THE SYNTHESIS OF ACETAMIDO-DEOXY KETOSES BY ACETOBACTER SUBOXYDANS

PART III

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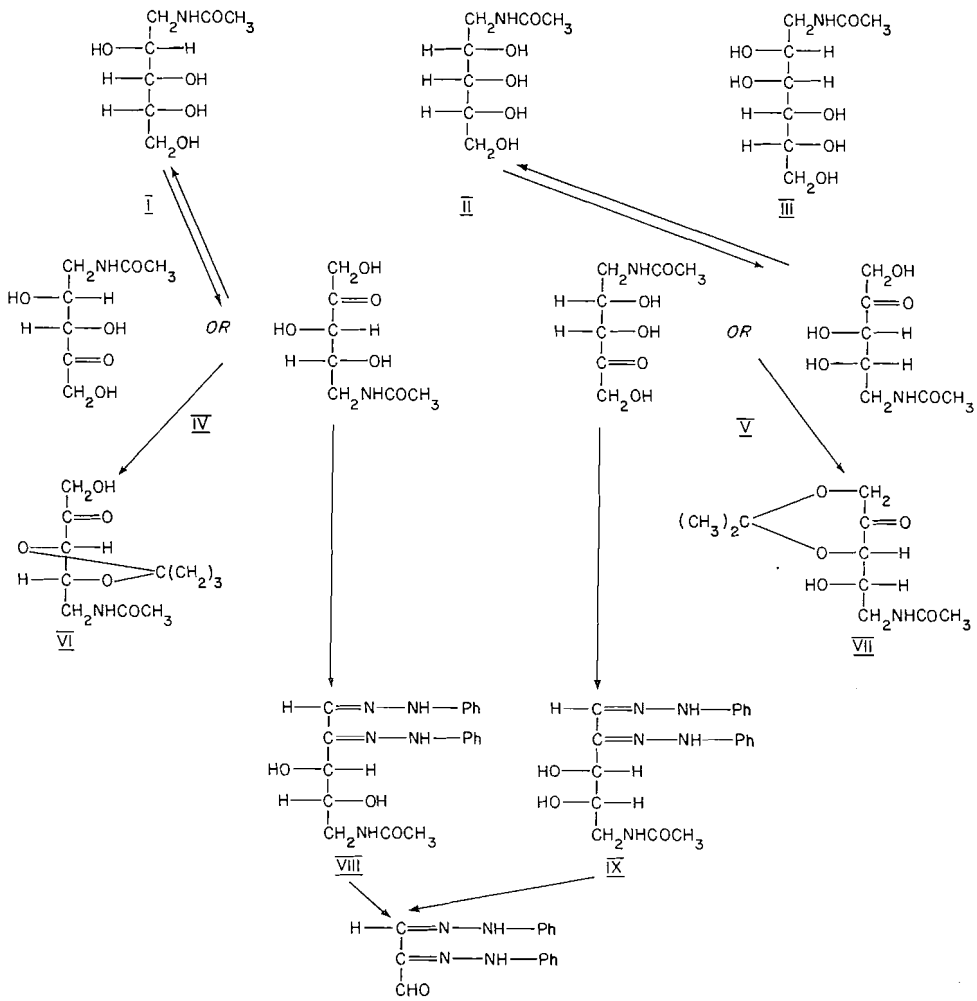
ABSTRACT

1-Acetamido-1-deoxy-D-arabinitol, 1-acetamido-1-deoxy-D-ribitol, and 1-acetamido-1-deoxy-D-mannitol were synthesized and characterized. Microbiological oxidation of 1-acetamido-1-deoxy-D-arabinitol and 1-acetamido-1-deoxy-D-ribitol gave the crystalline acyclic 2-pentuloses 5-acetamido-5-deoxy-D-*threo*-pentulose and 5-acetamido-5-deoxy-L-*erythro*-pentulose respectively.

RESULTS AND DISCUSSION

Crude 1-amino-1-deoxy-D-arabinitol, 1-amino-1-deoxy-D-ribitol, and 1-amino-1-deoxy-D-mannitol were prepared by the method of Holly *et al.* (1) and purified via the salicylidene Schiff's bases by the method of Kagan *et al.* (2). *N*-Acetylation of the pure amino-deoxy polyhydric alcohols with aqueous acetic anhydride (3) then gave 1-acetamido-1-deoxy-D-arabinitol (I), 1-acetamido-1-deoxy-D-ribitol (II), and 1-acetamido-1-deoxy-D-mannitol (III) respectively, which were characterized by periodate oxidation studies, elemental analyses, and infrared spectra.

The microbiological oxidation of acetamido-deoxy polyhydric alcohols by *Acetobacter suboxydans* has recently been investigated in this laboratory (4, 5). We now wish to report the microbiological oxidation of 1-acetamido-1-deoxy-D-arabinitol (I) to 5-acetamido-5-deoxy-D-*threo*-pentulose (IV) and of 1-acetamido-1-deoxy-D-ribitol (II) to 5-acetamido-5-deoxy-L-*erythro*-pentulose (V). Both oxidation products (IV, V) were obtained as strongly reducing crystalline solids which gave absorptions in the infrared corresponding to OH, NH, the amide linkage, and the saturated carbonyl group. Periodate oxidation studies yielded almost identical results in each case (periodate uptake 2.75 moles, formic acid 1.1 moles, formaldehyde 0.75 mole) and indicated that the compounds possessed a primary alcohol group. The results also indicate that approximately 0.2 mole glycollic acid was formed during the oxidation, which was then stable to further attack by periodate ion (6). It was concluded that the carbonyl group was located at carbon 2 in both cases and that cleavage by periodate ion was more rapid between carbons 1 and 2 than between carbons 2 and 3. Since both compounds were therefore probably 2-ketoses, the formation of furanose rings would be prohibited and the acyclic zigzag conformation would be adopted. The hydroxyl groups at carbons 3 and 4 of ketose IV would then be favorably situated for the formation of an isopropylidene derivative. Ketose IV, on reaction with acidified acetone, gave a strongly reducing syrupy isopropylidene derivative (VI) which gave absorptions in the infrared corresponding to OH, NH, the amide linkage, the saturated carbonyl group, and the isopropylidene group. The compound, on periodate oxidation, consumed 0.75 mole periodate, with the liberation of 0.63 mole titratable acid and 0.67 mole formaldehyde, indicating that carbons 1 and 2 were not involved in ketal formation and that the compound was the 3,4-*O*-isopropylidene derivative (VI). Ketose V under similar reaction conditions also gave a syrupy isopropylidene derivative (VII).



The infrared spectrum was similar to that of the 3,4-*O*-isopropylidene derivative (VI) except that the saturated carbonyl absorption was much stronger. However, the isopropylidene derivative VII was only weakly reducing and on periodate oxidation consumed 0.36 mole periodate, liberating 0.1 mole titratable acid and 0.1 mole formaldehyde, which suggested that hydrolysis to ketose V was occurring before oxidation. It was concluded that compound VII was probably the 1,3-*O*-isopropylidene derivative, which was possible since the carbonyl group distorted the carbon chain sufficiently to bring the primary alcohol group near carbon 3.

Ketose IV gave a crystalline phenylosazone (VIII) which, when oxidized with periodate by the method of Hough, Powell, and Woods (7), consumed 1.18 moles of periodate and released no formic acid or formaldehyde. A rapid formation of the 1,2-bisphenylhydrazone of mesoxalaldehyde (8) occurred. These results indicated that the phenylosazone (VIII) possessed free hydroxyl groups at carbons 3 and 4 and that the ketose (IV) from which it was derived was a 2-ketose. Ketose V also gave a crystalline phenylosazone (IX), which on periodate oxidation gave results closely similar to those

obtained from the oxidation of phenylosazone VIII, and the same conclusions were reached regarding the structure of phenylosazone IX and its parent ketose (V). In the case of IX, however, the precipitation of the 1,2-bisphenylhydrazone of mesoxalaldehyde occurred more slowly, which indicated that the free hydroxyl groups at carbons 3 and 4 of phenylosazone IX were less favorably situated for cleavage by periodate ion than those in the other phenylosazone (VIII), in agreement with the finding for the ketal formation of the free ketoses (IV and V).

Ketose IV on reduction with sodium borohydride gave crystalline 1-acetamido-1-deoxy-D-arabinitol (I), which indicated that the hydroxyl groups at carbons 3 and 4 of ketose IV were in the D-*threo* configuration, since the position of the carbonyl group had been fixed at carbon 2 by previous evidence. Ketose V on reduction with sodium borohydride gave a syrup which could not be satisfactorily crystallized, although paper chromatography and paper electrophoresis indicated the presence of a single compound. However, the syrup, when acetylated, gave a syrupy acetate which had infrared spectrum and retention time on gas–liquid chromatographic analysis identical with the syrupy acetate prepared from 1-acetamido-1-deoxy-D-ribitol (II), although the optical rotation was different. This indicated that some 1-acetamido-1-deoxy-D-ribitol (II) was present in the sodium borohydride reduction product and that the hydroxyl groups at carbons 3 and 4 of ketose V were in the L-*erythro* configuration, since the position of the carbonyl group had been fixed at carbon 2 by previous evidence.

The above evidence indicated that the biological oxidation product from 1-acetamido-1-deoxy-D-arabinitol (I) was the acyclic 2-pentulose 5-acetamido-5-deoxy-D-*threo*-pentulose (IV) and that the biological oxidation product from 1-acetamido-1-deoxy-D-ribitol (II) was the acyclic 2-pentulose 5-acetamido-5-deoxy-L-*erythro*-pentulose (V), in accordance with the Bertrand–Hudson rules for oxidation by *Acetobacter suboxydans* (9, 10).

Studies on the biological oxidation product from 1-acetamido-1-deoxy-D-mannitol (III) are in progress and will be the subject of a later communication.

EXPERIMENTAL

Solutions were concentrated under reduced pressure (ca. 15 mm) below 40° C. Melting points are uncorrected and optical rotations were measured at 23±3° C in water unless otherwise stated. Paper chromatography was carried out by the descending method (11) using Whatman No. 1 paper in the following solvent systems (v/v):

(A) butan-1-ol/ethanol/water, 9:3:3;
(B) ethyl acetate/acetic acid/formic acid/water, 18:3:1:4;
(C) butan-1-ol/pyridine/water, 5:3:2.

Rates of movements of compounds on paper chromatograms are given relative to that of rhamnose (R_{rh} value). Ketose sugars were detected on paper chromatograms with the orcinol – trichloroacetic acid spray reagent (12), other reducing compounds with the *p*-anisidine hydrochloride spray reagent (13), and non-reducing compounds with the alkaline silver nitrate spray reagent (14). Infrared spectra were measured in chloroform solution or as a dispersion in a potassium bromide pellet, using a Perkin–Elmer Model 21 spectrophotometer. Formaldehyde produced in periodate oxidations was determined by the chromotropic acid method (15).

Preparation of 1-Acetamido-1-deoxy Polyhydric Alcohols

1-Amino-1-deoxy polyhydric alcohols were prepared by the method of Kagan *et al.* (2) in which the free aldose sugar was dissolved in liquid ammonia and hydrogenated with Raney nickel catalyst at 2000 p.s.i. and 85° C for 2.5 hours. The 1-amino-1-deoxy polyhydric alcohols were isolated from the crude reaction mixture as the crystalline salicylidene Schiff's bases. Hydrolysis of the Schiff's bases with dilute hydrochloric acid then gave the corresponding 1-amino-1-deoxy polyhydric alcohol hydrochlorides which were deionized in aqueous solution on columns of Amberlite IRA 400 anion-exchange resin to yield the pure 1-amino-1-deoxy polyhydric alcohols. Physical constants of products and intermediates are listed in Table I.

TABLE I

Physical constants of products and intermediates in the preparation of 1-amino-1-deoxy polyhydric alcohols
(Literature values are given in parentheses (2))

Compound	M.p. (°C)	$[\alpha]_D$
Salicylidene 1-amino-1-deoxy-D-arabinitol	188–190 (187–188)	
Salicylidene 1-amino-1-deoxy-D-ribitol	125–127 (126–128)	
Salicylidene 1-amino-1-deoxy-D-mannitol	199–201	
1-Amino-1-deoxy-D-arabinitol hydrochloride	136.5–137.5	+15°
1-Amino-1-deoxy-D-ribitol hydrochloride	132.5–134	−8°
1-Amino-1-deoxy-D-mannitol hydrochloride	163–165	+5°
1-Amino-1-deoxy-D-arabinitol	114–120 (decomp.)	+4°
1-Amino-1-deoxy-D-ribitol	syrup	+5°
1-Amino-1-deoxy-D-mannitol	134–135 (decomp.)	+1°

1-Acetamido-1-deoxy polyhydric alcohols were prepared by *N*-acetylation in aqueous acetic anhydride (3) of the corresponding pure 1-amino-1-deoxy polyhydric alcohols. Yields, physical constants, and elemental analyses are listed in Table II, and infrared data and the results of periodate oxidation studies are listed in Table III.

TABLE II

1-Acetamido-1-deoxy polyhydric alcohols

Compound	% yield after three recrystallizations	M.p. (°C)	$[\alpha]_D$	R_{rh} Solvent: A	B	C	Analysis (%) Calc. C	H	N	Found C	H	N
1-Acetamido-1-deoxy-D-arabinitol	59	146.5–147.5	+23°	0.83	0.94	0.76	43.5	7.8	7.3	43.6	7.9	7.2
1-Acetamido-1-deoxy-D-ribitol	57	91.5–92	−24°	0.89	1.07	0.82	43.5	7.8	7.3	43.4	7.7	7.1
1-Acetamido-1-deoxy-D-mannitol	59	152.5–153	+13°	0.70	0.77	0.65	43.1	7.6	6.3	43.0	7.7	6.1

TABLE III

Infrared data and results of periodate oxidation studies on 1-acetamido-1-deoxy polyhydric alcohols

Compound	Absorptions in the infrared (cm^{-1})	Periodate oxidation (unbuffered aqueous solution) Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)
1-Acetamido-1-deoxy-D-arabinitol	OH(3400), NH(3300), amide I (1630), amide II (1600)	0.08 1.00 20	3.03 3.04 3.05	1.98 1.98 1.98
1-Acetamido-1-deoxy-D-ribitol	OH and NH (3340), amide I (1610), amide II (1570)	0.08 1.0 3.25	3.04 3.01 3.02	1.93 1.97 1.97
1-Acetamido-1-deoxy-D-mannitol	OH and NH (3350), amide I (1635), amide II (1555)	0.08 1.00 3.00	3.94 3.97 3.97	2.91 2.94 2.94

SECTION A. STUDIES ON 5-ACETAMIDO-5-DEOXY-D-*threo*-PENTULOSE

5-Acetamido-5-deoxy-D-threo-*pentulose*

1-Acetamido-1-deoxy-D-arabinitol (10 g), sorbitol monohydrate (0.5 g), potassium dihydrogen phosphate (0.05 g), and yeast extract powder (0.5 g) were dissolved in tap water (100 ml), sterilized, and innoculated with *Acetobacter suboxydans* in the usual way (4). After 10 days, when Somogyi estimations (16) of the copper-reducing power of the medium indicated an 81% conversion to ketose sugar, the medium was poured into 2 volumes of ethanol, filtered, and the filtrate was deionized by rapid passage through small columns of Amberlite IR 120 (H^+) and Duolite A4 (OH^-) resins at 5° C and concentrated to dryness. The syrup obtained was fractionated on a cellulose column, butan-1-ol half-saturated with water being used as irrigant, and 5-acetamido-5-deoxy-D-*threo*-pentulose was obtained as a chromatographically pure syrup which crystallized after desiccation for 1 month. The ketose was recrystallized from ethanol/ether to give needles, m.p. 105–106° C, $[\alpha]_D$ +34°, which reduced Fehling's solution immediately at room temperature. Absorptions in the infrared were recorded at 3340 cm^{-1} (OH and NH), 1720 cm^{-1} (saturated carbonyl group), 1640 cm^{-1} (amide I), and 1580 cm^{-1} (amide II). The ketose had R_{rh} 0.94 (solvent A), 1.12 (solvent B), and 0.97 (solvent C), and gave an immediate intense spot with the alkaline silver nitrate spray reagent. Anal. Calc. for $C_7H_{13}O_5N$: C, 44.0%; H, 6.8%; N, 7.3%. Found: C, 43.8%; H, 6.9%; N, 7.5%.

Periodate Oxidation of 5-Acetamido-5-deoxy-D-threo-*pentulose*

The ketose was oxidized with an approximately twofold excess of sodium metaperiodate in unbuffered aqueous solution. The results are recorded in Table IV.

TABLE IV

Periodate oxidation of 5-acetamido-5-deoxy-D-*threo*-pentulose

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.08	2.20	1.09	0.73
2	2.74	1.11	0.73
3	2.75	1.11	—
4	2.75	1.11	0.73

5-Acetamido-5-deoxy-3,4-O-isopropylidene-D-threo-*pentulose*

5-Acetamido-5-deoxy-D-*threo*-pentulose (300 mg) was shaken at room temperature with dry acetone (150 ml) containing concentrated sulphuric acid (4 drops) for 18 hours. The solution was then neutralized with barium carbonate, filtered, and evaporated to dryness. The residual syrup was separated from a trace of unreacted ketose by chromatography on Whatman No. 3 MM paper in solvent A overnight, and obtained as a chromatographically pure syrup (180 mg), $[\alpha]_D$ +17° (*c*, 1.75 in ethanol), R_{rh} 2.3 (solvent A), 1.84 (solvent B), 1.54 (solvent C). The syrup reduced Fehling's solution rapidly at room temperature and gave the following infrared absorptions: 3460 cm^{-1} (OH), 3360 cm^{-1} (NH), 1725 cm^{-1} (saturated carbonyl group), 1665 cm^{-1} (amide I), 1525 cm^{-1} (amide II), 1390, 1380 cm^{-1} (CH of isopropylidene group).

Periodate Oxidation of 5-Acetamido-5-deoxy-3,4-O-isopropylidene-D-threo-*pentulose*

The isopropylidene ketose was oxidized in 50% aqueous ethanol solution (unbuffered) with a twofold excess of sodium metaperiodate. The results are recorded in Table V. (A fourfold excess of periodate was used for the estimation of formaldehyde.)

TABLE V

Periodate oxidation of 5-acetamido-5-deoxy-3,4-*O*-isopropylidene-D-*threo*-pentulose

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.08	0.14	0.07	0.19
1.17	0.29	0.29	0.40
5	0.42	0.38	0.51 (4 hours)
26	0.62	0.56	0.59 (22.5 hours)
52	0.75	0.63	0.67 (70 hours)

5-Acetamido-5-deoxy-D-threo-*pentose Phenylosazone*

The phenylosazone was prepared by the usual method, using freshly distilled phenylhydrazine and glacial acetic acid. Several recrystallizations from aqueous ethanol gave bright yellow needles, m.p. 197–199° C. The phenylosazone gave absorptions in the infrared at 3260 cm^{-1} (OH and NH), 3080 cm^{-1} (aromatic CH), 1660 cm^{-1} (amide I), 1640 cm^{-1} (amide II), and 1605, 1500, 745, 685 cm^{-1} (aromatic ring). Anal. Calc. for $C_{19}H_{23}O_3N_5.H_2O$: C, 58.9%; H, 6.5%; N, 18.1%. Found: C, 59.6%; H, 6.5%; N, 18.1%.

Periodate Oxidation of 5-Acetamido-5-deoxy-D-threo-*pentose Phenylosazone*

The phenylosazone was oxidized in 50% aqueous ethanol by the method of Hough, Powell, and Woods (7). The results of the oxidation are shown in Table VI. One minute after oxidation had started, yellow needles separated from the solution. The crystals were centrifuged off and the supernatant was returned to the flask for oxidation studies. The crystals were recrystallized from aqueous ethanol and had m.p. 187–189° C. An authentic specimen of the 1,2-bisphenylhydrazone of mesoxalaldehyde had m.p. 194° C, and the mixed m.p. was 189–191° C. The infrared spectra of the authentic and derived specimens of the 1,2-bisphenylhydrazone of mesoxalaldehyde were identical over the range 4000–600 cm^{-1}.

TABLE VI

Periodate oxidation of 5-acetamido-5-deoxy-D-*threo*-pentose phenylosazone

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.33	1.18	0.00	0.00
1	1.16	0.00	0.00
2.5	1.15	0.00	—

Sodium Borohydride Reduction of 5-Acetamido-5-deoxy-D-threo-*pentulose*

5-Acetamido-5-deoxy-D-*threo*-pentulose (200 mg) was reduced with an equal weight of sodium borohydride in aqueous solution at 0° C for 3 hours. After removal of sodium borohydride and sodium borate the product was obtained as a clear syrup (200 mg). The syrup was dissolved in ethanol, cooled, and seeded with 1-acetamido-1-deoxy-D-arabinitol. Crystallization occurred and the crystals were filtered off, dried, and recrystallized from ethanol and had m.p. 145–147° C (47 mg). 1-Acetamido-1-deoxy-D-arabinitol had m.p. 146.5–147.5° C, and the mixed m.p. was 145–147° C. The infrared spectra of the authentic and derived specimens were identical over the range 4000–600 cm^{-1}. The derived specimen had $[\alpha]_D$ +22.6° and the authentic specimen had $[\alpha]_D$ +23°.

Section B. Studies on 5-Acetamido-5-deoxy-L-*erythro*-pentulose

5-Acetamido-5-deoxy-L-erythro-*pentulose*

1-Acetamido-1-deoxy-D-ribitol was oxidized by *Acetobacter suboxydans* using exactly the same procedure as that described for 1-acetamido-1-deoxy-D-arabinitol (Section A) to give an 83% conversion to ketose sugar after 10 days. After 21 days the medium was worked up in the usual way and the syrup obtained was fractionated on a cellulose column using butan-1-ol half-saturated with water as irrigant. 5-Acetamido-5-deoxy-L-*erythro*-pentulose was obtained as a chromatographically pure syrup which crystallized after desiccation for 1 week. The ketose was recrystallized from aqueous ethanol to give prisms, m.p. 160–164° C (decomp.), $[\alpha]_D$ +7°, which reduced Fehling's solution immediately at room temperature. Absorptions in the infrared were recorded at 3480 cm^{-1} (OH), 3310 cm^{-1} (NH), 1725 cm^{-1} (saturated carbonyl group), 1630 cm^{-1} (amide I), 1565 cm^{-1} (amide II). The ketose had R_{rh} 1.0 (solvent A), 1.15 (solvent B), 1.02 (solvent C), and gave an immediate intense spot with the alkaline silver nitrate spray reagent. Anal. Calc. for $C_7H_{13}O_5N$: C, 44.0%; H, 6.8%; N, 7.3%. Found: C, 43.8%; H, 6.9%; N, 7.5%.

Periodate Oxidation of 5-Acetamido-5-deoxy-L-erythro-*pentulose*

The ketose was oxidized with an approximately twofold excess of sodium metaperiodate in an unbuffered aqueous solution. The results are recorded in Table VII.

5-Acetamido-5-deoxy-1,3(?)-O-isopropylidene-L-erythro-*pentulose*

5-Acetamido-5-deoxy-L-*erythro*-pentulose (200 mg) was shaken with dry acetone (150 ml) containing concentrated sulphuric acid (4 drops), at room temperature, for 18 hours. The reaction mixture was neutralized with barium carbonate and filtered, the filtrate was evaporated to dryness, and the residue was examined on paper chromatograms. The orcinol – trichloroacetic acid spray reagent revealed three components, the major one having R_{rh} 2.74 (solvent A), 1.72 (solvent C), and this was separated by chromatography on Whatman No. 3 MM paper in solvent A. The material was obtained on elution as a

TABLE VII

Periodate oxidation of 5-acetamido-5-deoxy-L-*erythro*-pentulose

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.08	2.16	1.07	0.76
1.25	2.73	1.08	0.77
2.5	2.72	1.08	—
3.75	2.74	1.09	0.74

yellow syrup (83 mg). The optical rotation could not be measured due to the color of the solution. The syrup gave absorptions in the infrared at 3450 cm^{-1} (OH), 3350 cm^{-1} (NH), 1740 cm^{-1} (saturated carbonyl group), 1660 cm^{-1} (amide I), 1525 cm^{-1} (amide II), 1390, 1380 cm^{-1} (CH of the isopropylidene group). The syrup did not reduce Fehling's solution at room temperature but did so when heated; it gave a slow, weak reaction with the alkaline silver nitrate spray reagent.

*Periodate Oxidation of 5-Acetamido-5-deoxy-1,3(?)-O-isopropylidene-*L-erythro-*pentulose*

The isopropylidene ketose was oxidized in 50% aqueous ethanol solution (unbuffered) with a twofold excess of sodium metaperiodate. The results are recorded in Table VIII.

TABLE VIII

Periodate oxidation of 5-acetamido-5-deoxy-1,3(?)-*O*-isopropylidene-L-*erythro*-pentulose

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.17	0.05	0.02	0.00
1.42	0.09	0.05	0.08 (1.58 hours)
4	0.12	0.05	0.08
23.5	0.36	0.11	0.10 (22.5 hours)

*5-Acetamido-5-deoxy-*L-erythro-*pentose Phenylosazone*

The phenylosazone was prepared by the usual method, using freshly distilled phenylhydrazine and glacial acetic acid. Several recrystallizations of the product from ethanol gave bright yellow needles, m.p. 180–182° C. The phenylosazone gave absorptions in the infrared at 3550 cm^{-1} (OH), 3310 cm^{-1} (NH), 3080 cm^{-1} (aromatic CH), 1650 cm^{-1} (amide I), 1630 cm^{-1} (amide II) and 1605, 1495, 745, 690 cm^{-1} (aromatic ring). Anal. Calc. for $C_{19}H_{23}O_3N_5$: C, 61.8%; H, 6.2%; N, 19.0%. Found: C, 61.2%, 61.7%; H, 6.5%, 7.0%; N, 19.7%, 19.4%. Good analyses were not obtained despite repeated recrystallizations.

*Periodate Oxidation of 5-Acetamido-5-deoxy-*L-erythro-*pentose Phenylosazone*

The phenylosazone was oxidized under the same conditions as those used for 5-acetamido-5-deoxy-D-*threo*-pentose phenylosazone (Section A). The results of the oxidation are shown in Table IX. Fifteen

TABLE IX

Periodate oxidation of 5-acetamido-5-deoxy-L-*erythro*-pentose phenylosazone

Time (hours)	Periodate uptake (moles/mole)	Formic acid (moles/mole)	Formaldehyde (moles/mole)
0.17	1.24	0.00	0.00
1.17	1.15	0.00	0.00
2.5	1.14	0.00	—
4	1.14	0.00	—

minutes after oxidation had commenced, a precipitate of the 1,2-bisphenylhydrazone of mesoxalaldehyde appeared and was isolated as described in Section A. It had m.p. 185–187° C and an authentic specimen had m.p. 192–193° C; mixed m.p. was 185–187° C. The infrared spectra of the authentic and derived specimens of the 1,2-bisphenylhydrazone of mesoxalaldehyde were identical over the range 4000–600 cm^{-1}.

Sodium Borohydride Reduction of 5-Acetamido-5-deoxy-L-erythro-*pentulose*

5-Acetamido-5-deoxy-L-*erythro*-pentulose (300 mg) was reduced with an equal weight of sodium borohydride in aqueous solution at 0° C for 4 hours. After removal of sodium borohydride and sodium borate the product was obtained as a pale yellow syrup (315 mg) which was dissolved in ethanol, seeded with 1-acetamido-1-deoxy-D-ribitol, and cooled. Crystallization occurred but on attempted filtration the crystals immediately liquefied, and repeated attempts to isolate the material failed. The syrup gave one spot on paper chromatograms R_{rh} 0.91 (solvent A), 1.0 (solvent B), 0.83 (solvent C). Paper electrophoresis in pH 9.2 sodium borate buffer at 500 volts for 5 hours gave one spot with a rate of movement slightly less than that of 1-acetamido-1-deoxy-D-ribitol. The syrup was acetylated with acetic anhydride in pyridine solution and gave a syrupy product (466 mg) which had $[\alpha]_D$ −15° (*c*, 3.78 in chloroform). Acetylation of 1-acetamido-1-deoxy-D-ribitol gave a syrupy acetate which had $[\alpha]_D$ +3° (*c*, 4.1 in chloroform). When subjected to gas–liquid chromatographic analysis (column packing D, reference 17) at a flow rate of 100 ml/minute and temperatures of 213° C or 225° C, the two acetates had identical retention times and a mixture of the two gave a single symmetrical peak. The two acetates had practically identical infrared spectra and gave absorptions at 3440 cm^{-1} (NH), 1740 cm^{-1} (carbonyl group of *O*-acetate), 1680 cm^{-1} (amide I), and 1520 cm^{-1} (amide II). It was concluded that the sodium borohydride reduction product from 5-acetamido-5-deoxy-L-*erythro*-pentulose contained mainly 1-acetamido-1-deoxy-D-ribitol and an isomeric 1-acetamido-1-deoxy pentitol.

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