A Synthesis of 2-Amino-2,6-dideoxy-D-(and L-)galactose (Fucosamine) and 2-Amino-2,6-dideoxy-D-(and L-)talose (Pneumosamine)[1]

MALCOLM B. PERRY AND VIRGINIA DAOUST
Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

Received October 10, 1972

5-Deoxy-D-lyxose underwent base-catalyzed addition with nitromethane to give a mixture of 1,6-dideoxy-1-nitro-D-galactitol and 1,6-dideoxy-1-nitro-D-talitol (*ca.* 2:1). Acetylation of the crystalline 1,6-dideoxy-1-nitro-D-galactitol gave 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol which on treatment with methanolic ammonia afforded 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol and 2-acetamido-1,2,6-trideoxy-1-nitro-D-galactitol (*ca.* 3:1) which under the modified Nef reaction conditions gave 2-acetamido-2,6-dideoxy-D-talose and 2-acetamido-2,6-dideoxy-D-galactose respectively. The glycoses were converted to 2-amino-2,6-dideoxy-D-talose hydrochloride and 2-amino-2,6-dideoxy-D-galactose hydrochloride on hydrolysis with hydrochloric acid.

A similar reaction sequence applied to 5-deoxy-L-lyxose afforded the L-enantiomorphic intermediates, and gave 2-amino-2,6-dideoxy-L-talose hydrochloride and 2-amino-2,6-dideoxy-L-galactose hydrochloride as final products.

Le déoxy-5-D-lyxose s'additionne sur du nitrométhane en milieu basique pour conduire au mélange de didéoxy-1,6-nitro-1-D-galactitol et de didéoxy-1,6 nitro-1-D-talitol (*ca.* 2:1). L'acétylation du didéoxy-1,6 nitro-1-D-galactitol cristallin fournit le tétra-*O*-acétyl-2,3,4,5 didéoxy-1,6 nitro-1-D-galactitol qui, en présence d'ammoniac méthanolique, conduit à l'acétamido-2 tridéoxy-1,2,6 nitro-1-D-talitol et à l'acétamido-2 tridéoxy-1,2,6 nitro-1-D-galactitol (*ca.* 3:1); dans les conditions de la réaction modifiée de Nef, ce mélange donne respectivement l'acétamido-2 didéoxy-2,6-D-talose et l'acétamido-2 didéoxy-2,6-D-galactose. Les glycoses sont convertis en chlorhydrates d'amino-2 didéoxy-2,6-D-talose et d'amino-2 didéoxy-2,6-D-galactose dans l'hydrolyse par l'acide chlorhydrique.

La même séquence réactionnelle sur le déoxy-5-L-lyxose conduit aux intermédiaires L-énantiomorphes puis aux chlorhydrates d'amino-2 didéoxy-2,6-L-talose et d'amino-2 didéoxy-2,6-L-galactose comme produits finals. [Traduit par le journal]

Can. J. Chem., **51**, 974 (1973)

The following 2-amino-2,6-dideoxyhexoses have been identified as components of bacterial polysaccharides: 2-amino-2,6-dideoxy-D-glucose (quinovosamine) (1–5), 2-amino-2,6-dideoxy-L-mannose (rhamnosamine) (6, 7), 2-amino-2,6-dideoxy-D-galactose (fucosamine) (8–13), 2-amino-2,6-dideoxy-L-galactose (14–16), and 2-amino-2,6-dideoxy-L-talose (pneumosamine) (15, 17, 18). A survey of the carbohydrate components of *Pseudomonas* species made in this laboratory revealed many unusual aminoglycoses, including 2-amino-2,6-dideoxyhexoses. The synthesis of the series of these latter compounds was undertaken to provide glycoses for the development of analytical procedures and for the preparation of methyl ethers required in structural studies.

Although methods have been described for the synthesis of 2-amino-2,6-dideoxy-D-talose (18), 2-amino-2,6-dideoxy-L-talose (19, 20), 2-amino-2,6-dideoxy-L-galactose (20, 21), and 2-amino-2,6-dideoxy-D-galactose (13), it was considered that the series might be conveniently synthesized from available 5-deoxypentoses by the nitromethane method which has found general application in the synthesis of 2-amino-2-deoxyaldoses (22). This paper records the successful synthesis of 2-amino-2,6-dideoxy-D-talose and 2-amino-2,6-dideoxy-D-galactose from 5-deoxy-D-lyxose, and the corresponding L-enantiomorphs from 5-deoxy-L-lyxose, using the nitromethane method.

5-Deoxy-D-lyxose, prepared by the degradation of D-fucose diethyl dithioacetal (21, 23) underwent addition with nitromethane in the presence of sodium methoxide and the resulting precipitated sodium salts of 1,6-dideoxy-1-nitro-D-galactitol (66%) and 1,6-dideoxy-1-nitro-D-talitol (34%) were deionized with hydrogen form ion-exchange resin and the product afforded crystalline 1,6-dideoxy-1-nitro-D-galactitol which on acetylation gave 2,3,4,5-tetra-*O*-acetyl-1,6-

---

[1] NRCC No. 12975.

dideoxy-1-nitro-D-galactitol. Treatment of the 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol with saturated methanolic ammonia (24) afforded a mixture of 2-acetamido-1,2,6-trideoxy-1-nitro-D-galactitol (27%) and 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol (73%), the latter compound being obtained pure by crystallization from ethanol solution. The 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol on treatment under the mild modified Nef conditions (24) gave chromatographically pure 2-acetamido-2,6-dideoxy-D-talose. The crude 2-acetamido-1,2,6-trideoxy-1-nitro-D-galactitol remaining after the removal of crystalline 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol, underwent the modified Nef reaction to give a mixture of 2-acetamido-2,6-dideoxy-D-talose and 2-acetamido-2,6-dideoxy-D-galactose, the latter compound being separated by crystallization from the ethanol solution of the mixture.

The 2-acetamido-2,6-dideoxy-D-talose and 2-acetamido-2,6-dideoxy-D-galactose were each hydrolyzed with hot dilute hydrochloric acid to yield crystalline 2-amino-2,6-dideoxy-D-talose hydrochloride and 2-amino-2,6-dideoxy-D-galactose hydrochloride respectively which had physical properties in agreement with those recorded in the literature for these compounds.

The synthesis of the two 2-acetamido-2,6-dideoxy-hexoses performed without the isolation of the intermediates gave improved yields. The final products of 2-acetamido-2,6-dideoxy-D-talose and 2-acetamido-2,6-D-galactose were obtained in 44 and 17% yields respectively, based on 5-deoxy-D-lyxose used. The final mixture can be separated by preferential crystallization of the 2-acetamido-2,6-dideoxy-D-galactose leaving essentially pure 2-acetamido-2,6-dideoxy-D-talose which is readily purified by conversion to 2-amino-2,6-dideoxy-D-talose hydrochloride which is obtained pure in good yield. Alternatively, the two 2-acetamido-2,6-dideoxy-hexoses are easily separated by cellulose column chromatography using aqueous 1-butanol as the mobile phase.

5-Deoxy-L-lyxose, prepared either by the degradation of L-fucose diethyl dithioacetal (21) or from D-galactono-1,4-lactone (25), underwent the same synthetic reaction sequence as that described for 5-deoxy-D-lyxose to yield the corresponding L-enantiomorphic intermediates and to give, as final products, 2-amino-2,6-dideoxy-L-talose hydrochloride and 2-amino-2,6-dideoxy-L-galactose hydrochloride.

Experimental

Paper chromatography was performed by the descending method (26) on Whatman No. 1 filter paper using either (A) pyridine – ethyl acetate – water (2:5:5 v/v; top layer) or (B) 1-butanol–ethanol–water (4:1:5 v/v; top layer) as the mobile phase. Glycoses were detected with either (*i*) 2% silver nitrate in acetone followed by 3% sodium hydroxide in ethanol (27), (*ii*) 2% *p*-anisidine hydrochloride in ethanol (28), or (*iii*) 2% ninhydrin in acetone. The rates of movement of the glycoses are quoted relative to D-galactose (R_{Gal}) or to 2-amino-2-deoxy-D-glucose hydrochloride (R_{GN}).

Gas–liquid partition chromatography (g.l.p.c.) was carried out using a Hewlett-Packard model 402 gas chromatograph with a hydrogen flame detector and fitted with glass U-tubes (4 ft × 6 mm × 3 mm internal diameter) packed with 10% neopentyl-glycol sebacate polyester on 80–100 mesh acid washed Chromosorb W. Retention times of the compounds are quoted relative to penta-*O*-acetyl-L-arabinitol (T_{A}) or to 2-acetamido-2-deoxy-1,3,4,5,6-penta-*O*-(trimethylsilyl)-D-glucitol (T_{GN}).

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

(A) Synthesis of 2-Amino-2,6-dideoxy-D-talose Hydrochloride and 2-Amino-2,6-dideoxy-D-galactose Hydrochloride

(1) 1,6-Dideoxy-1-nitro-D-talitol and 1,6-Dideoxy-1-nitro-D-galactitol

To a solution of 5-deoxy-D-lyxose (21) (4.4 g) in a mixture of methanol (50 ml) and nitromethane (15 ml) was added 1.7 *N* sodium methoxide in methanol (23 ml) and the mixture was kept at 20 °C for 18 h. Following the addition of ether (140 ml), the precipitated product was collected by filtration, washed with cold methanol, ether, and light petroleum (b.p. 30–60 °C) and dried under vacuum. The product dissolved in cold water (70 ml) was passed down a column of Rexyn 101(H^+) ion-exchange resin (120 ml) and the eluate and water washings were concentrated to a syrup (5.5 g).

A portion of the product (20 mg) was dissolved in 2 *N* sodium hydroxide (0.2 ml) and the solution was added dropwise to 6 *N* sulfuric acid (0.3 ml) at 0 °C. After 2 h at room temperature the mixture was diluted with water (5 ml) and following neutralization ($BaCO_3$), filtration, and passage of the filtrate through a column of mixed Rexyn 101(H^+) and Rexyn RG6(OH^-) ion-exchange resins (2 ml), the solution was concentrated to a syrup (*ca.* 12 mg). Paper chromatographic examination of the syrup (solvent A) revealed two spots having R_{Gal} 2.37 and 4.26 corresponding in mobilities and color reaction, with authentic 6-deoxy-D-galactose and 6-deoxy-D-talose respectively (visual ratio 2:1). G.l.p.c. (180 °C) of a reduced ($NaBH_4$) and acetylated (29, 30) portion of the latter syrup gave two peaks corresponding with penta-*O*-acetyl-6-deoxy-D-talitol (T_{A} 0.72, 34%) and penta-*O*-acetyl-D-6-deoxy-D-galactitol(T_{A} 0.77, 66%).

On keeping, a methanolic solution of the mixed 1,6-dideoxy-1-nitro-hexitols (5.4 g) gave crystals (2.8 g), m.p. 170–176 °C (mixture of *talo*- and *galacto*-epimers, *ca.* 1:5 by Nef reaction) which after three recrystallizations from ethanol afforded pure 1,6-dideoxy-1-nitro-D-galactitol (2 g) having m.p. 180 °C and $[\alpha]_D$ +6° (*c*, 0.3 in water).

Anal. Calcd. for $C_6H_{13}O_6N$: C, 36.92; H, 6.71; N, 7.18. Found: C, 37.10; H, 6.53; N, 6.99.

A small sample of the pure product on treatment under the Nef conditions (as above) gave only 6-deoxy-D-galactose.

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

1,6-Dideoxy-1-nitro-D-galactitol (2 g) in acetic anhydride (20 ml) was treated with 1 drop of concentrated sulfuric acid and the mixture was heated on a boiling water bath for 30 min. The cooled reaction mixture was poured onto crushed ice (150 ml) and the precipitated derivative (3.9 g) was collected and washed with cold water. The product after two recrystallizations from ethanol gave crystalline 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol having m.p. 138–139 °C and $[\alpha]_D$ −18.5° (*c*, 0.7 in chloroform).

Anal. Calcd. for $C_{14}H_{21}O_{10}N$: C, 46.28; H, 5.83; N, 3.86. Found: C, 46.41; H, 5.86; N, 3.76.

Acetylation of the mixed 1,6-dideoxy-1-nitro-D-galactitol and -D-talitol (3.4 g) remaining after removal of the -D-galactitol component afforded further crystalline 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol (1.6 g) and a syrup mixture of 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol and 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-talitol (4.3 g).

(3) 2-Acetamido-1,2,6-trideoxy-1-nitro-D-galactitol and 2-Acetamido-1,2,3-trideoxy-1-nitro-D-talitol

2,3,4,5-Tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol (4.1 g) in dry methanol (45 ml) was cooled to 0 °C and ammonia gas was passed into the solution for 30 min and the saturated mixture was then kept for 18 h at 20 °C. The mixture was concentrated to a syrup which was triturated with warm chloroform (3 × 30 ml) to remove acetamide and the light brown syrup remaining was dissolved in hot ethanol, treated with charcoal (2 g), filtered, and, following concentration of the ethanol solution, crystalline 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol (1.2 g) was obtained, which had, after recrystallization from ethanol, m.p. 166–167 °C and $[\alpha]_D$ +20° (*c*, 0.4 in water).

Anal. Calcd. for $C_8H_{16}O_6N_2$: C, 40.67; H, 6.83; N, 11.86. Found: C, 40.83; H, 6.76; N, 11.69.

A portion of the product (10 mg) resulting from the action of ammonia on the 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol on treatment under the Nef conditions gave two 2-acetamido-2,6-dideoxy-hexoses which on paper chromatography gave two spots having R_{Gal} 3.02 and 4.10 corresponding in mobility and color reactions with 2-acetamido-2,6-dideoxy-D-galactose and 2-acetamido-2,6-dideoxy-D-talose respectively (visual ratio 1:2) while quantitative g.l.p.c. analysis (190 °C) of the trimethylsilylated product (31) indicated the mixture to be composed of 27% 2-acetamido-2,6-dideoxy-D-galactose and 73% 2-acetamido-2,6-dideoxy-D-talose.

(4) 2-Amino-2,6-dideoxy-D-talose Hydrochloride

2-Acetamido-1,2,6-trideoxy-1-nitro-D-talitol (0.96 g) was dissolved in a solution of $Ba(OH)_2 \cdot 8H_2O$ (1.18 g) in water (18 ml) and the mixture was added dropwise with stirring to a solution of concentrated sulfuric acid (1.2 ml) in water (11 ml) cooled in ice. The mixture was kept at 20 °C for 18 h and following neutralization ($BaCO_3$) and filtration, the filtrate was treated with Dowex-1 (CO_3^{2-}) ion-exchange resin (8 ml) and 4 drops of acetic anhydride and, after 20 min, the solution was passed down a column of mixed Rexyn 101(H^+) and Rexyn RG6(OH^-) ion-exchange resins and the eluate and washings were concentrated to dryness (0.62 g).

Paper chromatographic analysis of the product (solvent A) gave a single spot having R_{Gal} 4.10 corresponding with authentic 2-acetamido-2,6-dideoxy-D-talose and g.l.c. (190 °C) of the trimethylsilylated (31) equilibrated product showed four peaks having T_{GN} 0.53 (17%), 0.62 (46%), 0.98 (25%), and 1.07 (12%). The 2-acetamido-2,6-dideoxy-D-talose (0.6 g) which failed to crystallize was hydrolyzed with 3 *N* hydrochloric acid for 2 h at 100 °C and following concentration to dryness the product afforded pure 2-amino-2,6-dideoxy-D-talose hydrochloride (0.48 g) which gave a single ninhydrin positive spot on paper chromatography (solvent B) with R_{GN} 1.70 and had m.p. 164–165 °C and $[\alpha]_D$ $+7 \rightarrow -10°$ (*c*, 0.5 in water) (lit. (18) m.p. 161.5–163.5 °C and $[\alpha]_D$ $+8 \rightarrow -10°$ (water); L-enantiomorph (20) m.p. 162–163 °C and $[\alpha]_D$ $-4 \rightarrow +10°$ (water) and (19) m.p. 163–164 °C and $[\alpha]_D$ +9° (water)).

Anal. Calcd. for $C_6H_{14}O_4NCl$: C, 36.09; H, 7.07; N, 7.01; Cl, 17.75. Found: C, 36.12; H, 7.02; N, 7.15; Cl, 17.55.

(5) 2-Acetamido-2,6-dideoxy-D-galactose

The syrupy mixture of 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol and 2-acetamido-1,2,6-trideoxy-1-nitro-D-galactitol (1.42 g) remaining from the ammonia treatment of 2,3,4,5-tetra-*O*-acetyl-1,6-dideoxy-1-nitro-D-galactitol and removal of the crystalline 2-acetamido-1,2,6-trideoxy-1-nitro-D-talitol (section 3 above) was treated under the modified Nef conditions (as in section 4 above) to give a mixture of 2-acetamido-2,6-dideoxy-D-talose and 2-acetamido-2,6-dideoxy-D-galactose (1.1 g) which from concentrated ethanol solution gave crystalline 2-acetamido-2,6-dideoxy-D-galactose (0.48 g) which was removed leaving essentially pure 2-acetamido-2,6-dideoxy-D-talose as a syrup.

The 2-acetamido-2,6-dideoxy-D-galactose on paper chromatography (solvent A) gave a single spot R_{Gal} 3.02 and after recrystallization from ethanol the crystals (0.37 g) had m.p. 201–202 °C and $[\alpha]_D$ $+109 \rightarrow +87°$ (*c*, 0.4 in water) (lit. (13) m.p. 196–197 °C and $[\alpha]_D$ $+129 \rightarrow +92°$ (water); L-enantiomorph (21) m.p. 197–198 °C and $[\alpha]_D$ $-119 \rightarrow -82°$ (water)).

Anal. Calcd. for $C_8H_{15}O_5N$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.69; H, 7.44; N, 7.01.

G.l.c. (190 °C) of the trimethylsilylated (31) crystalline 2-acetamido-2,6-dideoxy-D-galactose gave a single peak T_{GN} 1.03 while the water equilibrated glycose gave two peaks having T_{GN} 1.03 (56%) and 1.75 (44%).

(6) 2-Amino-2,6-dideoxy-D-galactose Hydrochloride

2-Acetamido-2,6-dideoxy-D-galactose (0.2 g) after hydrolysis with 3 *N* hydrochloric acid for 2 h at 100 °C afforded crystalline 2-amino-2,6-dideoxy-D-galactose hydrochloride from methanol–acetone solution which gave a single ninhydrin positive spot on paper chromatography (solvent B) with R_{GN} 1.52 and had m.p. 192–193 °C and $[\alpha]_D$ $+120 \rightarrow +93°$ (*c*, 0.4 in water) (lit. (13) m.p. 192 °C and $[\alpha]_D$ $+117 \rightarrow +92°$ (water); L-enantiomorph (21) m.p. 192–193 °C and $[\alpha]_D$ $-119 \rightarrow -92°$ (water)).

Anal. Calcd. for $C_6H_{14}O_4NCl$: C, 36.09; H, 7.07; N, 7.01: Cl, 17.75. Found: C, 36.01; H, 6.98; N, 7.10; Cl, 17.60.

*(B) 2-Amino-2,6-dideoxy-*D*-talose Hydrochloride and 2-Amino-2,6-dideoxy-*D*-galactose Hydrochloride*

*(1) 2-Acetamido-2,6-dideoxy-*D*-talose and 2-Acetamido-2,6-dideoxy-*D*-galactose*

5-Deoxy-L-lyxose (21, 25) (5 g) was condensed with nitromethane (as in Section A.1) to yield the sodium salts of the 1,6-dideoxy-1-nitro-hexitols which were deionized (Rexyn 101(H$^+$)) and concentrated to a syrup (6.4 g). Acetylation of the syrup (as in Section A.2) gave the tetra-*O*-acetates of 1,6-dideoxy-1-nitro-L-talitol and 1,6-dideoxy-1-nitro-L-galactitol (11.3 g) which were treated with methanolic ammonia (as in Section A.3) and, following the removal of acetamide, the mixture of 2-acetamido-1,2,6-trideoxy-1-nitro-L-talitol and 2-acetamido-1,2,6-trideoxy-1-nitro-L-galactitol (7 g) was obtained as a syrup. The mixed 2-acetamido-1,2,6-trideoxy-1-nitro-hexitols were treated under the modified Nef reaction conditions (as in Section A.4) to yield 2-acetamido-2,6-dideoxy-L-talose and 2-acetamido-2,6-dideoxy-L-galactose (4.9 g). On keeping at room temperature, the concentrated ethanol solution of the product gave crystals of 2-acetamido-2,6-dideoxy-L-galactose (0.98 g) leaving essentially pure (*ca.* 90%) 2-acetamido-2,6-dideoxy-L-talose as a syrup (3.7 g).

The 2-acetamido-2,6-dideoxy-L-galactose after recrystallization from ethanol gave a single spot on paper chromatography (solvent A) R_{Gal} 3.02 and g.l.p.c. of the trimethylsilylated product gave a chromatogram identical with the D-enantiomorph. The crystals had m.p. 195–198 °C and $[\alpha]_D -116 \rightarrow -83^\circ$ (*c*, 0.2 in water).

Anal. Calcd. for $C_8H_{15}O_5N$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.59; H, 7.30; N, 7.02.

*(2) 2-Amino-2,6-dideoxy-*L*-galactose Hydrochloride*

2-Acetamido-2,6-dideoxy-L-galactose (0.3 g) was hydrolyzed with 3 *N* hydrochloric acid for 3 h at 100 °C and the concentrated product gave crystalline 2-amino-2,6-dideoxy-L-galactose (0.23 g) which gave a single ninhydrin positive spot on paper chromatography R_{GN} 1.52 (solvent B) and had m.p. 191–193 °C and $[\alpha]_D -115 \rightarrow -95^\circ$ (*c*, 0.5 in water).

Anal. Calcd. for $C_6H_{14}O_4NCl$: C, 36.09; H, 7.07; N, 7.01. Found: C, 36.00; H, 7.11; N, 7.07.

*(3) 2-Amino-2,6-dideoxy-*L*-talose Hydrochloride*

The impure 2-acetamido-2,6-dideoxy-L-talose (3.7 g) was hydrolyzed with 3 *N* hydrochloric acid (50 ml) for 3 h at 100 °C and following concentration, the methanol–acetone solution of the residue gave crystalline 2-amino-2,6-dideoxy-L-talose hydrochloride (2.3 g) which gave a single ninhydrin positive spot on paper chromatography R_{GN} 1.71 (solvent B) and had m.p. 163–164.5 °C and $[\alpha]_D -5 \rightarrow +10^\circ$ (*c*, 0.4 in water).

Anal. Calcd. for $C_6H_{14}O_4NCl$: C, 36.09; H, 7.07; N, 7.01. Found: C, 36.02; H, 7.11; N, 7.00.

1. E. J. Smith. Biochem. Biophys. Res. Commun. **15**, 593 (1964).
2. O. Lüderitz, J. Gmeiner, B. Kickhöfen, H. Meyer, and R. Wheat. J. Bacteriol. **95**, 490 (1968).
3. R. R. Colwell, E. J. Smith, and G. B. Chapman. Can. J. Microbiol. **14**, 165 (1968).
4. N. Suzuki, A. Suzuki, and A. Fukasawa. J. Jap. Biochem. Soc. **42**, 130 (1970).
5. S. G. Wilkinson and K. A. Carby. J. Gen. Microbiol. **66**, 221 (1971).
6. B. Jann and K. Jann. Eur. J. Biochem. **5**, 173 (1968).
7. F. Ørskov, I. Ørskov, B. Jann, E. Müller-Seitz, and O. Westphal. Acta path. microbiol. scandinav. **71**, 339 (1967).
8. M. J. Crumpton and D. A. L. Davies. Biochem. J. **70**, 729 (1958).
9. R. Wheat, E. L. Rollins, and J. Leatherwood. Nature, **202**, 492 (1958).
10. R. W. Wheat, E. L. Rollins, and J. M. Leatherwood. J. Biol. Chem. **238**, 26 (1963).
11. J. D. Higginbotham and M. Heidelberger. Carbohydr. Res. **23**, 165 (1972).
12. N. Sharon, I. Shif, and U. Zehavi. Biochem. J. **93**, 210 (1964).
13. U. Zehavi and N. Sharon. J. Org. Chem. **29**, 3654 (1964).
14. G. T. Barry and E. Roark. Nature, **202**, 493 (1964).
15. S. A. Barker, J. S. Brimacombe, M. J. How, and M. Stacey. Nature, **189**, 303 (1961).
16. J. A. Cifonelli, P. A. Rebers, M. B. Perry, and J. K. N. Jones. Biochem. **5**, 3066 (1966).
17. S. A. Barker, M. Stacey, and J. M. Williams. Bull. Soc. Chim. Biol. **12**, 1611 (1960).
18. J. S. Brimacombe and M. J. How. J. Chem. Soc. 5037 (1962).
19. P. M. Collins and W. G. Overend. Chem. Ind. (London), 375 (1963).
20. J. S. Brimacombe, J. G. H. Bryan, and M. Stacey. Carbohydr. Res. **1**, 258 (1965).
21. R. Kuhn, W. Bister, and W. Dafeldecker. Ann. **628**, 186 (1959).
22. H. H. Baer. Advan. Carbohydr. Chem. Biochem. **24**, 67 (1969).
23. L. Hough and T. J. Taylor. J. Chem. Soc. 3544 (1955).
24. C. Satoh and A. Kiyomoto. Chem. Pharm. Bull. Tokyo, **12**, 615 (1964).
25. R. K. Hulyalkar and M. B. Perry. Can. J. Chem. **43**, 3241 (1965).
26. S. M. Partridge. Biochem. J. **42**, 238 (1948).
27. W. E. Trevelyan, D. D. Procter, and J. S. Harrison. Nature, **166**, 444 (1950).
28. L. Hough, J. K. N. Jones, and W. H. Wadman. J. Chem. Soc. 1702 (1950).
29. S. W. Gunner, J. K. N. Jones, and M. B. Perry. Chem. Ind. (London), 255 (1961).
30. S. W. Gunner, J. K. N. Jones, and M. B. Perry. Can. J. Chem. **39**, 1892 (1961).
31. M. B. Perry. Can. J. Biochem. **42**, 451 (1964).