



In view of the possible errors in the assumed data, we feel that the above dissociation energies are subject to an uncertainty of about ± 2 k.cal./mole.

Butler and Polanyi⁵ have measured the C—I dissociation energy in phenyl iodide by means of pyrolytic decomposition. Szwarc⁶ has repeated this work and obtained a higher value. Also, Szwarc and Williams⁷ have found the C—Br dissociation energy in phenyl bromide.

From these results and the heats of formation of gaseous phenyl iodide, phenyl bromide and benzene, the heat of formation of the phenyl radical and the C—H dissociation energy in benzene may be derived.

C—hal. dissociation energy in k.cal./mole	$Q_f(\text{C}_6\text{H}_5)$ in k.cal./mole	$D(\text{C}_6\text{H}_5 - \text{H})$ in k.cal./mole
$D(\text{Ph} - \text{I}) \sim 55$ (ref. 5)	~ -67.9	~ 100
$D(\text{Ph} - \text{I}) > 57$ (ref. 6)	~ -70	~ 102
$D(\text{Ph} - \text{Br}) = 70.9$ (ref. 7)	-69.7	102

Finally, the measured heats of formation enable us to calculate the sum of the Hg—C dissociation energies in the compounds investigated:

$D(\text{Hg} - \text{Me}_2) = 57.1 \pm 2$ k.cal./mole	} limits of error uncertain
$D(\text{Hg} - \text{Et}_2) = 48.5$ k.cal./mole	
$D(\text{Hg} - \text{Ph}_2) = 60$,,	

We should like to add that our experimental results could not have been extended so widely but for the valuable work carried out on the thermochemistry of these mercury compounds by Skinner and his co-workers in Manchester.

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¹ Berthelot, *C.R. Acad. Sci., Paris*, **129**, 918 (1899).

² Gilman and Brown, *J. Amer. Chem. Soc.*, **51**, 928 (1929); **52**, 3314 (1930).

³ Hartley, Pritchard and Skinner, *Trans. Farad. Soc.*, **46**, 1019 (1950).

⁴ Hartley, Pritchard and Skinner, *Trans. Farad. Soc.*, **47**, 254 (1951).

⁵ Butler and Polanyi, *Trans. Farad. Soc.*, **39**, 19 (1943).

⁶ Szwarc, thesis (University of Manchester, 1947).

⁷ Szwarc and Williams, *J. Chem. Phys.* (in the press).

Precursors of Protoporphyrin in *Chlorella*

ON the basis of studies of *Chlorella* mutants a biosynthetic chain has been formulated leading from protoporphyrin through Mg protoporphyrin, Mg vinyl pheoporphyrin and protochlorophyll finally to chlorophyll¹. We have recently isolated a *Chlorella* mutant which promises to reveal some of the precursor porphyrins leading up to protoporphyrin.

This mutant, *W₅B-17*, arose from an irradiation with ultra-violet light of the protoporphyrin-producing *W₅B* cells. The *W₅B-17* cells appear almost colourless or pale brown. On solid medium they leak out porphyrins which are more soluble than protoporphyrin and discolour the agar pink. It has been found possible to grow this mutant in liquid culture without diminishing the pigment yield. Starting with a colourless medium, by the end of the week the medium turns a deep chocolate-brown colour due to the accumulation of porphyrins produced by the mutant. From fifteen litres of medium it is estimated that a total of approximately 1.5 gm. of porphyrins is produced.

Preliminary studies of the porphyrins from this mutant indicate that it consists of a number of components. From the R_F values of the paper chromatograms² it is concluded that there are present, in this mixture, porphyrins containing 2, 3, 4, 5 and possibly

8 carboxyls. The fraction containing two carboxyl groups per molecule represents most of the porphyrin produced: it consists of protoporphyrin and two additional main porphyrin components. One of these main components may be an immediate precursor of protoporphyrin since its absorption spectrum indicates that it contains one vinyl group in contrast to the two vinyl groups of protoporphyrin.

In the past, workers who have attempted a study of porphyrin precursors have been limited in material primarily to the porphyrins excreted by patients with some metabolic lesion in their porphyrin metabolism. Such studies have been difficult because the disease is rare, the isolation of the pigments tedious and the yields small. This new mutant now makes available unlimited quantities of several of the protoporphyrin precursors. It is hoped that studies on this alga will not only provide information on the important biosynthetic chain of heme and chlorophyll but also may eventually contribute to an understanding of porphyrinuric diseases in man.

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¹ Granick, S., *Ann. Rev. Plant Physiol.*, **2**, 115 (1951).

² Nicholas, R. E. H., and Rimington, C., *Scand. J. Clin. Lab. Invest.*, **1**, 12 (1949).

Structure of Lanostenol

RECENTLY, the molecular structure of lanostadienol (lanosterol), $\text{C}_{30}\text{H}_{50}\text{O}$, an important 'triterpenoid' constituent of wool-wax, has been studied intensively. Ruzicka *et al.*¹ and Barton, McGhie *et al.*² have suggested three possible formulæ and, considering the evidence available, were unable to decide between them. Earlier, we had begun an X-ray structure analysis to provide unequivocal proof of the molecular structure of lanostadienol. This investigation has provided, in addition, a complete description of the stereochemistry of the molecule, avoiding the complex orthodox methods of stereochemistry. From earlier work, lanostadienol is known to contain four rings, one inert double-bond and one active double bond in the terminal *isopropylidene* group of the long side-chain. Hydrogenation of the active double-bond yields lanostenol, and the iodoacetate of this compound³ was selected as a suitable 'heavy-atom' derivative for the structure analysis.

The crystals of lanostenol iodoacetate, $\text{C}_{32}\text{H}_{53}\text{O}_2\text{I}$, are orthorhombic, the space group being $P2_12_12_1$. There are four molecules in the unit-cell of dimensions: $a = 7.6$, $b = 10.9$, $c = 38.6$ Å. The x , y and z parameters of the iodine atoms were determined from Patterson F^2 syntheses of the projections along the a and b axes. The first Fourier syntheses, $\rho(0yz)$ and $\rho(x0z)$ were computed with the majority of signs fixed by the contributions of the iodine atoms, and from these electron-density distributions the general disposition of the molecule in the unit cell was evident. Due to the existence of false peaks adjacent to the iodine atoms, the initial difficulty in solving the structure was the location of the acetate group. However, after testing various molecular models, the detailed configuration of the molecule was achieved, refinement proceeding by successive Fourier syntheses until the reliability factors, $\frac{\sum |F_o - F_c|}{\sum |F_o|}$, were reduced to 22 and 25 per cent