

pletely reversed by the addition of reduced glutathione to the inhibited extract. The reaction occurs at once even in the presence of a ten-fold excess of the inhibitor, and clearly shows that the action of iodoacetate does not involve irreversible destruction of the enzyme itself. Further, in a dialysed extract activated by a known amount of glutathione, the quantity of iodoacetate required to stop lactic acid formation is approximately equivalent to the glutathione added to that extract. Thus the powerful activity of the purified extract, conditioned by the presence of added glutathione in  $10^{-4}$  to  $3 \times 10^{-5}$  molar concentration, is rapidly retarded or inhibited by iodoacetic acid in the same molecular concentration.

On the other hand, the glyoxalase activity of the crude extract is quite unaffected by this concentration of iodoacetate; it must be increased about a hundred-fold in order to arrest or retard the lactic acid formation. The behaviour of fresh liver slices, studied by Warburg's method, I find much more nearly corresponds with that of the purified extracts; with concentrations of iodoacetate down to  $1.5-5 \times 10^{-4}$  molar, the inhibition of glyoxalase action is well marked, and here also the activity is immediately restored by the addition of reduced glutathione ( $10^{-3}$  molar) to the contents of the vessels.

These results suggest the occurrence of a direct interaction between glutathione and iodoacetic acid; and this has in fact been observed. If dilute neutral solutions of iodoacetic acid and purified glutathione are mixed, a vigorous reaction occurs in which acid (HI) is liberated and the sulphhydryl group of the glutathione is attacked. The progress of the reaction is followed by mixing the bicarbonate solutions of the two reactants in an atmosphere of nitrogen and carbon dioxide (pH of solution 7.4) and measuring manometrically the carbon dioxide evolution due to acid production. It is then found that for each molecule of reactant decomposed one equivalent of acid is set free; the kinetics and chemistry of this reaction are now being further investigated.

How far the other actions of iodoacetate may be referred to a similar mechanism, or to oxidative reactions in the way suggested by Waldschmidt-Leitz and Schäffner<sup>4</sup> and by Bersin<sup>5</sup> is not yet clear.

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- <sup>1</sup> *Biochem. J.*, **25**, 439; 1931.  
<sup>2</sup> *Biochem. Z.*, **236**, 444; 1931.  
<sup>3</sup> *Biochem. Z.*, **254**, 332; 1932.  
<sup>4</sup> *Naturwiss.*, **20**, 122; 1932.  
<sup>5</sup> *Biochem. Z.*, **248**, 3; 1932.

### Structural Formulæ of the Chlorophylls

SOMEWHAT more than a year ago, a structural formula for chlorophyll-*a* was suggested<sup>1</sup> in which a carbomethoxy residue was placed in the  $\beta$ -position of one pyrrole ring. This seemed necessary as a monomethyl ester (phæopurpurin 7) was obtained as one of the products of an oxidative hydrolysis ('phase test') and the position of the methoxyl group in this phæopurpurin was clearly established. We have now found that the purest samples of the phæophorbides of the 'a' series do not yield any phæopurpurin 7. Under special conditions of oxidative hydrolysis, a monomethyl compound can be isolated (as the sole product) and the carbomethoxy group in this sub-

stance can be shown to be part of the side chain attached to the bridge (the so-called  $\gamma$ -position). This finding is in accord with the position of the methoxyl group in Fischer's formula for chlorophyll-*a*.

We have found in the mother liquors from the purification of the phæophorbides, considerable quantities of a material very similar to the normal members of the 'a' series but which on oxidative hydrolysis yields phæopurpurin 7 (a monomethyl ester). The presence of this material in our original samples was thus responsible for the phæopurpurin 7 which we obtained. It is difficult to separate this substance from phæophorbide-*a*, which it appears to resemble closely in physical and chemical properties. There seems no escape from the conclusion that we are dealing with a substance very similar to phæophorbide-*a*, but differing in the position of the methoxyl group. The oxidative hydrolysis of crude chlorophyll or of chlorophyllides has shown that a precursor of phæopurpurin 7 is present to the extent of 1-5 per cent in a variety of plants. The mother liquors from crystalline ethyl chlorophyllides from *Datura* contain as much as 20 per cent. It would appear that there are two forms of chlorophyll-*a*, and we are now engaged in an attempt to isolate in a pure state the second form (or the corresponding chlorophyllide). There are some indications that a similar situation exists in regard to chlorophyll-*b*, but there has been no definite evidence as yet published establishing the position of the methoxyl group in the 'b' series.

If there are two very similar forms of chlorophyll-*a*, differing only in the position of a methoxyl group, a formula must be found which allows of the interchange of the methoxyl group between two potential carboxyl groups without serious structural modification. This interchange must involve the carboxyl group of the pyrrole ring and that of the bridge. The lactam formula, which we mentioned previously<sup>2</sup> as an alternative of our anhydride formula, satisfies these requirements; the anhydride formula does not, nor do the formulae containing a carbocyclic ring connecting the pyrrole nucleus and the bridge.

The analyses of the pure phæophorbides present a difficulty as we have realised for many months, and has recently been emphasised by Stoll<sup>3</sup> and Fischer<sup>4</sup>. We are strongly inclined to the opinion that on isolating and drying the crystalline compounds, water is lost, leaving an unsaturated grouping which then adds water again in solution, regenerating the hydroxy compound.

A more detailed discussion of the structural formulæ of chlorophyll-*a* and -*b* will be given in a series of papers to be published shortly.

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- <sup>1</sup> *J. Amer. Chem. Soc.*, **53**, 2382; 1931.  
<sup>2</sup> *Ibid.*, **53**, 2384; 1931.  
<sup>3</sup> *Ann.*, **499**, 84; 1932.  
<sup>4</sup> *Helv. Chim. Acta*, **15**, 1128; 1932.

### 'Raw' Weather

I EXPECT that Sir Leonard Hill's remarks in NATURE of January 7 (p. 28) on this subject go a long way towards answering the inquiry about the physiological effects of raw weather, but I doubt if they cover the case of deep-seated pain to bedridden rheumatic people. Yet such people are sometimes