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THE REACTION OF CARBOHYDRATES WITH AMMONIA

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David John Giltrap
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ABSTRACT

A feature of typical carbohydrate/ammonia reactions is the formation of complex mixtures of imidazoles (among other products). These imidazole mixtures have proved difficult to separate in many cases. A theory for cation exchange chromatography of bases has been developed in this work and applied to the separation of imidazole mixtures. The technique used appears to be capable of separating mixtures of imidazoles more effectively than other previously used.

D-Glucosone (D-arabo-hexosulose) was prepared by the action of benzaldehyde on glucosazone (d-arabo-hexosephenylosazone) and its reaction with ammonia investigated. It was found that the reaction mixture included a number of imidazoles. These imidazoles were separated by the ion exchange technique developed earlier and a total of sixteen compounds giving a positive reaction with the imidazole-specific. Pauly reagent (diazotised sulphanilic acid) were detected. Fifteen of these compounds were isolated and six were identified by mass spectrometry and/or nuclear magnetic resovance spectrometry.

It was also intended to investigate the reaction of 4-O-methyl-D-glucose and ammonia. It was proposed to prepare this compound by methylation of methyl-2,3,4-tri-O-acetyl- -D-glucopyranoside with methyl iodide in the presence of silver oxide. Under these conditions an acetyl migration from the 4-O to 6-O position occurs with the methylation to give methyl-2,3,6-tri-O-acetyl-4-O-methyl- -D-glucopyranoside which may be hydrolysed to give 4-O-methyl-D-glucose. It was intended to prepare the starting material for this reaction (methyl-2,3,4-tri-O-acetyl- -D-glucopyranoside) from D-glucose by the following steps.

(1) Methanolysis of D-glucose catalysed by an H^+ cation exchange resin to give methyl- -D-glucopyrunoside.

(2) Blocking of the 6-O position with triphenylchloromethane.

(3) Acetylation with acetic anbydride to give methyl-6-O-triphenylmethyl-2,3,4-tri-O-acetyl- -D-glucopyranoside.

(4) Removal of the triphenylmethyl blocking group to give the required methyl-2,3,4-tri-O-acetyl- β D-glucopyranoside.

In fact at the time of this writing the first three steps had been accomplished but attempts to remove the triphenylmethyl blocking group while leaving the ocetyl groups intact had proved unsuccessful.

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TABLE OF CONTENTS

ABSTRACT ii

INTRODUCTION

Alkaline Degradation of Sugars 1.

Aldolisation and Dealdolisation 1

Formation of α -Desoxyosones 3

Reactions of the Desoxyosones 3

(1) Alkaline Fission 3

(2) Saccharinic Acid Formation 3

The Effect of Substitution 7

(1) Non-reducing hexoses 7

(2) 1-O-substituted 2-ketohexoses 7

(3) 2-O-substituted aldohexoses 7

(4) 3-O-substituted hexoses 7

(5) 4-O-substituted hexoses 8

(6) 6-O-substituted hexoses 8

Formation of Heterocyclic Compounds 8

(1) Imidazoles 8

(2) Other Heterocyclic compounds 12

SEPARATION OF IMIDAZOLES BY CATION EXCHANGE CHROMATOGRAPHY 14

Theory of Ion-Exchange Separation of Bases 16

Criteria for separation 19

Separation of an Imidazole Mixture 23

THE REACTION OF D-GLUCOSONE AND AMMONIA 24

EXPERIMENTAL

Chromatography 26

Preparation of D Glucosone 27

D-arabo-hexosephenylosazone 27

D-arabo-hexosulose (D-Glucosone) 28

Separation of Imidazoles 30

D-Glucosone/Ammonia Reaction 32

Kinetic Study 32

Preparative Reaction 32

Ion exchange separation of bases 35

(Contents)

Results

Compound I 39
Compound IV 39
Compound VI 39
Compound XI 40
Compound XII 40
Compound XIII 40
Compound XV 41

RESULTS AND DISCUSSION

Identification of Products 42
Compound I 2,4(2,5)-bis(tetrahydroxybutyl)imidazole 42
Compound IV 43
Compound VI 4(5)-tetrahydroxybutylimidazole 43
Compound XI 4(5)-(2,3-dihydroxypropyl)imidazole 43
Compounds XII 4(5)-(2-hydroxyethyl)imidazole and XIII 2-hydroxymethyl-4(5)-methylimidazole 43
Compound XV 4(5)-methylimidazole 44
D-Glucosone/Ammonia Reaction 47
SECTION II 4-O-METHYL-D-GLUCOSE/AMMONIA 51

Experimental

Methyl- D-Glucopyranoside 54
Methyl-6-O-triphenylmethyl-2,3,4-tri-O-acetyl-β-D-glucopyranoside 54

LIST OF FIGURES AND TABLES

FIGURES

Fig.1 Lobry de Bruyn-Alberda Van Ekenstein Reactions 2
Fig.2 Mechanism of the Aldol Condensation 4
Fig.3 Isomerisation by the aldol Condensation 4
Fig.4 β-Elimination Mechanism 5
Fig.5 Alkaline Fission of Dicarbonyls 6
Fig.6 Saccharinic Acid Formation from β-Desoxyosones 9
Fig.7 The Effect of Substitution on Desoxyosone Formation 10
Fig.8 Formation of Heterocyclic Compounds 13
Fig.9 Preparation of D-Glucosone 25
Fig.10 Development of Imidazole Concentration with Time in Glucosone/Ammonia Reaction 34
Fig.11 Mass Spectra of Identified Imidazoles 45,46
Fig.12 Precursors of Imidazoles Identified in D-Glucosone/Ammonia System 48
Fig.13 Formation of Imidazoles from D-Glucosone 49
Fig.14 Degradation of 3-O-Methyl-D-Glucose 52
Fig.15 4-O-Methylation of Methyl-2,3,4-tri-O-acetyl- D-glucopyranoside 53

TABLES

Table I Results of Separation of Imidazole Mixture 31
Table II Spots located by Paper Chromatography of Glucosone/Ammonia Reaction Mixture 34
Table III Compounds in fractions from Ion-Exchange Chromatography 37
Table IV Compounds Isolated from Glucosone/Ammonia Reaction 38