199. *Amine*-N-*glycosides. Part I. Arylamine*-N-*glucosides.*

By JOHN HONEYMAN and A. R. TATCHELL.

Aniline and glucose react under various conditions to give the same aniline-*N*-glucoside, which mutarotates in several solvents. Acetylation of aniline-*N*-glucoside gives a mixture of α- and β-aniline-*N*-glucopyranoside tetra-acetates which can be deacetylated to the original aniline-*N*-glucoside.

p-Toluidine-*N*-glucoside is obtained in a pure crystalline form which has been acetylated to β-*p*-toluidine-*N*-glucopyranoside tetra-acetate.

The pyranose ring structure of these amine-*N*-glucosides is probable, but not certain.

THE reaction products obtained when sugars react with amines have been known for many years, but although much work has been carried out to determine their structure there is still no clear picture of their nature. The early workers (Schiff, *Annalen*, 1870, **154**, 30; Sorokin, *Ber.*, 1886, **19**, 513) prepared compounds whose structures were considered to be of the Schiff's base type (Schiff and Straus, *Ber.*, 1894, **27**, 1287) or of the cyclic glycosidic type (Marchlewski, *J. prakt. Chem.*, 1894, [ii], **50**, 95). The methylation studies of Irvine and his co-workers from 1908 to 1911 (*e.g.*, Irvine and Hynd, *J.*, 1911, **99**, 161) furnished strong evidence of the cyclic nature of these compounds. Their isolation of tetramethyl aniline-*N*-glucopyranoside was held to be evidence for considering the mutarotating aniline-*N*-glucoside to be α- and β-aniline-*N*-glucopyranosides. Since then, certain arylamine-*N*-pentosides have been prepared which have been assigned the furanose structure solely on the basis of their reaction with triphenylmethyl chloride. In particular, certain arylamine-*N*-pentosides have thus been held to be furanosides (Kuhn and Ströbele, *Ber.*, 1937, **70**, 773) although later workers claim to have shown that at least one of these is actually a pyranoside (mentioned by Howard, Kenner, Lythgoe, and Todd, *J.*, 1946, 855, but details not yet published). Similarly, xylidine-*N*-riboside prepared in boiling alcohol is considered to be a furanoside (Kuhn and Birkofer, *Ber.*, 1938, **71**, 621), whereas the xylidine-*N*-riboside prepared in alcohol at room temperature is thought to be a pyranoside (Berger and Lee, *J. Org. Chem.*, 1946, **11**, 75). Under similar conditions aniline reacts with ribose to give two aniline-*N*-ribosides (Berger and Lee, *loc. cit.*); these were cyclic because acetylation of each led to a triacetate; although the triacetates were glasses, no characteristic physical data were given, and they had acetyl contents somewhat lower than the theoretical. Berger and Lee held that they were distinct compounds. Removal of the aniline residue from each gave two amorphous ribose triacetates (Berger, Solmssen, Leonard, Wenis, and Lee, *J. Org. Chem.*, 1946, **11**, 91). These workers considered them to be ribose 2 : 3 : 4-triacetate (from aniline-*N*-ribopyranoside) and ribose 2 : 3 : 5-triacetate (from aniline-*N*-ribofuranoside). Examination of the data of these workers shows that one of the compounds, with acetyl content 40·9% (theoretical, 46·7%), had $[\alpha]_D^{30}$ −26·3°, while the other, of acetyl content 41·5%, had $[\alpha]_D^{30}$ −24·2°. It is considered, therefore, that there is no evidence that two distinct aniline-*N*-riboside triacetates have been prepared. On the contrary, other workers (Todd *et al.*, *loc. cit.*) have shown that the two aniline-*N*-ribosides are acetylated to the same aniline-*N*-ribopyranoside 2 : 3 : 4-triacetate. Furthermore, Berger and Lee have shown that benzoylation of the two aniline-*N*-ribosides, followed by hydrogenation, gives the same ribitylaniline tribenzoate. The sole remaining chemical evidence for the pyranose and furanose structures assigned to the aniline-*N*-ribosides rests on the reaction of the compounds with triphenylmethyl chloride. This reagent is now known to be unsatisfactory for detecting primary alcohol groups such as would be present in aniline-*N*-ribofuranoside and absent in aniline-*N*-ribopyranoside, for it reacts with secondary as well as with primary alcohol groups (Hockett and Hudson, *J. Amer. Chem. Soc.*, 1931, **53**, 4456; McIlroy, *J.*, 1946, 100). Crystalline triphenylmethyl derivatives of β-methylxylopyranoside, a compound similar in structure to aniline-*N*-ribopyranoside, have been isolated (Jackson, Hockett, and Hudson, *J. Amer. Chem. Soc.*, 1934, **56**, 947).

Indeed, the work of Berger and Lee really confirms the unsatisfactory nature of this reagent. From the compound they consider to be aniline-*N*-ribofuranoside they isolated a tan-coloured amorphous product giving the elementary analysis of a monotrityl aniline-*N*-riboside combined with 1·75 molecules of water. No attempt was made to show that the trityl residue was attached to $C_{(5)}$. Under similar conditions the aniline-*N*-ribopyranoside gave a tarry product which could not be purified. It is clear that Berger and Lee have not shown that this second isomer reacts less readily with triphenylmethyl chloride. Methylation studies have been unproductive (Berger and Lee, *loc. cit.*), probably because of the instability of the *N*-glycosides to alkali. Oxidation with periodate has also been found to be of no value (Berger and Lee, *loc. cit.*; Howard, Kenner, Lythgoe, and Todd, *J.*, 1946, 861). It seems fair to say, therefore, that there

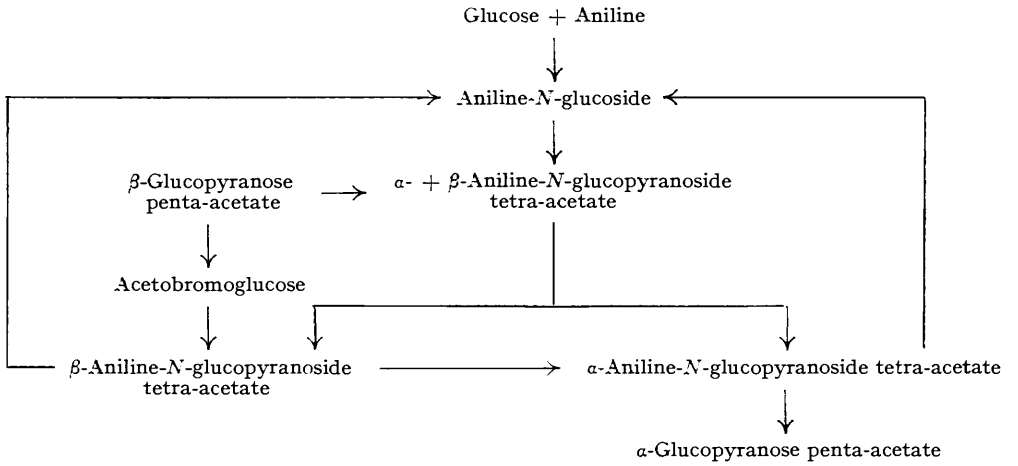
has been no chemical evidence presented so far for assigning the furanose structure to one of the aniline-*N*-ribosides. No derivative with this structure has been isolated. Of the physical data the melting points, as Berger and Lee point out, are unreliable. For 3 : 4-xylidine-*N*-ribofuranoside Kuhn and Birkofer (*loc. cit.*) give m. p. 118°, whereas this compound prepared identically was found by Berger and Lee to have m. p. 128—130°. The corresponding pyranoside of these workers has m. p. 110—112°. For aniline-*N*-ribopyranoside Todd and his co-workers give m. p. 119°, whereas Berger and Lee give m. p. 125—127°. For the corresponding furanoside the former workers give m. p. 126—127°, whereas the latter record m. p. 138—140°. In addition, Berger and Lee have found that mixing the two aniline-*N*-ribosides does not, as a rule, lead to a depressed melting point.

It remains to consider the specific rotations, and here lies the sole evidence for the existence of the two ring-isomers of arylamine-*N*-ribosides. The 3 : 4-xylidine-*N*-ribopyranoside has $[\alpha]_D^{24}$ $+171{\cdot}7^\circ \longrightarrow +56{\cdot}5^\circ$ (*c*, 0·5 in pyridine), while the corresponding furanoside has $[\alpha]_D^{25}$ $+94{\cdot}5^\circ \longrightarrow +53{\cdot}0^\circ$ (*c*, 1 in pyridine). The final values are so close that no conclusion that they represent α- + β-ribopyranosides and α- + β-ribofuranosides, respectively, is tenable. It might as well be that the former compound is, say, pure α-pyranoside mutarotating to an equilibrium mixture of α- + β-pyranoside, whereas the latter is a mixture of α- and β-pyranosides, richer in the β-anomer, mutarotating to the same equilibrium mixture of α- + β-pyranosides. With the aniline-*N*-ribosides the difference in specific rotation is marked and appears to be conclusive. The product of condensation in boiling alcohol, considered by Berger and Lee to be aniline-*N*-ribofuranoside, has $[\alpha]_D^{27}$ $+176{\cdot}5^\circ \longrightarrow +156{\cdot}6^\circ$ (*c*, 3 in pyridine) (Berger and Lee; Todd *et al.*), whereas the product of condensation in alcohol at room temperature, considered to be the pyranoside, has $[\alpha]_D^{24}$ $+63{\cdot}4^\circ \longrightarrow +48{\cdot}6^\circ$ (*c*, 1 in pyridine) (Berger and Lee; Todd *et al.*), and, since the two compounds mutarotate in the same direction but not to the same final equilibrium value, there appears to be a strong case for believing that two different ring-isomers have been obtained. There is, however, no acceptable evidence for deciding which has the furanose and which the pyranose structure. Thus, Berger and Lee's belief that the pyranose compound was converted into the more stable furanose compound simply by refluxing in alcohol or slowly at room temperature in alcohol, or by drying over phosphoric oxide in a vacuum, requires further investigation. (This investigation has already been begun in our laboratories.)

The case of the aniline-*N*-D-arabinosides must also be mentioned. The product of condensation in alcohol at room temperature, considered by Berger and Lee (*J. Org. Chem.*, 1946, **11**, 84), by analogy with the ribosides, to be aniline-*N*-arabinopyranoside, has m. p. 130°, $[\alpha]_D^{28}$ $+8{\cdot}9^\circ \longrightarrow -13{\cdot}2^\circ$ (*c*, 1·9 in methanol, after 48 hours), $[\alpha]_D^{29}$ $+68^\circ \longrightarrow -4{\cdot}2^\circ$ (*c*, 3 in pyridine, after 48 hours). The product, prepared in boiling alcohol by following the same procedure as an earlier worker [Hanaoka, *J. Biochem.* (*Japan*), 1940, **31**, 95], had m. p. 130°, $[\alpha]_D^{29}$ $+27{\cdot}4^\circ \longrightarrow -8{\cdot}0^\circ$ (*c*, 1·6 in methanol, after 24 hours), $[\alpha]_D^{29}$ $+82^\circ \longrightarrow +1{\cdot}48^\circ$ (*c*, 2 in pyridine, after 24 hours). Hanaoka cites m. p. 130°, $[\alpha]_D^{20}$ $+34^\circ \longrightarrow +2{\cdot}5^\circ$ (*c*, 1 in methanol). Again the values are too similar for certainty that different ring forms are present: the alternative explanation advanced in the case of the xylidine-*N*-ribosides appears to be equally valid.

It was in the light of the papers discussed above that the present work was started. During the course of this investigation it has been found that glucose reacts with aniline in boiling alcohol (Sorokin, *loc. cit.*), in aqueous alcohol at room temperature, and in boiling water (Weygand, *Ber.*, 1939, **72**, 1663), to give the same aniline-*N*-glucoside, mutarotating in methanol from an initial value of about $+10^\circ$ to a final value of about -52°. Despite many attempts to prepare this compound and to obtain it in a pure stable form it has invariably been obtained as a white solid which is not truly crystalline. It is precipitated from several solvents in a jelly-like form from which the last traces of solvent are difficult to remove, owing, it is considered, to the physical form of the product. When dry it is a hard white powder which, however, is unstable, becoming brown on storage at room temperature, even in a vacuum desiccator. Aniline-*N*-glucoside, like all compounds of this type, is readily hydrolysed by dilute acids. It is also attacked by aqueous alkali, and it therefore reduces Fehling's solution rapidly. No reproducible melting point was obtained for this product. Acetylation was successfully achieved with acetic anhydride in pyridine; under somewhat different conditions a similar mixture of tetra-acetates was obtained. The components of the mixture were shown to have pyranose structure since the removal of the aniline residue, followed by acetylation with acetic anhydride and zinc chloride, gave the known α-glucopyranose penta-acetate. Furthermore, the same mixture of aniline-*N*-glucoside tetra-acetates was obtained from α- or β-glucopyranose penta-acetate by hydrolysing the acetyl group from $C_{(1)}$ and treating the product with aniline (Frèrejacque, *Compt. rend.*, 1936,

202, 1190). This mixture of aniline-*N*-glucopyranoside tetra-acetates, while differing somewhat in melting range and specific rotation in different preparations, was invariably separable by fractional crystallisation or through the carbon tetrachloride complex of one of them (Frèrejacque, *loc. cit.*) into the two pure isomers. One of these, also obtained when acetobromoglucose reacts with aniline, is β-aniline-*N*-glucopyranoside, m. p. 97—98°, $[\alpha]_D^{16}$ −57° (*c*, 0·4 in chloroform); the other is α-aniline-*N*-glucopyranoside tetra-acetate, m. p. 149—150°, $[\alpha]_D^{16}$ +179° (*c*, 0·4 in chloroform). When the β-form is kept in methanol containing a trace of aqueous ammonia at room temperature it is slowly converted into the less soluble α-anomer. All the tetra-acetates mentioned here are deacetylated by methanol containing aqueous ammonia to the same aniline-*N*-glucoside which is obtained by direct condensation. These experiments show that aniline-*N*-glucoside is a mixture which reacts, when acetylated in pyridine, in the pyranose form only. It would appear probable although not certain, therefore, that the aniline-*N*-glucosides mentioned are mixtures of α- and β-aniline-*N*-glucopyranoside. These reactions are summarised in the annexed chart.



When *p*-toluidine is used instead of aniline rather different results are obtained. Thus, although prepared by different workers by different methods, only one *p*-toluidine-*N*-glucoside has been isolated which has well-defined crystalline form and sharp melting point. Acetylation of this glucoside has now been found to give a single tetra-acetate, m. p. 145—146°, $[\alpha]_D^{16}$ −34·2° in chloroform, which must be a derivative of β-*p*-toluidine-*N*-glucopyranoside, since it is identical with the compound prepared from acetobromoglucose and *p*-toluidine.

Although *p*-toluidine-*N*-glucoside is more stable than the corresponding aniline compound they both decompose on storage at room temperature. After about a year in specimen tubes both substances have decomposed to black tars. However, the tetra-acetates of both are stable at room temperature.

In all the cases recorded so far aniline- and *p*-toluidine-*N*-glucosides react to give derivatives with the pyranose ring-structure.

Experimental.

(The light petroleum used throughout had boiling range 60—80°.)

Aniline-N-glucoside.—Glucose (18 g., 1 mol.) was refluxed in absolute alcohol (150 ml.) with freshly re-distilled aniline (9·3 g., 1 mol.) for 2 hours. On cooling, a solid separated and was collected. This was recrystallised from absolute alcohol and washed with dry ether before being dried in an evacuated desiccator at room temperature. The almost white solid (15 g.), $[\alpha]_D^{18}$ +5·1° ⟶ −51·7° (after 24 hours) (*c*, 1·6 in methanol), melted with decomposition at temperatures varying between 110° and 150°, depending on the rate of heating. A further crop of product (6 g.), $[\alpha]_D^{18}$ +11·25° ⟶ −51·9° (after 24 hours) (*c*, 0·4 in methanol), was obtained by partial concentration of the reaction mother-liquor. Further concentration gave more product (3 g.), $[\alpha]_D^{18}$ +5° ⟶ −52·3° (total yield, 95%). Irvine and Gilmour give $[\alpha]_D$ +10° ⟶ −52° for the first fraction and $[\alpha]_D$ −20·1° ⟶ −52° for later fractions.

Glucose (5 g., 1 mol.) in absolute alcohol (15 ml.) and water (5 ml.) was left at room temperature for a week with aniline (8 g., 3 mols.). The solution was then evaporated to dryness over silica gel in an evacuated desiccator. The solid was purified by repeated washing with cold absolute alcohol and then with ether and dried as above. The appearance of the product (4 g., 53%), $[\alpha]_D^{18}$ +6° ⟶ −52·3° (*c*, 0·4 in methanol), was similar to the previous one.

Aniline-*N*-glucoside, prepared by the method of Weygand (*loc. cit.*), was a cream-coloured powder,

$[\alpha]_D^{18}$ $+10\cdot3 \longrightarrow -52\cdot5°$ (*c*, 0·4 in methanol). Weygand gives m. p. 140°, but does not mention the specific rotation. This method was the normal one used hereafter for preparing aniline-*N*-glucoside.

The solid products were examined microscopically under polarized light and were seen to be non-crystalline.

Mutarotation of Aniline-N-glucoside.—The mutarotation of aniline-*N*-glucoside in methanol and ethanol proceeds smoothly. In dry pyridine no change in rotation takes place but rapid mutarotation in pyridine–acetic acid was observed. The following values were obtained: $[\alpha]_D^{16}$ $-12\cdot5°$ (*c*, 2·0 in pyridine); $[\alpha]_D^{16}$ $-11\cdot3° \longrightarrow -62\cdot5°$ (after 24 hours) (*c*, 0·4 in pyridine containing a trace of glacial acetic acid); $[\alpha]_D^{16} \longrightarrow -60\cdot0°$ (equilibrium value after 6 minutes) (*c*, 0·8 in pyridine, 66 ml.; acetic acid 34 ml.).

Aniline-*N*-glucoside, $[\alpha]_D^{16}$ $+10\cdot5° \longrightarrow -52\cdot5°$ (*c*, 0·8 in methanol), was recovered by allowing the methanolic solution to evaporate at room temperature.

Acetylation of Aniline-N-glucoside.—Aniline-*N*-glucoside (20 g.) was dissolved in pyridine, and acetic anhydride (80 ml.) was added gradually at 0°. After 24 hours at room temperature the pyridine solution was poured on ice. After several hours the product was filtered off, washed with water, and dried in a vacuum at room temperature. The crude crystals (23 g., 64%), m. p. 80—85°, were recrystallised from absolute alcohol–light petroleum. During this recrystallisation an oil separated first, followed by a larger crop of crystals, m. p. 92—105°, $[\alpha]_D^{16}$ $+40\cdot2°$ (*c*, 2·5 in chloroform). These, after several recrystallisations, were a mixture of aniline-*N*-glucoside tetra-acetates, m. p. 88·5—92·5°, $[\alpha]_D^{16}$ $+45\cdot8°$ (*c*, 2·5 in chloroform) (Found: C, 56·4; H, 5·9; N, 3·3. $C_{20}H_{25}O_9N$ requires C, 56·7; H, 5·95; N, 3·3%). The oil which separated during the recrystallisation subsequently solidified and was purified by recrystallisation from a small volume of methanol and then from absolute alcohol–light petroleum. This product, which was subsequently proved to be *α-aniline-N-glucopyranoside tetra-acetate*, was a single substance, m. p. 149—150°, $[\alpha]_D^{16}$ $+180°$ (*c*, 2·5 in chloroform) (Found: C, 56·9; H, 6·0; N, 3·3%).

The product of another acetylation was separated by the method of Frèrejacque (*loc. cit.*). Aniline-*N*-glucoside tetra-acetate, m. p. 88—92·5°, $[\alpha]_D^{16}$ $+45\cdot7°$ (10 g.), was separated into *β*- (6 g., 60%), m. p. 97—98°, $[\alpha]_D^{16}$ $-57°$ (*c*, 0·4 in chloroform), $[\alpha]_D^{16}$ $-68\cdot3°$ (*c*, 0·4 in 90% aqueous alcohol) and *α*-aniline-*N*-glucopyranoside tetra-acetate (4 g., 40%), m. p. 149—150°, $[\alpha]_D^{16}$ $+179°$ (*c*, 0·4 in chloroform).

In another experiment aniline-*N*-glucoside (5 g.) was heated on a water-bath in pyridine (20 ml.) and acetic anhydride (20 ml.). After 20 minutes' heating the solution was allowed to cool and left overnight at room temperature. The product was isolated as in the previous preparation, and after recrystallisations from alcohol–light petroleum it was shown similarly to be a mixture of *α*- and *β*-aniline-*N*-glucopyranoside tetra-acetates (5 g., 62%), m. p. 92—110°, $[\alpha]_D^{16}$ $+55\cdot3°$ (*c*, 2·4 in chloroform).

A similar product was obtained by treating aniline-*N*-glucoside for 30 minutes in pyridine with acetic anhydride in the presence of a small amount of perchloric acid.

In another experiment the lævorotatory form of aniline-*N*-glucoside was acetylated. Aniline-*N*-glucoside (5 g.) in pyridine (20 ml.) containing acetic acid (0·5 ml.) was kept at room temperature for 3 days before addition of acetic anhydride (20 ml.) at 0°. After a further day at room temperature the product was isolated as before. After recrystallisations from alcohol–light petroleum there remained a mixture of *α*- and *β*-aniline-*N*-glucopyranoside tetra-acetates (5 g., 62%), m. p. 88—95°, $[\alpha]_D^{16}$ $+67\cdot4°$ (*c*, 0·8 in chloroform).

Conversion of β- into α-Aniline-N-glucopyranoside Tetra-acetate.—If a saturated solution of any of the above mixed *α*- and *β*-aniline-*N*-glucopyranoside tetra-acetates, or of the pure *β*-anomer, in methanol containing a drop of aqueous ammonia (10%) was kept at room temperature, then a gradual separation of crystalline material took place. This material, on recrystallisation, was found to be *α*-aniline-*N*-glucopyranoside tetra-acetate (80% yield), m. p. 149—150°, $[\alpha]_D^{16}$ $+180°$ (*c*, 0·4 in chloroform).

Conversion of Aniline-N-glucopyranoside Tetra-acetates into α-Glucopyranose Penta-acetate.—The hydrolysis of aniline-*N*-glucopyranoside tetra-acetates was successfully achieved by the method of Berger and Lee (*loc. cit.*). The crude glucose tetra-acetate was obtained as a viscous red syrup (3·5 g., 87%) which did not crystallise. This syrup (2 g.) was heated on a boiling-water bath for 30 minutes with acetic anhydride (25 ml.) and powdered anhydrous zinc chloride (0·5 g.). After being poured into water and kept for several hours the product was extracted with chloroform. The extract was washed free from acid and dried before the chloroform was evaporated off, leaving a syrup which crystallised from alcohol. The product was *α*-glucopyranose penta-acetate (1·7 g., 78%), m. p. 110—111°, $[\alpha]_D^{16}$ $+100\cdot9°$. A mixed m. p. with authentic *α*-glucopyranose penta-acetate, m. p. 110—111°, showed no depression.

Preparation of Aniline-N-glucopyranoside Tetra-acetates from β-Glucopyranose Penta-acetate.—The method of Frèrejacque (*loc. cit.*) was used. The product was recrystallised from alcohol–light petroleum and was a mixture of *α*- and *β*-aniline-*N*-glucopyranoside tetra-acetates, m. p. 88—92·5°, $[\alpha]_D^{16}$ $+46\cdot1°$ (*c*, 0·9 in chloroform). This mixture was separated by the procedure already described into *α*-aniline-*N*-glucopyranoside tetra-acetate and the corresponding *β*-anomer.

Preparation of β-Aniline-N-glucopyranoside Tetra-acetate from Acetobromoglucose.—The method of Baker (*J.*, 1928, 1583) was used. After recrystallisation from ether–light petroleum there was obtained pure *β*-aniline-*N*-glucopyranoside tetra-acetate, m. p. 96—97°, $[\alpha]_D^{16}$ $-70\cdot3°$ (*c*, 0·4 in 90% alcohol), $[\alpha]_D^{16}$ $-55°$ (*c*, 0·4 in chloroform). Baker (*loc. cit.*) gives m. p. 98°, $[\alpha]_D^{16}$ $-73\cdot3°$ (in 90% alcohol).

Deacetylation of Aniline-N-glucopyranoside Tetra-acetates.—The standard procedure was to allow the tetra-acetate (4 g.) to remain in methanol (40 ml.) containing aqueous ammonia (5 ml., *d* 0·880) at room temperature for 3 days. After removal of the solvent at room temperature under reduced pressure the product was purified by recrystallisation from alcohol. In different experiments, *α*-aniline-*N*-glucopyranoside tetra-acetate, the *β*-anomer, and mixtures of *α*- and *β*-anomers were used. In each case aniline-*N*-glucoside was obtained: $[\alpha]_D^{18}$ *ca.* $+10° \longrightarrow -52°$ (in methanol), *i.e.*, identical with the substance prepared directly from glucose and aniline.

p-Toluidine-N-glucoside.—Glucose (5·4 g., 1 mol.) was heated with *p*-toluidine (3·2 g., 1 mol.) and water (1 ml.) on a boiling-water bath until homogeneous (15 minutes). Ether (100 ml.) was added and the precipitated solid (6 g., 86%) filtered off. Recrystallisation from ether–alcohol gave needle-shaped crystals of *p*-toluidine-*N*-glucoside, m. p. 117—118°, $[\alpha]_D^{24}$ $-101\cdot2° \longrightarrow -45\cdot8°$ (*c*, 0·5 in methanol).

This same compound has been obtained by different procedures by Irvine and Gilmour (*J.*, 1909, **95**, 1548) and Kuhn and Dansi (*Ber.*, 1936, **69**, 1745).

β-p-*Toluidine-N-glucopyranoside Tetra-acetate.*—*β*-*p*-Toluidine-*N*-glucoside tetra-acetate was prepared from acetobromoglucose by the method of Baker (*loc. cit.*). After recrystallisation from absolute alcohol pure *β*-*p*-toluidine-*N*-glucopyranoside tetra-acetate was obtained, having m. p. 144—145°, $[\alpha]_D^{18}$ −33·4° (*c*, 0·4 in chloroform).

p-Toluidine-*N*-glucoside (5 g.) was dissolved in pyridine (20 ml.) and acetic anhydride (20 ml.) at 0°. After 24 hours at room temperature the solution was poured on ice. After several hours the solid product was collected and recrystallised from alcohol. This was *β*-*p*-toluidine-*N*-glucopyranoside tetra-acetate (5 g., 70%), m. p. 145—146°, $[\alpha]_D^{16}$ −34·2° (*c*, 0·5 in chloroform), mixed m. p. with the compound prepared above, 144—145°. For this compound Kuhn and Dansi (*loc. cit.*) cite m. p. 144—145°, $[\alpha]_D^{18}$ −57·5° (in methyl acetate).

UNIVERSITY OF LONDON, KING'S COLLEGE. [*Received, December 19th*, 1949.]