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).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO
RECEIVED OCTOBER 4, 1950

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°.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO
RECEIVED OCTOBER 5, 1950

---

[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.