tions of the sugars themselves and for those of their acetates. From the results it is possible now to specify more precisely certain stereochemical features of the structures of the biose and triose. The rotations of the alpha forms of amylobiose octa-acetate and amylotriose hendeka-acetate (amorphous substances) in chloroform solution have been measured.

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NOTES

Acetyldiphenylamine from Ketene.—In a recent interesting article,[1] J. van Alphen concerned himself chiefly with reactions of the ketenes with hydrazines. In a digression from this topic, he stated[2] that ketene was entirely without action on a solution of diphenylamine in ether. Van Alphen expected the acetyl derivative to precipitate from the ether, and this it failed to do. His observation of the non-precipitation is correct, as would also have been a statement that diphenylamine does not react instantly with ketene. To state, however, that the two do not react is quite erroneous.

An excess of ketene was bubbled through an ice-cold solution of diphenylamine in ordinary ether. No precipitation ensued. The escaping gases were shown to contain much ketene by passing them into an ethereal solution of *p*-phenetidine. Phenacetin precipitated so readily that the wide-mouthed delivery tube soon became clogged.

To separate the unchanged diphenylamine from its acetyl derivative, dry hydrogen chloride was passed into the ethereal solution. Diphenyl-ammonium chloride separated. It was filtered off, and the filtrate was tested with more hydrogen chloride. In the absence of further precipitation, the solution was left to evaporate. Water was then poured on the oily residue. Gradually, this converted the oil to a solid, which was later collected upon a filter, rinsed, and pressed on a porous plate. With no further purification, the melting point was 98–100°, which indicated that the product was nearly pure. The best yield obtained was 33%, based on the original diphenylamine. A low yield of 8% was obtained when the reaction flask was not cooled with an ice-bath. The yield, instead of being bettered, was lessened when ketene was passed into pure molten diphenylamine.

The diphenylamine is, of course, easily recovered from its hydrochloride by suspending it in hot water, a reaction which proceeds more smoothly if a little hydroxide is added.

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[1] van Alphen, *Rec. trav. chim.*, **43**, 826 (1924).

[2] Ref. 1, p. 860.

The Efficiency of Photosynthesis by *Chlorella*.[1]—In a study of the influence of wave length on energy transformation in carbon dioxide assimilation, Warburg and Negelein[2] found that in photosynthesis by the alga *Chlorella* slightly over four quanta per molecule of carbon dioxide assimilated are required in the case of red light and also of green light. In the case of blue light over five quanta per molecule are required, but this is to be expected in view of the presence of other plant pigments with an absorption in the blue.

Warburg and Negelein also calculated the efficiency on the basis of the heat of combustion of dissolved glucose, 674 Cal./mole. The calculated efficiency is, naturally, greatest in the case of red light, the mean result being 59% and the highest single observation, 63.5%.

Since there is every reason to believe that glucose is not the immediate product of the photosynthetic process, it has seemed worth while to examine into the results that would be obtained by using, instead of the heat of combustion of glucose, the heat absorbed in the reaction $CO_2 + 3H_2O = 2H_2O_2 + HCHO$ (all in solution). Taking data from the 1923 "Chemiker Kalender," the heat of combustion of gaseous formaldehyde is +137.0; of solution, +15.0; the heat of solution of carbon dioxide, +5.6, and the heat of formation of hydrogen peroxide (dissolved) from liquid water and gaseous oxygen, —21.7 Cal./mole. Whence the heat of the above reaction is $-137.0 + 15.0 - 5.6 - 2 \times 21.7 = -171.0$ Cal./mole.

The wave lengths of the red-absorption maxima for *a*- and *b*-chlorophyll are, respectively, 0.666μ and 0.640μ, whence taking for cNh/J the value, 28.46 Cal. μ/mol. (calculated from the Fundamental Constants and Conversion Factors as used in the "International Critical Tables"),

$$Nh\nu_a = 42.7 \text{ Cal./mole quantum}$$
$$Nh\nu_b = 44.5 \text{ Cal./mole quantum.}$$

For two quanta absorbed by each the energy would be $2(42.7 + 44.5) = 174.4$ Cal./mole, which is only slightly greater than that required for the reaction above. The maximum efficiency to be expected on a glucose basis, since 6 molecules of formaldehyde are required to form one of glucose, would be $674/(6 \times 174.4) = 64.4\%$ and, correspondingly, Warburg and Negelein's results become, on a formaldehyde + hydrogen peroxide basis: $59 \div 64.4 = 91.6\%$, and $63.5 \div 64.4 = 98.6\%$, for the mean efficiency in the red, and the maximum observed efficiency, respectively.

At this point, a few words as to the structure and reactions of chlorophyll, better, of the chlorophylls, are necessary. Willstätter[3] considers

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Washington, April, 1924.

[2] Warburg and Negelein, *Z. physik. Chem.*, **106**, 191–218 (1923).

[3] Willstätter and Stoll, "Untersuchungen über Chlorophyll," Julius Springer, Berlin, **1913**, p. 23. Compare Willstätter, This Journal, **37**, 323 (1915).

that *b*-chlorophyll is an oxidation product of *a*-chlorophyll, containing an atom of oxygen in place of two atoms of hydrogen. Reasons will be given below for considering that it contains one atom each more of carbon and oxygen, and the same number of hydrogens. Assuming Willstätter's formula for *a*-chlorophyll, $C_{55}H_{72}O_5N_4Mg$, his formula for *b*-chlorophyll is $C_{55}H_{70}O_6N_4Mg$, while that just suggested is $C_{56}H_{72}O_6N_4Mg$.

The differences in ultimate composition are shown in Table I.

TABLE I

Element	*a*-Chlorophyll $C_{55}H_{72}O_5N_4Mg$	Willstätter diff.	*b*-Chlorophyll $C_{55}H_{70}O_6N_4Mg$	Adams *b*-Chlorophyll $C_{56}H_{72}O_6N_4Mg$	(A.-W.) diff.
C	73.98	−1.15	72.83	73.03	+0.20
H	8.08	−0.35	7.73	7.83	+ .10
O	8.97	+1.63	10.60	10.44	− .16
N	6.28	−0.09	6.19	6.09	− .10
Mg	2.69	− .04	2.65	2.61	− .04

Experiment has shown that in crude chlorophyll solutions protected from carbon dioxide and exposed to light, the *b*-chlorophyll absorption tends to disappear, and reappears when the solution is exposed to air and light. Willstätter and Stoll[4] found the ratio, *a*-chlorophyll : *b*-chlorophyll, consistently greater for leaves growing in sunlight than for leaves growing in the shade. They give for the mean values of the ratio, respectively, 2.93 and 2.61, or a difference of 0.32, but if the results for the different species be weighted according to the number of observations, instead of being given equal weight, the mean values of the ratio become 2.93 and 2.43, respectively, and the difference, 0.50. Their data also show that on cloudy days the ratio diminishes, that is, tends toward the "shade" value. It is to be expected that during active photosynthesis the local carbon dioxide concentration would be lower than in the general atmosphere.

The chlorophyll may be pictured as going through a cycle of four reactions, two of them associated with the absorption of two quanta each of radiation, and two follow-reactions requiring water and carbon dioxide, but not light:

[ ] Represents $[C_{55}H_{72}O_4N_4Mg]$

$\therefore$ [ ] O is *a*-Chlorophyll [ ] CO_2 is *b*-Chlorophyll

$$\begin{aligned}
[\ ]\,O + H_2O + 2\text{ Quanta }\lambda 666\text{ m}\mu &\longrightarrow [\ ] + H_2O_2\\
[\ ] + CO_2 &\longrightarrow [\ ]\,CO_2\\
[\ ]\,CO_2 + H_2O + 2\text{ Quanta }\lambda 640\text{ m}\mu &\longrightarrow [\ ]\,CO + H_2O_2\\
[\ ]\,CO + H_2O &\longrightarrow [\ ]\,O + HCHO
\end{aligned}$$

As to the 2-quantum absorption, two types of explanation are available: first, the teleological one, since the energy required for either stage of the photosynthetic process exceeds the quantum for the wave length of light

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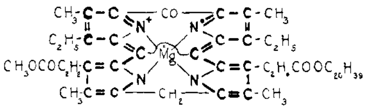
[4] Ref. 3, pp. 112–116.

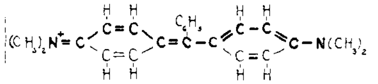
available to plants, the plants were obliged to develop substances which could pick up two quanta at a time; second, from the structure of chlorophyll.

The structure given in Fig. 1 is slightly different from that given by Willstätter for *a*-chlorophyll, but the difference does not affect the discussion to follow.

Comparison with the cation of malachite green shows that chlorophyll contains *two* conjugated chains of the same length (11 atoms) as the chain of the former. Simultaneous absorption of two quanta of red light is therefore to be expected. Since the differences between *a*- and *b*-chlorophyll do not involve these chains, only a slight difference in wave length of light absorbed is to be expected.



a-Chlorophyll



Malachite Green (Cation)

Fig. 1.

Summary

1. The structure of chlorophyll, *a*- and *b*-, alike, is such that it would be expected to absorb simultaneously two quanta of red light.

2. The energy of the four quanta so absorbed, 174.4 Cal./mole, is sufficient to cause the chlorophyll to pass through a cycle of four reactions, the outcome of which is the conversion of one molecule of carbon dioxide and three of water into two of hydrogen peroxide and one of formaldehyde, for which 171.0 Cal./mole is required.

3. Since six molecules of formaldehyde are required to produce one molecule of glucose, whose heat of combustion (dissolved) is 674 Cal./mole, the maximum possible efficiency of glucose production is $674 \div (6 \times 174.4) = 64.4\%$, which is to be compared with Warburg and Negelein's results with *Chlorella.* They found for the mean efficiency using red light, 59%, and the highest single value, 63.5%.

4. The formula for *b*-chlorophyll required, $C_{56}H_{72}O_6N_4Mg$, agrees within the usual limits of organic quantitative analysis with the formula, $C_{55}H_{70}O_6N_4Mg$, assigned to it by Willstätter.

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