Course -M.Sc. Botany Part-II, Paper-IX

(Group-"B")

Topic- Chemical Structure of Chlorophyll

(Bio-Chemistry)

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Chemical structure of Chlorophyll

Chlorophyll is a chlorin pigment, related to the porphyrin containing iron compound known as heme. At the centre of the ring is a magnesium ion. The side chains vary somewhat between the different forms of chlorophyll found in different organisms - chlorophyll *a* is always present, but chlorophylls *b* and *c* also occur in various groups.

Chlorophyll a contains a magnesium ion encased in a large ring structure known as a chlorin. The chlorin ring is a heterocyclic compound derived from pyrrole. Four nitrogen atoms from the chlorin surround and bind the magnesium atom. The magnesium centre uniquely defines the structure as a chlorophyll molecule.

Forms of chlorophyll

Chlorophyll consists of two forms, a and b.

a: $C_{55}H_{72}O_5N_4Mg$

b: $C_{55}H_{70}O_6N_4Mg$

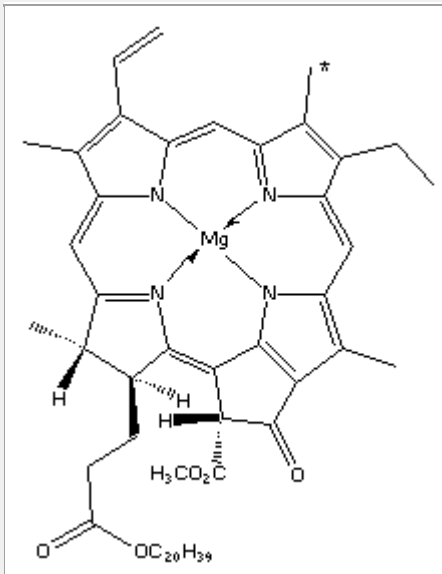
In both cases the magnesium atom is central in the molecule.

This green pigment is what gives green plants their colour. It is involved in photosynthesis by absorbing energy from visible light.

Chlorophyll is a green compound found in leaves and green stems of plants. Initially, it was assumed that chlorophyll was a single compound but in 1864 Stokes showed by spectroscopy that chlorophyll was a mixture. If dried leaves are powdered and digested with ethanol, after concentration of the solvent, 'crystalline' chlorophyll is obtained, but if ether or aqueous acetone is used instead of ethanol, the product is 'amorphous' chlorophyll.

In 1912, Willstatter *et al.* showed that chlorophyll was a mixture of two compounds, chlorophyll-*a* and chlorophyll-*b*:

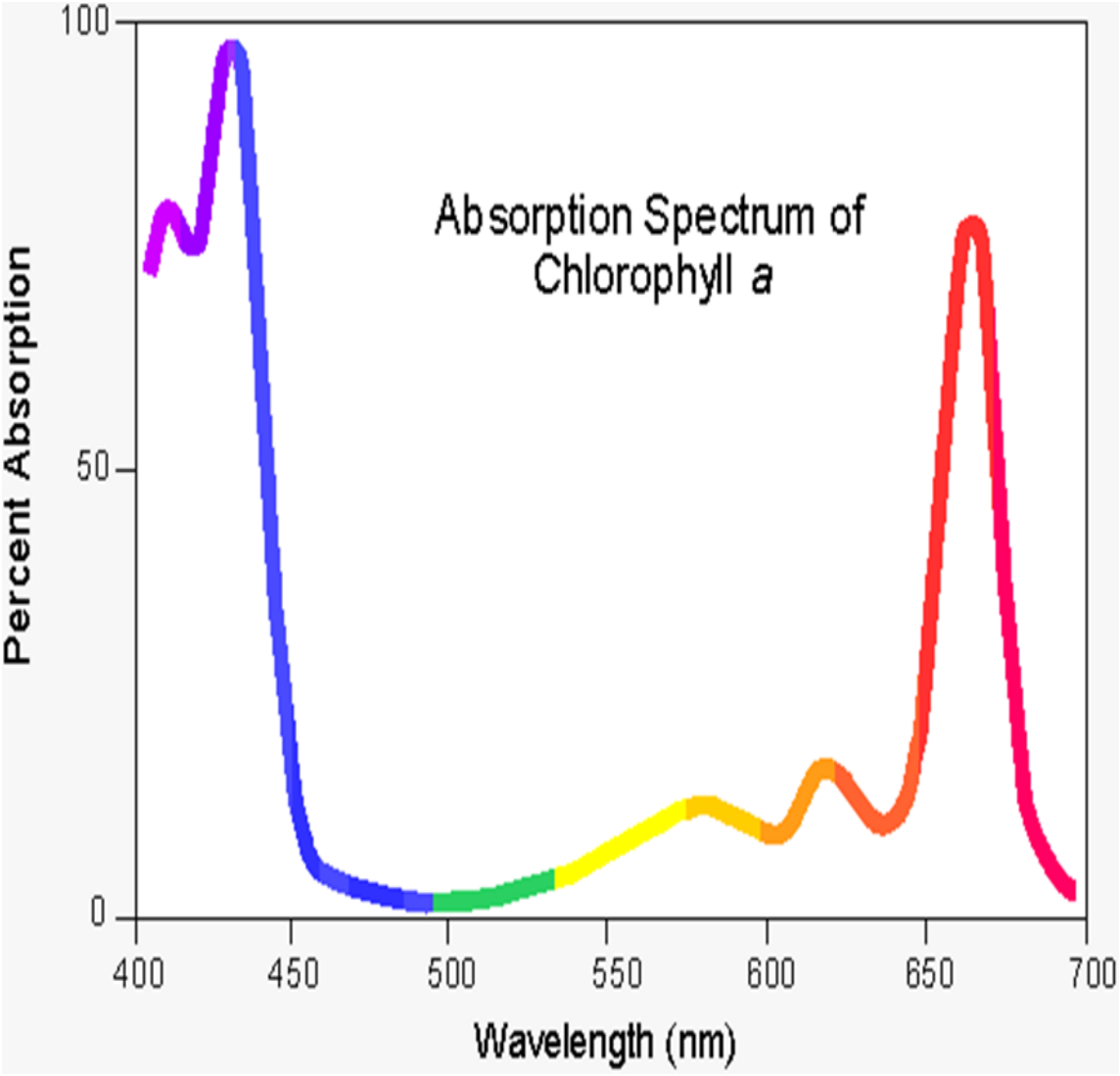
Apart from this fucoxanthin and phycoerythrin are important component of chlorohyll.



Chlorophyll-*a* ($C_{55}H_{72}MgN_4O_5$, mol. wt.: 893.49). The methyl group marked with an asterisk is replaced by an aldehyde in chlorophyll-*b* ($C_{55}H_{70}MgN_4O_6$, mol. wt.: 906.51).

The two components were separated by shaking a light petroleum solution of chlorophyll with aqueous methanol: chlorophyll-*a* remains in the light petroleum but chlorophyll-*b* is transferred into the aqueous methanol. Cholorophyll-*a* is a bluish-black solid and cholorophyll-*b* is a dark green solid, both giving a green solution in organic solutions. In natural chlorophyll there is a ratio of 3 to 1 (of *a* to *b*) of the two components.

The intense green colour of chlorophyll is due to its strong absorbencies in the red and blue regions of the spectrum, shown the below figure. Because of these absorbencies the light it reflects and transmits appears green.



The uv /visible adsorption spectrum for chlorophyll.

The different structures of chlorophyll are summarized below:

	Chlorophyll *a*	Chlorophyll *b*	Chlorophyll *c1*	Chlorophyll *c2*	Chlorophyll *d*
Molecular formula	$C_{55}H_{72}O_5N_4Mg$	$C_{55}H_{70}O_6N_4Mg$	$C_{35}H_{30}O_5N_4Mg$	$C_{35}H_{28}O_5N_4Mg$	$C_{54}H_{70}O_6N_4Mg$
C3 group	-CH=CH2	-CH=CH2	-CH=CH2	-CH=CH2	-CHO
C7 group	-CH3	-CHO	-CH3	-CH3	-CH3
C8 group	-CH2CH3	-CH2CH3	-CH2CH3	-CH=CH2	-CH2CH3
C17 group	-CH2CH2COO-Phytyl	-CH2CH2COO-Phytyl	-CH=CHCOOH	-CH=CHCOOH	-CH2CH2COO-Phytyl
C17-C18 bond	Single	Single	Double	Double	Single
Occurrence	Universal	Mostly plants	Various algae	Various algae	cyanobacteria

Function of chlorophyll

Due to the green colour of chlorophyll, it has many uses as dyes and pigments. It is used in colouring soaps, oils, waxes and confectionary.

Chlorophyll's most important use, however, is in nature, in photosynthesis. It is capable of channelling the energy of sunlight into chemical energy through the process of photosynthesis. In this process the energy absorbed by chlorophyll transforms carbon dioxide and water into carbohydrates and oxygen:

$CO_2 + H_2O \quad (CH_2O) + O_2$

Note: CH_2O is the empirical formula of carbohydrates.

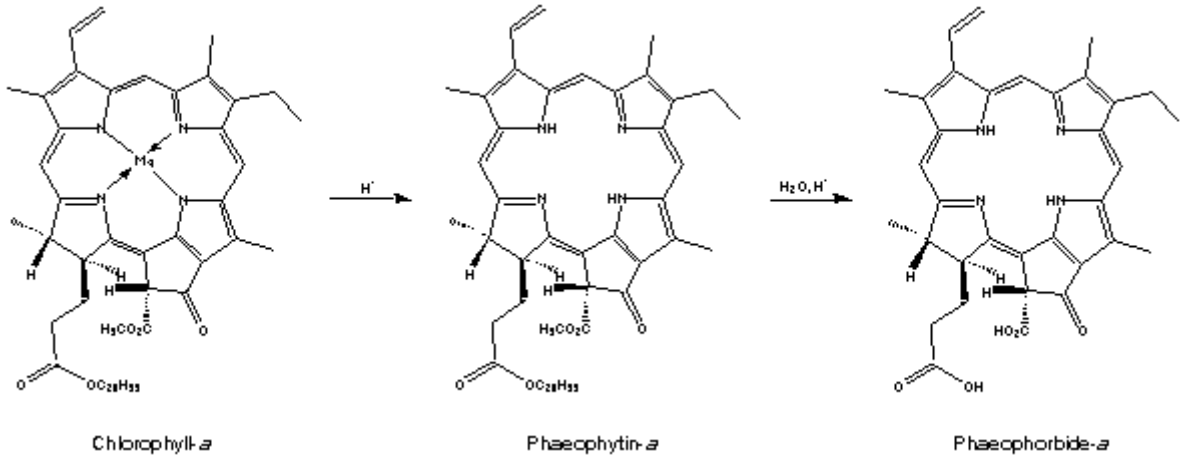
The chemical energy stored by photosynthesis in carbohydrates drives biochemical reactions in nearly all living organisms.

In the photosynthetic reaction electrons are transferred from water to carbon dioxide, that is carbon dioxide is reduced by water. Chlorophyll assists this transfer as when chlorophyll absorbs light energy, an electron in chlorophyll is excited from a lower energy state to a higher energy state. In this higher energy state, this electron is more readily transferred to another molecule. This starts a chain of electron-transfer steps, which ends with an electron being transferred to carbon dioxide. Meanwhile, the chlorophyll which gave up an electron can accept

an electron from another molecule. This is the end of a process which starts with the removal of an electron from water. Thus, chlorophyll is at the centre of the photosynthetic oxidation-reduction reaction between carbon dioxide and water.

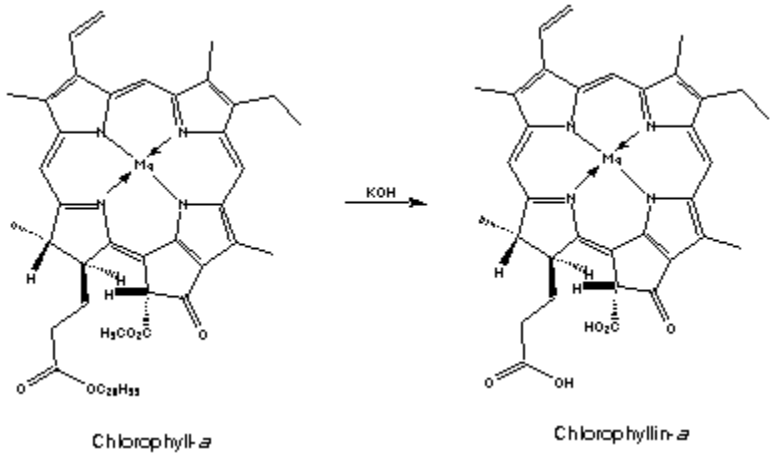
Simple reactions of chlorophyll

Treatment of cholorophyll-a with acid removes the magnesium ion replacing it with two hydrogen atoms giving an olive-brown solid, phaeophytin-a. Hydrolysis of this (reverse of esterification) splits off phytol and gives phaeophorbide-a. Similar compounds are obtained if chlorophyll-b is used.



Overall reaction scheme for the hydrolysis of chlorophyll.

Chlorophyll can also be reacted with a base which yields a series of phyllins, magnesium porphyrin compounds. Treatment of phyllins with acid gives porphyrins.



Overall scheme for the reaction of alkaline with chlorophyll.

Thanks and Regards

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