"THE ACTION OF AMMONIA ON CARBOHYDRATES AND RELATED CARBONYL COMPOUNDS"

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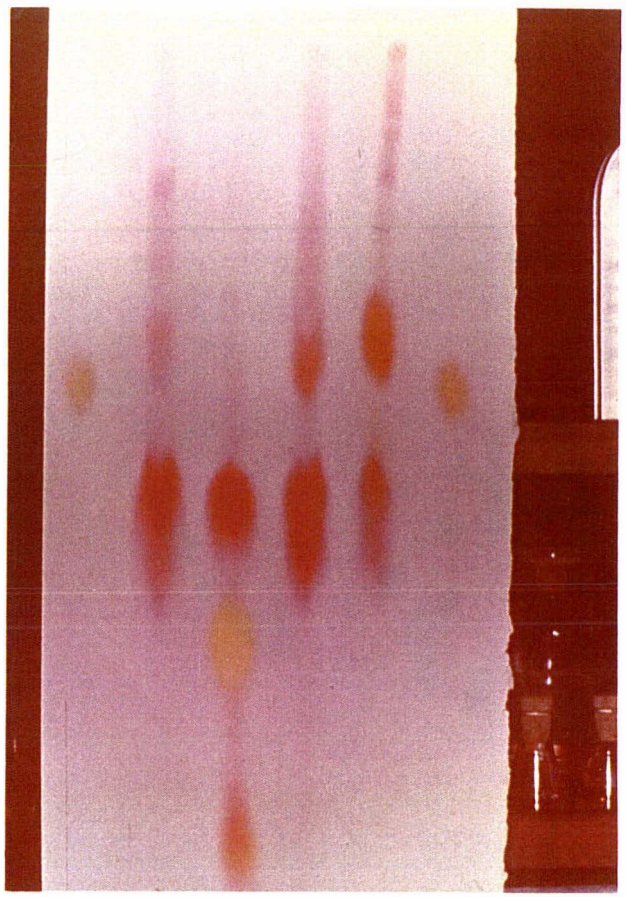
1965



Paper Chromatogram showing Imidazoles formed from: (L to R)
(i) Imidazole (marker); (ii) Glyceraldehyde/NH_3;
(iii) Pyruvaldehyde/NH_3; (iv) Dihydroxyacetone/NH_3;
(v) Hydroxypyruvaldehyde/NH_3; and (vi) Imidazole (marker).

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ABSTRACT

The chromatography of imidazoles has been studied and a method developed for their quantitative estimation.

The following facts have been brought to light:-

(i) Formaldehyde does not form imidazoles at room temperature in ammoniacal solution.

(ii) From the complex mixture resulting from the interaction of glyoxal with aqueous ammonia imidazole and 2,2'-bis-imidazole have been isolated and identified, while 2-formyl-imidazole has been tentatively identified.

(iii) Glycolaldehyde reacts with aqueous ammonia to form imidazole and 2-hydroxymethylimidazole.

(iv) DL-Glyceraldehyde reacts with aqueous ammonia to form a complex mixture of neutral and basic compounds. Dihydroxy-acetone, glucose, fructose, mannose, arabinose, lyxose and xylose have been tentatively identified by paper chromatography while ribose was suspected in low concentration. 2-Hydroxy-methyl—4(5)-methylimidazole, 4(5)-methylimidazole, 4(5)-(2-hydroxyethyl)imidazole and 4(5)-hydroxymethylimidazole have been isolated and characterised, and their orders and rates of formation studied.

(v) Pyruvaldehyde reacts exothermically with concentrated ammonia solution to form four imidazolic compounds. Three of these have been isolated and characterised as 2-acetyl-

4(5)-methylimidazole, 2,4(5)-dimethylimidazole and 4(5)-methylimidazole. The latter two compounds were formed in approximately equimolecular proportions. These results fail to confirm Bernhauer's finding that pyruvaldehyde cannot act as a source of formaldehyde in imidazole formation.

(vi) Hydroxypyruvaldehyde browns rapidly in aqueous ammonia forming 2-hydroxymethyl-4(5)-methylimidazole, 4(5)-methylimidazole and 4(5)-hydroxymethylimidazole. The yields of the latter two compounds have been found to be higher than from a similar mixture of dihydroxyacetone with ammonia.

(vii) Both diacetyl and acetoin react with ammonia to form 2,4,5-trimethylimidazole.

(viii) 4(5)-(2-Hydroxyethyl)imidazole has been tentatively identified from the mixture resulting from the interaction of 1,4-dihydroxybutan-2-one with aqueous ammonia.

(ix) Arabinose reacts with aqueous ammonia to form a complex mixture of imidazoles from which 4(5)-methylimidazole has been isolated and identified.

(x) A chromatographic study has been carried out to determine the orders of formation of imidazoles resulting from the interactions of a number of carbohydrates and their degradation products with aqueous ammonia. Arising from this study have come the following main results:-

(a) It appears that, contrary to the findings of Komoto, a number of imidazoles with low R_f values (probably polyhydroxy-

alkyl-substituted) are formed more rapidly than 4(5)-methyl-imidazole from hexose sugars with ammonia.

(b) Differently linked reducing disaccharides give markedly different patterns of imidazoles under ammoniacal conditions.

(xi) As a result of (b) above, a micro-method has been developed for determination of the position of the glycosidic link in reducing hexose disaccharides and homogeneously-linked oligosaccharides.

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