount of 8 g. of *aldehydo*-D-glucose pentaacetate[30] was treated with the diazomethane generated by the decomposition of 9–10 ml. of the urethan. Reaction occurred slowly and some crystalline material first separated and then redissolved as the reaction progressed. The solution was allowed to stand overnight at room temperature. A crystalline residue was obtained on solvent removal from the filtered solution; yield 6.5 g., m.p. 87–89°. Pure material was obtained after four recrystallizations from 50% ethanol; yield 4.5 g., m.p. 90–91°, m.p. 79–86° on admixture with 1-deoxy-*keto*-D-*gluco*-heptulose pentaacetate of m.p. 90.5–93.5° (see below), $[\alpha]^{26}D$ +11.5° (*c* 3.7, abs. $CHCl_3$), no mutarotation in U.S.P. chloroform, pronounced absorption maximum at 2830 Å.[11] in U.S.P. chloroform; X-ray powder diffraction data[19–21]: 9.56s(2), 7.33vs(1), 7.98vw, 5.75w, 4.92m(3,3), 4.60w, 4.35m(3,3), 4.10vw, 3.94w, 3.77vw, 3.55w, 3.43vw, 3.30w. The substance reduced Fehling solution, gave a negative Schiff aldehyde test and exhibited the usual solubility properties of a sugar acetate.

Anal. Calcd. for $C_8H_{11}O_6(CH_3CO)_5$: C, 51.68; H, 6.26; CH_3CO, 11.96 ml. 0.1 *N* NaOH per 100 mg. Found: C, 51.86; H, 6.01; CH_3CO,[22] 12.10 ml.

(b) **From Penta-*O*-acetyl-D-gluconic Acid.**—An amount of 5.0 g. of penta-*O*-acetyl-D-gluconic acid was converted to the acid chloride.[31] The product was not crystallized, but 1 g. of the sirupy material was allowed to react with 340 mg. of diazoethane and processed in the same manner as indicated above for the D-galactose analog. A light yellow sirup was obtained which effervesced on acidification and showed the expected absorption at 4.83 and 6.17 μ.[13]

This sirup was dissolved in 15 ml. of chloroform and was then treated with 4 ml. of 47% hydriodic acid. The mixture was processed in the manner indicated above for the D-galactose analog. The bright yellow sirup thus obtained was dissolved in 10 ml. of benzene and chromatographed on a Magnesol[27]–Celite[28] (5:1 by wt.) column (4.4 × 21 cm.) using 500 ml. of benzene:*t*-butyl alcohol (100:1 by vol.) as developer. Alkaline permanganate streaking[29] revealed four zones located at 0–0.7, 2–4, 7.5–9 and 12–15 cm. from the column top. The top zone was bright yellow and was only weakly indicated by alkaline permanganate (discarded). The zone below this and the effluent gave sirups which did not crystallize; yields 160 mg. and 60 mg. (effluent). The bottom zone was eluted with acetone and the eluate evaporated under reduced pressure to yield a light yellow sirup which crystallized on scratching; yield 190 mg., m.p. 99–102° unchanged on admixture with authentic ethyl penta-*O*-acetyl-D-gluconate[31,32] of like melting point.

The middle zone was processed as indicated above for the bottom zone and gave crystalline material; yield 30 mg., m.p. 79.5–82°, X-ray powder diffraction pattern identical with that reported above in part (a) for 1,2-dideoxy-3-*keto*-D-*gluco*-octulose pentaacetate. The product was recrystallized from ethanol; m.p. 83–86° and m.p. 85–88.5° on admixture with the pure material (m.p. 90–91°) described in part (a) above.

1-Deoxy-*keto*-D-*gluco*-heptulose Pentaacetate. (a) **From *aldehydo*-D-Glucose Pentaacetate.**—To a solution of 20 g.

(30) M. L. Wolfrom, *ibid.*, **51**, 2188 (1929); M. L. Wolfrom, M. Konigsberg and D. I. Weisblat, *ibid.*, **61**, 574 (1939).

(31) R. T. Major and E. W. Cook, *ibid.*, **58**, 2477 (1936).

(32) F. Volpert, *Ber.*, **19**, 2622 (1886).

of *aldehydo*-D-glucose pentaacetate[30] in a mixture of 80 ml. of U.S.P. chloroform and 20 ml. of methanol, cooled to 0–5°, was added 460 ml. of an absolute solution of diazomethane (2.5 molar ratio) in ether. The mixture was maintained at room temperature for 40 hr. Decolorizing carbon was then added and the mixture was warmed and filtered. The filtrate was concentrated by a stream of dry air. An ether solution (60 ml.) of the resulting sirup deposited crystalline material in two crops; 14.6 g. (combined), m.p. 84–90°. Upon extensive fractionation from aqueous alcohol and from acetone–ether–petroleum ether, pure material was obtained; yield 4.6 g., m.p. 91–92°, $[\alpha]^{21}D$ +7° (*c* 3.9, U.S.P. $CHCl_3$); X-ray powder diffraction data[19–21]: 10.05m, 8.29vw, 6.86vs (1,1), 6.22w, 5.44m, 4.88vs(1,1), 4.61vw, 4.17vw, 3.90m, 3.71w, 3.57vw, 3.33s(3), 3.07vw, 2.91w.

The pure substance reduced Fehling solution and was readily soluble in chloroform, acetone and hot ethanol, moderately so in ether and hot water and was insoluble in petroleum ether and cold water. It gave a light yellow precipitate with the characteristic odor of iodoform on treatment of an alkaline solution with iodine in potassium iodide. The crude product contained small amounts of a higher melting material which was not further investigated.

Anal. Calcd. for $C_7H_9O_6(CH_3CO)_5$: C, 50.49; H, 5.98; CH_3CO, 53.2. Found: C, 50.34; H, 5.93; CH_3CO, 53.2.

(b) **From 1-Deoxy-1-diazo-*keto*-D-*gluco*-heptulose Pentaacetate.**[33]—To a solution of 1.32 g. of crystalline 1-deoxy-1-diazo-*keto*-D-*gluco*-heptulose pentaacetate[9] in 15 ml. of chloroform was added 4 ml. of 47% hydriodic acid. Gas evolution was immediate and the mixture turned dark red. After about 5 min., when gas evolution had ceased, the chloroform solution was washed with water, sodium thiosulfate solution and again with water. The sirup obtained on solvent removal, under reduced pressure, from the dried chloroform extract, was dissolved in 10 ml. of benzene and chromatographed on a Micro Cel C[34] column (4.4 × 19.5 cm.) using 200 ml. of benzene:*t*-butyl alcohol (100:1 by vol.) as developer. Alkaline permanganate streaking[29] revealed two zones located at 3–5.5 and 9–12.5 cm. from the column top.

The top zone yielded a light yellow sirup which resisted crystallization. The bottom zone was eluted with acetone and evaporation of the eluate gave a bright yellow sirup which crystallized on scratching. This was recrystallized from ether; yield 370 mg. (two crops). Recrystallization was effected from ether and ether–petroleum ether (b.p. 30–60°); m.p. 91–92°, $[\alpha]^{20}D$ +6° (*c* 4.8, abs. $CHCl_3$), X-ray powder diffraction data identical with the product described in (a) above. The crude material was contaminated with a higher melting material which was not further investigated.

(33) Preliminary experiments were carried out in this Laboratory by Drs. S. M. Olin and B. S. Wildi.

(34) A synthetic magnesium silicate produced by Johns-Manville Co., New York, N. Y.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE NORTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION[1]]

Chlorous Acid Oxidation of Periodate Oxidized Cornstarch[2]

BY B. T. HOFREITER, I. A. WOLFF AND C. L. MEHLTRETTER

RECEIVED JULY 1, 1957

Periodate oxystarches prepared from cornstarch and containing from 5 to 100% of dialdehyde units have been quantitatively converted to the corresponding dicarboxyl derivatives by oxidation with chlorous acid. The reactions take place in aqueous acid medium and the products are isolated in good yield by precipitation with alcohol. Following investigation of reaction variables, preferred conditions found for the oxidation were: 1 *M* sodium chlorite, 0.5 *M* acetic acid, mole ratio sodium chlorite/aldehyde of 4, 25° and 3 hours reaction time.

The present study is part of an extensive program for the investigation of periodate oxystarches and their derivatives. Interest in these materials was stimulated by the development at this Laboratory of an economic electrolytic process for their preparation.[3,4] A recent publication[5] has described in some detail the physical and chemical properties of periodate oxystarches having a wide range of dialdehyde contents. Although undegraded oxidation or reduction products of periodate oxystarches have not been prepared *per se*, quantitative reduction is employed analytically,[6] and both oxidation and reduction, followed by hydrolysis, have been used for structural studies and preparation of monomeric materials.[7–9]

The purpose of the present work was the preparation of a series of carboxylated derivatives through selective oxidation of the carbonyl groups in periodate oxidized cornstarches. This objective was accomplished, and the products, referred to as dicarboxyl starches, are polyelectrolytes which have both theoretical and practical interest. For example, comparison of the pasting characteristics of dicarboxyl starches, both as free acid and as the sodium salt with those of the parent dialdehyde starches, will provide information on the influence of the various functional groups either on granule gelatinization or on viscosity characteristics of pastes derived from the respective polymeric materials. Further, the dicarboxyl starches in their general structural relationship to such natural and synthetic hydrophilic colloids as alginates, pectins, vegetable gums and carboxymethylated polysaccharides should possess similar valuable physical properties.

Chlorous acid was chosen as the oxidant because of its known specificity for the oxidation of aldehyde to carboxyl groups in acid medium,[10] a reaction condition particularly desirable because of the known sensitivity of periodate oxystarches to alkali. As established by Jeanes and Isbell[10] for the course of reaction of chlorous acid with

(1) One of the Divisions of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956, Abstracts p. 14-D.

(3) W. Dvonch and C. L. Mehltretter, THIS JOURNAL, **74**, 5522 (1952).

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