$C_{21}H_{24}N_2O_3$; C, 71·58; H, 6·82; O, 13·64; N, 7·95; one OCH_3 8·8%; one CCH_3 4·3%; two active H, 0·57. Calc. for $C_{21}H_{26}N_2O_3$: C, 71·19; H, 7·32; O, 13·56; N, 7·91; one OCH_3 8·7%; one CCH_3 4·2; two active H, 0·56%).

Hydrolysis of Lochnericine. Lochnericine (11 mg) and 10% alcoholic sodium hydroxide (0·6 ml) was sealed and heated in the water-bath for 30 min. The deep orange yellow solution on careful additions of sulphuric acid gave at the isoelectric point of about 7 pH, a sparingly soluble yellowish brown amorphous solid, soluble in and forming salts with acids and alkalies.

Acknowledgement—For the analytical results, U.V. and I.R. spectra we are indebted to Dr. A. Hofmann, Vize Direktor Der Sandoz A.G. Basel, Switzerland.

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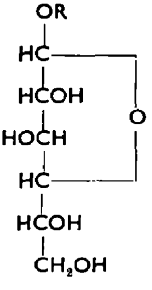
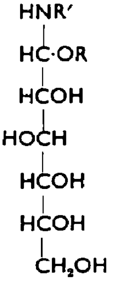
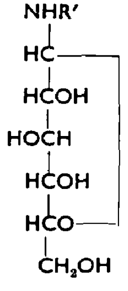
A novel trans-glycosylation reaction

(*Received* 12 *December* 1958)

THE replacement of one aglycone in an O- or N-glycoside by another aglycone has been variously termed 'transglycosidation'[1] or 'transglycosylation'.[2,3] Such a process has been found to occur only with difficulty when one O-aglycone replaces another,[1] but proceeds readily under mildly acidic conditions for the replacement of one N-aryl group by another in the N-aryl-glycosylamines.[2,3] So far no case has been recorded of the replacement of an O-aglycone by a N-aglycone. In the course of an investigation of some colour reactions of arylamines and sugars, we have noted such a replacement, and shown that in certain cases it may proceed readily under mildly acidic conditions. Treatment of methyl-glucofuranoside (I, R = CH_3) with *p*-nitroaniline in anhydrous methanol containing 0·01 to 0·1 mol of hydrogen chloride, leads to rapid formation of a mixed O- and N-glycoside (II, R = CH_3: R′ = $pNO_2{\cdot}C_6H_4$) which on prolonged treatment yields the N-*p*-nitrophenyl-D-glucosylamine (III, R′ = $pNO_2{\cdot}C_6H_4$).


I


II


III

Similarly *p*-chloroaniline under the same conditions reacts with methyl-glucofuranoside to yield a compound II, (R = CH_3:R′ = $pCl{\cdot}C_6H_4$). In contrast methyl-α-D-glucopyranoside was recovered unchanged even on prolonged boiling under these conditions. Similar results were observed with the ethyl- and *n*-propyl- glucosides, and with the corresponding galactose compounds.

When methyl-3:6-anhydro-α-D-glucopyranoside was added to a methanolic solution of *p*-nitroaniline or *p*-chloroaniline containing catalytic proportions of hydrochloric acid, a similar reaction occurred.

[1] W. Pigman and R. O. Laffre, *J. Amer. Chem. Soc.* 73, 4994 (1951).

[2] R. Bognar and P. Nanasi, *Nature, Lond.* 171, 475 (1953).

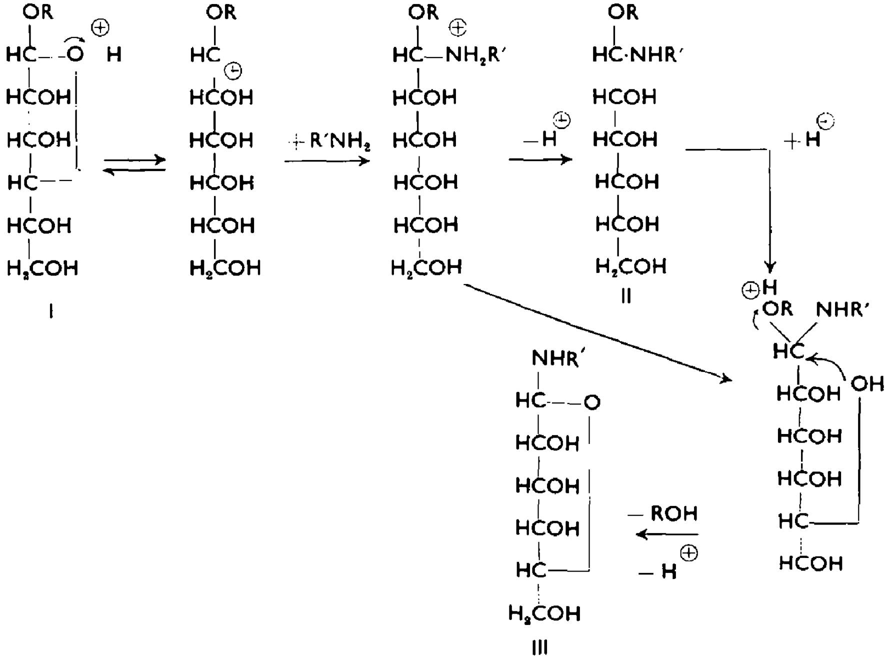
[3] (a) R. Bognar and P. Nanasi, *J. Chem. Soc.* 189 (1955); (b) W. G. Overend and J. B. Lee, unpublished observations.

It would appear that reaction only occurs readily when the labile furanose ring is present, or when the (usually stable) pyranose ring system is rendered labile[4] as in the bridged ring system of the 3:6-anhydro-glycosides. As the reaction proceeds readily in anhydrous conditions it cannot involve hydrolysis and recombination.

The isolation of compounds of type II, suggests that these may be formed intermediately in the conversion of the O-glycoside (I) to the, normally pyranose,[5] N-aryl-glycosylamine. Proton addition to the ring oxygen, yielding a [C(1)] carbonium ion to which the amine may then add, the charged product expelling a proton, or upon prolonged treatment eliminating the O-alkyl group, is suggested, as illustrated below.

The well-known conversion of methyl-3:6-anhydro-glucopyranosides to the furanose form, and of the corresponding galactose compound to the open chain form, proceeds readily under anhydrous conditions,[4] suggesting an analogous intermediate carbonium ion formation with which, in the presence of an arylamine, formation of an N-aryl-glycosylamine occurs. Alternatively the protonated arylamine may react directly with the O-glycoside.

This study has not been extended to include more basic arylamines: these may react less readily as studies have shown[3(b)] that the arylamine–hexose bond becomes weaker with increasing basicity of the amine.



Solutions of amine hydrochlorides, particularly the nitro-anilines, are useful spray reagents for paper chromatographic detection of alkyl-O-glycofuranosides and alkyl-3:6-anhydro-O-glycosides, rapidly yielding coloured spots at room temperature thus readily differentiating these compounds from the corresponding alkyl-O-glycopyranosides which yield spots only very slowly (ca. 24 hr) under the same conditions. The basis of these colour reactions would appear therefore to depend upon the primary formation of the glycosylamine, followed possibly by rearrangements of the type reported by Amadon.[6]

EXPERIMENTAL

1-O-*Methyl*-N-p-*chlorophenyl*-D-*aldehydo-glucosylamine*. *p*-Chloro-aniline (0·8 g) and methanolic hydrogen chloride (1 drop, 17 %) were added to a hot methanolic solution of methyl α-D-glucofuranoside, (0·92 g). After 5 min the solution was cooled, neutralised (barium carbonate), filtered and

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[4] W. Haworth, N. Owen and F. Smith, *J. Chem. Soc.* 88, (1941).

[5] J. Honeyman and A. R. Tatchell, *J. Chem. Soc.* 967 (1950).

[6] N. Amadon, *Atti. Acad. Lincei* [6], 2, 337 (1925); 13, 72 (1931).

evaporated to dryness at the pump. Extraction of the residue with hot methanol yielded a solution of 1-O-methyl-N-*p*-chlorophenyl-D-aldehydoglucosylamine (II: $R' = p\text{Cl}\cdot C_6H_4$. $R = CH_3$), deposited on cooling as white cubes, m.p. 145°, $[\alpha]_D^{16}$ +85° (*c* 0·165 in pyridine). (Found: C, 48·0, H, 5·9, N, 4·3; $C_{13}H_{20}O_6NCl$ requires: C, 48·5, H, 6·2, N, 4·3%).

1-O-*Methyl*-N-p-*nitrophenyl*-D-*aldehydoglucosylamine*. *p*-Nitro-aniline (1·5 g) and hydrochloric acid (30%, one drop) were added to a hot methanolic solution (15 ml) of methyl α-D-glucofuranose (1·4 g) and the clear solution allowed to cool. Bright yellow needles were deposited. Recrystallisation from methanol yielded 1-O-methyl-N-*p*-nitrophenyl-D-aldehydo-glucosylamine, (II; $R' = p\text{-}NO_2\cdot C_6H_4$. $R = CH_3$), m.p. 162–3°, $[\alpha]_D^{18}$ +46° (*c* 0·228 in pyridine). (Found: C, 44·4; H, 5·9; N, 7·1; $C_{13}H_{20}N_2O_8\cdot H_2O$. Requires: C, 44·6; H, 6·2; N, 8·0%).

(a) Methyl α-D-glucopyranoside (2·0 g) was treated with *p*-chloroaniline in methanol containing hydrogen chloride (3 drops, 17%). The mixture was refluxed (20 min). On cooling methyl α-D-glucopyranoside (1·1 g m.p., and m.p. on admixture with an authentic sample, 164·5–165°) separated. A further portion (0·6 g, m.p. 163–165°) was recovered from the mother liquor. Unchanged material also was recovered using *p*-nitroaniline in place of *p*-chloroaniline under the same conditions.

Under the above conditions ethyl *β*- and α-D-glucofuranosides yielded, with *p*-nitroaniline, N-*p*-nitrophenyl-D-glucosylamine, m.p. 183–185°, $[\alpha]_D^{28}$ −190° (*c* 1·1 in pyridine). Bognar[3(a)] reports m.p. 185°, $[\alpha]_D$ −193° (*c* 1·3 in pyridine). Similarly *n*-propyl-D-glucofuranose (α:*β* mixture) yielded a product m.p. 180°, giving no depression on admixture with an authentic sample. This compound yielded a tetra-acetate, yellow needles m.p. 168°, $[\alpha]_D^{18}$ −77·5° (*c* 0·109 in pyridine). (Found: C, 51·5; H, 4·5; N, 5·9; $C_{20}H_{24}N_2O_{11}$. Requires: C, 51·3; H, 5·1; N, 6·0%).

A mixture of methyl-α- and *β*-D-galactofuranosides with *p*-nitroaniline under the above conditions yielded yellow needles, m.p. 200–201°, $[\alpha]_D^{18}$ −191° (*c* 2·0 in pyridine). Frerejacques[7] reports m.p. 203°, $[\alpha]_D$ −202°, for N-*p*-nitrophenyl-D-galactosylamine. Methyl-*β*-D-galactopyranoside did not react under the same conditions.

(b) Methyl-3:6-anhydro-α-D-glucopyranoside (0·7 g) was added to *p*-nitroaniline (1·2 g) in hot methanol containing a trace of hydrogen chloride. The solution upon slow evaporation deposited deep-red plates, recrystallised from methanol, (0·4 g), m.p. 141–143°, $[\alpha]_D^{18}$ −200° (*c* 0·8 in pyridine). (Found: C, 51·7; H, 4·3; $C_{18}H_{20}N_4O_8$. Requires: C, 51·4; H, 4·7%).

Acknowledgment—The authors wish to express their thanks to Professor W. Cocker for his interest in this work.

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[7] J. Frerejacques, *C. R. Acad. Sci., Paris* **207**, 638–640 (1938).