## Letters to the Editor.

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## An Aspect of the Biochemistry of the Sugars.

As is well known, the d-galactose configuration may be derived from that of d-glucose by a simple optical inversion at position 4 as shown in the annexed conventional symbols:

$$\begin{array}{c|cccc} H & OH & & H & OH \\ HO & H & & HO & H \\ H & OH & \longrightarrow & HO & H \\ H & OH & & H & OH \\ \hline \textit{$d$-Glucose.} & & \textit{$d$-Galactose.} \end{array}$$

Although no suggestions as to a probable mechanism of this important transformation have hitherto been advanced, the explanation becomes obvious when certain developments in the theory of the Walden inversion and related simple optical inversions are taken into account. Lapworth, in the course of his studies of the mechanism of the formation and hydrolysis of esters, has pointed out that carboxylic esters and sulphonic esters are normally hydrolysed, and suffer fission generally, at the points shown by the dotted lines:

$$R-O$$
  $CO-X$   $R$   $OSO_2-X$   $H$   $OH$   $HO$   $H$ 

In harmony with the requirements of this theory, Phillips has found that optical inversion occurs in the fission, for example, the acetolysis of d-benzylmethylcarbinyl p-toluenesulphonate. The results are summarised by the scheme:

$$\begin{array}{ccccc} \operatorname{Ph} \cdot \operatorname{CH}_2 & \operatorname{OSO}_2 \cdot \operatorname{C}_6\operatorname{H}_4 \cdot \operatorname{Me} & \operatorname{Ph} \cdot \operatorname{CH}_2 & \operatorname{Me} \\ (\operatorname{I.}) & & & & & & & & \\ \operatorname{H} & \operatorname{Me} & & & & & & & \\ \end{array}$$

with inversion;

$$(II.) \xrightarrow{\text{Ph.CH}_2} C \xrightarrow{\vdots} COR \xrightarrow{\text{Ph.CH}_2} C \xrightarrow{\text{Me}} H$$

without inversion.

In reactions of type I., inversion is normal but not inevitable, since special conditions may induce a direct replacement. Thus there is little doubt that inversions in the carbohydrate group, though not occurring in the hydrolysis of acetates, carbonates, acetone compounds, etc., could be brought about by the formation and hydrolysis of sulphate or arylsulphonyl compounds. The theory which applies to derivatives of sulphuric acid applies also to derivatives of phosphoric acid since, putting it crudely, phosphorus has much affinity for oxygen, and having once acquired the element will be difficult to part from it. Therefore hydrolysis of phosphoric esters will be in

accordance with the scheme  $R = \frac{1}{2}O(PO)(OH)_2$ , and if

the oxygen atom is directly attached to an asymmetric carbon atom, optical inversion should be observed.

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Bearing in mind, then, the occurrence of hexosephosphates in Nature, it seems certain that the galactose configuration results from the hydrolysis of a glucosephosphoric acid which may occur as such or form part of a larger molecule. An interesting side-issue is the indication of the probable constitution of the glucosephosphoric acid, and the fact that the present hypothesis, permissible on the basis of Haworth's six-ring glucose formula, would be excluded if glucose contained the butylene oxide ring. The reverse change from galactose to glucose will naturally have the same mechanism.

In discussing the matter recently with Prof. W. N. Haworth and Dr. E. L. Hirst, it was pointed out that the above suggestion throws an interesting light on the nature of the pentose in the nucleic acid derived from vegetable nucleo-proteins. Levene has obtained from this source a pentose-phosphoric acid which on hydrolysis yields d-ribose and phosphoric acid and is therefore considered to be a ribosephosphoric acid. It is much more likely to be d-xylosephosphoric acid, the ribose being produced in accordance with the scheme:

$$\begin{array}{c|cccc} (HO)_2(PO)O & H & OH & H_2O & H & OH \\ H & OH & \longrightarrow & H & OH + H_3PO_4 \\ d\text{-Xylosephosphoric acid.} & & & & d\text{-Ribose.} \end{array}$$

The circumstance that we are able in this way to regard nucleic acid as a derivative of the relatively widely distributed xylose instead of the rare or unique ribose must undoubtedly be regarded as strongly supporting the thesis advanced. The d-ribose could also be obtained from a d-arabinose-phosphoric acid or from l-lyxosephosphoric acid, but d-arabinose and l-lyxose do not appear to occur naturally, and consequently the assumption of the origin from d-xylose is preferable. Finally, without going into detail, it may be pointed out that a consideration of the facts in relation to the theory of hydrolysis and optical inversion indicates that the first stage, involving fission of a bond, in the hydrolysis of a glucoside is the opening of the oxide ring.

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The University, Manchester, June 24.

## Friction of Solids.

There seems to be but very little published information regarding the subject of solid friction, and such as there is is chiefly concerned with the effects of lubrication at considerable velocities and at comparatively low pressures.

I think, therefore, it is worth while to contribute a short note on some experiments which I have recently made, in which the pressure between the solids range from those ordinarily met with in mechanical practice up to the highest which the material can withstand <sup>1</sup> and in which the velocities are almost vanishingly small. A list of the materials tried and of their coefficients of friction is given below.

The point worthy of remark is the small difference which exists between the coefficients for the various metals notwithstanding their strong contrasts in other respects. Another point which seems remarkable is that when the pressure is high, the presence of a lubricant nearly always increases instead of diminishing the coefficient of friction.<sup>2</sup>

¹ An example of friction at destructive pressures is presented by the driving-band on the projectiles of large guns. The great volume of smoke which 'smokeless' powder produces when such guns are fired consists almost entirely of powdered driving-band, i.e. of finely divided copper

divided copper.

2 The effect of a 'drop' in the saucer in preventing a cup from slipping is very generally known.