heads were 'loose' in appearance and their spores echinulate; if of *U. levis* the heads were 'covered' in appearance and their spores smooth; if one of the cultures was of *U. avenae* and the other of *U. levis* the infected heads were somewhat variable in appearance, but upon close examination they proved to be of the 'loose' type, and their spores were echinulate.

(3) The sporidia of *U. avenae*, like those of *U. levis*, are of two kinds, (+) and (-); the sporidia of one species mate without difficulty with sexually opposite sporidia of the other species.

These results indicate that *U. avenae* and *U. levis* are genetically distinct with respect to the characters by which they are differentiated, but the ease with which crosses can be made between them suggests that they are closely related species.

A full report of the investigation is being prepared for publication.

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Synthesis of a Methoxyketose.

A 5-METHOXYKETOSE has been prepared by the condensation of dioxycetone, $\text{CH}_2\text{OH} \cdot \text{CO} \cdot \text{CH}_2\text{OH}$, and α -methoxyglyceric aldehyde, $\text{CH}_2\text{OH} \cdot \text{CH}(\text{OCH}_3) \cdot \text{CHO}$. The method of synthesis is proof of the position of the methoxyl group and such a structure cannot form a furan ring.

Pure dioxycetone was obtained from nitromethane by the method of Henry and Piloty. Neither α -methoxyglyceric aldehyde nor its acetal had been prepared but the latter was obtained by methylating α -chlor- β -oxypropiondiethylacetal with sodium methylate, α -chlor- β -oxypropionacetal being formed from acrolein through the intermediary of β -chlorpropionacetal and acroleinacetal by a modification of the methods described by Wöhl and Witzemann. The required acetal was obtained as a colourless liquid distilling at $100^\circ\text{--}102^\circ\text{C}/6\text{mm}$. This was readily hydrolysed by dilute mineral acids and the aldehyde produced was converted into the bromphenylhydrazine derivative and into the condensation product with phloroglucinol. The preparation of these derivatives and the analysis of the acetal proved the identity of the aldehyde.

The conditions used by Fischer in his synthesis of α -acrose were modified to suit the condensation of dioxycetone and α -methoxyglyceric aldehyde and the optimum results were obtained by allowing a 5 per cent aqueous solution containing 0.25 per cent of barium hydroxide to stand at room temperature for a period of three weeks.

Dioxycetone is in equilibrium in aqueous solution with glyceric aldehyde, and hence, theoretically, it should be possible to obtain as a result of this condensation four inactive 5-monomethoxyketoses, the corresponding eight inactive 5-monomethoxyaldoses, and the twelve racemic forms of the non-methylated hexoses. The number of possible osazones is only eight and it was not considered likely that the non-methylated osazones would be formed in any quantity. Further, from analogy with the work of Fischer and Schmidt it was expected that the bulk of the product would consist of a single racemic form. These expectations were realised, but it may be noted that for the purpose in hand the actual identity of the substance produced was immaterial, the aim being to synthesise a ketose which could not possess a furan structure.

Treatment of the reaction mixture with phenylhydrazine under the usual conditions gave an impure, crystalline substance and a tarry mass. The former proved to be acetylphenylhydrazine, whilst from the

latter a mixture of osazones was isolated with considerable difficulty. Repeated fractional crystallisations from ethyl acetate gave two main fractions of osazones, a larger fraction melting at 183°C . and a smaller fraction melting at 130°C . These gave analytical figures corresponding to a pure monomethoxyhexosazone. From analogy with the work of Fischer on α -acrose and on a consideration of the melting points of the known methylated and non-methylated osazones the former product was considered to be inactive 5-monomethoxyfructosazone and the latter inactive 5-monomethoxysorbosazone.

The monomethoxyhexosazone (m.p. 183°), of which 35 grams were obtained (from 5600 grams of acrolein), was converted through the osone into the corresponding monomethoxyketose by a modification of Fischer's method. Five grams of a crystalline material melting at $80^\circ\text{--}85^\circ\text{C}$. were obtained which gave analytical figures corresponding to a pure monomethoxyhexose. Treatment at room temperature with methyl alcohol containing 1 per cent HCl showed that fructoside formation was complete only after 48 hours. This was evidence in favour of a sugar which cannot exist in the γ -form since the formation of γ -methylfructoside is complete after one hour. The monomethoxymethylhexoside was methylated by treatment with methyl sulphate followed by two successive methylations with Purdie's reagents. Towards alkaline permanganate this tetramethoxymethylhexoside behaved as a normal sugar derivative and the rate of hydrolysis also corresponded to that of normal tetramethoxymethylfructoside. Hydrolysis of the synthesised hexoside was complete on refluxing with 3 per cent aqueous HCl for three hours and the product was isolated as a syrup in the usual way. From this syrup tabular crystals were obtained by extraction with light petroleum which, after repeated crystallisations, melted at $95^\circ\text{--}96^\circ\text{C}$. There was no depression of melting point on mixing with an authentic specimen of normal tetramethoxyfructose.

Nitric acid oxidation gave a trimethyl-lactol acid which on further oxidation with alkaline permanganate yielded a trimethylarabonolactone. The curve of apparent specific conductivity plotted against time obtained by observations during the hydrolysis of the lactone derived from the synthesised tetramethoxyhexose was almost identical with the curve given under similar conditions by the lactone derived from normal tetramethoxyfructose but was sharply differentiated from that given by the lactone corresponding to tetramethoxy- γ -fructose.

From these experiments it is shown that the synthesised 5-methoxyhexose and its derivatives have exactly similar properties to those of the methylated derivatives of normal fructose, and that the synthesised hexose was in fact the racemic form of 5-monomethoxyfructose. Since the methoxyhexose produced by condensation could not possess a 5-atom ring, and of the other possible ring structures the pyranose is considered to be the most likely, this evidence, obtained from a field hitherto unexploited, proves conclusively that normal fructose and its derivatives cannot possess a furanose structure and lends support to the accepted pyranose constitution.

A parallel experiment is in progress with the object of synthesising a 6-methoxyhexose.

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