ethanol was hydrogenated over a 10% palladium-on-charcoal catalyst, 314 ml. (0.0126 mole) of hydrogen being absorbed. The yield of 3-phenylcyclopentanone, b.p. 110–111° (1 mm.), n^{25}D 1.4533 (lit.[32] b.p. 90–95° (0.05 mm.)), was 1.85 g. (91.5%). The 2,4-dinitrophenylhydrazone of the ketone, m.p. 154–154.5° (lit.[32] 154–155°) was obtained in 99% yield. The infrared spectrum of the ketone[19,20] has a band at 1760 cm.$^{-1}$ ($C{=}O$ in a five-membered ring).

3-Phenyl-1,2-cyclopentanedione (XVIIa).—A solution of 1.0 g. (0.00625 mole) of 3-phenylcyclopentanone, 0.69 g. (0.00625 mole) of selenium dioxide and 2 drops of acetic acid in a mixture of 10 ml. of water and 30 ml. of dioxane was boiled under reflux for 3 hours. The selenium which was separated by filtration amounted to 0.42 g. (85%). The filtrate was concentrated and the residue dissolved in a hot benzene–hexane mixture. The crude solid which separated from the cold solution afforded 0.20 g. (18%) of 3-phenyl-1,2-cyclohexanedione, m.p. 189–191°, after recrystallization from benzene. An additional recrystallization sharpened the melting point to 190–191°. The product was shown to be identical with the sample obtained from 2,3-epoxy-3-phenylcyclopentanone both by a mixed melting point determination and by comparison of the infrared and ultraviolet spectra of the two samples.

Rearrangement of 2,3-Epoxy-3-methylcyclopentanone (XVIb).—A solution of 0.5 g. (0.0045 mole) of the epoxy ketone and 0.5 ml. (0.004 mole) of boron trifluoride etherate in 30 ml. of benzene was allowed to stand for 2 minutes and then worked up in the usual manner. The product, the **enol form of 3-methyl-1,2-cyclopentanedione**, crystallized from hexane as white needles, m.p. 99–100° (lit.[33] 100°), yield 0.40 g. (80%). The bis-2,4-dinitrophenylhydrazone of the diketone separated as red plates, m.p. 220–230° dec., yield 99%. Recrystallization from an ethanol–ethyl acetate mixture raised the melting point of the derivative to 237–238° dec. (lit.[33] 238°). The enolic diketone gave a violet color with alcoholic ferric chloride. The infrared spectrum[20,30] of the enolized diketone has bands at 3350 cm.$^{-1}$ (associated O—H), 1695 cm.$^{-1}$ (conjugated $C{=}O$ in a five-membered ring) and 1635 cm.$^{-1}$ (conjugated $C{=}C$); the ultraviolet spectrum has a maximum at 259 mμ (ε 9,000).

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[32] F. Winternitz, M. Mousseron and G. Rouzier, *Bull. soc. chim. France*, 190 (1953).

[33] T. Enkvist, B. Alfredsson, M. Merikallio, P. Pääkkönen and O. Järvelä, *Acta Chem. Scand.*, **8**, 51 (1954); *C. A.*, **48**, 6690 (1954).

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Further Evidence for the Existence of Three Different Free Hydroxyl Groups in Acetone-soluble Cellulose Acetate

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The free hydroxyl groups of an acetone-soluble cellulose acetate were replaced by tosyloxy groups which were in turn replaced by pyrrolidino groups. In the course of the second reaction, the acetyl groups were removed. Hydrolysis of the resulting pyrrolidinopolysaccharide yielded, in addition to D-glucose, three nitrogen-containing hexoses. Determination of the position of the pyrrolidino group in each hexose led to the conclusion that the free hydroxyl groups in acetone-soluble cellulose acetate are distributed among the 2-, 3- and the 6-positions of the anhydroglucose unit.

A considerable amount of effort has been spent on the investigation of the positions occupied by the free hydroxyl groups of acetone-soluble cellulose acetate.[2] Gardner and Purves studied the kinetics of the tosylation of a cellulose acetate containing 0.56 free hydroxyl group per anhydroglucose unit. Interpretation of the rate curve resulted in the assignment of 0.197 free hydroxyl group to the 6-position, 0.139 to the 3-position and 0.223 to the 2-position. Malm, Tanghe and Laird[3] have shown that the distribution of free hydroxyl groups is influenced by the amount of water present in the bath during hydrolysis of the cellulose acetate.

We believed that a substitution of the free hydroxyl groups with an amine, followed by hydrolysis and identification of fragments, would be of considerable value in studying this problem. An acetone-soluble cellulose acetate[4] containing 0.73 free hydroxyl group per anhydroglucose unit was allowed to react with *p*-toluenesulfonyl (tosyl) chloride in pyridine. This tosylated cellulose acetate was then treated with pyrrolidine by refluxing for 30 hr. A quantitative and stoichiometric replacement of tosyl groups by pyrrolidino groups took place. At the same time acetyl groups were completely replaced by hydroxyl groups. It may be assumed that the pyrrolidino groups occupy the positions originally occupied by the free hydroxyl groups of the cellulose acetate. It is to be expected that the replacement of tosyl groups by pyrrolidino groups would result in inversion of the carbon atom. As far as we know there is no previous report in the literature of a quantitative and stoichiometric replacement of tosyl groups by amino groups in cellulose derivatives.[5]

This pyrrolidinopolysaccharide was then hydrolyzed with hydrochloric acid. The resulting mixture of sugars was separated on a column of Dowex-50 using a technique described by Gardell.[6] When the column was developed with 0.3 *N* hydrochloric acid, D-glucose came through immediately (zone 1). This was followed by three well-defined zones (zones 2, 3 and 4). We did not succeed in crystallizing the three amino sugars, but analysis of the

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[1] Abstracted from the 1955 Thesis of S. G. Sunderwirth, du Pont teaching fellow 1954–1955.

[2] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind. Japan*, **37**, Supplementary Binding, 604 (1934); F. B. Cramer and C. B. Purves, THIS JOURNAL, **61**, 3458 (1939); T. S. Gardner and C. B. Purves, *ibid.*, **64**, 1539 (1942); C. J. Malm, L. J. Tanghe and C. B. Laird, *ibid.*, **70**, 2740 (1948).

[3] C. J. Malm, L. J. Tanghe and C. B. Laird, THIS JOURNAL, **72**, 2674 (1950).

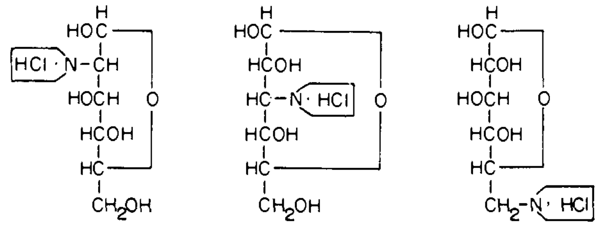
[4] The cellulose acetate used was supplied by Eastman Kodak Co., Rochester, N. Y. Repeated analysis in our laboratory gave consistent results from 37.9–38.00% acetyl, corresponding to 0.73 free hydroxyl group per anhydroglucose unit.

[5] P. Karrer and W. Wehrli, *Helv. Chim. Acta*, **9**, 591 (1926); I. Sakurada, *J. Soc. Chem. Ind., Japan*, **32**, 11 B (1929); K. Hess and N. Ljubitsch, *Ann.*, **507**, 68 (1933); Ssokolowa, *Chem. Zentr.*, **108**, II, 319 (1937); T. S. Gardner, *J. Polymer Sci.*, **1**, 121 (1946); J. F. Haskins, U. S. Patent 2,136,299 (Nov. 8, 1939); A. H. Weinstein, Ph.D. thesis, The Ohio State University, 1950.

[6] Sven Gardell, *Acta Chem. Scand.*, **7**, 207 (1953)

dried sirups gave, in each case, compositions consistent with the predicted formula, $C_{10}H_{19}O_5N \cdot HCl$.

If the free hydroxyl groups in acetone-soluble cellulose acetate are distributed among the 2-, 3- and 6-positions of the anhydroglucose units, the hydrolysis of this pyrrolidinopolysaccharide would result in the formation of the following compounds in addition to D-glucose. (It is assumed that inversion takes place during replacement of tosyloxy groups.)



2-deoxy-2-pyrrolidino-D-mannose hydrochloride (I)
3-deoxy-3-pyrrolidino-D-allose hydrochloride (II)
6-deoxy-6-pyrrolidino-D-glucose hydrochloride (III)

In order to correlate the compounds obtained from the three zones, periodate reactions were run. The compound from zone IV consumed 4 moles of periodate and that from zone III consumed 3 moles. Since it is known that a tertiary amine function alpha to an alcohol function gives an element of stability not easily overcome by periodate,[7] the compounds of zones IV and III would be consistent with formulas III and II, respectively. The compound from zone II consumed one mole of periodate rapidly and then very slowly consumed more. This behavior is consistent with formula I if we assume that the presence of the amine hydrochloride on the second carbon atom stabilizes the hemiacetal to such a degree that the periodate gives rapid cleavage only between the third and forth carbon atoms. This is, in all probability, a valid assumption.

Since these compounds have not been reported in the literature, it seemed advisable to characterize them further. The R_G values using 40–11–19 butanol–ethanol–water on a paper chromatogram were; I, 1.13; II, 0.76; III, 1.21. The equilibrium specific rotations were: I, $[\alpha]^{27}D$ +47.8° (water); II, $[\alpha]^{25}D$ +41.3° (water); III, $[\alpha]^{25}D$ −9.76° (water).

The isolation and identification of the three compounds is considered to be direct evidence that the free hydroxyl groups of acetone-soluble cellulose acetate are distributed among the 2-, 3- and 6-positions of the anhydroglucose units.

We also wish to report in the course of this work the preparation, isolation and identification of three new amino sugars. These are: 2-deoxy-2-pyrrolidino-D-mannose hydrochloride, 3-deoxy-3-pyrrolidino-D-allose hydrochloride and 6-deoxy-6-pyrrolidino-D-glucose hydrochloride.

Experimental

Acetyl Analysis.—The procedure of Genung and Mallatt[8] was followed.

Tosylation of Cellulose Acetate.—The procedure of Cramer and Purves[2] was followed in its essentials; 20 g. of cellulose acetate (37.95% acetyl) yielded 24.1 g. of tosylated cellulose acetate. Analysis showed sulfur 4.82%; acetyl, 28.43%; corresponding to a degree of substitution of 0.496 tosyl group and 2.18 acetyl groups per anhydroglucose unit of the cellulose.

Preparation of the Pyrrolidinopolysaccharide.—A 6-g. sample of tosylated cellulose acetate was dissolved in 60 ml. of pure, dry pyrrolidine, and the solution was refluxed for 30-hr. The reaction mixture was then poured into a cellophane bag and dialyzed for seven days. The dispersion remaining in the bag was dried by ice sublimation. The resulting product weighed 3.1 g. and was a white fibrous material. Analysis showed 3.8% nitrogen, no sulfur and no acetyl. This corresponds to a degree of substitution of 0.514 pyrrolidino group per anhydroglucose unit. Many reactions were carried out with consistent results.

Hydrolysis of the Pyrrolidinopolysaccharide.—Into a 250-ml. round-bottomed flask was placed 3.7 g. of the pyrrolidinopolysaccharide and 200 ml. of 3 *N* hydrochloric acid was added. This dissolved the pyrrolidinopolysaccharide. The solution was refluxed for 10 hr. The resulting dark colored solution was decolorized with charcoal and concentrated to a syrup; yield 3.5 g.

Separation of the Sugars.—One-half gram of the mixture of sugars was dissolved in 10 ml. of 0.3 *N* HCl and the solution placed on a column of Dowex 50[9] (200–400 mesh). The size of the column of resin was 25 × 500 mm. After the solution had passed completely into the column, the latter was developed by 0.3 *N* HCl, using a hydrostatic pressure of 4 feet. Under these conditions the rate of flow through the column was about 120 ml. an hour. Fractions of 50 ml. were taken by means of an automatic fraction collector. Reducing zones were detected by means of a spot test using alkaline potassium permanganate on a spot plate. The first zone was eluted with the first 200 ml. of developer, a second zone came through from 2500 to 2725 ml., a third from 3000 to 3300 ml. and a fourth from 3800 to 4050 ml. No more zones were found. The material in each zone was evaporated to a sirup, dried in a drying pistol and weighed. Typical yields (starting with 0.5 g. of the mixture of dried sirups) were: zone I, mostly D-glucose, 0.0963; zone II, compound I, 0.0142; zone III, compound II, 0.0356; and zone IV, compound III, 0.0120 g. This represented a yield of 31.6% of the material placed on the column. The yields were sometimes higher but never exceeded 36.6%. The relative amounts of material from each zone were always in the same order.

Analysis of Zones.—The material in the first zone was identified by paper chromatography as consisting essentially of D-glucose, although some as yet unidentified substances were also present. Analytical data for the substances present in the other zones are shown below.

	Analyses, %		
	Carbon	Hydrogen	Nitrogen
Zone 2	42.57	7.70	4.77
Zone 3	44.10	7.77	5.25
Zone 4	43.27	7.74	5.23

Calculated for $C_{10}H_{20}O_5NCl$ the composition is C, 44.5%; H, 7.42%; N, 5.18%.

Reactions of the Pyrrolidinosugars with Periodate.—The periodate reactions were run using from 300 to 700 mg. of the dried sirups and 0.1251 *M* sodium metaperiodate, 0.0252 *N* sodium arsenite and 0.252 *N* iodine solution. A slight modification had to be made for zone 2, since the uptake was only one mole of periodate per mole of compound.

The material from zone II consumed one mole of periodate rapidly and then very slowly consumed more. The material, from zone III consumed three moles of periodate rapidly and that from zone IV consumed four moles of periodate rapidly.

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(7) P. Fluery, J. Courtoir and M. Grandchamp, *Bull. Soc. Chim., France*, 88 (1949).

(8) L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, 13, 369 (1941).

(9) Manufactured by the Dow Chemical Company, Midland, Michigan.