solution was decanted and the residue was washed with dry ether. To the prepared magnesium was added 20 ml. of anhydrous ether, 13.6 g. of ethyl α-bromopropionate, 30 ml. of dry benzene and 16 g. of 2-methoxy-6-propionaphthone. The mixture was refluxed for 3 hours and decomposed with ice and hydrochloric acid. The reaction product was isolated and dehydrated as described above. The mixture of unsaturated esters was separated by chromatographic adsorption. The isomers obtained in 51% yield were identical with the substances described above: (II), m. p. 103–104°, yield 1.90 g.; (II), m. p. 94–96°, yield 8.45 g.; (III), m. p. 78–80°, yield 2.25 g.

Ethyl 2-Methyl-3-(6-methoxy-2-naphthalene)-pentanoate.—The unsaturated esters (1.75 g. each), dissolved in 80 ml. of acetic acid, were hydrogenated with 200 mg. of platinum oxide at room temperature. Under identical conditions (II), m. p. 103–104°, m. p. 94–96°, and (III) required 70, 15 and 360–480 minutes, respectively, to take up the theoretical amount of hydrogen.

The oily products, after removal of solvent and catalyst, were taken up in Skellysolve B and were chromatographed on aluminum oxide. Two bands were visible under ultraviolet light. They were cut apart and extracted with hot methanol. Crystallization from aqueous methanol yielded the racemate melting at 43–45° (IVa) from the lower band and the isomer, m. p. 64–65° (IVb) from the upper band (Table I).

TABLE I

HYDROGENATION RESULTS

Unsaturated ester	Yield (IVa), g.	Yield (IVb), g.	Total yield, %
II, m.p. 103–104°	1.32	0.25	90
II, m.p. 94–96°	0.25	1.40	95
III, m.p. 78–80°	0.75	0.65	80

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 76.00; H, 8.00. Found: (IVa) C, 76.09; H, 8.07; (IVb) C, 76.10; H, 8.03.

2-Methyl-3-(6-methoxy-2-naphthalene)-pentanoic Acid.—The mixture of isomeric esters (IVa and IVb, 12.0 g.) was hydrolyzed by refluxing for 3 hours with 125 ml. of 30% aqueous sodium hydroxide and 300 ml. of propylene glycol. After cooling, 200 ml. of water was added, the mixture was acidified with hydrochloric acid and extracted with ether. The extract yielded 10.8 g. of a glassy product which resisted all attempts at crystallization.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.72; H, 9.80. Found: C, 74.39; H, 9.73.

Several attempts to obtain crystalline acids by hydrolyzing crystalline esters only gave non-crystallizable glassy substances.

3-Methyl-4-(6-hydroxy-2-naphthalene)-2-hexanone.—The glassy acid mixture (IV) (8.0 g.) was converted to the acid chloride with oxalyl chloride according to Wilds.[9] The acid chloride (7.8 g.), dissolved in 50 ml. of dry ether, was added to a solution of dimethylcadmium prepared from 1.0 g. of cadmium chloride and methylmagnesium iodide (from 1.0 g. of methyl iodide). After the reaction subsided, the mixture was warmed on a steam-bath for 1 hour. Dilute sulfuric acid was added to the cooled mixture until the white precipitate dissolved. The mixture was extracted with ether, separated, and the ether layer was washed successively with water, dilute base and water, dried and evaporated. Attempts to crystallize the resulting reddish oil failed. The oil was taken up in Skellysolve B and chromatographed on aluminum oxide. The single main band yielded 3.35 g. of oily product. Further purification by conversion to the oily oxime and hydrolysis only gave an oily ketone, yield 3.0 g.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.81. Found: C, 79.49; H, 7.58.

Catalytic Hydrogenation.—The oily ketone (3 g.) was hydrogenated with Raney nickel (W-2, aged three weeks under absolute alcohol) at 240 atm. and 165° in sodium ethoxide solution containing 0.02 g. of sodium.[6] After removal of catalyst and solvent, the product was taken up in benzene and chromatographed on alumina. One single major band was eluted with the same solvent and yielded 2.7 g. of glassy product which was Folin-negative.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.27; H, 11.08. Found: C, 77.10; H, 10.86.

Absorption Spectra.—The ultraviolet absorption spectra of (II) and (III) were determined in 95% ethanol in concentrations of 6.29, 9.73 and 8.66 mg. per 25 ml.[10]

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[9] Wilds and Shunk, THIS JOURNAL, **70**, 2427 (1948).

[10] Absorption spectra by Dr. E. E. Pickett, University of Missouri, Columbia, Missouri.

CHEMISTRY DEPARTMENT
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A Simple Acetolysis of Nitrate Esters[1]

BY M. L. WOLFROM, R. S. BOWER AND G. G. MAHER

The nitrate esters of carbohydrates may be effectively denitrated by any of several methods involving metallic agents such as alkali metal hydrosulfides,[2] aluminum and mercuric chloride,[3] Devarda's alloy in a highly alkaline medium,[4] and iron dust (or zinc and iron dust) in glacial acetic acid.[5,6] A combined denitration and acetylation can be produced with zinc and anhydrous hydrogen chloride (or dry pyridine) in acetic anhydride.[7] A catalytic regeneration of the original alcohol from a nitrate ester has been effected by high pressure hydrogenolysis[8] and by the employment of hydrazine.[9] All of these methods employ reducing agents.

This report concerns a very simple acetolysis applicable to nitrate esters of small carbohydrate units. It has been developed from the observations of Kuhn[10] that ethyl nitrate in cold sulfuric acid produces considerable amounts of NO_2^+ and from the observations of Wolfrom and Montgomery[11] that in cold absolute sulfuric acid carbohydrate sulfate esters are converted to the acetates in the presence of acetic anhydride. The nitrate ester is dissolved in a small amount of sulfuric acid–acetic anhydride reagent in the cold and after subsequent hydrolysis of excess reagent, the acetate is separated by extraction of the hydrolyzate with some suitable solvent. No reducing environment is needed. Acetate derivatives were obtained in good yield (Table I) from the nitrates of cellobiose, D-glucose, pentaerythritol, erythritol, D-mannitol and levoglucosan (1,6-anhydro-β-D-glucopyranose). These acetolysis conditions are similar to those employed to anomerize β-acetates to the α-forms.[12,13] Thus the isolation of members of the α-D-series is to be expected. Our procedure is somewhat related to that of Clémente and Rivière[14] for producing cellulose acetate from cellulose nitrate. These authors employed acetic acid, acetic anhydride and

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[1] This work was carried out under a contract (W33-019ord-6279; supervising agency, Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland) between the Ordnance Department and The Ohio State University Research Foundation (Project 313).

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

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

[4] 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] D. O. Hoffman, R. S. Bower and M. L. Wolfrom, THIS JOURNAL, **69**, 249 (1947).

[8] L. P. Kuhn, *ibid.*, **68**, 1761 (1946).

[9] L. P. Kuhn, *Abstracts Papers Am. Chem. Soc.*, **117**, 2-0 (1950).

[10] L. P. Kuhn, THIS JOURNAL, **69**, 1974 (1947).

[11] M. L. Wolfrom and R. Montgomery, *ibid.*, **72**, 2859 (1950).

[12] Edna Montgomery and C. S. Hudson, *ibid.*, **56**, 2463 (1934).

[13] K. Freudenberg and K. Soff, *Ber.*, **69**, 1245 (1936).

[14] L. Clémente and C. Rivière, U. S. Patent 1,168,164 (1916).

TABLE I

ACETOLYSIS OF NITRATE ESTERS OF SUGARS AND SUGAR DERIVATIVES

		Acetate derivative			
		Found[a]		Accepted	
Original substance	Yield, %[b]	M.p., °C.	$[\alpha]^{25}D$, $CHCl_3$	M.p., °C.	$[\alpha]D$, $CHCl_3$
Cellobiose octanitrate[c]	83[d]	224–226	+ 41°	229.5	+ 41°
β-D-Glucose pentanitrate[e]	85[f]	112–113	+101	114	+102
Levoglucosan (1,6-anhydro-β-D-glucopyranose) trinitrate	72[f]	104–107	+99.5	114	+102
Erythritol tetranitrate	88	86–88	*meso*	89	*meso*
Pentaerythritol tetranitrate	92	83–84	....	84	...
D-Mannitol hexanitrate	87	120–121.5	+25.5	120	+26

[a] On recrystallized material. [b] Unrecrystallized material of good purity. [c] W. R. Ashford, T. H. Evans and H. Hibbert, *Can. J. Research*, B25, 155 (1947). [d] α-Cellobiose octaacetate was the product. [e] G. Fleury and L. Brissaud, *Compt. rend.*, 222, 1051 (1946). [f] α-D-Glucose pentaacetate was the product.

sulfuric or benzenesulfonic acid and by this means cellulose nitrates of low nitrogen content were successfully acetolyzed.

Experimental

The following procedure for the preparation of D-mannitol hexaacetate from D-mannitol hexanitrate is typical of the acetolysis method in general. One gram of crystalline D-mannitol hexanitrate was dissolved in 25 ml. of a solution of acetic anhydride and 100% sulfuric acid, 10:1 by volume, at 0°. The solution was allowed to stand for 24 hours in an ice–salt-bath. It was then poured into 400 g. of ice and water to hydrolyze the excess acetic anhydride. The hydrolyzate was extracted with five 40-ml. portions of chloroform. The extract, after washing with a saturated water solution of sodium bicarbonate and then with water, was dried over anhydrous calcium chloride. Evaporation of the solvent left a crude residue; yield 0.85 g. The residue was recrystallized from 95% ethanol and its physical constants were determined (Table I).

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Chromatography of Sugars and Their Derivatives; Aldonamides[1]

BY M. L. WOLFROM, R. S. BOWER AND G. G. MAHER

In a previous publication on the chromatography of sugars and their derivatives a general method for separations was described and a table or classification was established in which the following principal groups appeared: (I) sugars, sugar alcohols and glycosides; (II) acetylated sugars; and (III) methylated sugars.[2] To this list there may now be added a fourth group, the aldonamides. These are readily available derivatives of the aldonic acids. Using the same adsorbent as before, Silene EF–Celite in admixture, and dioxane as a developer a number of such amides have been zoned and put into classes. As a continuation of the aforementioned classification this new group appears in Table I. To test the subdivision a single pair, L-fuconamide and D-gluconamide, were separated, with good recovery of each effected. Coleman[3] has developed a related chromatographic separation on silicic acid of aldonamides as their O-*p*-azophenylbenzoates.

TABLE I[a]

CHROMATOGRAPHIC ADSORPTION SERIES OF SOME SUGARS AND DERIVATIVES (ARRANGED IN DECREASING ORDER OF ADSORPTIVE STRENGTH)

Adsorbent, 0.9 x 10 cm.[b] of 5:1 Silene EF[c]–Celite[d]; adsorbate soln., noted with group heading; developer, noted with class heading.

Group IV. Aldonamides (0.5 cc. of 90%[e] dioxane[f] followed immediately by a solution of 2 mg. of substance in 0.2 cc. of 90% dioxane).

Class 1. (10 cc. of 90% dioxane)	D-Gluco-D-*gulo*-heptonamide D-Galactonamide, D-gluconamide
Class 2. (5 cc. of 90% dioxane)	D-Lyxonamide D-Ribonamide L-Fuconamide

[a] Designed as an addition to Table I of ref. 2. [b] Column dimensions are those of the adsorbent. [c] Product of the Columbia Chemical Division, Pittsburgh Plate Glass Co., Barberton, Ohio. [d] Celite 535, a product of Johns–Manville Co., New York, N.Y. [e] Prepared by diluting 90 cc. of absolute dioxane with 10 cc. of water. [f] Purified by the procedure of K. Hess and H. Frohm, *Ber.*, 71B, 2627 (1938), as modified by L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

Experimental

The general techniques of the previously cited work were followed. D-Gluconamide and L-fuconamide, 400 mg. of each in 40 cc. of 90% dioxane, were placed on a column of Silene EF–Celite (5:1 by wt.) prewet with 50 cc. of 90% dioxane. Development was made with 450 cc. of 90% dioxane. The column was extruded and the zones detected by a brush streak[4] with a freshly prepared 1% solution of potassium permanganate in 2.5 *N* sodium hydroxide. Zones were located at 60–92 mm. and 115–150 mm. from the column top. The zones were eluted and their organic substituents purified as described previously.[2] From the upper zone a 74% recovery of D-gluconamide was effected; m.p. 143–144.5°, $[\alpha]^{18}D$ +30.5° (*c* 4, water), accepted values 145° and $[\alpha]^{20}D$ +31°. From the lower zone L-fuconamide was recovered in 66% yield, m.p. 179.5–180.5°, $[\alpha]^{18}D$ −31° (*c* 4, water), accepted values 180.5° and $[\alpha]^{20}D$ −31°.

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(1) This work was carried out under a contract (W33-019ord-3978; supervising agency, Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland) between the Ordnance Department and The Ohio State University Research Foundation (Project 212).

(2) L. W. Georges, R. S. Bower and M. L. Wolfrom, THIS JOURNAL, 68, 2169 (1946).

(3) G. H. Coleman, private communication.

(4) This is best effected by holding the solution in a medicine-dropper whose tip is drawn to a fine capillary and bent nearly at a right angle.