

(indicated by the dotted line in Fig. 2). If the acetylated dextrin were composed of fibrillar molecules, its solution would easily be torn into threads, and its films obtained by evaporation would exhibit a considerable solidity such as has been found for amylose acetate and the irregularly constituted lichenin acetate<sup>8</sup>. If it is branched, on the other hand, it would behave like acetylglycogen or analogous products, that is, the films would be extremely brittle. In fact, we found this to be the case: the acetyldextrin evaporated on a glass-plate could not even be detached as film. This behaviour is definitely against the Haworth formula and is in favour of our own assumption.

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- <sup>1</sup> Meyer, V., and Jacobson, P., "Lehrbuch der org. Chemie", 1, 2 Teil, 1624 ff. (1913).  
<sup>2</sup> Meyer, K. H., Mark, H., "Aufbau der Hochpolymeren" (Leipzig, 1930).  
<sup>3</sup> Staudinger, H., and Husemann, E., *Ann. Chemie*, **195**, 212 (1937).  
<sup>4</sup> Haworth, W. N., *Nature*, **129**, 365 (1932). Hirst, E. L., Plant, M. M. T., and Wilkinson, M. D., *J. Chem. Soc.*, 2375 (1932).  
<sup>5</sup> Meyer, K. H., Wertheim, M., and Bernfeld, P., *Helv. Chim. Acta*, **23**, 865 (1940).  
<sup>6</sup> Haworth, W. N., *Proc. Roy. Soc., A*, **186**, 1 (1946).  
<sup>7</sup> Meyer, K. H., and Bernfeld, P., *Helv. Chim. Acta*, **23**, 875 (1940).  
<sup>8</sup> Meyer, K. H., and Gürtler, P., *Helv. Chim. Acta*, **30**, 751 (1947).

PROF. MEYER'S brief sketch of the history of the development of starch structures neglects some essential facts. Before starch could be formulated as consisting of repeating maltose units, proof had to be provided that maltose was preformed in starch and was not a product of synthesis by the enzymes present during starch degradation<sup>1</sup>. Moreover, the constitutional formula of maltose had to be determined before any such formulation of starch could be attempted<sup>2</sup>. The end-group method of assay showed that if starch were represented as a very large molecule, it possessed many end-groups. As early as 1936<sup>3</sup>, in an article on the size of polysaccharide molecules, I made these statements: "it has never been claimed by the present author that the chemical end-group method of determination of chain length corresponds with the particle size", and also "a measurement of particle size must take account of the physical molecule and the molecular aggregate. This may involve not only aggregation to increase the length of chain but also the lateral combination of the chains."

In 1934<sup>4</sup>, I advanced the hypothesis that large molecules containing many end-groups could be formulated by the cross-linking or mutual combination of polymeric units of limited chain-length, and I illustrated this concept in a formula for xylan. In 1937<sup>5</sup>, I advanced the same hypothesis in the laminated formulae for both starch and glycogen. The nature of this polymeric bond uniting chains of limited length was postulated as an ordinary covalency link although alternatives were not excluded. The nature of this link between adjacent chains was determined later<sup>6</sup>. It has been the procedure of this School to advance formulations only with accompanying experimental evidence. It has been preferred to proceed stage by stage in accordance with the growth

of evidence, rather than to present highly speculative formulations with little experimental background.

Evidence that amylose should be represented as continuous chains of ninety or more glucose units, largely unbranched, was published in 1942<sup>7</sup> after examination of a specimen of the synthetic amylose of C. S. Hanes. This extended and confirmed the view of K. H. Meyer, who had separated amylose by Baldwin's method<sup>8</sup> and had shown that it was completely broken down to maltose by  $\beta$ -amylase, and that it did not give dextrin-A as a by-product as does amylopectin<sup>9</sup>. The laminated formula for amylopectin was advanced as a first approximation only, and is not to be regarded as the final or complete structure of amylopectin. It still serves to explain most of the known experimental facts. The multibranching structure advanced by K. H. Meyer is a development of the same concept; but at the present stage of our knowledge it seems to be premature and needlessly complex.

The point made by him above that acetylated dextrin-A should, on the basis of our formulation, yield films resembling amylose acetate rests on very slender evidence, and much more adequate experimental investigation will be necessary to support his contention.

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<sup>3</sup> Haworth, W. N., *Monatshefte für Chemie*, **69**, 314 (1936).  
<sup>4</sup> Haworth, W. N., Hirst, E. L., and Oliver, E., *J. Chem. Soc.*, 1917 (1934).  
<sup>5</sup> Haworth, W. N., Hirst, E. L., and Isherwood, F. A., *J. Chem. Soc.*, 577 (1937).  
<sup>6</sup> Barker, C. C., Hirst, E. L., and Young, G. T., *Nature*, **147**, 296 (1941), and others.  
<sup>7</sup> Haworth, W. N., Heath, R. L., and Peat, S., *J. Chem. Soc.*, 55 (1942).  
<sup>8</sup> Baldwin, M. E., *J. Amer. Chem. Soc.*, **52**, 2907 (1930).  
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### neoPentyl Alcohol and Steric Hindrance

IN a note under this title, Gerrard and Nechvatal<sup>1</sup> have reported the conversion of neopentyl alcohol,  $(\text{CH}_3)_3\text{C}\cdot\text{CH}_2\cdot\text{OH}$  (here written ROH), by thionyl and phosphorus halides into the esters RO.SOCl and RO.PCl<sub>2</sub>, *inter alia*. They remark that Whitmore and Rothrock<sup>2</sup> demonstrated the resistance of neopentyl alcohol to the replacement of its hydroxyl group by halogen, through the agency of thionyl chloride and phosphorus tribromide. They add that we<sup>3</sup> have attributed this to the steric hindrance of what they call "end-on approach" to the  $\alpha$ -carbon atom. They state that Whitmore and Rothrock leave the impression that neopentyl alcohol does not react at all with the halides specified; but that the work of Gerrard enabled Gerrard and Nechvatal to predict the probability of an easy "broadside approach" of the reagents. We should like to add some points to this statement of the relation between the different investigations.

Whitmore and Rothrock first showed that neopentyl alcohol exhibits considerable resistance to the substitution of its hydroxyl group as a whole, for example, by halogens; though they reported some displacement of the hydroxyl group by means of hydrogen bromide and phosphorus tribromide. They also, however, observed a fairly facile substitution of the hydrogen atom of the hydroxyl group in the