$$\begin{array}{c} \mathrm{C_{10}H_{14}O_{9}N_{2}+3H_{2}O} = \mathrm{C_{3}H_{5}O_{4}N+CO_{2}+NH_{3}+}\\ \mathrm{hiptagin} \\ \mathrm{C_{8}H_{12}O_{6}} \\ \mathrm{C_{9}Hecce} \end{array}$$

The acid was later isolated from another crystalline glycoside, karakin, m.p. 122° C., extracted from the berries of the karaka tree, *Corynocarpus lævigata*, by Carrie², who identified his acid by a mixed melting point with a specimen of Gorter's acid.

Later work by Carter³ showed that the two glycosides have identical composition and properties apart from different melting points and optical rotation, and appear to be stereoisomeric forms of the formula

 $C_{10}H_{14}O_{9}N_{2}, \frac{1}{2}H_{2}O.$

When karakin is boiled in aqueous solution for six hours or more, it is almost completely hydrolysed to hiptagenic acid and an amino-sugar which loses carbon dioxide according to the equations:

$$\begin{array}{lll} \mbox{(a)} & C_{10} H_{14} O_9 N_2 \, + \, 2 H_2 O \, = \, C_3 H_5 O_4 N \, + \, C_7 H_{13} O_7 N \\ \mbox{(b)} & C_7 H_{13} O_7 N \, & = \, C_6 H_{11} O_5 N H_2 \, + \, C O_2. \end{array}$$

Recently, Carter and McChesney, from a consideration of the properties of β -nitropropionic acid, and bearing in mind the fact that Gorter had obtained a small yield of sodium nitrite from hiptagenic acid by the action of sodium ethylate, prepared some of the former acid from β -iodopropionic acid and silver nitrite. The synthetic acid gave no depression of the melting point when mixed with hiptagenic acid, and proved to be in other respects identical with the acid obtained from natural sources.

Hiptagenic acid is probably the first organic nitro-compound to be isolated from plants, and it is also probable that the nitro group is present in the hiptagin and karakin molecules, since a comparison of the ultra-violet absorption spectra of hiptagenic acid and of karakin shows the same characteristics.

C. L. CARTER W. J. McChesney

Department of Chemistry, University of Otago. April 5.

¹ Gorter, Bull. Jard. Bot. Buitenzorg, (III), 2, 187 (1920).

A New Method for Forming Vinyl Polymers in Wool

When ethylene sulphide is polymerized from the vapour phase in wool¹, reduction of the cystine is considered to occur², the cysteine side-chains so produced then taking part in polymerization as follows:

To nows:
$$\frac{-\text{CH}_2 \cdot \text{SH}}{-\text{CH}_2 \cdot \text{SH}} + \frac{\text{CH}_2}{n} \cdot \text{S} \longrightarrow \\ \frac{-\text{CH}_2 \cdot \text{S}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{S})_{n-1} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SH}}{-\text{CH}_2 \cdot \text{S}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{S})_{n-1} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SH}}.$$
 In support of this, Blackburn and Phillips (loc. cit.)

In support of this, Blackburn and Phillips (loc. cit.) found that more polymerization occurs if the cystine in the wool is previously reduced with thiolacetic acid, although sodium bisulphite was ineffective.

These findings have now been extended to the polymerization of vinyl compounds in wool, using aqueous solutions. With such systems, it is usual to introduce some external form of initiator, such as iron (Fe⁺⁺) and hydrogen peroxide^{3,4}; but it has now been found that the wool can provide its own catalyst in the form of reduced cystine.

A conditioned sample (2.5 gm.) of purified all-wool flannel was immersed in 30 c.c. of a 10 per cent solution of thiolacetic acid for 3 hours at 30° C. A second

sample was placed in 50 c.c. of a 2 per cent solution of sodium bisulphite, raised to the boil in five minutes and boiled for three minutes; a third sample was similarly treated with a 2 per cent solution of sodium hydrosulphite. After treatment, each was washed in running water and then immersed in 50 c.c. of a 4 per cent solution of methacrylic acid for sixteen hours at 22° C. After washing for eight hours in running water, the samples were conditioned and weighed. Increases in weight due to polymer deposition were as follows: (i) pretreated with thiolacetic acid, 14·5 per cent; (ii) pretreated with sodium bisulphite, 10·7 per cent; (iii) pretreated with sodium hydrosulphite, 3·1 per cent.

Wool without pretreatment did not show any significant increase in weight. Pretreatments with thiolacetic acid and sodium bisulphite are each very effective in promoting polymerization, and the general mechanism is probably similar to that postulated for ethylene sulphide, the polymer being chemically bound as follows:

Council for Scientific and Industrial Research, Wool Textile Research Section,

Geelong, Australia. April 11.

¹ Barr and Speakman, J. Soc. Dyers and Colourists, 60, 238 (1944).

Blackburn and Phillips, J. Soc. Dyers and Colourists, 61, 203 (1945).
 Lipson and Speakman, Nature, 157, 590 (1946).

⁴ Lipson and Speakman, Nature, 157, 736 (1946).

A New Method of Peptide Synthesis

It has been observed previously that an acylphosphate, the phosphoric group of which is bound in an ester linkage, reacts readily at 37° in aqueous solution of pH 7·4 with the amino-group of a free amino-acid, forming the corresponding acylated amino-acid¹.

The same reaction can be applied to the synthesis of true peptides.

Phenyl carbobenzoxyglycyl phosphate

$$\mathbf{C_{6}H_{5}\cdot CH_{2}\cdot O\cdot CO\cdot NH\cdot CH_{2}\cdot CO\cdot O\cdot P} = \mathbf{O}$$

$$\mathbf{O\cdot C_{6}H}$$

has been prepared by the reaction of carbobenzoxy-glycyl chloride with disilver phenylphosphate. Phenyl carbobenzoxyglycylphosphate reacts very rapidly with amino-acids, forming the corresponding carbobenzoxyglycylpeptides, from which the free peptides can be obtained by catalytic hydrogenation.

Up to the present, glycylglycine, glycyltryptophane and glycylglycyltryptophane have been prepared in this way.

A remarkable feature of this new method is that it permits the synthesis of oligopeptides without isolation of the intermediary products (dipeptide, tripeptide, . . .) by alternately adding the phenyl carbobenzoxyaminoacylphosphate and hydrogenating the resulting carbobenzoxypeptide. All the operations are carried out in aqueous solution at 37° and pH~7.4; the yields are high, even in M/100 concentration of both reacting substances.

² Carrie, J. Soc. Chem. Indust., 53, 288T (1934).

³ Carter, J. Soc. Chem. Indust., 62, 238 (1943).