this hypothesis would be to measure the viscosity of the polyacrylate in a solvent such as methanol, where cross bonds could not form: considered from the point of view of hydrogen bonding, methanol is monofunctional while water is bifunctional.

Sodium polyacrylate is insoluble in methanol. Tetrabutylammonium polyacrylate was therefore prepared by the following procedure:

A 50-g. sample of aqueous acrylic acid was evaporated to dryness as before, taken up in absolute methanol and standardized by titration with potassium hydroxide solution, using phenolphthalein as indicator; normality found, 0.391. Tetrabutylammonium hydroxide in methanol was prepared by shaking fresh silver oxide (washed with methanol) with a methanol solution of tetrabutylammonium bromide. After filtration, a sample of the solution was titrated with standard hydrochloric acid, using methyl orange; normality found, 0.0407. Equivalent volumes of the polyacrylic acid and of the tetrabutylammonium hydroxide solutions were then mixed and diluted to 0.01956 normal.

Viscosities of the quaternary polyacrylate in methanol were measured at several concentrations, with the results shown in Table II. (A lower range of concentrations than that of our previous work was used, in order to avoid possible complications due to mechanical entangling of the polyions.)

TABLE II

VISCOSITIES OF TETRABUTYLAMMONIUM POLYACRYLATE IN METHANOL

C	η_r	η_{sp}/C	c	η_{sp}/c
0.6132	1.839	1.368	0.01956	42.9
.3054	1.532	1.742	.00974	54.6
.1479	1.302	2.042	.00472	64.0

A comparison of these results with the data of Table III for sodium polyacrylate in water over a comparable range of concentration shows that the aqueous solutions have a much higher viscosity. (Both weight and equivalent concentration scales are used because the monomer weights are so different: $CH_2CHCO_2N(C_4H_9)_4 = 313.5$ and $CH_2CHCO_2Na = 94.05$.) For example, at $C = 0.2$ g./100 ml., the aqueous solution has seven times the reduced viscosity of the methanol concentration; at $C = 0.01$ monomole per liter, the aqueous solution has 3.5 times the reduced viscosity of the methanol solution.

TABLE III

VISCOSITIES OF SODIUM POLYACRYLATE IN WATER

C	η_r	η_{sp}/C	c	η_{sp}/c
0.2701	4.26	12.05	0.02873	113
.1397	3.26	16.18	.01486	152
.0708	2.56	22.0	.00753	207

Based on these experimental results, we therefore conclude that the unusually high viscosity of sodium polyacrylate solutions is due to cross-linking through hydrogen bonds with water molecules. This result is probably general; *i. e.*, polymers which contain groups which can bond to hydrogen will give much higher viscosities in water than in other protonic solvents because water is bifunctional.

As concentration is increased, the reduced viscosity concentration curve for the sodium polyacrylate in water goes through a minimum; our previous data give $\eta_{sp}/c = 450$ at $c = 0.0442$ and $\eta_{sp}/c = 800$ at $c = 0.287$. In this range of concentration, the volumes occupied by polyanions are beginning to overlap[3] and we would then expect hydrogen-bond cross-linking to have a tremendous effect on viscosity.

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Sulfonic Acid Esters of Sucrose

BY R. C. HOCKETT[1] AND MORRIS ZIEF

Although *p*-toluenesulfonyl (tosyl) and methanesulfonyl (mesyl) esters are important intermediates for the synthesis of iodo and anhydro sugars, it is surprising that sulfonic acid esters of sucrose have not hitherto been described in the literature. Raymond and Schroeder[2] report treating acetone solutions of trimesyl and tritosylsucrose with sodium iodide, but the starting materials were not isolated or described. In connection with a study of anhydride formation among sugars and polyhydric alcohols, the sucrose derivatives listed in Table I have been prepared by the present authors. Thus far it has not been possible to obtain these products in a crystalline condition. Even though these derivatives are amorphous, however, purification by several precipitations from acetone and water gave fairly pure compounds. These showed compositions, on analysis, that correspond very closely to those predicted for esters in which the degree of substitution is as indicated in the table.

Experimental

Octamesyl and Octatosylsucrose.—Mesyl or tosyl chloride (0.088 mole) was added in small portions to a stirred mixture of 3.42 g. (0.01 mole) of sucrose and 80 cc. of pyridine at 0°. The reaction mixture was stirred for three hours and was then allowed to stand at room temperature for twenty-four hours. The reaction product was poured with stirring into ice-water, the powdery product was filtered off, dried and dissolved in acetone. The acetone solution was decolorized, filtered, and poured with stirring into ice-water. After two more precipitations from acetone and water, colorless, amorphous powders were obtained.

Tritosylsucrose.—Tritosylsucrose, prepared from 0.01 mole of sucrose and exactly 0.03 mole of tosyl chloride under similar conditions, separated as a gum when the reaction mixture was poured into ice-water. A chloroform solution of this gum was washed with dilute sulfuric acid, saturated sodium bicarbonate solution and finally with

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[2] Raymond and Schroeder, U. S. Patent 2,365,776.

TABLE I

Substance	M. p., °C. (uncor.)	Rotation, $[\alpha]_D$ o	Temp., °C.	c	Solvent	Analyses, % Carbon Calcd.	Found	Found	Hydrogen Calcd.	Found	Found	Sulfur Calcd.	Found	Found
Octamesylsucrose	86–94	+43.7	30.0	2.29	Acetone	24.8	24.7	24.7	3.93	3.89	3.95	26.5	26.4	26.2
Octatosylsucrose	82–86	+41.78	25.9	7.623	Chloroform	51.84	51.5	51.3	4.45	4.48	4.49	16.27	16.3	16.1
Tritosylsucrose[a]	66–69	+42.35	27.6	2.42	Chloroform	49.2	48.9	48.7	4.97	4.91	4.86	11.94	12.3	12.5
Pentaacetyltritosylsucrose[a]	58.5–61	+53.3	24.9	3.94	Chloroform	50.86	51.0	50.9	4.93	5.15	5.37	9.46	9.39	9.30

[a] Since the derivatives described here are not crystalline, their degree of homogeneity is not proved nor have their structures been determined by rigid methods. Nevertheless, because of the relatively great reactivity of primary hydroxyl groups in reactions of this type (*cf.* Hockett and Downing, THIS JOURNAL, **64**, 2463 (1942)) a strong presumption may be established to the effect that the *tri*substitution products described here consist almost entirely of the isomers to be expected from selective reaction at the three primary groups. The preparation of partially esterified sucrose derivatives gives rise to the need for a system of numbering the positions in the parent disaccharide. Helferich, Bohn and Winkler, *Ber.*, **63**, 994 (1930), have established a precedent for numbering the positions in a *reducing* disaccharide, cellobiose, by using plain numerals in the reducing moiety and numbers prime in the non-reducing section. In the case of sucrose, which is an unsymmetrical, non-reducing disaccharide, and in analogous cases we propose that plain numerals be used for numbering in the glucose moiety and numbers prime in the non-glucose part. Names for the two tosyl derivatives described above would be: 6,1′,6′-tri-(*p*-toluenesulfonyl)-sucrose and 2,3,4,3′,4′-pentaacetyl-6,1′,6′-tri-(*p*-toluenesulfonyl)-sucrose.

water. After drying over calcium chloride and removal of the chloroform *in vacuo*, a colorless amorphous product was collected. Pentaacetyltritosylsucrose was prepared by acetylating tritosylsucrose in pyridine according to conventional methods.

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Mechanism of the Formation of "Aldose Acetamides" in the Reaction of Acetylated Aldonic Acid Nitriles with Ammonia

BY R. C. HOCKETT, V. DEULOFEU AND J. O. DEFERRARI

When a fully acetylated aldonic acid nitrile is treated with aqueous ammonia, the main product is usually an open-chain "diacetamide derivative" of the aldose sugar having one less carbon atom[1]:

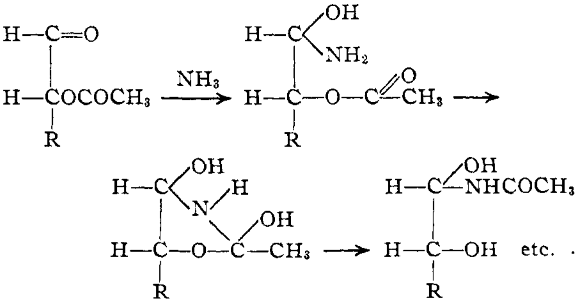
$$CH_2OAc(CHOAc)_4CN + NH_3 \longrightarrow CH_2OH(CHOH)_3CH(NHCOCH_3)_2 + NH_4CN + 3CH_3CONH_2$$

There is little doubt that the initial step of reaction is hydrolysis of the cyanide group as a pseudohalogen since in the presence of silver salts, silver cyanide is precipitated.[1b] The other product of such hydrolysis accompanied by deacetylation, would be expected to appear as the sugar with one less carbon atom in the chain.

The mechanism of the reaction whereby this newly formed aldose becomes combined with acetamide has been the subject of considerable experiment and speculation. Free aldoses do not show any tendency to combine directly with preformed acetamide, though this lack of affinity can be attributed reasonably to the hemiacetal structure of aldoses that have reached a state of equilibrium.

The assumption, moreover, that *aldehydo*aldose derivatives might combine directly with acetamide[2,1c] has not been sustained by later experimental findings. Pentaacetyl-*aldehydo*-D-glucose did not combine directly with acetamide under a variety of conditions, although this glucose derivative is converted by aqueous ammonia to the same glucose acetamide derivative which is the product of reaction of ammonia with the corresponding acetylated D-glucoheptonic acid nitrile.[1c,3]

It has therefore appeared that the observed sugar-acetamide derivatives must arise either as the products of interaction between acetamide and some unidentified sugar derivative that has only transitory existence during the course of the reactions, or through a mechanism that does not involve preformed acetamide at all. Isbell and Frush[4] have proposed a mechanism in line with modern theories of organic chemical reactions. They suggest that an acetylated *aldehydo* sugar may first add ammonia at the aldehyde group and that acetyl may then migrate to nitrogen from an ester group suitably located spacially in the same molecule to produce the acetamide-like structure



To test this hypothesis, we have caused tetraacetyl-L-arabonic acid nitrile to react with ethanolic ammonia in which 6.2 atom per cent. of the nitrogen is N^{15} while an excess of acetamide containing normal nitrogen was present in the alcohol solution. These results were obtained:

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(1) (a) Maquenne, *Compt. rend.*, **130**, 1402 (1900); (b) *cf.* Wohl, *Ber.*, **26**, 730 (1893); (c) Hockett and Chandler, THIS JOURNAL, **66**, 957 (1944).

(2) Brigl, Mühlschlegel and Schinle, *Ber.*, **64**, 2921 (1931); Deulofeu, *J. Chem. Soc.*, 2974 (1932).

(3) The product obtained in this case was actually "glucose monoacetamide" or N-acetyl-D-glucofuranosylamine, but the reaction mechanism involved in its formation is undoubtedly closely analogous to that which forms "aldose diacetamides" in other cases.

(4) Abstracts of papers for the 114th meeting of the American Chemical Society, Sept., 1948.