Distillation *in vacuo* followed by g.l.c. purification gave a pure sample of *cis*-1-methyl-2-phenylcyclopropane (74% yield). The i.r. and n.m.r. data were quite identical with those of the authentic one (15).

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Synthesis of 2-acetamido-2-deoxy-D-gulose, 2-acetamido-2-deoxy-D-idose, and 2-deoxy-D-*xylo*-hexose from 3,4,5,6-tetraacetoxy-D-*xylo*-1-nitro-1-hexene[1]

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3,4,5,6-Tetraacetoxy-D-*xylo*-1-nitro-1-hexene with methanolic ammonia afforded a mixture of 2-acetamido-1,2-dideoxy-1-nitro-D-gulitol and 2-acetamido-1,2-dideoxy-1-nitro-D-iditol which were converted *via* a Nef reaction to 2-acetamido-2-deoxy-D-gulose and 2-acetamido-2-deoxy-D-idose.

Reduction of 3,4,5,6-tetraacetoxy-D-*xylo*-1-nitro-1-hexene afforded 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol which was converted *via* the Nef reaction to 2-deoxy-D-*xylo*-hexose.

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2-Acetamido-2-deoxy-D-gulose and 2-acetamido-2-deoxy-D-idose were prepared in 32 and 4% yields respectively from 3,4,5,6-tetraacetoxy-D-*xylo*-1-nitro-1-hexene by the general procedure in which polyacetoxy-1-nitro-1-alkenes are treated with ammonia to yield epimeric 2-acetamido-1,2-dideoxy-1-nitroglycitols which may be converted *via* a modified (1) Nef (2) reaction to the corresponding 2-acetamido-2-deoxyglycoses (3–7). This procedure had previously been applied to the preparation of 2-amino-2-deoxy-D-gulose in about 15% yield from the intermediate acetoxylated nitroalkene (8); 2-amino-2-deoxyidose was detected chromatographically in the reaction products.

2-Amino-2-deoxy-D-gulose and 2-amino-2-deoxy-D-idose have been synthesized from D-xylose in 8 and 38% yields respectively by the condensation of D-xylose with hydrogen cyanide and aniline or *p*-toluidine followed by controlled hydrogenation of the products (9). 2-Amino-2-deoxy-D-gulose has been synthesized from 2-amino-2-deoxy-D-galactose by configurational inversion at C-3 (10) and 2-amino-2-deoxy-D-idose has been made by ammonolysis of methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside in the presence of sodium methoxide and subsequent *N*-acetylation to yield methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside from which 2-amino-2-deoxy-D-idose could be obtained (11).

3,4,5,6-Tetraacetoxy-D-*xylo*-1-nitro-1-hexene (12) with saturated methanolic ammonia solution gave a mixture of 2-acetamido-1,2-dideoxy-1-nitro-D-gulitol and 2-acetamido-1,2-dideoxy-1-nitro-D-iditol which could not be separated by fractional crystallization. The mixed 2-acetamido-1,2-dideoxy-1-nitroglycitols on treatment with sulfuric acid afforded a mixture of 2-acetamido-2-deoxy-D-gulose and 2-acetamido-2-deoxy-D-idose and a small proportion of the corresponding free aminoglycoses. The product after

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treatment with aqueous acetic anhydride, was shown by paper chromatography, to contain only the 2-acetamido-2-deoxygulose and 2-acetamido-2-deoxyidose derivatives in the visual ratio of about 10:1. The mixture was fractionated by cellulose column chromatography to yield pure samples of 2-acetamido-2-deoxy-D-gulose and 2-acetamido-2-deoxy-D-idose. This preparative procedure gives a simple and direct route to the synthesis of the 2-acetamido-2-deoxyglycoses from readily available and inexpensive precursors and should be of practical value.

2-Deoxy-D-*xylo*-hexose was prepared in 25% yield from 3,4,5,6-tetraacetoxy-D-*xylo*-1-nitro-1-hexene by reduction with hydrogen to give 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol which underwent the Nef reaction to yield the 2-deoxy-D-*xylo*-hexose. 2-Deoxy-D-*xylo*-hexose which has been reported to be a constituent of a glycoside isolated from *Erysimum perowskianum* (13) has been synthesized from methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-gulopyranoside by reduction with lithium aluminium hydride to methyl 4,6-*O*-benzylidene-2-deoxy-D-*xylo*-hexopyranoside, which on mild hydrolysis afforded 2-deoxy-D-*xylo*-hexose (14).

Experimental

Paper chromatography was performed by the descending method (15) on Whatman No. 1 filter paper using pyridine – ethyl acetate – water (2:5:5 v/v, top layer) as the mobile phase. The glycoses were detected with (*A*) 2% silver nitrate in acetone followed by 2% sodium hydroxide in ethanol (16), (*B*) 2% *p*-anisidine hydrochloride in ethanol (17), or (*C*) 0.02 *M* sodium metaperiodate followed by ethylene glycol – acetone – sulfuric acid (50:50:0.3 v/v) and 6% sodium 2-thiobarbiturate (18). The rates of movement of the glycoses on the chromatograms are quoted relative to D-galactose (R_{gal}).

Gas–liquid partition chromatography (g.l.c.) was carried out using a Hewlett–Packard 402 chromatograph with a hydrogen flame detector and fitted with glass U tubes (4ft × 6mm × 3mm internal diameter) packed with 10% neopentylglycol sebacate polyester on 80–100 mesh acid-washed Chromosorb W, maintained at 225 °C. Dry helium was used as the carrier gas and retention times of the compounds are quoted relative to 2-acetamido-2-deoxy-1,3,4,5,6-penta-*O*-(trimethylsilyl)-D-glucitol (T_{GN}) or 1,2,3,4,5,6-hexa-*O*-acetyl-D-glucitol (T_G).

Melting points were determined on a Fisher–Johns apparatus and are corrected. Solutions were concentrated under reduced pressure, below 40 °C. Optical rotations were determined at 20 °C using a Perkin–Elmer 141 polarimeter.

*2-Acetamido-2-deoxy-*D*-idose and 2-Acetamido-2-deoxy-*D*-gulose*

A solution of 3,4,5,6-tetraacetoxy-D-*xylo*-1-nitro-1-hexene (20 g) (12), in methanol (150 ml) cooled to 0 °C, was saturated with dry ammonia (about 1 h) and the mixture was then allowed to stand at room temperature for 20 h. The reaction mixture was concentrated to a syrup which was triturated with warm chloroform (4 × 100 ml) to remove acetamide. The residual syrup (13 g) was then dissolved in a solution of $Ba(OH)_2 \cdot 8H_2O$ (16 g) in water (240 ml). This solution was added dropwise with vigorous stirring to a cold mixture of sulfuric acid (14 ml) in water (240 ml) and, after stirring at 10 °C for 2 h the mixture was left at 20 °C for 18 h. The neutralized ($BaCO_3$) reaction mixture was filtered and the filtrate after concentration to about 100 ml was treated with Dowex-1($CO_3^=$) ion-exchange resin (30 ml), methanol (10 ml), and acetic anhydride (0.8 ml). The mixture was then shaken for 30 min. The filtered solution was concentrated to a syrup (11 g) and paper chromatographic examination of the product showed two spots having R_{gal} 1.87 and 2.19 in the visual ratio of 10:1 which corresponded in rates of movement with 2-acetamido-2-deoxygulose and 2-acetamido-2-deoxyidose respectively.

The mixed 2-acetamido-2-deoxyhexoses were separated by cellulose column (4.5 × 85 cm) chromatography using butan-1-ol half saturated with water as the mobile phase. Chromatographically pure 2-acetamido-2-deoxy-D-idose (0.48 g) was eluted first and was followed by 2-acetamido-2-deoxy-D-gulose (3.90 g).

*2-Acetamido-2-deoxy-*D*-idose*

The product from the column which could not be crystallized showed a single spot on paper chromatography (R_{gal} 2.19) and had $[\alpha]_D$ −38° (*c*, 2 in water) (lit. (9) $[\alpha]_D$ −45°).

Anal. Calcd. for $C_8H_{15}O_6N$: C, 43.43; H, 6.84; N, 6.33. Found: C, 43.3; H, 6.8; N, 6.3.

The trimethylsilylated (19) 2-acetamido-2-deoxy-D-idose on gas chromatography gave four peaks having T_{GN} 0.58 (4%), 0.87 (48%), 1.06 (18%), and 1.13 (30%).

*2-Acetamido-2-deoxy-*D*-iditol*

2-Acetamido-2-deoxy-D-idose (0.1 g) in water (5 ml) was reduced with sodium borohydride (50 mg) for 3 h at room temperature and the isolated 2-acetamido-2-deoxy-D-iditol (65 mg) after recrystallization from ethanol had m.p. 139 °C and $[\alpha]_D$ +25° (*c*, 0.6 in water) and gave a single spot on paper chromatography (R_{gal} 1.13).

Anal. Calcd. for $C_8H_{17}O_6N$: C, 43.05; H, 7.68; N, 6.27. Found: C, 43.1; H, 7.8; N, 6.3.

The fully acetylated hexitol (20) on g.l.c. gave a single peak having T_G 3.23 corresponding in retention time with authentic 1,3,4,5,6-penta-*O*-acetyl-2-acetamido-2-deoxy-D-iditol.

*2-Acetamido-2-deoxy-*D*-gulose*

The product obtained crystalline from ethanol solution had m.p. 125–126 °C and $[\alpha]_D$ −66° (*c*, 2.5 in water) (lit. (9) $[\alpha]_D$ −59°) and gave a single spot on paper chromatography (R_{gal} 1.87).

Anal. Calcd. for $C_8H_{15}O_6N$: C, 43.43; H, 6.84; N, 6.33. Found: C, 43.4; H, 6.7; N, 6.4.

The trimethylsilylated crystalline 2-acetamido-2-deoxy-D-gulose on gas chromatography gave two peaks having T_{GN} 1.04 (26%) and 1.16 (74%) and the trimethylsilylated glycose after equilibration in water gave the same two peaks (29 and 71% respectively).

*2-Acetamido-2-deoxy-*D*-gulitol*

2-Acetamido-2-deoxy-D-gulose (0.15 g) was reduced as

described above for the preparation of 2-acetamido-2-deoxy-D-iditol to yield 2-acetamido-2-deoxy-D-gulitol which after recrystallization from methanol had m.p. 169–170 °C and $[\alpha]_D$ +6.2° (*c*, 0.5 in water) and gave a single spot on paper chromatography (R_{gal} 1.18).

Anal. Calcd. for $C_8H_{17}O_6N$: C, 43.05; H, 7.68; N, 6.27. Found: C, 43.0; H, 7.8; N, 6.2.

The fully acetylated hexitol on gas chromatography gave a single peak having T_G 3.59.

2-Deoxy-D-xylo-hexose

(a) 3,4,5,6-Tetra-O-acetyl-1,2-dideoxy-1-nitro-D-xylo-hexitol

3,4,5,6-Tetraacetoxy-D-*xylo*-1-nitro-1-hexene (10 g) in ethanol (200 ml) was shaken with hydrogen at atmospheric pressure in the presence of palladium black (0.4 g). One mole of hydrogen was absorbed in 20 min. The reaction mixture was filtered and the filtrate was concentrated to a syrup which crystallized. The 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol (7.8 g) after recrystallization from ethanol had m.p. 81 °C and $[\alpha]_D$ −5.9° (*c*, 1.5 in chloroform).

Anal. Calcd. for $C_{14}H_{21}O_{10}N$: C, 46.28; H, 5.83; N, 3.86. Found: C, 46.3; H, 6.0; N, 3.8.

(b) 2-Deoxy-D-xylo-hexose

3,4,5,6-Tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol (7.5 g) was dissolved in *N* sodium hydroxide (100 ml) and after 1 h at 20 °C the mixture was added dropwise with stirring to a solution of sulfuric acid (12 ml) in water (20 ml). The neutralized ($BaCO_3$) reaction mixture after filtration, was passed down columns of Rexyn 101(H^+) (200 ml) and Duolite A4(OH^-) (25 ml) ion-exchange resins and the eluate and washings were concentrated to a syrup (2.6 g) which was fractionated on a cellulose column (4 × 35 cm), using butan-1-ol half saturated with water as the mobile phase, to yield chromatographically pure 2-deoxy-D-*xylo*-hexose (1.1 g).

The 2-deoxy-D-*xylo*-hexose on paper chromatography had R_{gal} 2.70 and gave the characteristic red color with the periodate – thiobarbiturate spray reagents. It had $[\alpha]_D$ +9.4° (*c*, 0.5 in water) (lit. (14) $[\alpha]_D$ +12 ± 2°).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.0; H, 7.4.

The 2-deoxy-D-*xylo*-hexose (100 mg) on bromine oxidation gave 2-deoxy-D-*xylo*-hexonolactone (90 mg) having $[\alpha]_D$ −56° (*c*, 1.9 in acetone) (lit. (14) $[\alpha]_D$ −57°) which on treatment with phenylhydrazine afforded 2-deoxy-D-*xylo*-hexonic acid phenylhydrazide (38 mg) having m.p. 125–126 °C (lit. (14) m.p. 124–125 °C).

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Formation of a C_{22} dihydroxyketo acid by a yeast

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Saponification of extracellular lipids from the yeast NRRL YB-2501 yielded 8,9,13-trihydroxydocosanoic acid and a new keto dihydroxy acid of melting point 131–132 °C. The keto acid was shown to be 8,9-dihydroxy-13-oxodocosanoic acid by conversion to 5-ketotetradecanoic acid and suberic acid. By means of the method of Ames and Bowman (3), it was established that the vicinal hydroxyls of the new acid have the *erythro* configuration.

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In 1965 we reported (1) that 8,9,13-triacetoxydocosanoic acid is produced by a yeast closely related to *Torulopsis fujisanensis*. More recently, in a review (2) on the extracellular lipids of yeasts, we mentioned that this organism also forms at the same time a smaller amount of