LETTERS TO THE EDITORS

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A New Procedure for Correlating the Structure of Glycosides

WHEN a sugar glycoside is oxidized with periodate, the ring is severed and a dialdehyde is formed[1]. In the case of pyranosides, cleavage is accompanied by the elimination of the —CH(OH)— group at C_3 as formic acid, whereas in the cleavage of pentofuranosides no formic acid is formed. The elucidation of this reaction by recognition of the dialdehydic character of the periodate oxidation product[1] and an extensive study of the corresponding dibasic acids and their salts have enabled the ring structure of glycosides to be determined and have provided a simple method for correlating the structure of the various glycosides[2].

We wish to report another procedure for correlating the structure of glycosides, which consists of the reduction, either catalytically (in alcohol at 100° C. with 1,500 p.s.i. hydrogen and Raney nickel) or with sodium borohydride (in aqueous solution at 25° C.), of the dialdehydes formed by periodate oxidation and an examination of the corresponding alcohols so formed. The dialdehydes (I) from the hexopyranosides and pentofuranosides give the alcohol (II), while the dialdehydes (III) from the pentopyranosides furnish the alcohol (IV). Similarly, the dialdehydes (V) from the 6-deoxy-hexopyranosides yield the alcohol (VI).

When the dialdehyde (I) is hydrogenated under pressure in the presence of a palladium-charcoal catalyst at room temperature, only the aldehydic group at C_4 of the original glycoside is reduced.

There is only one centre of asymmetry in the alcohols II and IV. Consequently, all the α-methyl-D-hexopyranosides and all the β-methyl-L-hexopyranosides should give the same optically active alcohol (A). Similarly, all the β-methyl-D-hexopyranosides and all the α-methyl-L-hexopyranosides should furnish the same optically active alcohol (B) which is the enantiomorph of A. The same relationship should exist among the alcohols (IV) produced from the α- and the β-methyl-D- and L-pentopyranosides. Experiments carried out on the glycosides of D-glucose, D-mannose, D-galactose, D-xylose and L-arabinose have shown that these relationships do actually hold true.

The alcohols represented by the general formulæ II, IV and VI, which can be produced in almost quantitative yield, are colourless fairly mobile liquids and they can be distilled *in vacuo* without decomposition. The enantiomorphic alcohols (II) obtainable from the hexopyranosides and pentofuranosides give the corresponding enantiomorphic tribenzoates, melting point 66°, $[\alpha]_D^{20} + 21°$ and $- 21°$ (ethanol), and the *tris-p*-nitrobenzoates, melting point 110°, $[\alpha]_D^{20} + 24°$ and $- 24°$ (chloroform). The enantiomorphic alcohols (IV) from the dialdehydes (III) furnished by the pentopyranosides yield the enantiomorphic *bis p*-nitrobenzoates, melting point 113°, $[\alpha]_D^{20} + 10°$ and $- 10°$ (chloroform). The diasteroisomeric alcohols corresponding to (VI) from the aldehydes (V) provided by the 6-deoxy-hexopyranosides have been characterized as *bis p*-nitrobenzoates. The structures of the alcohols represented

* Denotes an asymmetric carbon atom.

by the formulæ II and IV have been established by acid hydrolysis and identification of the fragments, namely, glycerol (from II), ethylene glycol (from IV) and glycollic aldehyde (from II and IV). Confirmation of these results has been obtained from experiments carried out with the benzoyl and p-nitrobenzoyl derivatives of the alcohols.

Proof of the structure of the alcohols represented by VI may be illustrated by reference to that obtained from α-methyl-L-rhamnopyranoside. This particular alcohol affords upon hydrolysis glycollic aldehyde (2,4-dinitrophenylhydrazone, melting point 86°) and an optically active 1,2-propanediol (*bis* p-nitrobenzoate, melting point 109°, $[\alpha]_D^{23} + 48 \cdot 5°$ (acetone)), which proved to be identical with that obtained from L (dextro)-lactic acid and its methyl ester by reduction with lithium aluminium hydride.

We have also found that reduction of aldehydes, formed by periodate oxidation of glycosides, is also applicable to oligosaccharides. Thus β-methyl maltoside has given VII whereas sucrose has afforded VIII.

Furthermore, the fact that the latter, which contains only one asymmetric carbon atom (C_1 of the original D-glucose moiety), has a negative rotation shows that in sucrose the anomeric linkage at the glucose residue is of the α-type, inasmuch as all alcohols of the type represented by II (an analogue of VIII) derived from α-alkyl-D-glucopyranosides have a negative rotation, whereas all those derived from β-alkyl-D-glucopyranosides have a positive rotation.

Further details of this work will be published later.

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¹ Fleury, Herissey and Joly, *J. Pharm. Chim.*, **20**, 149 (1934).
² Hudson and Jackson, *J. Amer. Chem. Soc.*, **58**, 378 (1936); **59**, 994 (1937).

A New Synthesis of 2-Deoxy-D-ribose

IT has long been a matter of interest to synthesize 2-deoxy-D-ribose, a component sugar of deoxyribonucleic acid, and several methods have been reported¹. We wish to communicate some results which we obtained recently.

D-Arabinose was converted into ribulose by heating it in pyridine². Ribulose isolated as its o-nitrophenyl hydrazone was reduced as such with Raney's nickel catalyst to the 2-deoxy-2-amino-pentitols, the crystallization of which failed. The amino-alcohols were converted into deoxy-pentose by treatment with nitrous acid. The course of the reaction may be interpreted as a sort of 'semipinacolinic deamination'³. 2-Deoxy-D-ribose was isolated as its benzylphenyl hydrazone melting at 125·5–126·5° C., $[\alpha]_D^{11}$ being − 15·25°. The overall yield was about 3 per cent. The whole course of the reaction is represented as follows :

We are indebted to Prof. K. Makino and Mr. K. Ohta, of the College of Medicine, Kumamoto University, for an authentic specimen of deoxyribose, and we are grateful to Prof. S. Akabori, of the College of Science, Osaka University, for his suggestions and encouragement.

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¹ Sowden, J. C., *J. Amer. Chem. Soc.*, **71**, 1897 (1949). Kent, P. W., Stacey, M., and Wiggins, L. F., *J. Chem. Soc.*, 1232 (1949). Overend, W. G., Stacey, M., and Wiggins, L. F., *J. Chem. Soc.*, 1358 (1949). Ohta, K., *J. Biochem. (Japan)*, **38**, 31 (1951). Hough, L., *Chem. and Indust.*, 406 (1951).
² Glatthaar, C., and Reichstein, T., *Helv. Chim. Acta*, **18**, 80 (1935).
³ Matsushima, Y., *Bull. Chem. Soc. Japan*, **24**, 144 (1951).

Transglucosylation of Aromatic N-Glucosides

ALTHOUGH the transglucosylation of O-glucosides is not very practicable and has been described hitherto only in isolated cases¹, the same mechanism appears in the case of N-glucosides of primary aromatic amines and seems to be fairly easy and to proceed according to the reaction :

$$Ar-NH-\underset{\lfloor\underline{\quad\quad O\quad\quad}\rfloor}{CH-(CHOH)_3-CH}-CH_2OH + Ar'-NH_2 \rightarrow$$

$$Ar'-NH-\underset{\lfloor\underline{\quad\quad O\quad\quad}\rfloor}{CH-(CHOH)_3-CH}-CH_2OH + Ar-NH_2.$$

The first example of this reaction was given in 1936 by R. Kuhn and A. Dansi², who in this way prepared nitroxylidine-glucoside from p-toluidine-glucoside, but the yield was very low. In 1948, J. Inoue and K. Onodera described two further reactions, namely, the preparation of aniline-glucoside and m- or p-nitraniline-glucoside from p-toluidine-glucoside ; however, the description of the latter seems to me doubtful ("white tabular crystals (?), m.p. 120–122°, of aniline N-D-glucoside"³).

Since this process appears to be of significance both from the chemical and biochemical points of view, we have made detailed investigations of the conditions and mechanism of the reaction. Our conclusions can be summarized as follows :

(1) The reaction is dependent upon pH.

(2) It is in certain circumstances reversible (see examples 4–5, 6–7 and 8–9 in the accompanying table).

(3) The reaction will proceed to completion in solvents such as methyl alcohol and ethyl alcohol in a few minutes at low temperature with very satisfactory yields ; Inoue and Onodera heated the reaction mixtures for eight hours. We find that application of heat serves only to speed up the solution of the starting reactants.

(4) The reactions in absolute alcohols leave little doubt that the process is really transglucosylation rather than hydrolysis followed by redistributive reglucosylation. This conclusion is confirmed by the

CHO
|
HOCH
|
HCOH   →(Pyridine)
|
HCOH
|
CH₂OH

CH₂OH
|
CO
|
HCOH   →
|
HCOH
|
CH₂OH

CH₂OH
|
C=NNHC₆H₄NO₂(o)
|
HCOH   →(4H)
|
HCOH
|
CH₂OH

CH₂OH
|
CH(NH₂)
|
HCOH   →(HNO₂)
|
HCOH
|
CH₂OH

CHO
|
CH₂
|
HCOH
|
HCOH
|
CH₂OH