[CONTRIBUTION FROM THE BANTING AND BEST DEPARTMENT OF MEDICAL RESEARCH, UNIVERSITY OF TORONTO]

Synthesis of 6-Nitro-6-desoxy-D-glucose and 6-Nitro-6-desoxy-L-idose

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The synthesis of 6-carbon C-nitrodesoxy-aldoses, in which the hydroxyl group on carbon atom 6 is replaced by a nitro group, thus forming the grouping —CH_2NO_2, was of interest, since these compounds represent a new type of sugar derivative and also show, as was anticipated, a remarkable tendency to form cyclic compounds of the cyclohexane and benzene series, on which we shall report in a subsequent paper.

Two of these sugars, 6-nitro-6-desoxy-D-glucose and 6-nitro-6-desoxy-L-idose, have been prepared by the condensation of 1,2-acetone-D-*xylo*-trihydroxyglutaric dialdehyde (II) with nitromethane. Such a condensation reaction of an aldehyde with a nitroparaffin, which dates back to Henry[1] has received much attention in recent years.[2] It has been used previously in this Laboratory for the preparation of nitrolactaldehyde,[3] and recently for the preparation of carbohydrate C-nitroalcohols.[4] In the case under consideration the condensation was effected in ethanol with sodium methoxide in the presence of an excess of nitromethane. When no further change in optical rotation occurred (after eighteen hours), the solution was processed and a crystalline **Mixture A** of the two diastereoisomers III and IV was obtained in a yield of 50% of the theoretical amount (calcd. on the dialdehyde).

The 1,2-acetone-D-*xylo*-trihydroxyglutaric dialdehyde, which is made from monoacetone-D-glucose (I)[5] by oxidation with lead tetraacetate, has been described previously with a rotation of $[\alpha]^{10}D$ $+ 20 \pm 3°$.[6] On preparing this compound we obtained products of varying rotations. Therefore, in the experimental part we describe our method of preparing the dialdehyde for our present purpose. Further investigations of the sirupy dialdehyde are being conducted.

It was found impracticable to separate the two isomers from the mixture **A** by fractional crystallization. A very small amount of IV (less than 5%) was obtained on extraction with absolute ether and repeated crystallization from dibutyl ether. However, separation could be effected satisfactorily by a process we would like to call "fractional acetonation." We found that under similar conditions, IV was acetonated to a diacetone derivative in a yield of about 90%, whereas III was acetonated in a yield of only about 25%. Thus acetonation of the mixture **A** resulted in practically complete acetonation of IV and only partial acetonation of III. This mixture could then be separated easily into the monoacetone derivative III, the diacetone derivative VI, and a residual amount of a crystalline mixture of the two diacetone derivatives V and VI, from which V could not be separated. The latter was, however, obtained from acetonation of III.

On desacetonation of III and V, 6-nitro-6-desoxy-D-glucose was obtained as a white powder which crystallized on slow cooling from a mixture of butanol and dibutyl ether. The crystalline 6-nitro-6-desoxy-D-glucose shows a downward mutarotation in water. Acids slightly accelerate the mutarotation, whereas traces of alkali induce secondary reactions. The downward direction of the mutarotation indicates that the 6-nitro-6-desoxy-D-glucose crystallizes in its α-form.[7]

On desacetonation of IV and VI, 6-nitro-6-desoxy-L-idose was obtained as a resinous, slightly colored mass, which so far has resisted crystallization. The initial and final values of the rotation of this amorphous material were considerably dependent on the degree to which it had been previously dried. Acids accelerate the mutarotation whereas traces of alkali induce secondary reactions.

To establish the configuration of III, it was reduced to the known 1,2-acetone-6-amino-6-desoxy-D-glucose,[8] which was isolated in the form of its *p*-toluenesulfonate in a yield of 85%. Further evidence that III and V possess the D-glucose configuration was obtained by the reduction of V to the known 1,2,3,5-diacetone-6-amino-6-desoxy-D-glucose *p*-toluenesulfonate.[9] This establishes the D-glucose configuration for III and for V and for the acetone-free nitrodesoxysugar VII obtained from III and V. It leaves for IV, VI and VIII the L-idose configuration, as indicated in the table.

On reduction of VI, as above, the crystalline *p*-toluenesulfonate of 1,2,3,5-diacetone-6-amino-6-desoxy-L-idose could be isolated in a yield of 80%.

Experimental

(1) **Condensation of 1,2-Acetone-D-xylo-trihydroxyglutaric Dialdehyde with Nitromethane.**—One hundred grams of monoacetone-D-glucose (m. p. 159–160°) was added to 1.6 liters of dry benzene and the suspension just brought to the boil while stirring moderately. Then 205 g. of lead tetraacetate was added in five equal portions at intervals of about three minutes without further heating, and the stirring was continued for an additional quarter of an hour at 70°. Any slight excess of lead tetraacetate

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(1) L. Henry, *Compt. rend.*, **120**, 1265 (1895).

(2) Reviews by H. B. Hass and Riley, *Chem. Reviews*, **32**, 373 (1943); H. B. Hass, *Ind. Eng. Chem.*, **35**, 1146 (1943); Hass and Bourland, *C. A.*, **38**, 2969 (1944).

(3) H. O. L. Fischer, E. Baer and H. Nidecker, *Helv.*, **18**, 1079 (1935).

(4) J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, **66**, 1312 (1944); **67**, 1713 (1945); **68**, 1511 (1946); **69**, 1048, 1963 (1947).

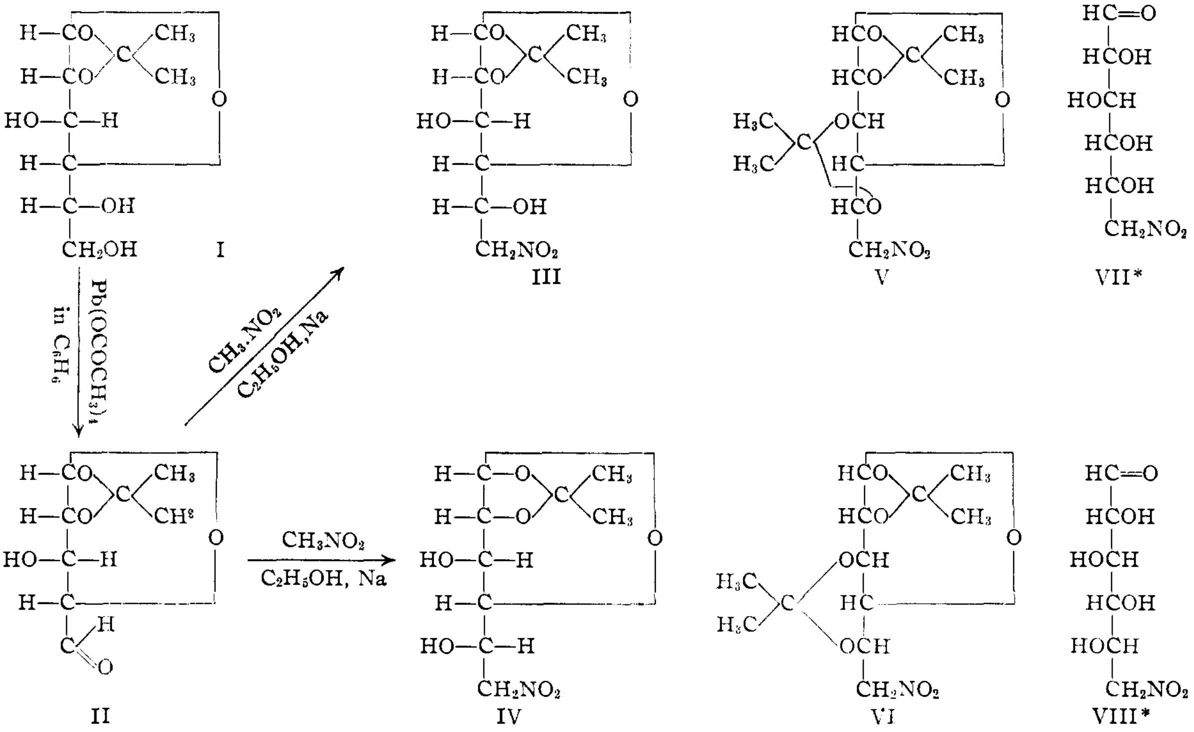
(5) Preparation according to Hixon, *ibid.*, **51**, 523 (1929).

(6) Koichi Iwadare, *Bull. Chem. Soc., Japan*, **16**, 40 (1941); *C. A.*, **35**, 4740 (1941).

(7) C. S. Hudson, THIS JOURNAL, **31**, 66 (1909).

(8) H. Ohle and L. v. Vargha, *Ber.*, **61**, 1206 (1928).

(9) H. Ohle and L. v. Vargha, *ibid.*, **62**, 2432 (1929).



* No ring form has been assigned

was then reduced with a few drops of ethylene glycol and, after cooling to room temperature, the precipitated lead diacetate was filtered off and washed with a little benzene. The combined filtrates, about 2 liters, were quickly extracted four or five times with 25 cc. of ice-water, until no more lead diacetate could be traced in the last aqueous extract, and the benzene solution was cleared from suspended water by filtration. On removal of the benzene under reduced pressure, about one-third of the amount of aldehyde formed remained as a viscous sirup. The optical rotation of this sirup was $[\alpha]^{25}\text{D}$ +50 ± 2° (c = 5) in ethanol. The combined aqueous extracts, about 125 cc., were kept at 0° and extracted quickly six to eight times with 25 cc. of chloroform. Thus the remaining aldehyde was almost entirely extracted from the aqueous solution, containing lead diacetate and acetic acid, and was obtained as a viscous sirup after drying and evaporating the chloroform under reduced pressure. The optical rotation of this sirup was $[\alpha]^{25}\text{D}$ +40 ± 2° (c = 5) in ethanol. The lower optical rotation of the product recovered from the chloroform solution, as compared with that recovered from the benzene solution, may be due to polymerization or to a partial desacetonation, resulting in an admixture of the optically inactive xylo-trihydroxyglutaric dialdehyde. However, both sirups, which may still contain small amounts of formaldehyde, gave the same mono-phenylhydrazone, m. p. 140.5–141°, $[\alpha]^{25}\text{D}$ −42° (c = 5.0) in chloroform, as described by Koichi Iwadare.[6] Over-all yield of the sirupy material was approximately 80%. For all further experiments these sirups were dissolved in ethanol and used together.

One hundred grams of the above 1,2-acetone-D-xylo-trihydroxyglutaric dialdehyde was dissolved in a mixture of 400 cc. of 95% ethanol and 200 cc. of nitromethane. The solution was made alkaline to litmus by the addition of 2 *N* sodium methoxide. An excess of 20 cc. of 2 *N* sodium methoxide was then added and the solution left at room temperature for eighteen hours. The solution was then concentrated *in vacuo* to about one-fifth of its volume, and, after addition of about 500 cc. of chloroform, it was extracted five to six times with about 20 cc. of water. The condensation products were then obtained as a viscous residue on evaporation of the organic solvents *in vacuo*. On addition of an equal amount of absolute ether to this residue and stirring until a homogeneous mixture was obtained, crystallization of the condensation products was soon induced and the crystals were filtered with suction and washed twice with absolute ether. The mother liquor and ether washings, containing an appreciable amount of condensation products, were collected and evaporated and the residue treated as above. This crystalline mixture of 1,2-acetone-6-nitro-6-desoxy-D-glucose and 1,2-acetone-6-nitro-6-desoxy-L-idose could be crystallized from dibutyl ether (25 parts), chloroform and ether-petroleum ether (b. p. 40–60°), but no appreciable separation of the isomers took place. The mixture melted between 105 and 120° and showed a specific optical rotation of between −21° and −25°. The yield of this mixture A of colorless crystalline nitrodesoxysugars was about 50% of the theoretical.

(2) **1,2-Acetone-6-nitro-6-desoxy-D-glucose.**—One hundred grams of mixture A, as under (1), was dissolved in 2 liters of absolute acetone, containing 10.0 cc. of concentrated sulfuric acid, and kept at room temperature for four days. The sulfuric acid was then just neutralized with concentrated ammonia (an excess of ammonia being avoided), the ammonium sulfate was centrifuged off, and the solution was concentrated *in vacuo* to about 200 cc. The residue was taken up in 2 liter of ether and extracted twice with 50 cc. and twice with 25 cc. of water and filtered clear. The ether was distilled off, leaving a crystalline sludge from which the remaining solvent was distilled off *in vacuo* at about 60°. The resulting crystalline mass was dissolved in about 150 cc. of hot ethanol and the solution was slowly diluted with 600 cc. of water. Most of the diacetone products crystallized out immediately, and, after standing overnight in the ice-box, the crystals (B) (about 40 g.) were filtered with suction and washed with a little water. The mother liquor was concentrated *in vacuo* to half its volume, heated shortly to 80° with a little charcoal, and filtered. On complete evaporation of the solvents *in vacuo* the unchanged 1,2-acetone-6-nitro-6-desoxy-D-glucose crystallized out and was recrystallized first from benzene and then from

dibutyl ether (1 g. in 25 cc.). In this way 40 g. of the almost pure isomer, m. p. 123–125°, $[\alpha]^{25}_{\mathrm{D}}$ −18 to −20°, was obtained. On repeating with this substance the entire acetonation and crystallization procedure as above, the purest isomer we could prepare, m. p. 126–127° and $[\alpha]^{24}_{\mathrm{D}}$ −16.8° in water (c = 4.2), was obtained. *Anal.* Calcd. for $C_9H_{15}O_7N$ (249): C, 43.3; H, 6.02; N, 5.62; acetone, 23.3. Found: C, 43.4; H, 6.17; N, 5.64; acetone, 23.1.

(3) **1,2-Acetone-6-nitro-6-desoxy-L-idose.**—On extraction of 5 g. of mixture A, as under (1), with absolute ether in a Soxhlet apparatus, about 0.5 g. of impure 1,2-acetone-6-nitro-6-desoxy-L-idose, m. p. 135–142°, remained undissolved. After three crystallizations from dibutyl ether this substance had a m. p. of 161–162° and $[\alpha]^{24}_{\mathrm{D}}$ −39.0° in water (c = 3.32) and no change of these constants was observed on recrystallization. *Anal.* Calcd. for $C_9H_{15}O_7N$ (249): C, 43.3; H, 6.02; N, 5.62; acetone, 23.3. Found: C, 43.6; H, 5.93; N, 5.55; acetone, 23.6.

(4) **1,2,3,5-Diacetone-6-nitro-6-desoxy-D-glucose.**—This was obtained on acetonation of our purest 1,2-acetone-6-nitro-6-desoxy-D-glucose, as under (2) and crystallization from ethanol, and subsequently from 50% aqueous methanol, in a yield of 25%, while 60% of the unchanged starting material was recovered; m. p. 106–107°, $[\alpha]^{23}_{\mathrm{D}}$ +18.8° in pyridine (c = 3.56). *Anal.* Calcd. for $C_{12}H_{19}O_7N$ (289): C, 49.8; H, 6.58; N, 4.84; acetone, 40.1. Found: C, 50.0; H, 6.49; N, 4.87; acetone 40.3.

(5) **1,2,3,5-Diacetone-6-nitro-6-desoxy-L-idose.**—On crystallizing the mixture B (40 g. as under (2)), once from 80% ethanol and three times from methanol, 20 g. of diacetone-6-nitro-6-desoxy-L-idose, m. p. 150–151° and $[\alpha]^{25}_{\mathrm{D}}$ −30.1° in pyridine (c = 2.80), was obtained. After five recrystallizations from methanol or ethanol the melting point was one-half degree higher, but the optical rotation was unchanged. *Anal.* Calcd. for $C_{12}H_{19}O_7N$ (289): C, 49.8; H, 6.58; N, 4.84; acetone, 40.1. Found: C, 49.7; H, 6.78; N, 4.75; acetone, 40.3. The mother liquors were combined and concentrated *in vacuo*, leaving a crystalline sludge, consisting mainly of the diacetone–glucose derivative. Fractional crystallization of this mixture from ethanol and water yielded further amounts of the diacetone–idose derivative. The main portion of about 15 g., however, could not be separated completely from its isomer and melted from about 95 to 105°.

Acetonation of 1,2-acetone-6-nitro-6-desoxy-L-idose, as under (2), yielded about 90% of diacetone-6-nitro-6-desoxy-L-idose.

(6) **6-Nitro-6-desoxy-D-glucose.**—The 1,2-acetone-6-nitro-6-desoxy-D-glucose (m. p. 124° and higher), was dissolved in five times its weight of 0.1 N sulfuric acid and kept for about seventy-five minutes in a water-bath at 75–80°. The diacetone-6-nitro-6-desoxy-D-glucose was treated in the same manner, except for the addition of about 20% of ethanol to facilitate its solution. The solutions were then freed from the sulfuric acid by careful addition, with stirring, of 80% of the theoretical amount of barium hydroxide solution and balanced out exactly with a 0.1 N solution of barium acetate. This solution should at no time become even slightly alkaline on account of the extreme sensitivity of the free nitrodesoxysugar. The barium sulfate was removed by centrifuging or filtering. On evaporation *in vacuo* of the water, the free sugar was obtained as a white powder, m. p. 152–154°, with an initial optical rotation of $[\alpha]^{23}_{\mathrm{D}}$ +40 ± 2° within five minutes after dissolution in water. Ten grams of this substance was dissolved in a boiling mixture of 500 cc. of *n*-butanol and 500 cc. of *n*-dibutyl ether and the solution seeded at about 100° with crystalline nitrodesoxyglucose. (Seeds were obtained by dissolving a sample of the nitrodesoxysugar in a mixture of the solvents as above, and letting stand overnight.) Approximately 5 g. of material crystallized in small white needles on slow cooling to 50° within six hours. On further cooling, the remaining substance came out as an amorphous precipitate from the mother liquor, and could be recovered completely by evaporation of the solvents *in vacuo*.

The crystalline 6-nitro-6-desoxy-D-glucose melts at 156–157° and shows the mutarotation (±0.5°).

Time	$[\alpha]^{23}_{\mathrm{D}}$ in H_2O (c = 2.90)	$[\alpha]^{23}_{\mathrm{D}}$ in 0.1 N H_2SO_4 (c = 2.81)
5 min.	+45° ± 0.5°	+44.6° ± 0.5°
10 min.	44.6°	44.0°
30 min.	43.6°	42.8°
60 min.	43.0°	40.9°
2 hours	41.0°	39.2°
3 hours	39.0°	37.9°
4 hours	37.8°	37.4°
5 hours	37.0°	37.0°
6 hours	36.7°	36.9°
12 hours	36.7°	36.8°
2 days	35.6°	36.8°
5 days	32.6°	36.8°
12 days	29.1°	..
18 days	24.9°	..

The end rotation was thus reached within six to seven hours in water and dilute acid. A very much slower change of the optical rotation was observed after that time in water, indicating that a secondary reaction took place. This was probably due to the slight alkalinity of the glass with which the solution came in contact, since no such change was observed in dilute acid. *Anal.* Calcd. for $C_6H_{11}O_7N$ (209): C, 34.5; H, 5.27; N, 6.70. Found: C, 34.6; H, 5.23; N, 6.94.

(7) **6-Nitro-6-desoxy-L-idose** was prepared from its diacetone derivative, as under (6). So far, it has not been obtained in a crystalline state, but only as a resinous, slightly colored mass. We have been unable, therefore, as yet, to determine accurately the optical properties of this compound, especially since sharp drying in high vacuum over phosphorus pentoxide resulted in a brittle, glassy mass with a very much smaller mutarotation than material dried to a viscous consistency. A representative experiment can be given as follows: 1.503 g. of diacetone-6-nitro-6-desoxy-L-idose, m. p. 150–151°, was dissolved in 20 cc. of boiling ethanol and kept at 75–80° for one hour after the addition of 10.0 cc. of N sulfuric acid; then 15 cc. of warm water was added and the solution kept at the same temperature for an additional hour. After cooling to room temperature and adjusting the volume of the solution to 50.0 cc. with water, the optical rotation was $[\alpha]^{20}_{\mathrm{D}}$ −13.8°. After removal of the sulfuric acid and the solvents, as under (6), and drying the residue to a viscous consistency, the initial optical rotation was $[\alpha]^{23}_{\mathrm{D}}$ −16.6° in water (c = 3.15), $[\alpha]^{23}_{\mathrm{D}}$ −12.3° in 0.1 N sulfuric acid (c = 2.63), and the rotation seven days later $[\alpha]^{23}_{\mathrm{D}}$ −20.9° in water, $[\alpha]^{23}_{\mathrm{D}}$ −26.0° in 0.1 N sulfuric acid. After drying the same sample to a brittle, glassy mass, which was crushed to a powder, the initial optical rotation was $[\alpha]^{23}_{\mathrm{D}}$ −10.4° in water (c = 4.36), $[\alpha]^{21}_{\mathrm{D}}$ −12.2° in 0.1 N sulfuric acid, and the rotation forty-eight hours later $[\alpha]^{22}_{\mathrm{D}}$ −12.9° in water, $[\alpha]^{22}_{\mathrm{D}}$ −14.0° in 0.1 N sulfuric acid.

(8) **1,2-Acetone-6-amino-6-desoxy-D-glucose *p*-Toluenesulfonate.**—1,2-Acetone-6-nitro-6-desoxy-D-glucose (1.01 g., m. p. 126°) was dissolved in 30 cc. of water and reduced with hydrogen at ordinary temperature and pressure in the presence of 8 g. of freshly prepared Raney nickel catalyst. Within the first ten minutes 250 cc. of hydrogen was absorbed and 55 cc. within the next fifty minutes (calcd., 307 cc. at 23° and 753 mm.). (This reduction was also carried out at room temperature and a hydrogen pressure of 20–30 atm. and was then complete in five minutes.) The catalyst was then centrifuged off and the solution neutralized with 0.5 N *p*-toluenesulfonic acid and evaporated to dryness *in vacuo*. The amorphous residue was dissolved in about 6–8 cc. of absolute ethanol and filtered. On gradual addition of about 300 cc. of absolute ether, in portions, 1.2 g. (85%) of the crystalline compound was obtained, m. p. 176–177°, $[\alpha]^{26}_{\mathrm{D}}$ −7.0°

in water (c = 3.7). These constants agree with those reported by Ohle[8] for the same compound (m. p. 176–177°, $[\alpha]^{20}\text{D}$ −7.02° in water, (c = 5.01)).

(9) **1,2,3,5-Diacetone-6-amino-6-desoxy-D-glucose *p*-Toluenesulfonate.**—An amount of 1.05 g. 1,2,3,5-diacetone-6-nitro-6-desoxy-D-glucose (m. p. 106–107°) was dissolved in 60 cc. of dioxane and reduced as under (8). The reduction was complete within forty-five minutes and the free amine was obtained as a viscous sirup after centrifuging off the catalyst and evaporating the dioxane *in vacuo* at 40°. This sirup was dissolved in 20 cc. of water, neutralized exactly with 0.5 N *p*-toluenesulfonic acid and filtered. On evaporating the water *in vacuo*, 1.3 g. (83%) of the salt was obtained and was crystallized once from benzene and once from dry ethyl acetate. *Anal.* Calcd. for $C_{19}H_{29}O_8NS$ (431): C, 52.8; H, 6.72; N, 3.25; acetone, 26.9. Found: C, 52.9; H, 6.62; N, 3.12; acetone, 26.7.

Since the melting point found for this substance did not entirely agree with that reported by Ohle, the physical constants of the salt were thoroughly examined by Mr. D. L. MacDonald of this Laboratory, who reports as follows:

"The melting point of this compound varied considerably with the rate of heating, and melting was accompanied by decomposition; as these characteristics were not reported by Ohle and v. Vargha, the compound was also prepared according to their method from 6-tosyl-1,2-monoacetone-D-glucose *via* 6-tosyl-1,2,3,5-diacetone-D-glucose.[9,10] The amine salt prepared by the two different methods was found to be identical as regards melting point (with decomposition), solubilities in various solvents, crystal form, optical rotation and dependence of melting point on rate of heating, as shown in the table. From the data, it can be concluded that the compound under consideration is identical with Ohle and v. Vargha's 1,2,3,5-diacetone-6-amino-6-desoxy-D-glucose *p*-toluenesulfonate. The slightly low rotation may indicate the presence of a small amount of the corresponding L-idose compound."

	Prepared according to:		
	Ohle and v. Vargha	Grosheintz and Fischer	Mixed melting point, °C.
From dry ethyl acetate:			
(1) Standing in bath for 20 minutes at	160°	160°	
(2) Heating at 1°/minute	172–172.5°	171.5–172°	171.5–172°
(3) Heating at 10°/minute	177–179°	176–179°	
(4) $[\alpha]\text{D}$ (1 dm. tube, H_2O)	+30.5° (c = 5.4, t = 25°)	+29.1 (c = 4.0, t = 24°)	

(10) **1,2,3,5-Diacetone-6-amino-6-desoxy-L-idose *p*-Toluenesulfonate.**—An amount of 2.35 g. of 1,2,3,5-diacetone-6-nitro-6-desoxy-L-idose (m. p. 150–151°) was dissolved in 100 cc. of dioxane, reduced, and the resulting amine was neutralized with *p*-toluenesulfonic acid as under (9). The crude salt was dissolved in a little warm methanol, treated with charcoal, and filtered. On addition of about 5 volumes of absolute ether to this solution 2.8 g. (80%) of substance crystallized immediately in long fine needles, m. p. 198–200° (dec.), $[\alpha]^{25}\text{D}$ +5.8° in 0.1 N NaOH (c = 3.8), $[\alpha]^{26}\text{D}$ +0.84° in absolute ethanol (c = 3.5), $[\alpha]^{26}\text{D}$ −7.0° in dry pyridine (c = 5.3). No optical rotation could be observed in water. *Anal.* Calcd. for $C_{19}H_{29}O_8NS$ (431): C, 52.8; H, 6.72; N, 3.25; acetone, 26.9. Found: C, 52.7; H, 6.55; N, 3.24; acetone, 26.8.

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Summary

The preparation of a new type of sugar derivative is described. 1,2-Acetone-D-*xylo*-trihydroxyglutaric dialdehyde was condensed with nitromethane to yield a mixture of 1,2-acetone-6-nitro-6-desoxy-D-glucose and 1,2-acetone-6-nitro-6-desoxy-L-idose. Separation of the two diastereoisomers could be effected. The free nitrodesoxysugars were obtained on desacetonation with dilute sulfuric acid.

The constitution and configuration of the glucose derivatives were established by the reduction of the mono- and diacetone-6-nitro-6-desoxy-D-glucose to the known 1,2-acetone-6-amino-6-desoxy-D-glucose and to 1,2,3,5-diacetone-6-amino-6-desoxy-D-glucose and subsequent isolation of their *p*-toluenesulfonates.

This leaves for the other isomer the L-idose configuration.

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[10] H. Ohle and E. Dickhäuser, *Ber.*, **58**, 2602 (1925); H. Ohle and L. v. Vargha, *ibid.*, **61**, 1208 (1928).

[CONTRIBUTION FROM THE BANTING AND BEST DEPARTMENT OF MEDICAL RESEARCH, UNIVERSITY OF TORONTO]

Cyclization of 6-Nitrodesoxyaldohexoses to Nitrodesoxyinositols

BY J. M. GROSHEINTZ AND HERMANN O. L. FISCHER

When an aldose, in which the primary hydroxyl group is replaced by a nitro group, is exposed to a mild alkali, condensation of the aldehyde group into the —CH_2NO_2 group may be expected[1] forming the group —$CH(NO_2)$—CH(OH)— with two new asymmetric carbon atom centers. Such a reaction, reminiscent of an aldol condensation, could produce either straight-chain or cyclic polymers or produce cyclic monoisomers. In the latter case the aldehyde group would condense with the nitromethylene group of the same molecule. It was with this reaction in mind that we synthesized 6-nitro-6-desoxy-D-glucose and 6-nitro-6-desoxy-L-idose,[2] since we expected intramolecular condensation, *i. e.*, cyclization of these nitrodesoxysugars to a number of nitrodesoxyinositol stereoisomers. We found our expectations confirmed and we were able to isolate some of these nitrodesoxyinositols under certain controlled conditions.

Evidence for the cyclohexane ring structure of our condensation products is shown by the quantitative transformation of these compounds to a known aromatic compound. Thus, on dissolving a pentaacetylnitrodesoxyinositol in warm pyridine

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[1] L. Henry, *Compt. rend.*, **120**, 1265 (1895).

[2] Grosheintz and Fischer, THIS JOURNAL, **70**, 1476 (1948).