gel which formed was broken up and heated on a steam-bath in an air stream to evaporate most of the excess water and acid. It was crushed, washed with water until no longer acid to litmus, and then dried at 70° for three or four days. The product was pure white.

Chromatographic Separations.—Columns were prepared by slowly pouring the gel (40–60 mesh) into a glass tube (20 × 500 mm.) and with rapid tapping of the sides to pack the adsorbent to a depth of 300 mm. or more. After it was wetted with the developing solution, there was added a solution of the *p*-phenylazophenyl polyacetyl-β-glycosides dissolved in a minimum volume of the developing agent. Separation was effected by further addition of the developing agent. The amount and composition of the latter is shown in Table I. The colored zones were removed and extracted with acetone in a Soxhlet extractor. Filtration and evaporation at reduced pressure left sirupy residues which were then weighed and recrystallized from *i*-propyl alcohol. Identity was determined from melting points and specific rotation.

The separation of a D-glucoside, D-xyloside, lactoside mixture offers typical results. After development with 450 ml. of benzene, the lactoside was present in a 25-mm. orange band at the top and was followed by a 35-mm. colorless band, an 80-mm. orange zone containing the glucoside, an 80-mm. colorless band, and finally a 175-mm. light orange band containing the xyloside.

Summary

p-Phenylazophenyl polyacetyl-β-glycosides related to D-xylose, D-glucose, D-galactose, lactose, maltose, and cellobiose have been prepared. From these the corresponding *p*-phenylazophenyl β-D-glycosides and *p*-phenylazophenyl polypropionyl-β-D-glycosides have been made.

Chromatographic separations of *p*-phenylazophenyl polyacetylglycosides have been carried out with mixtures of several carbohydrate types including pairs of reducing monosaccharides and a pair of reducing disaccharides.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 23, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CHAS. PFIZER AND CO., INC.]

5-Desoxy-L-sorbose[1]

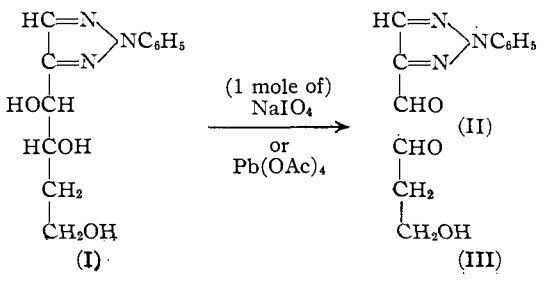
BY PETER P. REGNA

A new crystalline desoxy sugar, 5-desoxy-L-sorbose (IV) (synonym 5-desoxy-D-fructose), was isolated from the mother liquors of the large-scale production of L-sorbose which is obtained from sorbitol by submerged growths of *Acetobacter suboxydans*. The commercial sorbitol used in this particular fermentation was not prepared by the catalytic hydrogenation of D-glucose, but by the electro-reduction of the sugar under mild alkaline conditions. The desoxysorbose undoubtedly arises from the oxidative fermentation of 2-desoxy-D-sorbitol which has been recently demonstrated by Wolfrom, Konigsberg, Moody and Goepp[2] to be present in small amounts in the electro-reduction product.

The desoxy-L-sorbose crystallizes in needles from absolute ethanol, gives a Rosenthaler test similar to a methyl pentose and forms several well-defined derivatives: the tetraacetate and phenylosazone. The desoxysorbose tetraacetate gives a positive Pacsu keto-acetate test indicating the presence of a free ketone group in the molecule. The phenylosazone was converted to phenyl-5-desoxy-L-sorbosotriazole and from this was prepared the tribenzoate derivative.

The desoxysorbose was catalytically hydrogenated under high pressure to a mixture of 2-desoxy-D-sorbitol and 2-desoxy-L-iditol. The solution containing the mixed sugar alcohols was subjected to fermentation with a suspension of cells of *Acetobacter suboxydans* from which the desoxy sugar was isolated as phenyl-5-desoxy-L-sorbosazone. The fermentation of the alcohols produced about 65% of the desoxyketose and shows that the hydrogenation favors, in almost 2:1 ratio, the formation of the D-sorbitol isomer. The preparation of the sugar by oxidative fermentation indicates that the structure of the starting alcohol satisfies Bertrand's rule in that the two hydroxy groups, adjacent to the terminal primary alcohol group, are in *cis*-position; this establishes the position of the hydroxyl on C_3 of 5-desoxy-L-sorbose (IV).

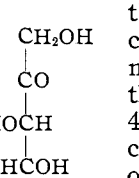
In a preliminary experiment, it was found that with an excess of sodium periodate the methyl desoxysorboside consumed less than 1.5 equivalents of oxygen suggesting that a single glycol grouping existed in the molecule. Further evidence of the structure of the desoxy sugar was obtained when phenyl-5-desoxy-L-sorbosotriazole (I) was oxidized by lead tetraacetate or sodium periodate. With one molecular equivalent of either reagent the osotriazole readily consumes two equivalents of oxygen and splits smoothly into two aldehydes which have been identified as 2-phenyl-4-formylosotriazole (II) and β-hy-



(1) The material in this paper was presented before the Division of Sugar Chemistry and Technology at the Chicago Meeting of the American Chemical Society in September, 1946.

(2) M. L. Wolfrom, M. Konigsberg, F. B. Moody and R. M. Goepp, Jr., THIS JOURNAL, **68**, 122 (1946).

droxypropionaldehyde (III), thus revealing the presence of a single glycol grouping as a portion of the structure of the osotriazole molecule. However, the glycol grouping must be at C_3 and C_4 to account for the quantitative yields of 2-phenyl-4-formylosotriazole and for the hydracrylic aldehyde fragment on periodic oxidation of the osotriazole. These facts establish the structure of the 5-desoxy-2-ketohexose (IV) but give no evidence for the *trans*-arrangement of the glycol grouping.



(IV)

Experimental

5-Desoxy-L-Sorbose.—The crude desoxy sugar obtained from the mother liquors of the crystallization of the sorbose fermentation was dissolved in water, treated with Darco decolorizing charcoal, filtered and evaporated to dryness *in vacuo*. The residue was extracted with several portions of hot methanol and the extract, upon cooling, deposited fine needles of L-sorbose (m. p. 165°; $[\alpha]^{26}D$ −43.0). After several days the sugar was filtered, the filtrate was evaporated to dryness *in vacuo*, and the residue was extracted with hot absolute ethanol. The combined extracts were treated with Darco decolorizing charcoal and after partial evaporation *in vacuo* the desoxy sugar was allowed to crystallize from solution at 5°. After several recrystallizations from absolute ethanol the desoxy sugar formed white needles melting at 110°; $[\alpha]^{23}D$ −67.0° (*c*, 1 in water). In the Rosenthaler[3] test the desoxyketose gives a permanent wine-red color. The sugar is very soluble in water, alcohols, dioxane, pyridine, acetic acid and is practically insoluble in ether, acetone and ethyl acetate.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 43.68; H, 7.20.

Hydrogenation of Sugar to a Mixture of 2-Desoxy-D-Sorbitol and 2-Desoxy-L-Iditol.—A solution of 10.0 g. of 5-desoxy-L-sorbose in 100 ml. of water containing 2 g. of Raney nickel catalyst was agitated in a high pressure autoclave (American Instrument Co.) at room temperature and 1500 lb. pressure. However, in order to obtain nearly complete reduction, it was necessary to carry out the hydrogenation over a period of twelve hours at 150° and a pressure of 2200 lb. After removing the catalyst by filtration, through a bed of "Filter-Cel," a Fehling reduction indicated less than 2% of unreduced sugar.

Fermentation of the Mixed Sugar-Alcohols.—The mixture of 2-desoxysorbitol and 2-desoxyiditol was made the basis of a fermentation medium according to the method of Visser't Hooft.[4] After concentrating the hydrogenation reaction to 200 ml., the solution was sterilized in a Fernbach flask and the medium was inoculated with a suspension of washed cells of *Acetobacter suboxydans*. Fermentation proceeded for five days at 30° when the Fehling reduction reached a maximum: 6.5 g. calculated as 5-desoxysorbose.

The fermentation solution was filtered, and the filtrate was concentrated *in vacuo* to dryness. The dehydrated sirup was extracted with absolute ethyl alcohol, filtered and again evaporated to dryness under diminished pressure. The residue was taken up with water and to the solution was added 23.0 g. of phenylhydrazine hydrochloride and 22.0 g. of sodium acetate trihydrate. The solution was heated for thirty minutes and allowed to crystallize overnight. The precipitate was filtered and triturated in *i*-propyl ether (9.9 g., yield 67%). After recrystallizing the osazone from 60% ethanol (m. p. 153°, $[\alpha]^{23}D$ −34.5° (*c*, 1 in absolute methanol)) a mixed melting point with an authentic specimen of the phenyl-5-desoxysorbosazone described below showed no depression.

5-Desoxy-L-Sorbose Tetraacetate.—Four grams of the pure sugar was dissolved in 30 ml. of anhydrous pyridine, cooled and treated with 50 ml. of acetic anhydride. After standing at room temperature for about thirty hours, the solution was poured onto ice and water (400 ml.). The oil was dissolved in ether and the aqueous solution extracted with ether. The combined ether extracts were washed with cold dilute sulfuric acid, water, saturated sodium bicarbonate solution and water. After drying over sodium sulfate, the ether solution was evaporated to a sirup. After several weeks the 5-desoxysorbose tetraacetate crystallized in prisms; it was separated and washed with a mixture of petroleum ether–*i*-propyl alcohol (3:2). The material was recrystallized from *i*-propyl alcohol and washed with the mixture of petroleum ether–*i*-propyl alcohol; yield 4.5 g., m. p. 123–124°; $[\alpha]^{24}D$ −33.0° (*c*, 1.1 in anhydrous chloroform).

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.59; H, 6.06; CH_3CO, 51.81. Found: C, 50.40; H, 6.38; CH_3CO, 52.50.

The presence of a free ketone group in the molecule of the tetraacetate was obtained by the Pacsu keto-acetate test.[5] To 0.1 g. of the derivative in 15 ml. of pure acetone was added 1 ml. of 0.1 *N* sodium hydroxide. The pale yellow color which developed during two minutes of shaking disappeared on adding two drops of dilute sulfuric acid. Small additions of a 0.05 *N* potassium permanganate solution were gradually absorbed during a five-minute period.

Phenyl-5-desoxy-L-sorbosazone.—Forty-five grams of the pure sugar was dissolved in 600 ml. of water and treated with 160 g. of phenylhydrazine hydrochloride and 150 g. of sodium acetate trihydrate. The mixture was heated on the steam-bath for forty minutes, allowed to stand overnight, filtered and washed with water. The osazone could not be treated with acetone as was suggested by Sattler and Zerban,[6] because of its ready solubility in the solvent. Instead the material was triturated several times in benzene and dried: yield (80%).

The product (95.0 g.) was recrystallized from one liter of 60% ethanol. After another recrystallization and drying in an Abderhalden apparatus at 100° for ten hours, the osazone melted at 153°; $[\alpha]^{23}D$ −34.5° (*c*, 1 in absolute methanol). The very fine needles are soluble in ethyl acetate, acetone, methanol, ethanol, pyridine and dioxane and are practically insoluble in chloroform and ether.

Anal. Calcd. for $C_{18}H_{22}O_3N_4$: C, 63.14; H, 6.48; N, 16.36. Found: C, 62.90; H, 6.67; N (Dumas), 16.19.

Phenyl-5-desoxy-L-sorbosotriazole (I).—The sorbosotriazole was prepared by the method of Haskins, Hann and Hudson.[7] A suspension of 83.0 g. of phenyl-5-desoxysorbosazone in 10 liters of water containing 60 g. of copper sulfate pentahydrate was heated to boiling (oil-bath) under a reflux condenser. At the boiling point there was complete solution of the osazone with an accompanying red color which darkened after five minutes. After boiling thirty minutes, the solution containing a fine red precipitate was treated with Norite and filtered over "Super-Cel." The filtrate was concentrated *in vacuo* to 2500 ml. when the sorbosotriazole crystallized in thin needles. After removing the first crop (40.4 g.) from the cooled solution, a second crop (9.3 g.) was obtained after further evaporation *in vacuo* of the mother liquor (total yield 49.7 g., 83%).

The first crop of the osotriazole (40.4 g.) was recrystallized by dissolving it in 1200 ml. of boiling water, treating with Norite and filtering the solution through a steam-jacketed Büchner funnel over a bed of "Filter-Cel." The phenyl-5-desoxy-L-sorbosotriazole crystallized in long thin colorless needles, m. p. 149°; $[\alpha]^{23}D$ −38.5° (*c*, 1 in absolute methanol). The substance is readily soluble

(3) L. Rosenthaler, *Z. anal. Chem.*, **48**, 165 (1909).

(4) F. Visser't Hooft, Dissertation from Technical High School of Delft, Nov. 3, 1925.

(5) E. Pacsu, THIS JOURNAL, **54**, 3649 (1932).

(6) L. Sattler and F. W. Zerban, *Ind. Eng. Chem.*, **37**, 1133 (1945).

(7) W. T. Haskins, R. M. Hann and C. S. Hudson, THIS JOURNAL, **67**, 939 (1945).

in pyridine, methanol, ethanol, acetone, glacial acetic acid and hot water and is practically insoluble in chloroform, ether, ethyl acetate, cold alcohols and cold water.

Anal. Calcd. for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.85. Found: C, 58.02; H, 6.03; N (Dumas), 16.90.

Phenyl-5-desoxy-L-sorbosotriazole Tribenzoate.—Pure phenyl-5-desoxysorbosotriazole (1 g.) was dissolved in anhydrous pyridine (10 ml.), cooled to 0° and treated with benzoyl chloride at 0° (3 ml.). The mixture was allowed to stand at room temperature for two days, cooled and treated with an excess of petroleum ether. The crystalline material was filtered, washed wth petroleum ether and recrystallized twice from absolute alcohol; the long needles had m. p. 123° and $[\alpha]^{23}D$ −14.0° (*c*, 1 in anhydrous chloroform).

Anal. Calcd. for $C_{33}H_{27}O_6N_3$: C, 70.58; H, 4.85; N, 7.48; C_6H_5CO, 56.20. Found: C, 70.37; H, 4.95; N, 7.85; C_6H_5CO, 56.90.

Sodium Periodate Oxidation of Methyl-5-desoxy-L-sorboside.—A preliminary periodate oxidation was made on the methyl desoxysorboside which was prepared by a modification of a method of Fischer.[8] Ten grams of desoxy sugar was dissolved in freshly distilled anhydrous methanol containing 1% hydrochloric acid. The reaction mixture was allowed to stand seventeen hours at 0°, and then mechanically agitated with an excess of dry silver carbonate. The silver chloride was removed by filtration and a Fehling reduction showed less than 0.5% of unreacted sugar. The alcoholic solution was evaporated to dryness *in vacuo* and the sirup was taken up in dry acetone. The slight amount of insoluble material was filtered and the acetone was evaporated *in vacuo* to constant weight. However, the sirup did not crystallize. A portion of the methyl desoxysorboside (1 g.) was dissolved in water, as quickly as possible, transferred into a solution containing two moles of sodium periodate, and the solution was kept at 20° while rotatory readings were made until a constant value was obtained (−0.07° → +0.32°) after three hours. The oxidation reaction was allowed to stand another fifteen hours when an analysis by the iodine-arsenite procedure[9] showed the reaction had consumed about 1.3 moles of the periodate, thus indicating that the molecule probably contained only a single glycol grouping.

Lead Tetraacetate Oxidation of Phenyl-5-desoxy-L-sorbosotriazole.—Lead tetraacetate was prepared by the method of McClenahan and Hockett,[10] and was recrystallized from glacial acetic acid. In 50 ml. of warm glacial acetic acid was dissolved 3.75 g. (0.015 mole) of phenyl-5-desoxysorbosotriazole. After cooling the mixture to 25°, 6.7 g. (0.015 mole) of lead tetraacetate was added, and the reaction was maintained at 25°. A test portion against starch–potassium iodide paper showed that all the lead tetraacetate had been consumed within three hours. After twenty-four hours the acetic acid solution was poured onto ice, neutralized at 20° with sodium bicarbonate and then extracted four times with peroxide-free ether. The ether layer was distilled under a current of nitrogen, and the dry residue was taken up in 10 ml. of water. The insoluble aldehyde was found to be 2-phenyl-4-formylosotriazole characterized as described elsewhere in this paper (2.1 g., yield 80%).

Sodium Periodate Oxidation of Phenyl-5-desoxy-L-sorbosotriazole.—To a solution containing 11.9 g. of sodium periodate (1.05 molecular equivalents) in 500 ml. of water was suspended 11.9 g. of desoxysorbosotriazole. Although an immediate odor of 2-phenyl-4-formylosotriazole was noted, the mixture was agitated at room temperature (25°) for sixteen hours. The insoluble aldehyde was filtered and found to have the properties described by Hann and Hudson[11]; m. p. 69–70°; yield 8.2 g.

Anal. Calcd. for $C_9H_7ON_3$: C, 62.42; H, 4.08; N, 24.26. Found: C, 62.65; H, 4.21; N, 24.60.

Aliquots of the filtrate showed complete consumption of the periodate by the iodine–arsenite procedure and no presence of acid by titration with standard sodium hydroxide. The remaining filtrate was extracted several times with peroxide-free ether and the combined extracts, after drying over sodium sulfate, were evaporated under reduced pressure in a current of nitrogen. The residue was taken up in about 10 ml. of water and a second crop (0.14 g.) of 2-phenyl-4-formylosotriazole was recovered by filtration (total yield 8.34 g., 95%). The filtrate was transferred to a large volume of 0.4% dimedone (dimethyldihydroresorcinal) in water and the precipitate was coagulated by mechanical shaking. After six hours the dimedone derivative was filtered, washed with water and dried; the substance sintered at 195° and melted at 198°.

The low yield (25%) of the dimedone derivative obtained from the ether-extracted periodate oxidation-liquor was compared with the yield obtained by altering the procedure in another experiment. After the 2-phenyl-4-formylosotriazole was removed by filtration following the completion of the periodate oxidation, an aliquot of the filtrate was added directly to a 0.4% dimedone solution: yield 80%.

The dimedone derivatives of both synthetic β-hydroxypropionaldehyde and that obtained from the periodate oxidation of the osotriazole readily formed the dimedone "anhydride" on boiling in 60% aqueous methanol and recrystallizing from the same solvent mixture. The dimedone "anhydride" obtained from the oxidation crystallized in the form of shining plates and melted at 203–204°.

Anal. Calcd. for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.92; H, 8.34.

A mixed melting point with an authentic specimen of the dimedone "anhydride" showed no depression. The pure β-hydroxypropionaldehyde for the derivative was prepared by a modification of the method of Nef.[12] To 68 ml. of water was added 17 ml. of acrolein and the mixture was mechanically shaken in a high pressure stainless steel autoclave for nine hours at 103°. The autoclave was cooled to room temperature and the solution was concentrated to dryness under diminished pressure under a current of nitrogen. Several additions of water and subsequent evaporations were required until no odor of acrolein could be detected. An aqueous portion of the dissolved residue was added to a 0.4% solution of dimedone and the precipitate converted to the "anhydride" as described above.

Acknowledgment.—The author wishes to express his thanks to Dr. Richard Pasternack for his suggestions, to Mr. Bernard Forscher for his technical assistance and to Dr. John Means for carrying out the microchemical analyses.

Summary

A new crystalline desoxy sugar, 5-desoxy-L-sorbose (synonym 5-desoxy-D-fructose) was isolated from the mother liquors of L-sorbose fermentation. Proof of the structure of the desoxy sugar has been obtained by catalytically hydrogenating the sugar and then subjecting the mixed sugar-alcohols to an *Acetobacter suboxydans* oxidation. To satisfy Bertrand's rule the hydroxyl groups on C_4 and C_5 of 2-desoxy-D-sorbitol must be in *cis*-positions, and this, in turn, establishes the position of a hydroxyl group on C_3 of the 5-desoxy-L-sorbose (IV). Preliminary evidence of a single glycol grouping and the presence of a hydroxyl group on C_4 of the molecule was obtained through the oxidation

(8) E. Fischer, *Ber.*, **28**, 1145 (1895).

(9) E. Muller and O. Freedburger, *Ber.*, **35**, 2655 (1902).

(10) W. S. McClenahan and R. C. Hockett, THIS JOURNAL, **60**, 2061 (1938).

(11) R. M. Hann and C. S. Hudson, THIS JOURNAL, **66**, 735 (1944).

(12) J. U. Nef, *Ann.*, **335**, 191 (1904).

of the methyl desoxysorboside by sodium periodate.

The structure of the 5-desoxy-2-ketohexose was established by oxidizing the phenyl-5-desoxy-L-sorbosotriazole with one mole of either lead tetraacetate or sodium periodate. When the latter reagent was employed, the osotriazole was cleaved smoothly into two fragments which were identified as 2-phenyl-4-formylosotriazole and β-hydroxypropionaldehyde. The former was obtained as the solid crystalline aldehyde and the latter was characterized through the dimedone "anhydride."

BROOKLYN, N. Y. RECEIVED AUGUST 21, 1946

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

The Reductive Acetolysis of Nitrate Esters

BY D. O. HOFFMAN,[1] R. S. BOWER[1] AND M. L. WOLFROM

The denitration of cellulose nitrate with ammonium and the alkali metal hydrosulfides[2,3] has been an established commercial process. Rassow and Dörr[3] were able to denitrate cellulose nitrate with aluminum, activated by mercuric chloride, in various solvents but were unable to separate the cellulosic product from the aluminum compounds formed. These investigators also denitrated cellulose nitrate with Devarda's alloy[4] in strongly alkaline solution, a medium which is known to produce profound chemical alterations in cellulose nitrate. The nitrate ester in several D-glucose derivatives has been reductively hydrolyzed to the parent alcohol by means of iron dust[5] (or zinc and iron dust[6]) and glacial acetic acid. All of these methods pose difficult isolation problems when applied to nitrates of water-soluble carbohydrates because of the large amounts of inorganic salts in the reaction mixtures. Kuhn[7] has reported an excellent method for the catalytic hydrogenolysis of nitrate esters to the parent alcohol, employing a supported palladium catalyst under pressure.

We wish to report herein a method by which a nitrate ester may be simultaneously denitrated and acetylated. A solution of the nitrate ester in acetic anhydride is reduced with zinc dust and a suitable promoter to a solution free of nitrate, as demonstrated by the very sensitive color test with diphenylamine and sulfuric acid. The most satisfactory promoter found was anhydrous hydrogen chloride. Dry pyridine gave a nitrate-free reaction mixture but the yield of acetate was lower.

The crystalline nitrate esters of methyl α-D-glucopyranoside, levoglucosan (1,6-anhydro-D-glucopyranose), erythritol (the *meso*-tetritol) and D-mannitol were converted in good yield to their acetates with the hydrogen chloride promoter (Table I). The same result but with a markedly lower yield, was obtained using pyridine and is illustrated with D-mannitol hexanitrate in the data of Table I.

TABLE I

SIMULTANEOUS DENITRATION AND ACETYLATION OF NITRATE ESTERS OF SUGAR DERIVATIVES AND OF POLYHYDRIC ALCOHOLS

Substance	Promoter for denitration	Yield, % Crude	Yield, % Recrystd.[a]	Acetate derivative Found M. p., °C.	Acetate derivative Found $[\alpha]^{20-25}D$, c 4–6, $CHCl_3$	Acetate derivative Accepted M. p., °C.	Acetate derivative Accepted $[\alpha]D$, $CHCl_3$
Methyl α-D-glucopyranoside tetranitrate	HCl	93	62	100–102	+130°	100–101	+131°
Levoglucosan trinitrate	HCl	83	59	108–109	− 47[b]	110	− 45.5[b]
Erythritol tetranitrate	HCl	81	65	87–88	*meso*	89	*meso*
D-Mannitol hexanitrate	HCl	75	69	120–121	+ 25.5	120	+ 26
D-Mannitol hexanitrate	Pyridine	34	29	118–119	+ 25	120	+ 26

[a] From 95% ethanol. [b] Solvent 95% ethanol. Found in chloroform, $[\alpha]^{25}D$ −59° (c 4).

A sample of high-viscosity cellulose nitrate of 13% nitrogen content was subjected to the

TABLE II

VISCOSITY CHARACTERISTICS OF PRODUCTS FROM THE SIMULTANEOUS DENITRATION AND ACETYLATION OF CELLULOSE NITRATE

Substance	Acetone solution, 25° Time of outflow, sec.[a]	Sp. gr.	c, g./100 ml. soln.
Cellulose nitrate (13% N)	446.5	0.792	0.709
Denitration product, hydrogen chloride promoter	81.0	.797	.788
Denitration product, pyridine promoter	65.3	.797	.709
Acetone	62.3	.788	

[a] Ostwald type viscometer.

(1) Research Associate of The Ohio State University Research Foundation (Project 212).

(2) H. de Chardonnet, German Patent 56,655 (1890).

(3) B. Rassow and E. Dörr, *J. prakt. Chem.*, **216**, 113 (1924).

(4) *Cf.* A. Devarda, *Z. anal. Chem.*, **33**, 113 (1894).

(5) J. W. H. Oldham, *J. Chem. Soc.*, **127**, 2840 (1925).

(6) J. Dewar and G. Fort, *ibid.*, 492, 496 (1944); J. Dewar, G. Fort and N. McArthur, *ibid.*, 499 (1944).

(7) L. P. Kuhn, THIS JOURNAL, **68**, 1761 (1946).