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Chemical transformations of chlorophyll and its application in the design of a new generation of environmentally safe dyes

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Abstract. Chemical transformations of chlorophyll and physicochemical properties of its derivatives are considered. These compounds can be used in the design of a new generation of chlorophyll- and porphyrin-based dyes environmentally more safe than currently used arene dyes and possessing renewable sources of raw materials. The first results on the use of chlorophyll derivatives for dyeing wool, acetate fibres and cotton are reported. The bibliography includes 91 references.

I. Introduction

Chlorophyll as one of the main representatives of the plant world has been a subject of keen interest for investigators for many years.[1–8] An important characteristic feature of chlorophyll is its ability to absorb solar energy and to transform it into chemical energy in a photochemical reaction of water with carbon dioxide occurring in plant cells:

$$6\,H_2O + 6\,CO_2 \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2. \qquad (1)$$

This process represents a key reaction of photosynthesis of carbohydrates and ATP in the green leaf. The energy liberated in the decomposition of ATP is utilised for the synthesis of all the other classes of biomolecules.[9–16]

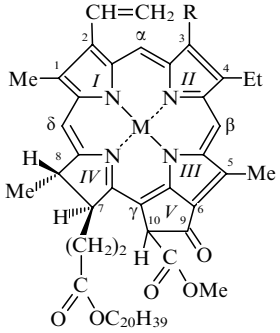
The specific chemical, photochemical and photophysical properties of chlorophyll attract attention with regard to the practical application of its derivatives in phototransformation of solar energy,[17] semiconductor engineering,[18] photochemical and electrochemical catalysis,[19] generation of singlet molecular oxygen,[20] thermo- and photostabilisation of fats and polymers,[21] *etc.*

Numerous vitally important applied problems (*e.g.*, purification of waste and heat-carrier gases, design of gas- and ion-sensitive electrodes, production of pure oxygen from atmospheric air, photodynamic therapy of cancerous diseases, *etc.*) that can be solved using chlorophyll derivatives and its structural analogues have been repeatedly discussed in the literature.[4, 22, 23]

One of the main challenges for investigators is the design of up-to-date high-quality dyes manifesting high chemical, thermal and photo stability, spectral colour purity and environmental safety as regards their manufacture and application in the textile, paint-and-varnish, printing, food and light industries. Complexes of Cu, Zn, Fe, Co, Ni and other metals with porphyrins and chlorins derived from chlorophyll meet all these requirements.

II. Structure and chemical transformations of chlorophyll

Specific chemical, spectral, chromophore and photochemical properties of chlorophyll **1** and pheophytin **2**, which determine their biological functions and natural coloristic characteristics, are due to the presence of a macrocyclic aromatic nucleus and functional groups in their molecules. These include a vinyl group, a cyclopentenone ring and two ester groups, *viz.*, a propionyl residue esterified by phytol in position 7 and a methoxycarbonyl group in position 10. Besides, the active reaction centre of chlorophyll **1** is represented by a Mg^{2+} ion coordinated to four pyrrole nitrogen atoms, while the active centre of pheophytin **2** contains two proton-donor (−NH−) and two basic (=N−) groups. The C(10)−H bond is strongly polarised due to the presence of three electronegative fragments (C=O, CO_2Me and the π-system of the macroring) and is therefore chemically active.



1, **2**

1: M = Mg, R = Me (**a**), CHO (**b**);
2: M = 2H, R = Me (**a**), CHO (**b**).

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It is impossible to consider the whole range of essential characteristics of chlorophyll and pheophytin in one review; therefore, we thought it expedient to highlight only chemical transformations of chlorophyll into its derivatives possessing all the properties of industrial dyes.

One of the main chemical features of chlorophyll is its ability to eliminate Mg^{2+} in acidic media to be converted into pheophytin:

$$MgChl + 2H_3O^+ \rightleftharpoons Mg^{2+}\cdot(H_2O)_2 + H_2Chl, \qquad (2)$$

where MgChl is chlorophyll and H_2Chl is pheophytin.

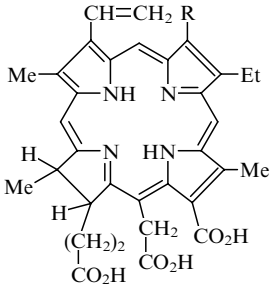
The dissociation of chlorophyll in various organic solvents has been studied in detail. The activation parameters and the mechanism of reaction (2) depending on the specific characteristics of the medium were established.[4] Pheophytin formed upon dissociation of chlorophyll reacts with metal salts in organic solvents (at high rates in carboxylic acids and alcohols and at low rates in pyridine and DMSO)[4] to give metallopheophytinates MChl.

$$MX_2(Solv)_{n-2} + H_2Chl \rightleftharpoons MChl + 2HX + (n-2)Solv, \qquad (3)$$

where MX_2 is the metal salt and Solv are the coordinated solvent molecules.

Pheophytin complexes with d-metals are much more stable than chlorophyll with the exception of Cd^{2+} and Hg^{2+} pheophytinates which, in contrast to MgChl, dissociate in carboxylic acids virtually instantaneously. Stable pheophytin metal complexes, like those of chlorophyll, can find application as dyes.

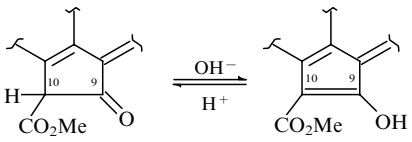
Yet another important feature of chlorophyll and pheophytin is their ability to undergo opening of the cyclopentenone ring. In contrast to four pyrrole rings (*I*–*IV*), the cyclopentenone ring (*V*) polarised by a keto group is insufficiently stable and contains a mobile hydrogen atom in position 10. The ring *V* causes significant distortions in the geometrical parameters of the planar chlorin macrocycle. The opening of the cyclopentenone ring occurs under the action of various reagents (*e.g.*, OH^-, O_2, amines, *etc.*). The oxidative destruction and opening of the cyclopentenone ring result in the formation of chlorin e_6 (**3**) from chlorophyll *a* (**1a**), and of rhodin g_7 (**4**) from chlorophyll *b* (**1b**).



3, 4

R = Me (**3**), CHO (**4**).

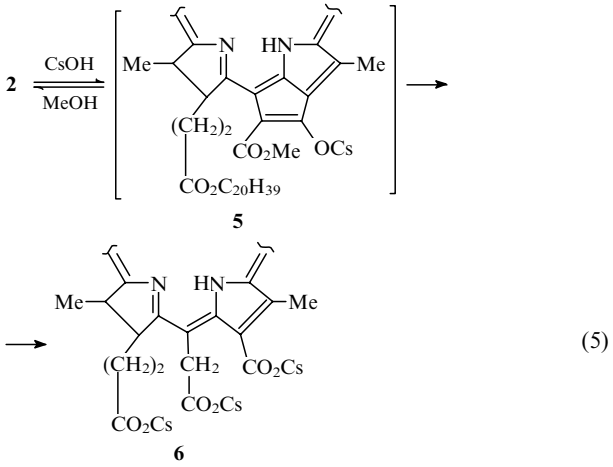
This reaction is most often preceded by keto–enol tautomerism:



(4)

The reaction of a ketone with the OH^- ion may follow two different routes: one of them leads to ionisation of the C(10)–H bond, while the other one entails nucleophilic addition of OH^- to the C(9) atom with subsequent elimination of the H_2O molecule. The enol thus formed is unstable and is rapidly and irreversibly decomposed in alkaline solutions with the opening of the cyclopentenone ring.

The kinetics of cleavage of the cyclopentenone ring was studied under various conditions.[24,25] The addition of 0.1 M CsOH causes changes in the electronic absorption spectrum of pheophytin *a* manifested in the appearance of strong absorption in the region of 460–520 nm and a decrease in the intensity of the first absorption band [λ_I = 667 nm in an ethyl acetate–methanol mixture (12 : 1)]. In this reaction, known in chlorophyll biochemistry as the Molisch 'phase test', an unstable yellow-coloured enol form of chlorophyll or pheophytin (**5**) is initially formed. The electronic spectrum recorded 135 min after the onset of the reaction resembles that of the original pheophytin owing to the formation of a tricaesium salt of chlorin e_6 (**6**):



(5)

The keto–enol equilibrium constants (K_{KE}) have been determined:[24,25]

$$\underset{\text{Ketone form}}{H_2Chl} + Cs^+MeO^- \rightleftharpoons \underset{\text{Enol form}}{HChl^-Cs^+} + MeOH, \qquad (6)$$

$$K_{KE} = \frac{[HChl^-Cs^+][MeOH]}{[H_2Chl][Cs^+MeO^-]}. \qquad (7)$$

The K_{KE} values for ethyl acetate–methanol–CsOH and ethyl acetate–ethanol–CsOH mixtures measured at 298 K are equal to $(3.2 \pm 0.3) \times 10^{-3}$ and $(8.2 \pm 1.2) \times 10^{-3}$, respectively. Obviously, the equilibrium (6) is strongly shifted towards the keto form H_2Chl, the enol form being stabilised by ethanol more effectively than by methanol. In this respect, it is of note that glycerol shifts the keto–enol equilibrium to the right more strongly than other alcohols as a result of additional stabilisation of the enol form of pheophytin by intermolecular hydrogen bonds.[26]

The effective rate constants for the opening of the cyclopentenone ring of pheophytin in the presence of alkali in some organic solvents were measured using spectrophotometry from the decrement in the intensity of the absorption band at 460 nm (Table 1).[24,25] The rate of the second step of reaction (5) is independent of the concentration of alkali, since it affects only the reaction equilibrium (6) (which is shifted to the right) and is not directly involved in the cleavage of the exocycle. The double bond C(10)=C(9) of the exocycle is oxidised by atmospheric oxygen present in the solution. The putative mechanism of reaction (5) has been discussed.[25]

The effective rate constant k_{eff} for the second step of reaction (5) is determined by the equation:

$$-\frac{dc_i}{dt} = k_{eff}c_i, \qquad (8)$$

where c_i is the concentration of the intermediate **5**.

Table 1. Effective rate constants for oxidative degradation (k_{eff}) of pheophytin *a* in mixed organic solvents in the presence of an alkali (298 K) (the operating wavelength $\lambda = 460$ nm, $c^0_{H_2Chl} = 2 \times 10^{-5}$ mol litre^{-1}, $c^0_{O_2} \approx 0.2$ ml cm^{-3}).[24, 25]

Solvent (volume ratio)	c_{CsOH} /mol litre^{-1}	k_{eff} /s^{-1}
$MeCO_2Et$ – MeOH (12 : 1)	$(1.5-80) \times 10^{-3}$	$(2.5 \pm 0.1) \times 10^{-4}$
$MeCO_2Et$ – EtOH (12 : 1)	4×10^{-2}	2.05×10^{-3}
$MeCO_2Et$ – n-$C_5H_{11}OH$ (12 : 1)	3.7×10^{-2}	1.3×10^{-3}
Et_2O – MeOH (12 : 1)	1.1×10^{-2}	6.9×10^{-4}
CCl_4 – MeOH (12 : 1)	1.1×10^{-2}	3.0×10^{-4}
MeOH [a]	0.4 – 0.9	5.4×10^{-4}
EtOH [b]	0.1 – 0.8	6.3×10^{-5}
n-C_3H_7OH [a]	0.4	8.0×10^{-5}
n-$C_5H_{11}OH$ [a]	0.01 – 0.4	9.5×10^{-5}

[a] $c^0_{H_2Chl} = 2.0 \times 10^{-4}$ mol litre^{-1}; [b] $c^0_{H_2Chl} = 2.2 \times 10^{-4}$ mol litre^{-1}.

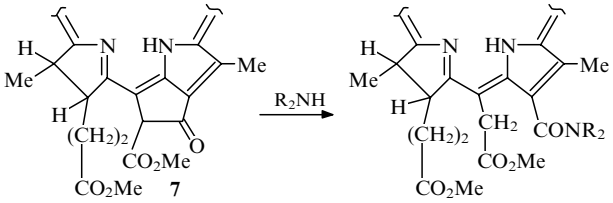
At the same time,

$$k_{eff} = k_v c_{O_2},$$

where k_v is the rate constant for the bimolecular reaction (5). With the molar concentration of O_2 in a saturated solution equal to 7×10^{-3} mol litre^{-1}, the rate constant for reaction (5) can be calculated by the formula:[24, 25]

$$k_v = \frac{k_{eff}}{c_{O_2}} = 1.4 \times 10^2 k_{eff}. \quad (9)$$

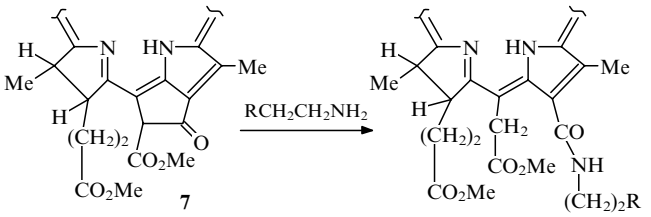
The opening of the cyclopentenone ring of methylpheophorbide *a* (**7**) under the action of amines has been studied.[27] These reactions result in the preferential amidation of one of the carboxy groups formed upon the opening of the exocycle to yield 6-monoamides of 7,γ-dimethyl ester of chlorin e_6.



R = Me, Et.

Analogously, the reaction of methylpheophorbide *a* with yet another nucleophilic reagent, *viz*., morpholine, results in the opening of the cyclopentenone ring. The amide groups of the chlorin derivatives manifest higher affinity for natural and synthetic polyamide fibres.

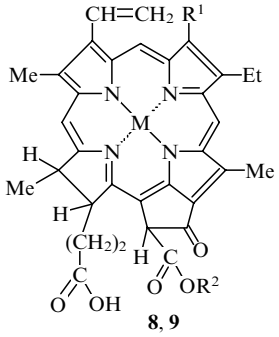
The aminolysis of methylpheophorbide (**7**) by ethylenediamine and ethanolamine is of considerable interest for the synthesis of chlorophyll dyes. In dilute aqueous solutions of carboxylic acids, monoamides of dimethyl ester of chlorin e_6 and their complexes with d-metals are converted into cationic dyes containing an active NH_3^+ group able to bind tightly to amide-type fibres containing terminal COOH groups.



R = NH_2, OH.

Reactions involving alkoxycarbonyl groups, *viz*., the phytyl propionate group in the pyrrole ring *IV* and the methoxycarbonyl group in the ring *V*, are extremely important for chlorophyll and pheophytin. Mild alkaline hydrolysis results in the splitting of phytol $C_{20}H_{39}OH$ and methanol, while the central metal ion is preserved; under these conditions, chlorophyll is transformed into chlorophyllin **8**. Acid hydrolysis leads to the loss of Mg^{2+} and the phytol residue resulting in the formation of pheophorbide **9**.

The extended size of the phytyl residue favours its incorporation into the solvation shell of chlorophyll and pheophytin and creates steric hindrance for the reagents; removal of phytol increases the rates of many chemical reactions.

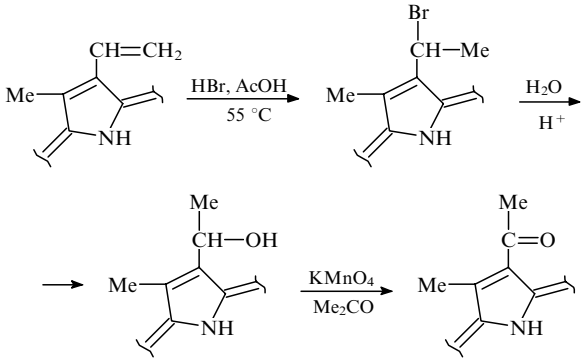


8, **9**

R^1 = Me, CHO; R^2 = H, M = Mg (**8**), R^2 = Me, M = 2 H (**9**).

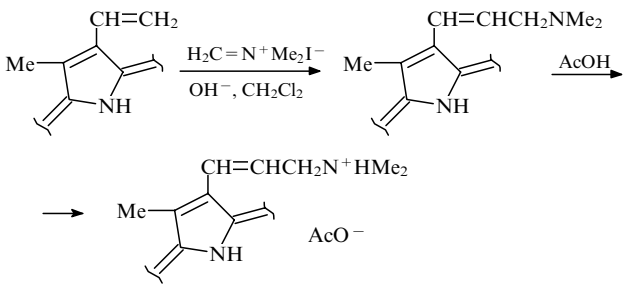
Free carboxy groups favour not only the solvation of pigment molecules in highly polar solvents, but also their association in weakly polar media. Therefore, prior to their chemical modification compounds **8** and **9** are methylated (5% methanolic H_2SO_4), resulting in their conversion into methylchlorophyllin and methylpheophorbide, commonly used in the synthesis of diverse chlorophyll derivatives.

The vinyl group of pheophytin, pheophorbide and other chlorophyll derivatives reacts easily with HBr in organic solvents.[28]

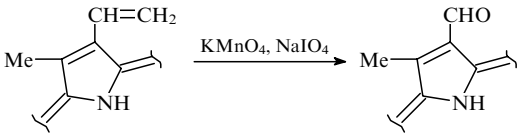


Bromine can be replaced by treatment with nucleophilic reagents,[29] which enables the preparation of chlorophyll derivatives with functional groups in position 2. For example, acid hydrolysis yields derivatives with an alcohol group which can be oxidised to the keto group by potassium permanganate.[30]

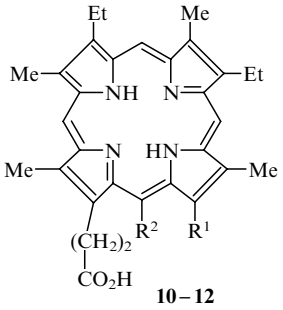
The reaction of chlorophyll with methylidenedimethylammonium iodide and subsequent treatment with acetic acid afford a cationic amino derivative [31] which is of interest in the chemistry of chlorophyll-based dyes due to its higher affinity for polyamide fibres. Quaternisation of tertiary amines affords chromophores that are readily soluble in water.



The oxidation of the vinyl group is an interesting approach to the modification of chlorophyll molecules. Treatment of chlorophyll *a* with $KMnO_4$ and then with $NaIO_4$ results in the incorporation of the aldehyde group into position 2 of the macrocycle which is not accompanied by the oxidation of the cyclopentenone ring. The formyl group can further be converted into a carboxy group.[32, 33]



Chlorophyll and its derivatives contain a chlorin macrocycle with a partially hydrogenated pyrrole ring. Chlorophyll derivatives can successfully be converted into porphyrins among which phylloporphyrin (**10**), pyrroporphyrin (**11**) and rhodoporphyrin (**12**) are of considerable practical interest by virtue of their peculiar structures, and high thermal and chemical stabilities. These compounds represent final products of chlorin conversions under the most drastic redox conditions. The preparation of pyrroporphyrin methyl ester from a mixture of pheophytins *a* and *b* by heating it in an autoclave with 30% KOH in methanol in the presence of a silver catalyst (8 h, 185 °C) has been described.[30, 34] Rhodoporphyrin dimethyl ester is synthesised from pheophytins *a* and *b* under similar conditions but at 145 °C. Phylloporphyrin is prepared from a mixture of pheophorbides *a* and *b* by heating it in pyridine in the presence of 30% methanolic KOH (138 – 140 °C).[34, 35] The reduction of the vinyl group is accompanied by simultaneous dehydrogenation of the C—C bond in the pyrrole ring *IV* of chlorin. It is noteworthy that the preparation of these porphyrins does not require any preliminary separation of a mixture of chlorophylls *a* and *b*.



10 – 12

R^1 = H: R^2 = Me (**10**), H (**11**); R^1 = CO_2H, R^2 = H (**12**).

Chemical modification of peripheral substituents of chlorophyll is possible owing to the extremely high stability of the aromatic porphyrin macroring in acidic, alkaline and various redox media.

III. Chromophore systems of chlorophyll, its derivatives and analogues

Electronic absorption spectra (EAS) provide valuable information about chromophore properties of molecules and the possibility of their use, in principle, as dyes. The electronic absorption spectra of tetrapyrrole aromatic macrocyclic compounds are considered comprehensively in monographs,[4, 18, 36] so there is no need to discuss them in detail. Suffice it to say that EAS of porphyrins, phthalocyanines and chlorophylls differ considerably.[36]

The electronic absorption spectra of porphyrins (Fig. 1) are characterised by low molar extinction coefficients (ε) in the visible region, high intensity of the Soret band at the boundary of visible and near-ultraviolet regions ($\lambda \approx 400$ nm), low sensitivity to the character of inert organic solvents and very high sensitivity to protonating and complex-forming reagents (acids, salts, *etc.*).[4, 36] The positions and intensities of bands in the EAS of porphyrins

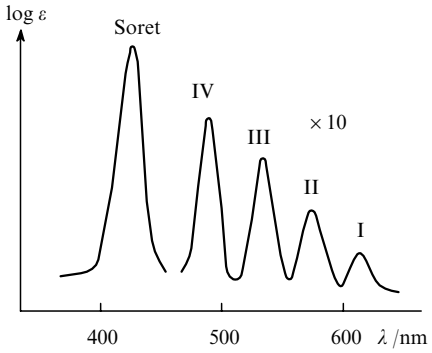


Figure 1. Electronic absorption spectrum of 1,3,5,7-tetramethyl-2,4,6,8-tetraethylporphin.

vary depending on the structures of the side substituents and their positions in the molecules.

In contrast to porphyrins, chlorins are characterised by a long-wave shift and high intensity of the first absorption band (Fig. 2), which enhances the chromophore properties of dyes.

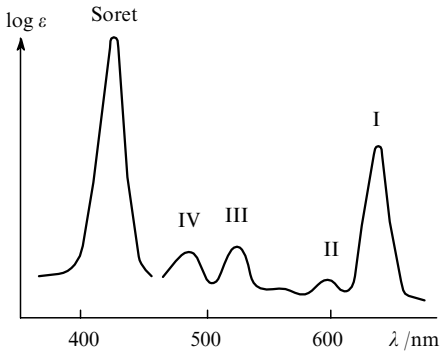


Figure 2. Electronic absorption spectrum of octaalkyl-7,8-dihydroporphin.

The intensities of the first absorption band of pheophytin (Table 2) and chlorophyll (Table 3) depend weakly on the nature of the solvent. In this case, its weak solvatochromic effect is determined by the symmetry of the macrocyclic chlorin chromophore, its atomic-electronic environment and, possibly, minor differences in the solvation of the ground and excited states of chlorophyll and pheophytin.

Special mention should be made of the relatively small dependence of the EAS of chlorins on the presence of substituents in the pyrrole fragments.

Incorporation of a metal atom into the centre of the chlorin molecule does not change the symmetry of the π-electron cloud of the chromophore. This is why EAS of metallochlorins do not differ significantly from that of pheophytin. In particular, the incorporation of Mg^{2+} or any other metal has little effect on the intensity of 'red' absorption bands of chlorins (see Tables 2, 3), since electron transitions in this band are permitted for both the ligand and the complexes.[36] However, the colour tones of crystalline chlorins, their complexes and solutions may vary widely, which is especially important for the chemistry of dyes.

In contrast, in the case of porphyrins the effects of metal cations on the electronic absorption spectra are very pronounced.[4] The complexation of metal ions with porphyrins results in degeneration of the energy levels for the electronic $\pi \rightarrow \pi^*$ transitions polarised along the coordination axes *x* and *y* in the plane of the macrocycle. The absorption bands I and III of free porphyrin corresponding to these transitions merge into one band (I) with an increase in the symmetry of metalloporphyrin mole-

Table 2. Wavelengths (λ /nm) and intensities ($\log \varepsilon$) of the absorption bands in the EAS of pheophytin *a* in organic solvents at 298 K.[36]

Solvent	λ ($\log \varepsilon$)				
	I	II	III	IV	Soret
Methanol	668 (4.417)	614 (3.688)	535 (3.702)	502 (3.876)	401 (4.852)
Ethanol	668 (4.504)	610 (3.834)	537 (3.852)	507 (3.901)	409 (4.814)
Pentanol	670 (4.583)	612 (3.884)	540 (3.933)	508 (3.951)	412 (4.888)
Acetone	666 (4.506)	608 (3.799)	535 (3.861)	505 (3.887)	410 (4.874)
DMF	669 (4.554)	610 (3.827)	535 (3.908)	506 (3.980)	411 (4.900)
Dioxane	670 (4.562)	611 (3.809)	537 (3.881)	507 (3.967)	412 (4.910)
Acetic acid	669 (4.547)	611 (3.882)	537 (3.872)	508 (3.902)	412 (4.922)
Pyridine	672 (4.516)	613 (3.785)	539 (3.861)	509 (3.920)	415 (4.870)
Quinoline	675 (4.570)	617 (3.839)	542 (3.928)	510 (3.945)	421 (4.911)
Glycerol – ethanol	695 (4.562)	640 (3.813)	—	518 (3.940)	415 (4.577)

Table 3. Positions (λ_1) and values of molar extinction coefficients (ε_1) of the first absorption band in the EAS of chlorophyll *a* in various organic solvents.[36]

Solvent	λ_1 /nm	$10^{-4}\varepsilon_1$	Solvent	λ_1 /nm	$10^{-4}\varepsilon_1$	Solvent	λ_1 /nm	$10^{-4}\varepsilon_1$
Methanol	666	6.66	Benzyl alcohol	672	6.66	Aniline	675	6.24
Ethanol	665	6.94	Isoamyl alcohol	667	7.33	Nitromethane	663	6.60
n-Pentanol	667	7.67	Acetonitrile	662	6.88	Carbon disulfide	672	6.80
Acetone	662	7.66	Acetophenone	668	7.65	α-Chloronaphthalene	670	6.94
DMF	664	7.39	Diethyl ether	661	8.51	Chloroform	665	7.15
DMSO	666	7.01	THF	664	8.18	Nitrobenzene	670	6.70
Dioxane	662	8.20	Ethyl acetate	662	7.94	Triethylamine	662	8.52
Pyridine	671	7.69	Benzene	666	7.82	Chlorobenzene	666	7.49
Quinoline	671	7.42						

cules. The intensity of this band increases, which is formally due to the fact that the corresponding electron transition becomes permitted, whereas the transitions I and III of free porphyrins are quasi-forbidden. The true reason for the increase in intensities of the absorption band I in the spectra of metalloporphyrins is that metalloporphyrins are more potent chromophores than the free porphyrins due to the rearrangements in their electronic and electronic-vibrational levels. The essence of these rearrangements is discussed in monographs.[36–38].

Coloured compounds are attributed to strong or weak chromophores based on the intensities of the absorption bands in the visible region of the spectrum. Of two coloured compounds with similar positions of the absorption bands, the one with a larger value of ε possesses more potent chromophore properties. The intensity of the absorption band I in the EAS of porphyrins increases 3–4-fold as a result of complexation, and a short-wave shift of this band by 40–60 nm occurs. In this respect, metalloporphyrins exhibit much more potent chromophore properties than the corresponding metal-free compounds (Tables 4 and 5).

IV. Photochemical stability of chlorophyll and its derivatives

Photochemical stability is a central problem in the design of novel dyes based on chlorophyll and related porphyrins. Chlorophyll and porphyrins are involved in diverse complex photochemical transformations; the theoretical aspects of these transformations are considered in detail in a monograph.[38] In this section, we shall discuss various problems connected with photochemical stabilities of chlorophyll and its derivatives in relation to their synthesis and application as dyes. Upon intense illumination, chlorophyll and porphyrins pass easily into singlet and triplet excited states characterised by high chemical activity and ability to generate singlet oxygen. Under these conditions, the macrocyclic chromophore passes into radical-cationic or radical-anionic forms in the presence of oxidants or reducing agents; their further conversions may lead to the cleavage of the macrocycle.[39] The cationic forms are generated in the presence of weak electron acceptors (O_2, quinones, Fe^{3+}, *etc.*), while stronger oxidants (H_2O_2, HNO_3, NO,

Table 4. Wavelengths (λ /nm) and intensities ($\log \varepsilon$) of the absorption bands in the EAS of pheophytin *a* and its complexes with metals.[36]

Compound	Solvent	λ ($\log \varepsilon$)				
		I	II	III	IV	Soret
H_2Chl *a*	EtOH	668 (4.50)	610 (3.83)	537 (3.85)	507 (3.90)	409 (4.814)
ZnChl *a*	EtOH	655 (4.68)	610 (4.01)	565 (3.74)	522 (3.51)	418 (4.94)
	AcOH	660 (4.71)	615 (4.04)	570 (3.77)	520 (3.59)	427 (4.84)
CuChl *a*	EtOH	650 (4.58)	610 (3.95)	548 (3.55)	501 (3.53)	411 (4.76)
	AcOH	651 (4.54)	610 (3.90)	550 (3.55)	502 (3.54)	411 (4.78)
CoChl *a*	EtOH	644 (4.50)	605 (3.95)	555 (3.66)	500 (3.39)	420 (4.65)
AgChl *a*	EtOH	650 (4.52)	605 (3.92)	555 (3.62)	510 (3.46)	422 (4.61)
MgChl *a*	EtOH	666 (4.73)	618 (4.10)	580 (3.84)	535 (3.54)	431 (4.78)
CdChl *a*	EtOH	665 (4.71)	618 (4.08)	582 (3.80)	532 (3.62)	434 (4.80)
NiChl *a*	AcOH	649 (4.50)	605 (4.00)	548 (3.55)	495 (3.46)	409 (4.67)
PdChl *a*	AcOH	638 (4.72)	595 (4.32)	536 (3.71)	493 (3.61)	393 (4.68)

Table 5. Positions (λ_1 /nm) and intensities ($\log \varepsilon_1$) of the absorption band I in the EAS of proto-, meso-, deutero- and hematoporphyrin and their complexes.[36]

Solvent	λ_1 ($\log \varepsilon_1$) in the spectrum of		
	porphyrin	copper complex	zinc complex
Protoporphyrin			
C_6H_6	634 (3.78)	571 (4.40)	579 (4.42)
Py	631 (3.77)	574 (4.30)	589 (4.26)
DMF	630 (3.75)	570 (4.38)	584 (4.33)
DMSO	630 (3.75)	570 (4.36)	586 (4.30)
EtOH	629 (3.76)	569 (4.32)	584 (4.33)
CCl_4	633 (3.81)	571 (4.41)	579 (4.32)
$CHCl_3$	630 (3.77)	570 (4.39)	561 (4.88)
AcOH	629 (3.44)	569 (4.38)	579 (4.18)
Mesoporphyrin			
C_6H_6	624 (3.79)	562 (4.47)	570 (4.43)
Py	622 (3.75)	564 (4.36)	579 (4.19)
DMF	621 (3.72)	560 (4.44)	579 (4.27)
DMSO	619 (3.73)	561 (4.41)	577 (4.24)
EtOH	619 (3.73)	561 (4.41)	575 (4.26)
CCl_4	626 (3.82)	564 (4.48)	570 (4.37)
$CHCl_3$	621 (3.75)	562 (4.42)	570 (4.34)
AcOH	593 (3.74)	560 (4.44)	569 (4.07)
Deuteroporphyrin			
C_6H_6	623 (3.71)	559 (4.41)	567 (4.34)
DMSO	620 (3.66)	557 (4.38)	571 (4.15)
$CHCl_3$	620 (3.70)	560 (4.38)	568 (4.25)
Hematoporphyrin			
C_6H_6	626 (3.75)	563 (4.41)	571 (4.38)
DMSO	621 (3.72)	562 (4.36)	577 (4.22)
$CHCl_3$	623 (3.74)	564 (4.38)	570 (4.34)

NO_2, $H_2S_2O_8$, *etc*.) result in the loss of chromophore properties. Abstraction of only two electrons from the binding π-orbitals of the porphyrin chromophore results in the disappearance of the absorption bands in the visible region of the spectrum. Thus, the absorption band I in the EAS of the radical cation of the magnesium octaethylporphyrin complex is characterised by lower intensity and has a bathochromic shift by 100 nm in comparison with its position in the spectrum of neutral porphyrin, whereas the corresponding dication is colourless. Pheophytin and its complexes manifest a similar behaviour. The alkyl groups, which represent σ-electron donors, favour the oxidation including photochemical oxidation. In contrast, protonation of porphyrins and chlorins prevents their oxidation. On the whole, chlorins are oxidised more easily than porphyrins. It should be remembered that the factors responsible for chemical and electrochemical oxidation can also influence photooxidation.[4,39]

Effects of metals on the oxidisability of complexes are of special interest. These metals can be divided into two groups that are different in principle. The metals of the first group (Mg, Cu, Zn, Cd, Ti) preserve their oxidation state in the transition of metalloporphyrins into radical-cationic and cationic forms. In this case, the electrons are abstracted from HOMO of the ligand, and the oxidation potential of the complex is lower than that of free porphyrin.[39]

The second group includes the metals (Mn, Fe, Co, Ni, Ag) the oxidation state of which changes upon transition into radical-cationic forms. As a result, the oxidation potentials of the complexes increase considerably.

The rate constants for photochemical destruction of metal analogues of chlorophyll are given in Table 6.[4]

Table 6. Rate constants (k_v) for the photochemical destruction of chlorophyll *a* and its metal complexes at different temperatures.[4]

Compound	Solvent	k_v /h^{-1}		
		20 °C	40 °C	60 °C
H_2Chl *a*	EtOH	very slow	very slow	very slow
	AcOH	0.019	0.039	0.081
MgChl *a*	EtOH	0.400	0.453	0.588
	AcOH	0.297	0.402	0.563
ZnChl *a*	EtOH	0.035	0.053	0.082
	AcOH	0.205	0.304	0.395
CdChl *a*	EtOH	0.460	0.466	0.493
HgChl *a*	EtOH	0.039	0.048	0.065
CoChl *a*	EtOH	–	–	0.025
	AcOH	–	–	0.006
CuChl *a*	AcOH	0.0101	0.015	0.024
PdChl *a*	AcOH	–	–	0.013
NiChl *a*	AcOH	–	–	0.0045
Fe(AcO)Chl *a*	AcOH	–	–	0.004

Ionic complexes with Cd and Mg and weakly covalent (Zn) complexes undergo photodestruction faster than pheophytin. The rate of photochemical oxidation of the covalent complexes with the metal ions (Cu, Co, Ni, Fe, Pd) that deactivate the triplet state and suppress the photogeneration of singlet oxygen is very low. This prompts an important practical conclusion that covalent metal-containing chlorin- and porphyrin-based dyes are much more resistant to photooxidation than free porphyrins.

V. Properties of chlorophyll and its derivatives in solutions. Solubility of porphyrins and energetics of solvation

Many natural porphyrins pass into a solution with difficulty. This is due to relatively high energies of their crystal lattices, low solvation energies of relatively non-polar chemical bonds and strong interactions of the π-systems of the neighbouring molecules. The solubility of porphyrins in organic solvents strongly depends on their structures.[40]

The structural and thermodynamic aspects of the solubilisation and solvation of the main types of porphyrins (chlorophyll, protoporphyrin and their derivatives, tetraphenylporphin, tetrabenzoporphin), their complexes and non-classical porphyrins (tetraazaporphyrins, phthalocyanines, chemical porphyrin dimers, *etc*.) have been investigated.[41–64] The main regularities of the thermodynamics of the solubilisation and solvation of porphyrins by various organic solvents and their binary mixtures have been established. The dependence of these processes on the conformational component of the free energy of solubilisation (ΔG_s), enthalpy (ΔH_s) and entropy (ΔS_s) of solubilisation caused by elimination of conformational strains in porphyrin molecules on phase transitions from the solid state to the solution has been established for the first time.

The energies of molecular lattices (ΔG_{lat}) for the majority of porphyrins are not determined. The contribution of the conformational component ΔG_{conf} for structurally similar porphyrins can be assessed only qualitatively. Therefore, a comparative analysis of experimental data on the solvation of porphyrins and their complexes is usually carried out based on the relative enthalpies of solubilisation of these compounds in a series of solvents with the least solvating one used as a standard.

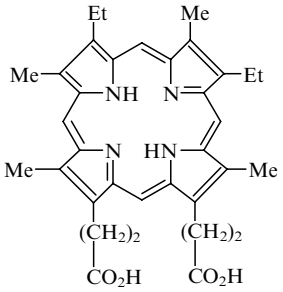
Chlorins are much more soluble in organic solvents than porphyrins. The enthalpies of the transfer from benzene to another organic solvent (Table 7) are negative and vary from -2.3 (for chlorin e_6 in pyridine) to -71 kJ mol^{-1} (for pheophorbide *a* in piperidine).

Table 7. Standard changes in the enthalpies of solubilisation (ΔH_s°) (±2%) and the transfer (ΔH_t°) of chlorins.[64]

Chlorin	Solvent	ΔH_s° /kJ mol^{-1}	ΔH_t° /kJ mol^{-1}
H_2Chl *a*	C_6H_6	30.6	0
	CCl_4	22.5	−8.1
	$C_6H_5NO_2$	20.3	−10.3
	$CHCl_3$	1.3	−29.3
	DMF	23.6	−7.0
	pyridine	16.4	−14.2
	piperidine	−35.9	−66.5
Pheophorbide *a*	C_6H_6	16.9	0
	CCl_4	11.9	−5.0
	$C_6H_5NO_2$	5.7	−11.2
	$CHCl_3$	−9.2	−26.1
	DMF	8.0	−8.9
	pyridine	8.6	−8.3
	piperidine	−53.8	−70.7
Chlorin e_6	C_6H_6	14.2	0
	$CHCl_3$	−2.2	−16.4
	DMF	−10.3	−24.5
	pyridine	11.9	−2.3
	piperidine	−25.8	−40.0
Pheophorbide *b*	C_6H_6	14.4	0
	$C_6H_5NO_2$	4.8	−9.6
	$CHCl_3$	−9.8	−24.2
	DMF	4.4	−10.0
	pyridine	3.8	−10.0

The data listed in Table 7 suggest that benzene is the worst solvent, especially for H_2Chl *a* the phytol residue in which prevents its solubilisation in all organic solvents studied. The difference in the ΔH_s° values for phytol-free and phytol-containing molecules in all solvents constitutes, on average, −15 kJ mol^{-1} (see Table 7). This suggests that the phytol residue creates conformational hindrances for the solubilisation (but not the solvation). Thus the ΔH_t° values for pheophytin *a* and pheophorbide *a* are virtually identical for each of the solvents chosen.

The energy characteristics of the solubilisation and solvation of methyl esters of porphyrins of the chlorophyll group, *viz.*, pyrroporphyrin (**11**), rhodoporphyrin (**12**) and mesoporphyrin (**13**), are given in Table 8.



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The endothermic character of solubilisation of porphyrin methyl esters in benzene increases considerably in the following order: **11** < **12** < **13**. Presumably, the appearance of a second methoxycarbonyl group in the porphyrin molecule creates steric hindrance (the absolute value of ΔG_{conf} for compound **13** is also increased) and hinders the solvation (ΔG_{solv}) in benzene. This order of changes in ΔH_s is preserved in CCl_4. The ΔH_t values of porphyrins with alkoxycarbonyl groups become highly negative in $CHCl_3$. The latter, being a weak acid, forms solvates with these compounds through hydrogen bonds. The solvation of porphyrins dissolved in DMF, pyridine or piperidine is determined by a weak acid – base interaction of porphyrins with solvent molecules of the type N−H···Solv.

Table 8. Standard changes in the enthalpies of solubilisation (ΔH_s°) (± 5%) and transfer (ΔH_t°) of porphyrins of the chlorophyll group.[64]

Porphyrin	Solvent	ΔH_s° /kJ mol^{-1}	ΔH_t° /kJ mol^{-1}
Pyrroporphyrin	C_6H_6	22.5	0
	CCl_4	15.1	−7.4
	$CHCl_3$	8.1	−14.4
	DMF	12.8	−9.7
	pyridine	15.3	−7.2
	piperidine	10.3	−12.2
Rhodoporphyrin	C_6H_6	42.8	0
	CCl_4	29.4	−13.4
	$CHCl_3$	21.0	−21.8
	DMF	35.3	−7.5
	pyridine	40.2	−2.6
	piperidine	24.1	−18.7
Mesoporphyrin	C_6H_6	53.2	0
	CCl_4	40.4	−12.8
	$CHCl_3$	16.5	−36.7
	DMF	20.9	−32.3
	pyridine	31.5	−21.7

Metal ions coordinated to chlorins and porphyrins change strongly their abilities for solvation in organic solvents. Such ions as Zn^{2+}, Cd^{2+} and Co^{2+} in metalloporphyrins take part in the coordination of molecules of electron-donor solvents (alcohols, pyridine, piperidine, DMF, DMSO, *etc.*),[4,39,65] which strongly increases the solubility of metalloporphyrins and favours their solvation. In contrast, virtually no solvation of copper and nickel complexes through axial coordination takes place (Table 9).

Table 9. Enthalpies of axial coordination (ΔH_{ec}°) of the solvent molecules by porphyrin complexes at 298 K.[41–46,62]

Complex	ΔH_{ec}° /kJ mol^{-1}		
	DMF	Py	Pip[a]
MgChl	−17.5	−33.6	–
CdPhe *a* (see[b])	−17.2	−55	−38.7
ZnChl	−17.6	−30.3	–
ZnPhe	−13.0	−29.2	−15.5
ZnPir[c]	−12.2	−36.1	−33.8
ZnGp[d]	−23.0	−42.9	−51.8
CoChl	−25.6	−84.1	−172.2
CoPhe	−23.4	−29.5	−57.6
CoRp[e]	−25.1	−38.5	–
CuChl	1.8	−5.6	–
NiChl	−1.7	−27.7	−7.0
NiPir	−2.8	−6.3	–

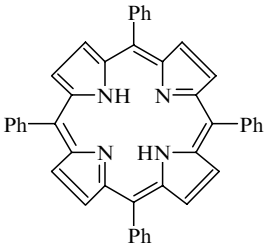
[a] Pip, piperidine; [b] Phe, pheophorbide; [c] Pir, pyrroporphyrin; [d] Gp, haematoporphyrin; [e] Rp, rhodoporphyrin.

The copper complex of tetraphenylporphin **14** is characterised by extremely low solubility in ethanol (Table 10).

Table 10. Solubilities of tetraphenylporphyrin and its complexes in ethanol at 298 K.[41–46, 62]

Compound	$10^3 S^{298}$ /mol litre^{-1}
H_2TPP [a]	0.018
	5.90 [b]
CoTPP	0.084
CuTPP	0.012
ZnTPP	0.682
CdTPP	0.802

[a] Tetraphenylporphyrin **14**; [b] in benzene.



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At the same time, the solubility of Co, Zn and Cd complexes is increased 7–60-fold due to the axial coordination of the solvent molecules to the fifth and sixth coordination positions along the *z* axis orthogonal to the porphyrin ring as a result of which the solvation energy decreases (on average, by 20–40 kJ mol^{-1}) depending on the electron-donor properties of the solvent.

Thermodynamic, thermochemical and spectral methods have been developed for the study of solvation of metalloporphyrins through axial coordination of solvent molecules.[39, 41, 63]

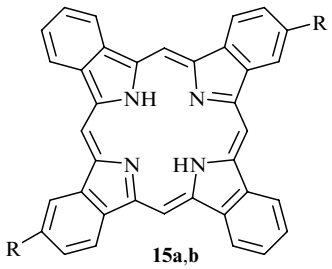
VI. Use of porphyrins and chlorins for dyeing textiles

The textile and light industries utilise an immense variety of synthetic dyes [66–72] many of which are toxic, irritate the skin and mucosa and cause otitis, laryngitis and various gastrointestinal disorders. Aniline dyes are especially hazardous in production and, possibly, application.[71, 72] Unfortunately, preventive measures are taken mostly during the production of synthetic dyes and, to a lesser degree, during colouration and utilisation of textiles. The effects of dyes on human skin in the course of wearing and laundering of dyed fabrics and their hazardous impact on living beings through waste waters have been little studied. One should not rule out the possibility that synthetic dyes of the arene series provoke cancerous and other severe diseases even in homeopathic doses. Therefore, in recent years the attention of investigators has been mainly focussed on natural dyes of plant origin.[73–76] A large body of literature data on this problem has been analysed.[75]

Chlorophyll, the most important natural dye, has a tetrapyrrole and not arene structure and is a component of foods consumed by warm-blooded animals. Therefore, chlorophyll itself, its derivatives and many porphyrins can be regarded as environmentally safe compounds. Dyes based on chlorophyll came into use as colouring matter for foodstuffs as early as the beginning of the 20th century and are currently widely used in medicine, perfumery and other areas.[34, 35] However, until recently the use of chlorophyll derivatives in the textile and light industries has been restrained due to the rapid progress in the chemistry of synthetic dyes and their ubiquitous application.

The necessity to find vast agricultural areas for growing plants as natural sources of dyes (*e.g.*, indigo) at the sacrifice of agricultural plants used as food for humans is the main obstacle to the transition to safe natural dyes.[73] No such problem exists for chlorophyll-based dyes, since chlorophyll is extracted from naturally abundant green plants (*e.g.*, nettle, conifers, algae, *etc.*). The annually renewable chlorophyll reserves on our planet constitute no less than 10^{12} tons.[11]

Several promising environmentally safe porphyrin dyes have been proposed,[77–81] and a simple, economic one-step procedure for the isolation of metallochlorophyll analogues from green plants has been developed.[82] Ni, Fe, Co, Cu, Mn complexes and complexes of other metals prepared by this method possess the entire set of characteristics required for them to be employed as dyes.



15a,**b**

R = CH_2N^+⟨pyridine⟩ Cl^- (**a**), $CH_2S^+{=}C(NMe_2)_2$ (**b**).

Pyridinium and thiouronium salts of tetrabenzoporphin **15a**,**b** were prepared in 98% yield by chloromethylation of tetrabenzoporphin [83–85] followed by heating of the reaction product with pyridine or tetramethylthiourea. These compounds are easily soluble in water and stable in weakly acidic solutions (1%–3% acetic acid). The derivatives **15a**,**b** impart an intensive bright green colouring to Nitron fibres in 40 min. Dyeing of cotton fibres with these salts also gave good results. Of substantial interest are active disperse porphyrin dyes for polyamide fibres based on tetra(*p*-chloromethylphenyl)porphin.[86, 87] The starting compounds for the synthesis of the latter are pyrrole, benzaldehyde and formaldehyde. The aforementioned porphyrin dyes can easily be converted into the corresponding metal complexes possessing enhanced chromophore properties.

Unique phthalocyanine pigments and dyes with a tetrabenzotetraazaporphin structure have been known for a very long time.[4, 88, 89] These compounds are prepared from phthalic acid derivatives and metal salts and are characterised by complete environmental safety owing to their extremely high chemical and photochemical stability which is not inherent in other classes of dyes.

The aforementioned properties of chlorophyll and the principles of its processing into chlorins and porphyrins enable its application as a potential source of environmentally safe dyes. Chlorophyll is isolated from green plant cells by extraction. In Russia, it is economically more effective to extract chlorophyll from nettle leaves.[4, 90] In the USA and European countries, food pigments have been prepared from chlorophyll extracted from finely ground alfalfa leaves since the early 1920's.[35] Acetone and light petroleum are used as extractants. Pheophytin is isolated by extraction with 96% ethanol and subsequent treatment with 6 M HCl. Treatment of plant tissues with acetone and 34% aqueous HCl yields a mixture of pheophorbides *a* and *b*.

Pheophorbide, chlorin e_6 and chlorin e_6 6-*N*-(2-aminoethyl)-amide dimethyl ester were tested as dyes for wool, cotton and acetate fibres in our laboratory.[91]

A wool specimen dyed with pheophorbide acquired a light green-brown colouring, while that dyed with chlorin e_6 was coloured bright green-brown. Dyeing with chlorin e_6 6-*N*-(2-aminoethyl)amide dimethyl ester gave the third specimen a khaki colour. Boiling of specimens dyed with chlorin e_6 and chlorin e_6 6-*N*-(2-aminoethyl)amide dimethyl ester with an aqueous solution of copper acetate resulted in complexation. In the former case, the colour of the specimen was bright blue-green, while in the latter it was green.

Chlorin e_6 6-*N*-(2-aminoethyl)amide dimethyl ester was used as a dye for conferring a khaki colour on acetate fibres. Subsequent boiling of the specimens with aqueous solutions of copper and nickel acetates gave the former an intensive light-green (lettuce) colour. After dyeing with chlorin e_6 and chlorin e_6 6-*N*-(2-aminoethyl)amide dimethyl ester by a pad-dry technique, which includes thermal treatment and steaming, the cotton specimens acquired green-yellow and khaki colouring, respectively. Subsequent boiling of the specimens with solutions of copper and nickel acetate gave dark-green and green colouring, respectively.

Chlorin e_6 was used for dyeing cotton fabrics by the colour-printing method which includes starch and cellulose thickening. The green-yellow coloured specimens appeared to be more sensitive to solar light than dyed wool specimens.

* * *

The state-of-the-art in chlorophyll chemistry allows gradual replacement of some environmentally unsafe classes of synthetic arene dyes by porphyrins and chlorophyll derivatives.

Chlorophyll and its derivatives, their cationic forms and metal complexes are potent chromophores characterised by purity of colour and photochemical stability. They can be used as direct, disperse, cationic and active dyes for regenerated protein (*e.g.*, wool, silk, *etc.*) and synthetic fibres giving stable and bright green tones. Chlorophyll-based porphyrins impart pink-red colouring to fabrics. The authors are currently engaged in the development of effective methods for extracting chlorophyll from natural raw materials (*e.g.*, nettle leaves, alfalfa powder, conifers, algae, *etc.*) and its modification into chemically stable and photostable derivatives possessing an ideal chromophore system and an affinity for textile fibres. The main practical results from their application give every reason to consider this class of chlorophyll dyes as promising industrially and operationally safe agents; their commercial production can be realised in the very near future.

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