

PROVISIONAL

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY  
and  
INTERNATIONAL UNION OF BIOCHEMISTRY

JOINT COMMISSION ON BIOCHEMICAL NOMENCLATURE\*†

**NOMENCLATURE OF TETRAPYRROLES**

(Recommendations, 1978)

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Comments on these proposals should be sent within 8 months of publication to the Secretary of the Commission:

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Comments from the viewpoint of languages other than English are encouraged. These may have special significance regarding the eventual publication in various countries of translations of the nomenclature finally approved by IUPAC-IUB.

IUPAC-IUB Joint Commission on Biochemical Nomenclature (JCBN),  
NOMENCLATURE OF TETRAPYRROLES  
(Recommendations 1978)

CONTENTS

Preface	2253
Introduction	2254
TP-0 General considerations	2256
TP-1 Fundamental Porphyrin Systems	
1.1 Porphyrin ring system	
1.2 Numbering	2257
1.3 Additional fused rings	
1.4 Skeletal replacement	2258
1.5 Skeletal replacement of nitrogen atoms	2259
1.6 Fused porphyrin replacement analogs	2260
1.7 Systematic names for substituted porphyrins	2261
TP-2 Trivial names and locants for certain substituted porphyrins	2263
2.1 Trivial names and locants	
2.2 Roman numeral type notation	2265
TP-3 Semisystematic porphyrin names	2266
3.1 Semisystematic names in substituted porphyrins	
3.2 Subtractive nomenclature	2269
3.3 Combinations of substitutive and subtractive operations	
3.4 Additional ring formation	2270
3.5 Skeletal replacement of substituted porphyrins	2271
TP-4 Reduced porphyrins including chlorins	
4.1 Unsubstituted reduced porphyrins	
4.2 Substituted reduced porphyrins. Systematic chlorin names	2272
4.3 Substituted reduced porphyrins, and close relatives of the chlorophylls. Trivial names and numbering	2273
4.4 Substituted chlorins. Semisystematic chlorin names	2276
TP-5 Ring-expanded and ring-contracted systems	2277
5.1 Ring expansion	
5.2 Skeletal replacement of ring-expanded systems	2278
5.3 Ring-contracted systems	2279
5.4 Sapphyrin	
TP-6 Linear tetrapyrroles	2280
6.1 Fundamental system	
6.2 Unsubstituted reduced bilins	
6.3 Systematic nomenclature, substituted bilins	2281
6.4 Trivially named substituted bilins	2283
6.5 Semisystematic names	2284
TP-7 Relatives of linear tetrapyrroles	2286
TP-8 Metal coordination complexes	
8.1 General description	
8.2 Coordination nomenclature	2287
8.3 Alternative order of the components of the name	2290
8.4 Trivial names	
TP-9 Metal coordination complexes - less common structural types	2293
9.1 Coordination complexes of unknown structure	
9.2 Coordination other than at central nitrogen	
9.3 Mononuclear coordination complexes with two tetrapyrrolic ligands	
9.4 Porphyrin as a bridging ligand	2294
9.5 Axial bridging ligands	
References	2295
Appendix 1 Trivially named porphyrins, chlorins, chlorophylls and bilins, fundamental parents	2296
Appendix 2 Comparison of the numbering of the trivially named porphyrins with numbering based on CNOC/CAS	2303

## PREFACE

In 1968 the IUPAC Commission on the Nomenclature of Organic Chemistry (CNOC) and the IUPAC-IUB Commission on Biochemical Nomenclature (CBN) set up a Joint Subcommittee to examine, and to make recommendations on, the nomenclature of tetrapyrroles (excluding hemoproteins). This group consisted of Professor S. Aronoff, Professor R. Bonnett, Dr. L. C. Cross, Dr. K. L. Loening and Professor C. Rimington, with Professor M. R. Lemberg as Convenor. The convenorship passed to Professor R. Bonnett in 1971, and two new members, Professors A. Eschenmoser and H. H. Inhoffen, joined the group.

Since 1968 six documents of increasing coverage were considered by the Subcommittee. The present document has been prepared on the basis of the Sixth Memorandum (April 1976) prepared by Professor R. Bonnett which in turn was a revision of a Fifth Memorandum (May 1975), with additions and emendations from the IUPAC-IUB Commission on Biochemical Nomenclature (CBN), the IUPAC Commission on Nomenclature of Organic Chemistry (CNOC) and the IUPAC Commission on Nomenclature of Inorganic Chemistry (CNIC). The Fifth Memorandum was based on the Report of April 1974 by the Joint Subcommittee set up in 1968. Since the Sixth Memorandum was issued the IUPAC-IUB Commission on Biochemical Nomenclature has become the IUPAC-IUB Joint Commission on Biochemical Nomenclature.

The views of a considerable number of chemists and biochemists were received and considered. Informal discussion sessions were held at a meeting on porphyrin chemistry in New York in 1972 [1] and at a meeting on bile pigment biochemistry at Hemsedal, Norway [2]. The cooperation of the organizers of these meetings in making arrangements for these sessions is appreciated. Throughout the work the contributions and guidance of Prof. R. Bonnett were invaluable.

## INTRODUCTION

"Tetrapyrrole" is a term used widely, but loosely, to refer to a member of a class of compounds whose molecules have four rings of the pyrrole type, generally linked together by single-atom bridges between the alpha<sup>a</sup> positions of the five-membered pyrrole rings. The common arrangements of the four rings for which this name is used are macrocyclic (as in the porphyrins) and linear (as in the bile pigments).

Tetrapyrroles and their relatives are of importance in several disciplines. The international nomenclature commissions have not previously put forward specific recommendations for this field. The nomenclature most generally used has been that of Fischer [3,4] which is based on a very large number of trivial names which continue to appear (e.g. pemptoporphyrin [5], harderoporphyrin [6]) and a numeration scheme, shown in Fig. 1 for the unsubstituted porphyrin ring system, which is simple but incomplete.<sup>b</sup> The availability of a more systematic nomenclature would be expected to help interdisciplinary communication, and would considerably diminish the need for new trivial names.

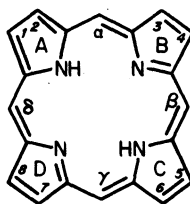


Fig. 1. Fischer numeration.

a. The alpha positions of the pyrrole ring are those adjacent to the nitrogen atom. This use of "alpha" should not be confused with its stereochemical meaning.

b. See also Table 1.

These recommendations provide for naming porphyrins, hydroporphyrins, ring contracted or expanded porphyrins, porphyrins fused with other rings, skeletally replaced porphyrins and porphyrin-metal coordination complexes together with corresponding linear arrangements of three and four pyrrole rings. The application of these recommendations permits these substances to be named more systematically using fewer trivial names than are now currently used in the literature. Fundamental porphyrin and bilin nuclei form the basis of a systematic tetrapyrrole nomenclature in accord with the recommendations of the provisional rules for natural products.<sup>a</sup>

In parallel, a semisystematic tetrapyrrole nomenclature is developed based on a few trivial names<sup>b</sup>, selected mainly from the Fischer system, that are so well established that it is desirable to retain them. The general rules for substitutive nomenclature, including operations of replacement, substitution and subtraction, are applied as appropriate. The application of these recommendations makes the use of a large number of trivial names no longer necessary. Trivial names are abandoned<sup>c</sup> except for the select few retained as the basis of the systematic and semisystematic tetrapyrrole nomenclature systems.

In addition, the incomplete Fischer numeration is abandoned for the porphyrin nucleus and the corresponding skeleton of the bile pigments. The 1-24 numbering scheme, already proven over an eighteen-year period with the closely related nucleus of the corrinoids<sup>d</sup>, is adopted as shown in TP-1.1 Fig. 2. A comparison of the 1-24 numbering scheme with the Fischer numeration for the unsubstituted porphyrin nucleus is given in Table 1.

Table 1. Comparison of the 1-24 numbering scheme with the Fischer numeration for the unsubstituted porphyrin nucleus.

Recommended:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Fischer:	-	1	2	-	$\alpha$	-	3	4	-	$\beta$	-	5	6	-	$\gamma$	-	7	8	-	$\delta$	-	-	-	-

Even though the 1-24 numbering scheme is used for the porphyrin and bilin nuclei, the numbering of the point of attachment of substituents on the nucleus may be different for systematic tetrapyrrole nomenclature than for semisystematic tetrapyrrole nomenclature. In systematic tetrapyrrole nomenclature the beginning and direction of numbering is determined by the rules for systematic substitutive nomenclature. Lowest locants are assigned according to the criteria of principal group named as suffix, substituents first cited, etc.<sup>e</sup> In contrast, in semisystematic tetrapyrrole nomenclature, the beginning and direction of numbering are the same as those established by Fischer for the trivially named porphyrins.<sup>f</sup> A comparison of the systematic and trivial numeration based on the 1-24 numbering scheme is presented in Appendix 2 for substituted porphyrins for which trivial names have been retained.

a. IUPAC, "Nomenclature of Organic Chemistry, Section F, Natural Products and Related Compounds." *Inf. Bull. Append. Provis. Nomencl. Symb. Terminol., Conv.* (IUPAC) No. 53, December 1976.

b. See Appendix 1.

c. Some of the abandoned Fischer trivial names are likely to persist, for example, in the discussion section of a paper. This is regarded as permissible provided that the systematic or semisystematic name appears by way of definition at least once in each paper.

d. IUPAC-IUB Commission on Biochemical Nomenclature, "Nomenclature of Corrinoids, Rules Approved 1975." *Pure Appl. Chem.* 48, 495-502 (1976) which supersedes IUPAC Commission on the Nomenclature of Biological Chemistry, "Definitive Rules for the Nomenclature of Vitamins." *J. Am. Chem. Soc.* 82, 5582 (1960), Rule V-15.

e. IUPAC, "Nomenclature of Organic Chemistry (1969)" Sections A, B and C combined. Butterworths, London, 1971, Rule C-15.1. See also TP-1.7.

f. See Appendix 1.

### Rule Tetrapyrrole 0. General Considerations

TP-0.1. The established international rules for naming organic compounds<sup>a</sup> and natural products<sup>b</sup> apply to tetrapyrroles, except where otherwise stated.

TP-0.2. Most of the structures considered here are based on delocalized  $\pi$ -electron systems: the double-bond distribution is represented in a formal way.

TP-0.3. Unless implied by a trivial name, the absolute configuration of a tetrahedral chiral center is designated by an *R* or *S* symbol assigned by the sequence-rule procedure. Similarly, the stereochemistry about a double bond is denoted by the prefixes *E* or *Z*. The symbols are assigned in accord with procedures given in the international recommendations for stereochemistry and are normally cited with their corresponding locants, when necessary, in front of the whole name.<sup>c</sup> Inversion of configuration or change in the configuration of a double bond from that implied by a name is expressed in front of the name in accord with IUPAC Rule F-6.3.

TP-0.4. The use of the diphthong (ae) or the single letter (e) in such words as haem, aetioporphyrin etc., is left to editorial discretion. (This vowel becomes (ä) in German). Here the single letter (e) is used throughout, hence additionally taking a terminal (e).

### Rule Tetrapyrrole 1. Fundamental Porphyrin Systems.

TP-1.1. The fundamental macrocyclic tetrapyrrolic ring system shown in Fig. 2 is named porphyrin. It is tautomeric with respect to the location of the two hydrogen atoms not involved in the peripheral conjugated system. The two hydrogen atoms may be associated with any two of the four nitrogen atoms. Unless stated to the contrary the representation of one tautomeric form does not imply the absence of another tautomer. However, for nomenclature purposes, the name "porphyrin" implies that the saturated nitrogen atoms are at positions 21 and 23 unless specifically indicated otherwise.

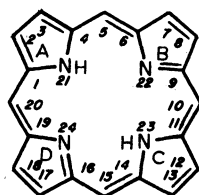


Fig. 2. Porphyrin 1-24 Numbering Scheme.

a. IUPAC, "Nomenclature of Organic Chemistry (1969)". Sections A, B and C combined. Butterworths, London, 1971; "Section D." *Inf. Bull. Append. Tentative Nomencl., Symb., Units, Stand.* (IUPAC) No. 31 August 1973.

b. IUPAC, "Nomenclature of Organic Chemistry, Section F, Natural Products and Related Compounds." *Inf. Bull. Append. Provis. Nomencl., Symb., Terminol., Conv.* (IUPAC) No. 53, December 1976.

c. IUPAC, "Rules for the Nomenclature of Organic Chemistry, Section E, Stereochemistry, Recommendations 1974." *Pure Appl. Chem.* **45**, 11-30 (1976) Rules E-2.2 and E-4.9..

d. The name "porphine" has also been used widely for the structure in Fig. 2. For further discussion see A. H. Corwin in "Organic Chemistry." (H. Gilman, ed.) Vol. 2. Wiley N. Y., 1943, p. 1272 and reference [1].

TP-1.2. *Numbering.* The 1-24 numbering system upon which the numbering system for corrinoids is based is adopted for the porphyrin nucleus and is shown in Fig. 2. The 2,3,7,8,12,13,17 and 18 positions have commonly been referred to generically as "beta-positions" (i.e. of the pyrrole rings). Similarly, positions at 1,4,6,9,11,14,16 and 19 have been referred to generically as "alpha-positions," while those at 5,10,15 and 20 are referred to generically as "meso-positions." However, in order to avoid possible ambiguity with stereochemical designations the use of these generic terms is discouraged.

TP-1.3. *Fused Systems.*<sup>b,c</sup> Compounds with extra rings ortho-fused or ortho-perifused to the porphyrin nucleus are of some importance. Tetrabenzoporphyrin is defined and the extra positions numbered as shown in Fig. 3. The name may be used without fusion letters to refer to tetrabenzob[*b,g,l,q*]porphyrin. Systems in which the porphyrin nucleus is fused with other cyclic hydrocarbons<sup>d</sup> may be named by analogy to the IUPAC Rules B-3 and A-21 for naming fused-ring systems, but adopting the porphyrin nucleus with the implied hydrogen atoms at positions 21 and 23 as the basic component to which other rings are fused. Fusion locants are derived according to IUPAC Rule A-21.5. Indicated hydrogen is determined on the basis of the presence of implied hydrogen atoms at positions 21 and 23 of the porphyrin ring in contrast to the form containing the maximum number of noncumulative double bonds as in IUPAC Rule A-21.6.

The component rings fused to the porphyrin base are numbered as substituent groups of the lowest possible position of the porphyrin ring.<sup>e</sup> However, where the "extra" rings are formally derived, such as for lactones, from the reaction of noncyclic substituents implied by the trivial name the numbering of the noncyclized substituent is retained as illustrated by example 4 of Rule TP-3.1 and the examples of Rule TP-3.4.

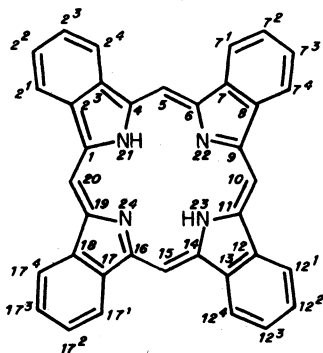
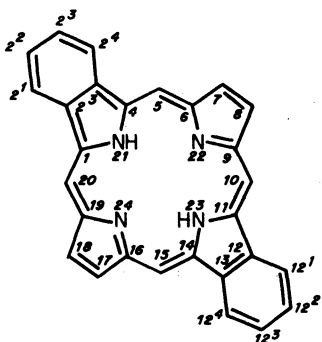


Fig. 3. Tetrabenzoporphyrin.

Examples:



Dibenzob[*b,l*]porphyrin

a. IUPAC-IUB Commission on Biochemical Nomenclature, "Nomenclature of Corrinoids, Rules Approved 1975." *Pure Appl. Chem.* **48**, 495-502 (1976).

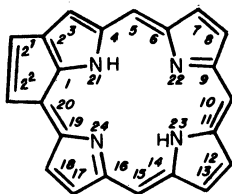
b. See also TP-3.4 for use of "cyclo".

c. See TP-1.6 for fused systems involving skeletally replaced porphyrins.

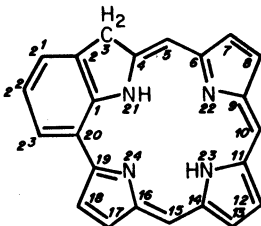
d. Fusion of the porphyrin ring system with heterocyclic rings, particularly one containing a bivalent atom may affect the tautomerism of the nitrogen atoms of the porphyrin ring system and needs further consideration.

e. See TP-2.1 Fig. 6. This practice is in contrast to established procedures of systematic organic nomenclature for orienting and numbering fused rings according to IUPAC Rules A-22 and B-3.4.

2.

Cyclopenta[ at ]porphyrin<sup>a</sup>

3.

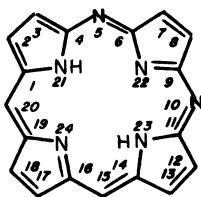


3H-Benzo[ at ]porphyrin

TP-1.4. *Skeletal Replacement.* <sup>b,c</sup> Replacement of a carbon atom of the porphyrin ring by an atom of another element may be denoted by adapting the IUPAC rules for systematic organic replacement nomenclature. The locants of replacement, followed by the appropriate multiplicative prefix (if any) and the replacement term of the element being introduced, are cited in front of the porphyrin name as directed in IUPAC Rules B-4, C-0.6 and D-1.6. When atoms of more than one kind of element are introduced, the replacement terms are cited in the order given in IUPAC Rule B-1.1, Table I. The porphyrin system is a "dihydro system" (i.e. contains one less than the maximum number of double bonds). "Indicated hydrogen," if needed, is assigned on the basis of implied hydrogen atoms at positions 21 and 23 of the porphyrin ring.

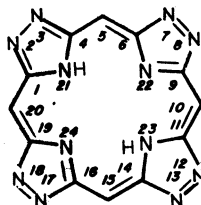
Examples:

1.



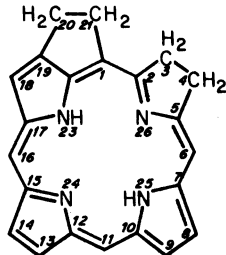
5,10-Diazaporphyrin

2.



2,3,7,8,12,13,17,18-Octaazaporphyrin

a. The name phorbine has been used for the tetrahydro derivative of this ring system, numbered and oriented as follows:

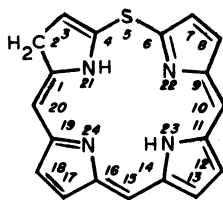


Phorbine

b. See TP-3.5 for skeletal replacement of substituted porphyrins.

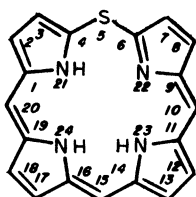
c. These rules have been developed in order to name the common replacement analogs. However further refinement is needed in order to name replacement analogs of other porphyrin types and for corrins and corroles.

3.



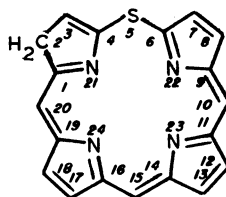
2H-5-Thiaporphyrin

4.



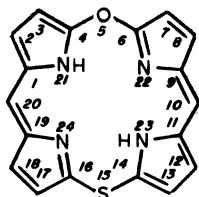
24H-5-Thiaporphyrin

5.



21,23-Didehydro-2H-5-thiaporphyrin

6.



5-Oxa-15-thiaporphyrin

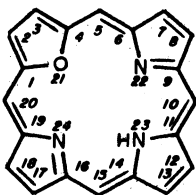
TP-1.5. *Skeletal Replacement of Nitrogen Atoms.* The replacement operation may be further extended *with caution* to denote the replacement of nitrogen atoms of the porphyrin ring.<sup>a</sup> The porphyrin system is a "dihydro system" containing one less double bond than the maximum possible. The two "extra" hydrogen atoms of the porphyrin system are tautomeric among the four nitrogen atoms. Thus in order to avoid ambiguity the convention that saturated nitrogen atoms are formally replaced before unsaturated nitrogen atoms is adopted, even if a tautomeric form other than the 21,23-dihydro form must be assumed as in example 3 below. Replacement of one -NH- group by a bivalent atom results in a structure with only one of the implied hydrogen atoms left. Hence this hydrogen atom is now denoted by indicated hydrogen in the usual way. The implied dihydro porphyrin structure is no longer assumed.

a. Systematic organic nomenclature requires that the parent upon which replacement is performed be a hydrocarbon (see IUPAC Rules B-4, C-0.6 and D-1.6). Thus, the replacement operation is generally limited to replacement of carbon atoms by atoms of other elements. For natural products IUPAC provisional rules F-4.11 to F-4.13 permit replacement of carbon atoms of a heterocyclic parent, and also the replacement of noncarbon atoms by carbon atoms. The replacement of noncarbon atoms by other noncarbon elements is introduced for porphyrin nomenclature, but needs further consideration.



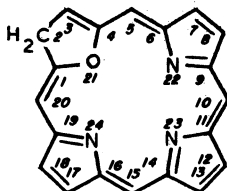
## Examples:

1.



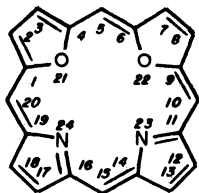
23H-21-Oxaporphyrin

2.



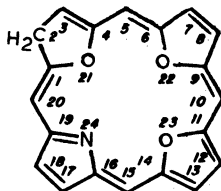
2H-21-Oxaporphyrin

3.



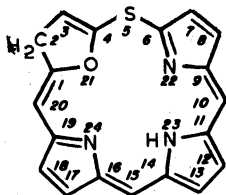
21,22-Dioxaporphyrin

4.



2H-21,22,23-Trioxaporphyrin

5.



2H,23H-21-Oxa-5-thiaporphyrin

TP-1.6. *Fused Porphyrin Replacement Analogs.* In denoting the fusion of a skeletally replaced porphyrin with cyclic hydrocarbons the procedures of TP-1.3 are followed using the skeletally replaced porphyrin as the base component.<sup>a</sup> As an exception, the name phthalocyanine is retained for the tetrabenzol[*b,g,l,q*]-5,10,15,20-tetraazaporphyrin system. The structure and numbering are as shown in Fig. 4.

a. This is in contrast to the procedures for systematic organic nomenclature in which the fusion operation is performed before skeletal replacement is carried out. See IUPAC Rule B-4.2.

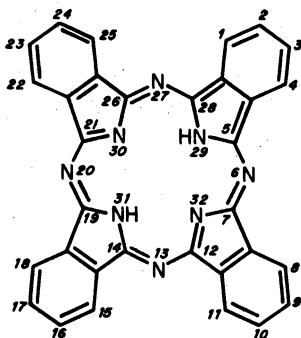
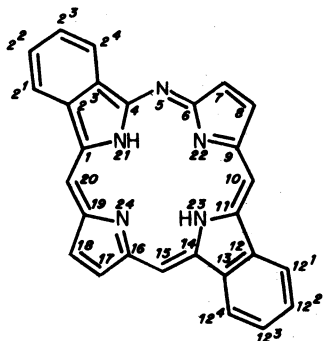


Fig. 4. Phthalocyanine.

Example:

Dibenzo[*b, l*]-5-azaporphyrin

TP-1.7. *Systematic Names for Substituted Porphyrins.* Substituted fundamental porphyrins may be named systematically on the basis of the fundamental porphyrin ring nuclei given in TP-1.1 or that are formed as directed in TP-1.3 to TP-1.6. All substituents on the fundamental porphyrin ring are expressed by prefixes and/or suffixes as in organic nomenclature.<sup>a</sup> Hydrogenation of unsaturated positions may be indicated in the customary manner by the prefixes, dihydro-, tetrahydro-, etc.<sup>b</sup>

Substituted porphyrins named systematically are numbered by the rules for systematic organic nomenclature, IUPAC Rule C-15.1. When there is a choice the starting point and direction of numbering around the porphyrin nucleus are chosen so as to give lowest locants to the following structural factors (if present), considered successively in the order listed until a decision is reached:

- hydrogen atoms expressed as "indicated hydrogen"<sup>c</sup>
- principal groups named as suffix
- substituents named as prefixes and hydro prefixes all considered together in one series in ascending numerical order
- the substituent named as a prefix, which is cited first in a name.

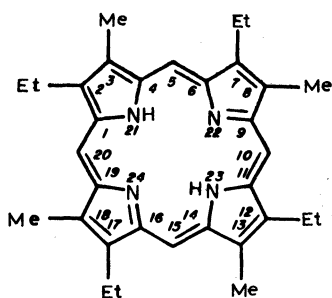
a. IUPAC, "Nomenclature of Organic Chemistry (1969)." Sections A, B and C combined. Butterworths, London, 1971.

b. But see also TP-4 for nomenclature of reduced porphyrins including chlorins.

c. Because the name "porphyrin" implies a "dihydro parent," which contains two more hydrogen atoms than the corresponding fully conjugated ring system, the notation of indicated hydrogen (a locant and a capital italic *H*), introduced in IUPAC Rule A-21.6, is adapted to denote one of several possible isomers of a particular parent porphyrin structure or a particular tautomer. See also TP-1.4.

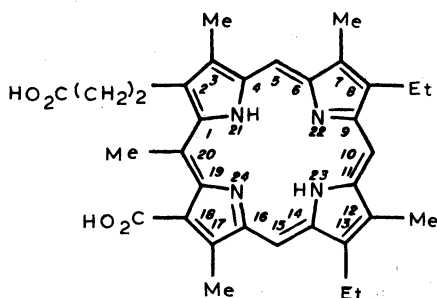
## Examples:

1.



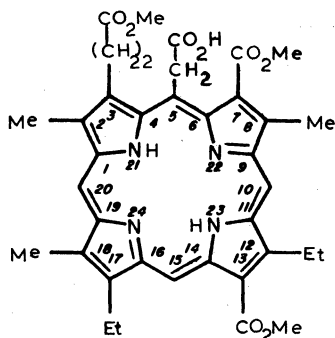
2,7,12,17-Tetraethyl-3,8,13,18-tetramethylporphyrin

2.

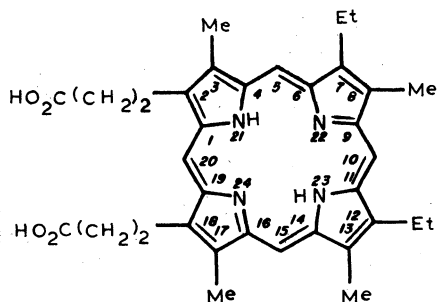


18-Carboxy-8,13-diethyl-3,7,12,17,20-pentamethylporphyrin-2-propionic acid

3.

12,17-Diethyl-7,13-bis(methoxycarbonyl)-3-[2-(methoxycarbonyl)ethyl]-2,8,18-trimethylporphyrin-5-acetic acid<sup>a</sup>

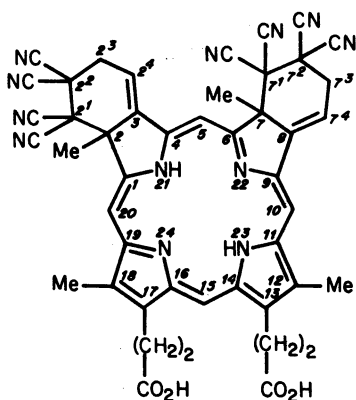
4.



7,12-Diethyl-3,8,13,17-tetramethylporphyrin-2,18-dipropionic acid

a. In line with IUPAC Rule C-10.3, a carboxylic acid is preferred to an ester. Thus the parent, porphyrin-5-acetic acid, is preferred to methyl porphyrin-3-propionate.

5.



2<sup>1</sup>,2<sup>1</sup>,2<sup>2</sup>,2<sup>2</sup>,7<sup>1</sup>,7<sup>1</sup>,7<sup>2</sup>,7<sup>2</sup>-Octacyano-2,2<sup>1</sup>,2<sup>2</sup>,2<sup>3</sup>,7,7<sup>1</sup>,7<sup>2</sup>,7<sup>3</sup>-octahydro-2,7,12,18-tetramethyldibenzo[*b,g*]porphyrin-13,-17-dipropionic acid

Rule Tetrapyrrole 2. Trivial Names and Locants for Certain Substituted Porphyrins.<sup>a</sup>

*TP-2.1. Trivial Names and Locants.* Eleven well-established trivial names and associated locants<sup>b</sup> are retained for naming certain substituted porphyrin structures containing the porphyrin nucleus.<sup>c</sup> They are listed in Tables 2 and 3. They are also explicitly shown in Appendix 1. In addition to these names the name phytoporphyrin is recommended for the hexacyclic structure numbered as shown in Fig. 5. Phylloerythrin, the name formerly used for this structure, is abandoned.

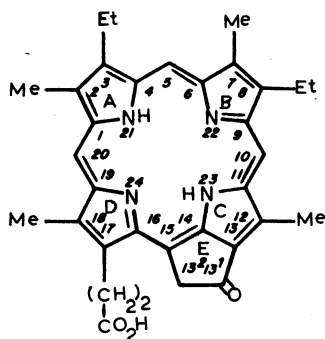


Fig. 5. Phytoporphyrin<sup>d</sup>.

a. See also TP-4.3 and TP-4.4 for trivial names of substituted reduced porphyrins including pheophorbides, pheophytins and chlorins.

b. The locants used with these trivial names are retained for semisystematic porphyrin names formed according to TP-3.1. However, they do not coincide with those used for systematic porphyrin names formed according to TP-1.7. A comparison of the locants of trivially named porphyrins with locants derived systematically is given in Appendix 2.

c. With the exception of the etioporphyrins, the structures denoted by these trivial names do not meet the criteria of IUPAC Rule F-2 regarding selection of parent structures for semisystematic names. However because of their firm establishment in the porphyrin field, these eleven names are carried over from the Fischer system. These names form the basis of a semisystematic nomenclature for naming other porphyrin derivatives.

d. A systematic porphyrin name of phytoporphyrin based on the fundamental ring named as in TP-1.3 would be: 7,12-Diethyl-2<sup>1</sup>,2<sup>2</sup>-dihydro-3,8,13,17-tetramethyl-2<sup>1</sup>-oxocyclopenta[*at*]-porphyrin-18-propionic acid.

Table 2. Trivial Names for Substituted Porphyrins<sup>a</sup>

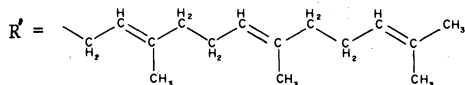
Trivial Name <sup>b</sup>	Rank	Substituents <sup>c</sup> and locants								
		2	3	7	8	12	13	15	17	18
Coproporphyrin I	9	Me	Cet	Me	Cet	Me	Cet	H	Me	Cet
Cytoporphyrin <sup>c</sup>	11	Me	-CH(OH)CH <sub>2</sub> R'	Me	Vn	Me	Cet	H	Cet	-CHO
Deuterioporphyrin <sup>d,e</sup>	1	Me	H	Me	H	Me	Cet	H	Cet	Me
Etioporphyrin I	3	Me	Et	Me	Et	Me	Et	H	Me	Et
Hematoporphyrin <sup>e</sup>	8	Me	-CH(OH)CH <sub>3</sub>	Me	-CH(OH)CH <sub>3</sub>	Me	Cet	H	Cet	Me
Mesoporphyrin <sup>e</sup>	7	Me	Et	Me	Et	Me	Cet	H	Cet	Me
Phylloporphyrin <sup>f</sup>	4	Me	Et	Me	Et	Me	H	Me	Cet	Me
Protoporphyrin <sup>e</sup>	6	Me	Vn	Me	Vn	Me	Cet	H	Cet	Me
Pyrroporphyrin <sup>f</sup>	2	Me	Et	Me	Et	Me	H	H	Cet	Me
Rhodoporphyrin <sup>f</sup>	5	Me	Et	Me	Et	Me	-CO <sub>2</sub> H	H	Cet	Me
Uroporphyrin I.	10	Cm	Cet	Cm	Cet	Cm	Cet	H	Cm	Cet
Phytoporphyrin	12	Me	Et	Me	Et	Me	-C(O)-CH <sub>2</sub> -	Cet	Me	

The side chains of trivially named porphyrins may be numbered using the number of the point of substitution in the porphyrin nucleus, with a following superscript numeral as shown in Fig. 6. The trivial names listed in Table 2 and TP-2.2., Table 3, may be used in deriving semisystematic names for other substituted porphyrins as directed in TP-3.1 and TP-3.2.

a. The porphyrins are arranged alphabetically. They are ranked according to (1) number of component rings (2) number of carbon atoms, (3) molecular weight. A porphyrin of higher rank number is preferred to one of lower rank for selection as parent for semisystematic names according to TP-3.1.

b. For explanation of Roman numerals associated with some of the trivial names see TP-2.2, and Table 3.

c. The following abbreviations are used; Cm for -CH<sub>2</sub>CO<sub>2</sub>H; Cet for -CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H; Me for -CH<sub>3</sub>; Et for -CH<sub>2</sub>CH<sub>3</sub>; Vn for -CH=CH<sub>2</sub>; see *Eur. J. Biochem.* **74**, 1-6 (1977). The use of the symbols A and P, which is a parochial practice in the field of porphyrin chemistry for -CH<sub>2</sub>CO<sub>2</sub>H and -CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, respectively, is not recommended.



*trans, trans*-farnesyl which is (2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrienyl. See *J. Chem. Soc. Chem. Commun.* **1977**, 278.

d. Not to be confused with deuterioporphyrin, a possible name for an isotopically labeled compound.

e. Formerly type IX.

f. Formerly type XV.

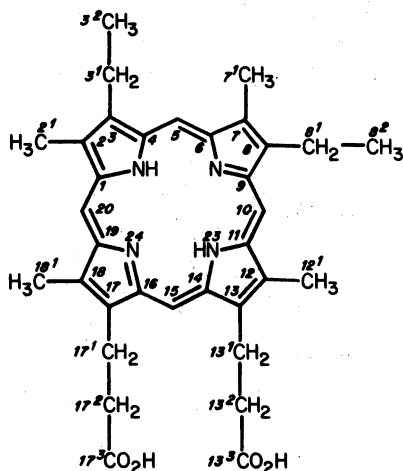
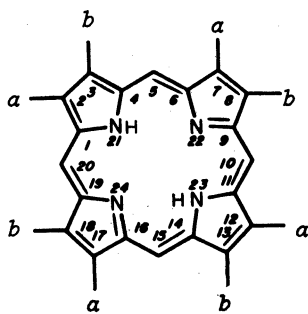
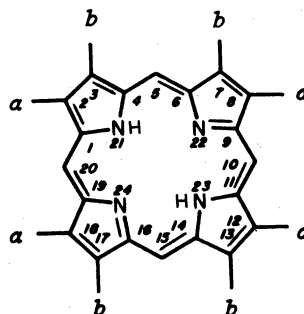


Fig. 6. Numbering of Mesoporphyrin.

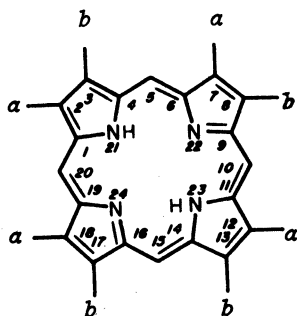
TP-2.2. *Roman Numeral Type Notation.* There are only four possible positional isomers for each of the 2,3,7,8,12,13,17,18-octasubstituted coproporphyrin, etioporphyrin and uroporphyrin structures in which (i) the substituents are of two sorts only, and (ii) one of each sort of substituent is present as a substituent in each of the component pyrrolic rings A, B, C and D.<sup>a</sup> The four positional isomers are distinguished by Roman numerals, I, II, III or IV applied to these substituted porphyrin rings, numbered and oriented<sup>b</sup> as shown below where substituent *a* is smaller than substituent *b*. The substituents and locants for these porphyrins are summarized in Table 3. The use of Roman numerals or "type nomenclature" is not recommended for more complex cases, or for porphyrins with more than four possible positional isomers.



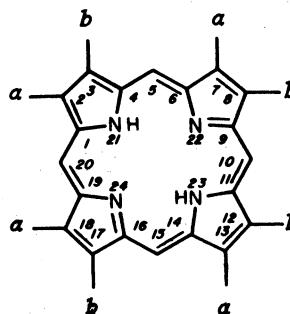
I



II



III



IV

a. S. Aronoff, "The number of biologically possible porphyrin isomers," *Ann. N.Y. Acad. Sci.* 244, 327-333 (1975).

b. In orienting these trivially named structures the following guidelines were followed: (a) in ring A the sequence "smaller substituent-larger substituent" is clockwise; and (b) insofar as it is possible this order "smaller substituent-larger substituent" continues in turn for ring B, C, D, in that priority.

Table 3. Positional Isomers

Name	Substituents <sup>a</sup> and locants								
	2	3	7	8	12	13	15	17	18
Coproporphyrin I	Me	Cet	Me	Cet	Me	Cet	H	Me	Cet
Coproporphyrin II	Me	Cet	Cet	Me	Me	Cet	H	Cet	Me
Coproporphyrin III	Me	Cet	Me	Cet	Me	Cet	H	Cet	Me
Coproporphyrin IV	Me	Cet	Me	Cet	Cet	Me	H	Cet	Me
Etioporphyrin I	Me	Et	Me	Et	Me	Et	H	Me	Et
Etioporphyrin II	Me	Et	Et	Me	Me	Et	H	Et	Me
Etioporphyrin III	Me	Et	Me	Et	Me	Et	H	Et	Me
Etioporphyrin IV	Me	Et	Me	Et	Et	Me	H	Et	Me
Uroporphyrin I	Cm	Cet	Cm	Cet	Cm	Cet	H	Cm	Cet
Uroporphyrin II	Cm	Cet	Cet	Cm	Cm	Cet	H	Cet	Cm
Uroporphyrin III	Cm	Cet	Cm	Cet	Cm	Cet	H	Cet	Cm
Uroporphyrin IV	Cm	Cet	Cm	Cet	Cet	Cm	H	Cet	Cm

### Rule Tetrapyrrole 3. Semisystematic Porphyrin Names

*TP-3.1. Semisystematic Names For Substituted Porphyrins.* As an alternative to a systematic name based on the porphyrin ring nucleus,<sup>b</sup> compounds closely related to the trivially named porphyrins listed in Rule TP-2, Tables 2 and 3, but differing in that one or more hydrogen atoms<sup>c</sup> have been replaced (substituted) by one or more other atoms or groups, may be named semisystematically based on one of the trivially named parent porphyrins. Prefixes, and/or a suffix of the new substituents are combined with the trivial name of the parent porphyrin. The functional group of highest priority,<sup>d</sup> not implied in the trivial parent name, may be expressed as a suffix. The remaining substituents not implied by the trivial name are expressed by prefixes. Locants and multiplying prefixes are added as appropriate, and the prefixes arranged in alphabetical order.

When there is a choice among trivially named parent porphyrins, the one with the highest possible rank number in Table 2 is preferred. However a porphyrin of lower rank may be selected where special emphasis is desired.

Functional derivatives such as esters and lactones are named similarly and in accord with the rules for organic nomenclature.<sup>e</sup>

a. Abbreviations used are Me for "methyl;" Cet for "carboxyethyl;" Et for "ethyl;" Cm for "carboxymethyl;" see *Eur. J. Biochem.* 74, 1-6 (1977).

b. See TP-1.7 for generation of systematic names.

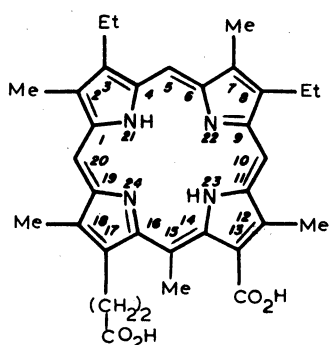
c. Precise guidelines for naming modified or substituted side chains of trivially named natural products are needed. In general, chain lengthening of substituent groups by substitution of hydrogen atoms by alkyl groups is less preferred than removal of the entire side group and the addition of the new group. See TP-3.2 for subtractive nomenclature.

d. See IUPAC Rule C-10.3.

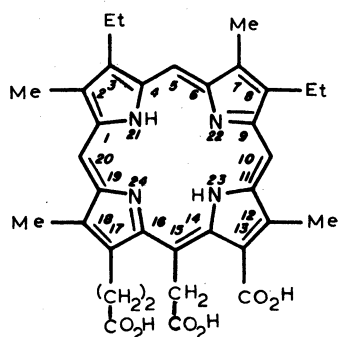
e. See Rule C-4.6 and C-4.7. See also TP-3.4

## Examples:

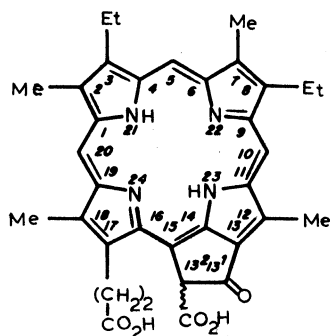
1.

Semisystematic:<sup>a</sup> 15-MethylrhodoporphyrinSystematic:<sup>b</sup> 18-Carboxy-8,13-diethyl-3,7,12,17,20-pentamethylporphyrin-2-propionic acid.Fischer: Chloroporphyrin  $e_4$ 

2.

Semisystematic:<sup>c</sup> Rhododoporphyrin-15-acetic acidSystematic:<sup>e</sup> 18-Carboxy-20-(carboxymethyl)-8,13-diethyl-3,7,12,17-tetramethylporphyrin-2-propionic acidFischer: Chloroporphyrin  $e_6$ 

3.

Semisystematic:<sup>c,d</sup> Phytodoporphyrin-13<sup>2</sup>-carboxylic acidSystematic:<sup>d,e</sup> 2<sup>2</sup>-Carboxy-7,12-diethyl-2<sup>1</sup>,2<sup>2</sup>-dihydro-3,8,13,17-tetramethyl-2<sup>1</sup>-oxocyclopenta [*a*] porphyrin-18-propionic acidFischer: Pheoporphyrin  $a_5$ 

a. Not phylloporphyrin-13-carboxylic acid. Rhododoporphyrin has a higher rank number than phylloporphyrin.

b. See TP-1.7 for generation of systematic names.

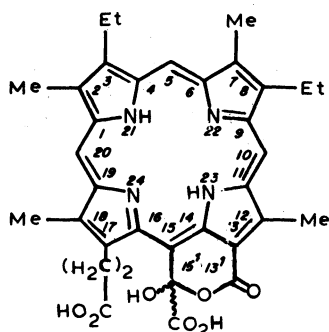
c. Note that in contrast to regular practices of substitutive nomenclature that the propionic principal group is unexpressed. In these rules a subordinate group may be cited as a suffix. Compare IUPAC Rule C-10.3.

d. If it is necessary to specify the absolute stereochemistry of this molecule, it should be indicated by *R* or *S* in accord with TP-0.3.

e. For systematic numbering see TP-1.1 and TP-1.7



4.

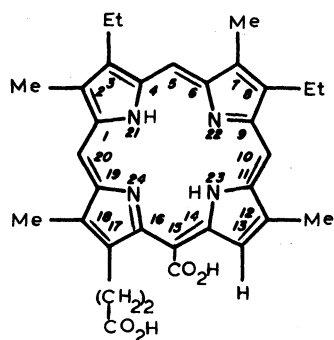


Semisystematic:<sup>a,b</sup> 15<sup>1</sup>,15<sup>1</sup>-Dihydroxy  
rhodoporphyrin-15-  
acetic acid  $\delta$ -lactone

Systematic:<sup>b,c,d</sup> 18-Carboxy-20-(carboxy  
dihydroxymethyl)-8,13-  
diethyl-3,7,12,17-tetra  
methylporphyrin-2-propionic  
acid  $\delta$ -lactone

Fischer: Pheoporphyrin  $\alpha_7$

5.

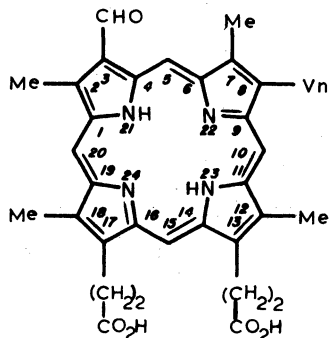


Semisystematic:<sup>e</sup> Phylloporphyrin-15<sup>1</sup>-oic  
acid

Systematic: 20-Carboxy-8,13-diethyl-3,7,12  
17-tetramethylporphyrin-2-propionic  
acid

Fischer:  $\gamma$ -Carboxypyrrporphyrin

6.



Semisystematic: 3-Formyl-8-vinyldeutero  
porphyrin

Systematic: 8-Formyl-3,7,12,17-tetramethyl-  
13-vinylporphyrin-2,18-dipropionic  
acid

Fischer: Chlorocruoroporphyrin

or

Spirographisporphyrin

a. Note that in contrast to regular practices of substitutive nomenclature that the propionic principal group is unexpressed. In these rules a subordinate group may be cited as a suffix. Compare IUPAC Rule C-10.3.

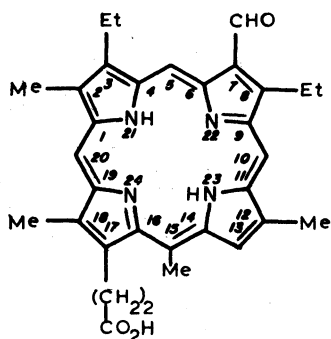
b. If it is necessary to specify the absolute stereochemistry of this molecule, it should be indicated by *R* or *S* in accord with TP-0.3.

c. For systematic numbering see TP-1.1 and TP-1.7.

d. Alternatively a name based on ring fusion principles could be formed, but see footnote d, TP-1.3.

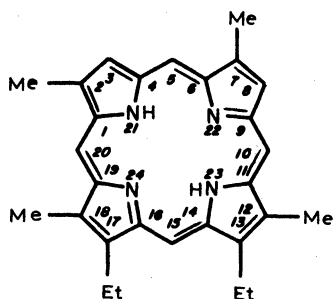
e. Not Pyrporphyrin-15-carboxylic acid. Phylloporphyrin ranks higher than pyrporphyrin in Table 2.

7.

Semisystematic: 7<sup>1</sup>-OxophylloporphyrinSystematic: 8,13-Diethyl-12-formyl- 3,7,  
17,20-tetramethylporphyrin  
2-propionic acidFischer: Rhodinoporphyrin g<sub>3</sub>

TP-3.2. *Subtractive Nomenclature.* The prefix "de" followed by the name of a substituent group is used to denote the removal of that substituent from the semisystematic parent porphyrin<sup>a</sup> and its replacement by the appropriate amount of hydrogen as in organic nomenclature.<sup>b</sup> These prefixes combined with a multiplicative prefix denote the loss of a corresponding number of substituents or atoms. "Dehydro" denotes the loss of one hydrogen atom. The "de" prefix is nondetachable from the name of the substituent group to which it refers.<sup>c</sup> Simple subtractive prefixes are alphabetized disregarding the multiplying prefixes, di, tri, tetra, penta, etc. When there is a choice, as low locants as possible are selected for the subtractive prefixes as in systematic substitutive nomenclature.<sup>d</sup>

Example:



Semisystematic: 3,8-Diethyletioporphyrin III

Systematic:<sup>e</sup> 3,7-Diethyl-2,8,12,17-  
tetramethylporphyrin

Fischer: Deuteroetioporphyrin IX

TP-3.3. *Combinations of Substitutive and Subtractive Operations.* The subtractive operations of TP3.2 may be combined with the operations of substitution of TP-3.1 to denote the removal of a group or atom from a position in the parent porphyrin and subsequent substitution at any position. The subtractive prefixes are alphabetized among the substitutive prefixes. As low locants as possible are selected for substitutive and subtractive prefixes considered together in one series. If this is not decisive, then the numbering is chosen that assigns the lowest locant to the first cited substituent or subtractive prefix. When a porphyrin structure can be considered as a derivative of two or more trivially named parent porphyrins listed in Tables 2 and 3, and shown in Appendix 1, the name that requires the fewest number of subtractive and substitutive operations combined is preferred. If this is not decisive, then the name that requires the smaller number of subtractive prefixes is preferred.

a. Further development of guidelines for choice of the trivially named parent porphyrin, its numbering, and limits of application of these operations is needed.

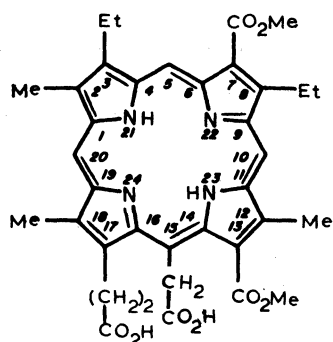
b. See IUPAC Rule C-41.

c. See IUPAC provisional Rules F-4.10 and F-4.13.

d. See IUPAC Rule C-15.11(d) and (e).

e. See TP-1.7 for formation of the systematic name.

Example:



Semisystematic: 7-Demethyl-7-(methoxy carbonyl)rhodoporphyrin 15-acetic acid 13-methyl ester<sup>a</sup>

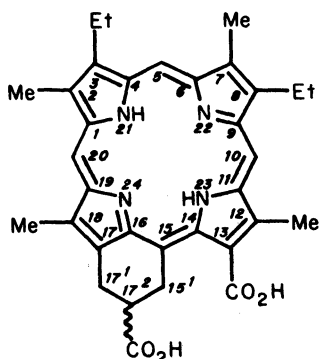
Systematic: 20-(Carboxymethyl)-8,13-diethyl-12,18,bis(methoxycarbonyl)-3,7,17-trimethylporphyrin-2-propionic acid

Fischer: Rhodinoporphyrin *g*<sub>8</sub> (as one of its dimethyl esters)

TP-3.4. *Additional ring formation.* Compounds closely related to the trivially named porphyrin of Rule TP-2 but in which an additional ring has been formed by means of a direct link between two atoms of the parent structure are named by prefixing "cyclo" preceded by the locants of the positions joined by the new bond.<sup>b</sup> Alternatively such compounds may be named according to the provisions for fused rings in Rule TP-1.3.

Examples

1.

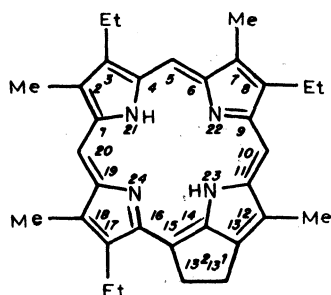


Semisystematic:<sup>c</sup> 15<sup>1</sup>,17<sup>2</sup>-Cyclophylloporphyrin-13-carboxylic acid

Systematic<sup>c,d</sup>: 8,13-Diethyl-2<sup>2</sup>,2<sup>3</sup>-dihydro-3,7,12,17-tetramethyl-2<sup>1</sup> *H*-benzo[*a*]porphyrin-2<sup>2</sup>,18-dicarboxylic acid

Fischer: Neoporphyrin 4

2.



Semisystematic: 13<sup>2</sup>,15-Cycloetioporphyrin III, or 17<sup>2</sup>-Decarboxy-13<sup>1</sup> deoxyphytoporphyrin

Systematic:<sup>d</sup> 7,12,18,Triethyl-2<sup>1</sup>,2<sup>2</sup>-dihydro-3,8,13,17-tetramethyl cyclopenta[*a*]porphyrin

Fischer: Deoxyphylloerythroetioporphyrin

a. Alternate formats for naming this diester should be considered such as 7-carboxy-7-demethyl-rhodoporphyrin-15-acetic acid 7,13-dimethyl ester, or 13-methyl 7-demethyl-7-(methoxycarbonyl)-rhodoporphyrin-15-acetate. Present IUPAC nomenclature rules are not definitive in this respect.

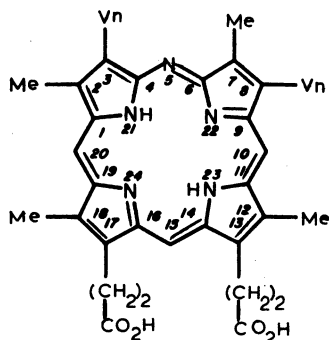
b. See IUPAC provisional Rule F-4.1.

c. If it is necessary to specify the absolute stereochemistry of this molecule, it should be by *R* or *S* according to TP-0.3.

d. See TP-1.3 for the systematic name and numbering of the fundamental ring.

TP-3.5. *Skeletal Replacement of Substituted Porphyrins.*<sup>a</sup> Trivially named porphyrins in which one or more of the atoms in the porphyrin ring nucleus have been replaced by atoms of other elements are named by prefixing to the trivial name, the appropriate locants with corresponding multiplicative and replacement prefixes. Where there is a choice due to the symmetry of substituents, the replacing atoms are numbered in line with IUPAC Rule B-4.

Example:



Semisystematic: 5-Azaporphyrin

Systematic:<sup>a</sup> 2,7,12,18-Tetramethyl-  
3,8-divinyl-5-azaporphyrin-  
13,17-dipropionic acid

Rule Tetrapyrrole 4. Reduced Porphyrins Including Chlorins.

TP-4.1. *Unsubstituted Reduced Porphyrins.* The most common reduced porphyrins are dihydroporphyrins in which saturated carbon atoms are located at the nonfused carbon atoms of one of the pyrrole rings. The parent compound of this series is called *chlorin*, which, defined in terms of the unsubstituted porphyrin ring, is 2,3-dihydroporphyrin (see Fig. 7). Tetrahydroporphyrins in which the saturated carbon atoms are located at nonfused carbon atoms of two diagonally opposite pyrrole rings are bacteriochlorins. Hexahydroporphyrins in which the nitrogen atoms and four meso positions are saturated are porphyrinogens. The unsubstituted bacteriochlorin and porphyrinogen ring systems are shown together with their systematic names and numbering in Figs. 8 and 9 respectively. Further hydrogenated derivatives of these specially named structures are to be named systematically as hydroporphyrins in preference to hydrochlorins, hydrobacteriochlorins, or hydroporphyrinogens. Other unsubstituted reduced porphyrin ring systems are also to be named systematically according to TP-1.7.

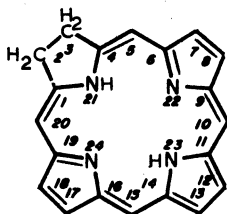


Fig. 7. Chlorin  
2,3-Dihydroporphyrin<sup>b</sup>.

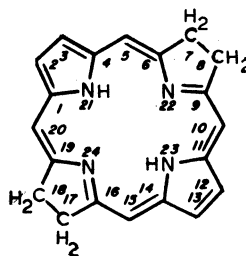


Fig. 8. Bacteriochlorin  
7,8,17,18-Tetrahydroporphyrin<sup>c</sup>.

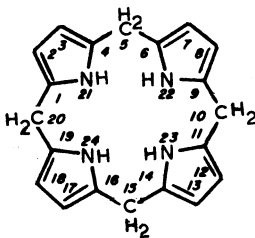


Fig. 9. Porphyrinogen  
5,10,15,20,22,24-Hexahydroporphyrin<sup>b</sup>.

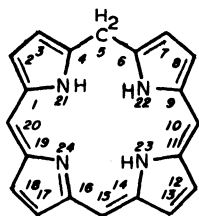
a. See TP-1.4 and TP-1.5 for systematic names and numbering of skeletally replaced fundamental porphyrin systems.

b. The presence of hydrogen atoms at positions 21 and 23 is implied by the name "porphyrin".

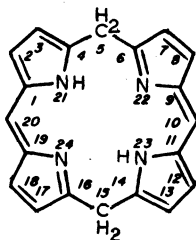
c. The 2,3,12,13-tetrahydroporphyrin with implied hydrogen atoms at 21 and 23 is not structurally possible.

Examples:

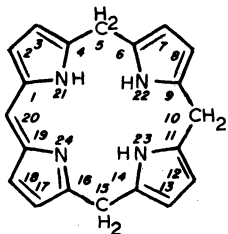
1.

5,22-Dihydroporphyrin  
(formerly named phlorin)

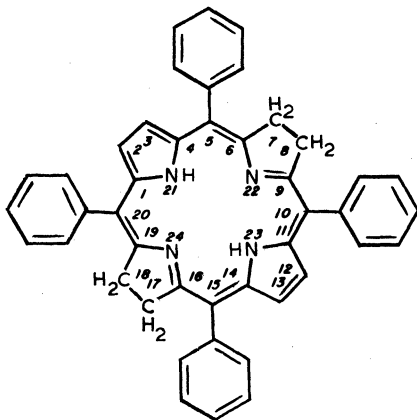
2.

5,15-Dihydroporphyrin  
(formerly named porphodimethene)

3.

5,10,14,22-Tetrahydroporphyrin  
(formerly named porphomethene)

TP-4.2 *Substituted Reduced Porphyrins. Systematic Chlorin Names.* Derivatives of chlorins and other reduced porphyrins may be named systematically based on one of the parent rings chlorin, bacteriochlorin, porphyrinogen, or porphyrin shown in Figs. 7, 8, 9 and 2 respectively.<sup>a</sup> Substituents are expressed by prefixes or suffixes as in organic nomenclature.<sup>b</sup>

Example:<sup>c</sup>

5,10,15,20-Tetraphenylbacteriochlorin

a. See also Appendix 1.

b. See also TP-1.7.

c. For more examples see TP-4.4.

TP-4.3. *Substituted Reduced Porphyrins and Close Relatives of the Chlorophylls. Trivial Names and Numbering.*

TP-4.3.1. The four trivial names listed in Table 4 may be used to name 17,18-dihydro derivatives of the four corresponding trivially named porphyrins in Table 2. These names may also be used to form semisystematic names as directed in TP-4.4. 17,18-Dihydro derivatives of other trivially named porphyrins are named systematically as directed in TP-4.2.

Table 4. Trivially named substituted chlorins corresponding to 17,18-dihydro derivatives of trivially named porphyrins

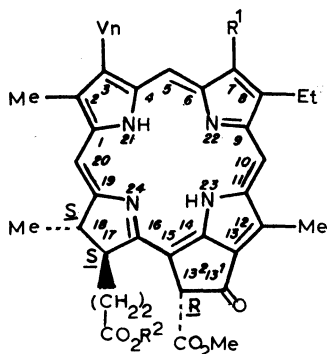
Trivial name	Rank No.	Substituents and locants								
		2	3	7	8	12	13	15	17	18
Phyllochlorin	2	Me	Et	Me	Et	Me	H	Me	Cet,H	Me,H
Phytochlorin	4	Me	Et	Me	Et	Me	-C(O)—CH <sub>2</sub> -	Cet,H	Me,H	Me,H
Pyrochlorin	1	Me	Et	Me	Et	Me	H	H	Cet,H	Me,H
Rhodochlorin	3	Me	Et	Me	Et	Me	-CO <sub>2</sub> H	H	Cet,H	Me,H

TP-4.3.2. Additional trivial names used to name chlorins, bacteriochlorins and porphyrins may be derived from the common chlorophyll names listed in TP-8.4 and Appendix 1. Compounds that may be formally derived by demetallation of the corresponding substituted naturally occurring chlorophyll shown in TP-8.4 are called pheophytins (if the ester of the 17-propionic acid group is phytlyl) or pheofarnesins (if the ester of the 17-propionic acid group is farnesyl). In naming such compounds, the word "pheophytin" (or "pheofarnesin") replaces "chlorophyll" in the original name.<sup>a</sup> Thus demetallation of bacteriochlorophyll *a* gives bacteriopheophytin *a*.

Compounds that are demetallated and also possess a free propionic acid or acrylic acid residue at position 17 are called pheophorbides,<sup>b</sup> and the names are related to those of the chlorophyll in the same way. Thus, on demetallation and hydrolysis of the phytlyl ester, chlorophyll *a* gives pheophorbide *a*.

Examples:

1.

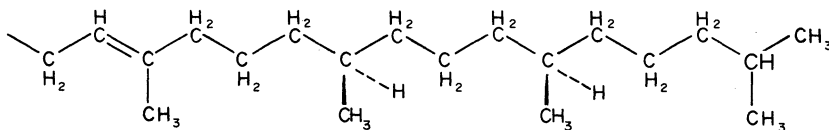


- Pheophytin *a* R<sup>1</sup> = -CH<sub>3</sub>; R<sup>2</sup> = phytlyl<sup>c</sup>  
 Pheophytin *b* R<sup>1</sup> = -CHO; R<sup>2</sup> = phytlyl<sup>c</sup>  
 Pheophorbide *a* R<sup>1</sup> = -CH<sub>3</sub>; R<sup>2</sup> = -H  
 Pheophorbide *b* R<sup>1</sup> = -CHO; R<sup>2</sup> = -H  
 Pheophorbide *a* methyl ester R<sup>1</sup> = -CH<sub>3</sub>;  
 R<sup>2</sup> = -CH<sub>3</sub>

a. At present this method is limited to the phytlyl and farnesyl ester groups. Even though a geranylgeranyl ester has been reported for bacteriochlorophyll, no trivial name has been accepted for the demetallation analog.

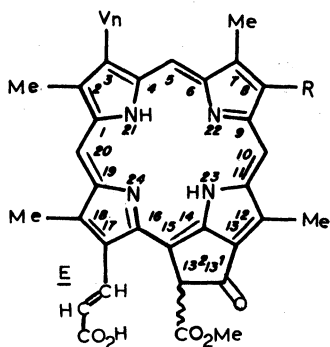
b. The ending "-ide" should not be confused with its meaning by IUPAC Rule C-84.3 in which it would designate an anion formed by removal of a proton from a carbon atom.

c. Phytlyl =

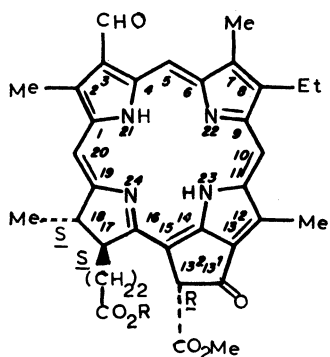


(2*E*)-(7*R*,11*R*)-3,7,11,15-tetramethyl-2-hexadecenyl.

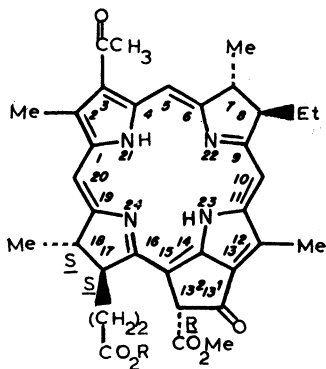
2.

a,b Pheophorbide  $c_1$  R =  $-\text{CH}_2\text{CH}_3$ a,b Pheophorbide  $c_2$  R =  $-\text{CH}=\text{CH}_2$ 

3.

Pheophytin  $d$  R = phytylPheophorbide  $d$  R = -H

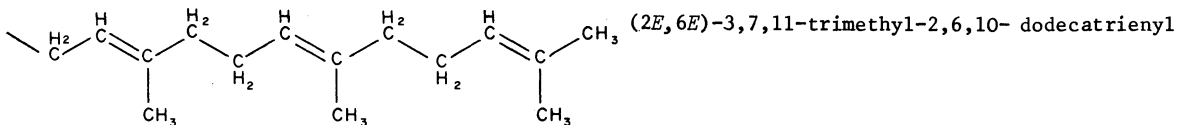
4.

Bacteriopheophytin  $\alpha$  R = phytylBacteriofarnesin  $\alpha$  R = farnesyl<sup>c</sup>Bacteriopheophorbide  $\alpha$  R = -H

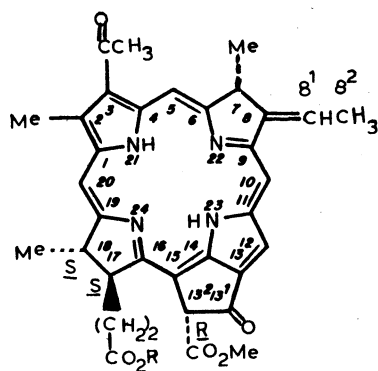
a. Chlorophylls  $c_1$  and  $c_2$  (which have a free acrylic acid residue at C-17) on demetallation yield the pheophorbides  $c_1$  and  $c_2$ , and are porphyrins rather than chlorins.

b. The configuration of the double bond is *E*, and is to be implied by these names. If it is necessary to specify the absolute configuration at C-13<sup>2</sup>, it should be indicated by *R* or *S* according to TP-0.3.

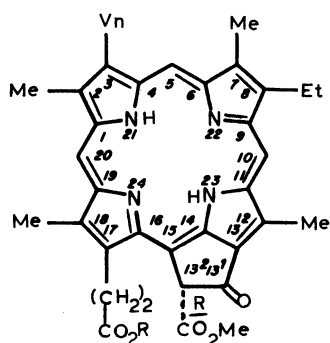
c. *trans,trans*-Farnesyl is



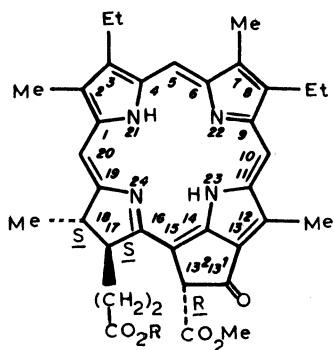
5.

Bacteriopheophytin  $b^a$  R = phytyl

6.

17,18-Didehydropheophytin  $a^b$  R = phytyl17,18-Didehydropheophorbide  $a^b$  R = -H

7.

Mesopheophytin  $a$  R = PhytylMesopheophorbide  $a$  R = -H

a. If it is necessary to specify the stereochemistry of the 8(8<sup>1</sup>) double bond, it should be indicated by *E* or *Z* according to TP-0.3.

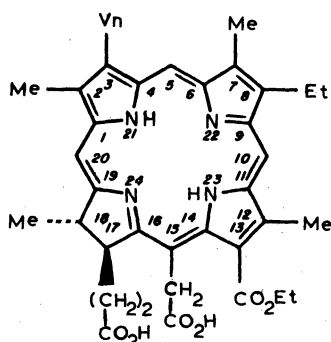
b. The names protopheophytin *a* and protopheophorbide *a* would be derived according to this rule from the Fischer name, protochlorophyll *a*. However "protochlorophyll *a*" is not included in the list of chlorophyll names in TP-8.4 because its substitution pattern differs from that of protoporphyrin (an ethyl group at position 8 is a vinyl group in protoporphyrin). Hence "protopheophytin *a*" and "protopheophorbide *a*" are not acceptable names in this document. These structures are easily named using the subtractive prefix "didehydro" combined with derivative terms, pheophytin *a* or pheophorbide *a* based on the parent structure, chlorophyll *a*.



TP-4.4. *Substituted Chlorins. Semisystematic Chlorin Names.* As an alternative to systematic chlorin names formed according to TP-4.2, chlorin derivatives closely related to the four trivially named chlorins in Table 4 of TP-4.3.1 may be named semisystematically. Subtractive and/or substitutive prefixes (or suffix) are combined with the appropriate trivial name. The procedures for forming semisystematic porphyrin names in TP-3 are followed.

Examples:

1.

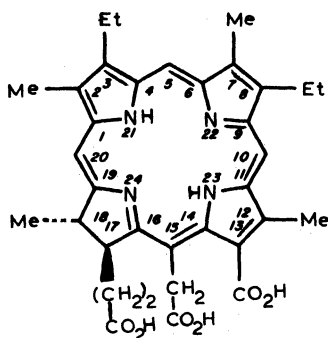


Semisystematic: 3<sup>1</sup>,3<sup>2</sup>-Didehydrorhodochlorin-15-acetic acid  
13-ethyl ester

Systematic: (2*S*,3*S*)-20-(Carboxymethyl)-18-(ethoxycarbonyl)-13-ethyl-3,7,12,17-tetramethyl-8-vinylchlorin-2-propionic acid

Fischer: Chlorin *e*<sub>6</sub> (as a monoethyl ester)

2.

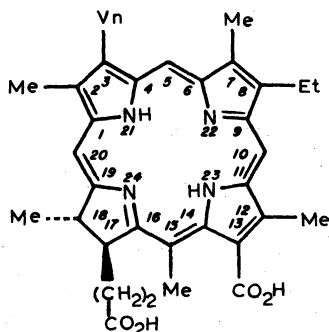


Semisystematic: Rhodochlorin-15-acetic acid

Systematic: (2*S*,3*S*)-18-Carboxy-20-(carboxymethyl)-8,13-diethyl-3,7,12,17-tetramethylchlorin-2-propionic acid

Fischer: Mesochlorin *e*<sub>6</sub>

3.

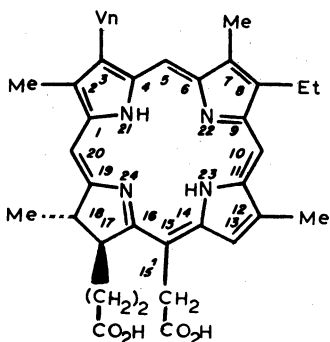


Semisystematic: 3<sup>1</sup>,3<sup>2</sup>-Didehydro-15-methylrhodochlorin

Systematic: (2*S*,3*S*)-18-Carboxy-13-ethyl-3,7,12,17,20-pentamethyl-8-vinylchlorin-2-propionic acid

Fischer: Chlorin *e*<sub>4</sub>

4.

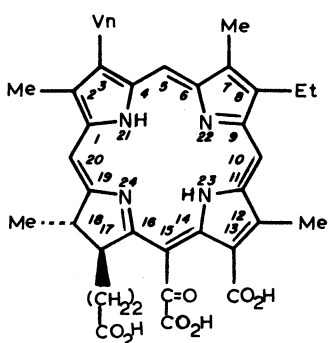


Semisystematic: 3<sup>1</sup>,3<sup>2</sup>-Didehydrophyllchlorin-15<sup>4</sup>-carboxylic acid

Systematic: (2*S*,3*S*)-20-(Carboxymethyl)-13-ethyl-3,7,12,17-tetramethyl-8-vinylchlorin-2-propionic acid

Fischer: Isochlorin e<sub>4</sub>

5.

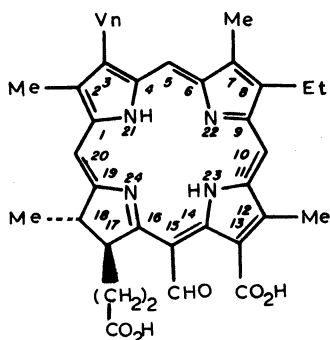


Semisystematic: 3<sup>1</sup>,3<sup>2</sup>-Didehydrorhodochlorin-15-glyoxylic acid

Systematic: (2*S*,3*S*)-18-Carboxy-13-ethyl-3,7,12,17-tetramethyl-20-oxalo-8-vinylchlorin-2-propionic acid

Fischer: Purpurin 7

6.



Semisystematic: 3<sup>1</sup>,3<sup>2</sup>-Didehydro-15-formylrhodochlorin

Systematic: (2*S*,3*S*)-18-Carboxy-13-ethyl-20-formyl-3,7,12,17-tetramethyl-8-vinylchlorin-2-propionic acid

Fischer: Purpurin 5

#### Rule Tetrapyrrole 5. Ring-expanded and Ring-contracted Systems.

*TP-5.1. Ring Expansion.* Inclusion of a methylene group (-CH<sub>2</sub>-) into a porphyrin ring sector is indicated by the prefix "homo" in accord with the guidelines established for natural products.<sup>a</sup> The homo prefix is preceded by a locant indicating the position of the inserted group. A locant for the inserted group is generated by adding the letter "a" to the locant of the highest possible numbered atom of the ring-sector that is not a bridgehead or junction<sup>b</sup> to which the group is added.

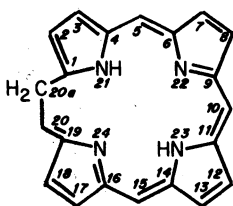
To denote ring expansion of the fundamental porphyrin nucleus, "homo" immediately precedes "porphyrin". To denote ring expansion of a trivially named porphyrin or reduced porphyrin, "homo" immediately precedes the appropriate trivial name.

a. IUPAC provisional Rule F-4.5.

b. Bridgehead and junction atoms are excluded to avoid ambiguity.

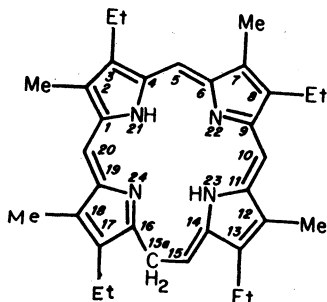
## Examples:

1.



20a-Homoporphyrin

2.

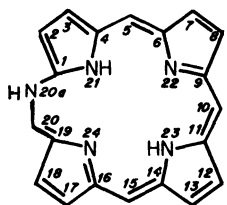


15a-Homoetioporphyrin III

TP-5.2. *Skeletal Replacement of Ring-expanded Systems.* Replacement prefixes with appropriate locants are added in front of the name of the ring-expanded porphyrin.<sup>a</sup>

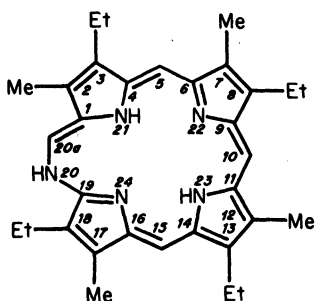
## Examples:

1.



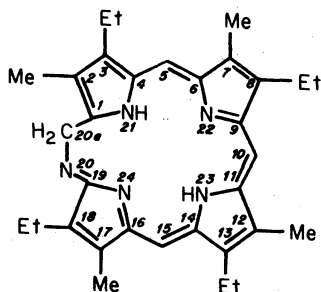
20a-Aza-20a-homoporphyrin

2.

20H-20-Aza-20a-homoetioporphyrin I<sup>b</sup>

a. General practice varies in related areas such as steroids and natural products as to the relative placement of ring modifying and skeletal replacement prefixes. Further study is needed. See IUPAC provisional Rule F-4.5.

b. "Indicated hydrogen" distinguishes this structure from the closely related one:



20-Aza-20a-homoetioporphyrin I

Because atom 19 is a bridgehead, the locant 19a may be ambiguous.

TP-5.3. *Ring-contracted systems.* The trivial names "corrin" and "corrole" [7] are retained for the ring-contracted structures shown in Figs. 10 and 11 respectively.<sup>a</sup> Skeletal replacement analogs are named by prefixing the appropriate locants with multiplicative and replacement prefixes to the parent name "corrole".<sup>b</sup> Other ring-contracted porphyrins are named systematically according to the rules for naming heterocycles.<sup>c,d</sup>

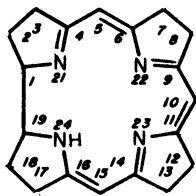


Fig. 10. Corrin.

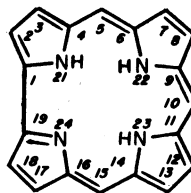
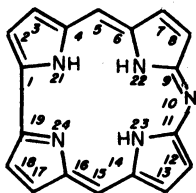


Fig. 11. Corrole.

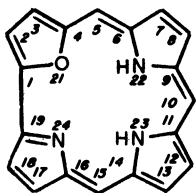
Examples:

1.



10-Azacorrole

2.



21-Oxacorrole

TP-5.4. The pentapyrrolic macrocycle Fig. 12 is called saphyrin [8], and is numbered as shown.

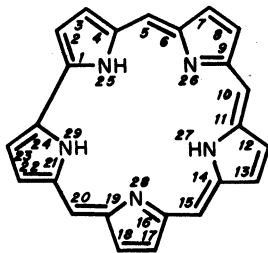


Fig. 12. Saphyrin.

a. For other trivial names such as cobyrinic acid, cobinic acid and vitamin B-12 that are retained for substituted derivatives of these ring systems, see IUPAC-IUB Commission on Biochemical Nomenclature, "Nomenclature of Corrinoids, Rules Approved 1975." *Pure Appl. Chem.* 48, 495-502 (1976).

b. As for skeletal replacement in porphyrins, replacement of saturated nitrogen atoms of corrin and corrole precede replacement of the unsaturated nitrogen atoms. See TP-1.5.

c. See IUPAC Rules B-1 to B-15.2.

d. The ring contraction prefix "nor", recommended for natural products in IUPAC provisional Rule F-4.4, at present denotes only the loss of a methylene (-CH<sub>2</sub>-) group from a ring system. Generally, ring contraction by use of "nor" has been restricted to saturated systems such as steroids. Extension of the meaning of "nor" to indicate loss of either a methylene (-CH<sub>2</sub>-) or methyne (-CH=) group needs further study with regard to indication of hydrogen present in the ring, priority of citation and numbering of heteroatoms and other ring modifying prefixes.

### Rule Tetrapyrrole 6. Linear Tetrapyrroles.

*TP-6.1. Fundamental System.* The structure in Fig. 13 is called "bilin". It is defined without oxygen substituents, and is numbered (omitting C-20) to agree with the numbering of the unsubstituted porphyrin ring system (see Fig. 2). Unless otherwise specified it is implied that the nitrogen atom at position 22 is saturated. If it is necessary to specify the stereochemistry of the 4(5)-, 5(6)-, 9(10)-, 10(11)-, 14(15)- and/or 15(16)- double bonds, it should be indicated by *E* or *Z* according to TP-0.3.

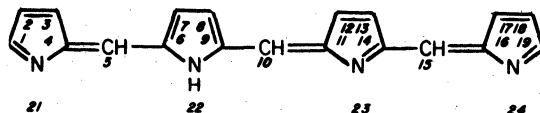


Fig. 13. Bilin (22H-form drawn conventionally).

*TP-6.2. Unsubstituted Reduced Bilins.* Unsubstituted reduced bilins may be named systematically on the basis of the bilin structure in Fig. 13. The trivial names "bilinogen" and "1,19-secocorrin" may be used in place of 5,10,15,21,23,24- hexahydrobilin and 1,2,3,7,8,12,13,17,18,19-decahydrobilin shown in Figs. 14 and 15, respectively [9].

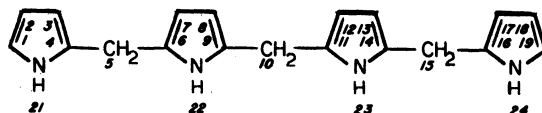


Fig. 14. Bilinogen  
5,10,15,21,23,24-Hexahydrobilin

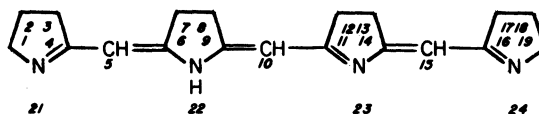
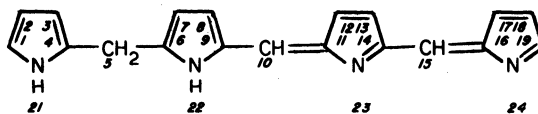


Fig. 15. 1,19-Secocorrin  
1,2,3,7,8,12,13,17,18,19-Decahydrobilin

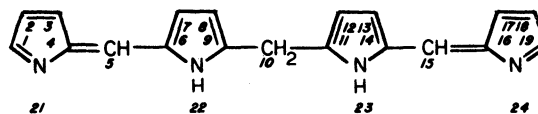
Examples:

1.



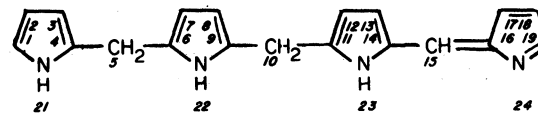
5,21-Dihydrobilin

2.



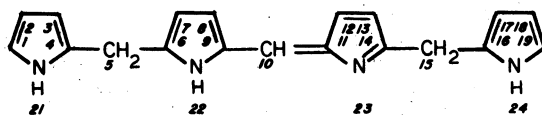
10,23-Dihydrobilin

3.



5,10,21,23-Tetrahydrobilin

4.

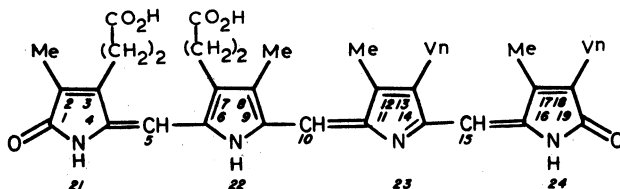


5,15,21,24-Tetrahydrobilin

TP-6.3. *Systematic Nomenclature.* Substituted bilins may be named systematically on the basis of the fundamental bilin structure shown in Fig. 13. All substituents are expressed by prefixes and/or suffixes as in systematic organic nomenclature.<sup>a</sup> Positions of substitution are determined in accord with IUPAC Rule C-15.11 (b) to (e) based on the 22H form. Hydrogenation of unsaturated positions may be indicated by the prefixes, dihydro- tetrahydro-, etc.

Examples:<sup>b</sup>

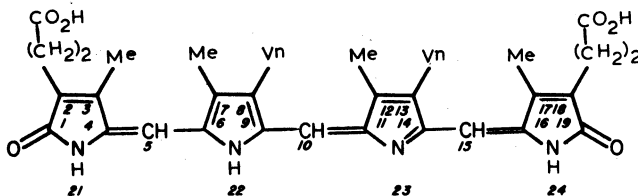
1.



1,19,21,24-Tetrahydro-2,8,12,17-tetramethyl-1,19-dioxo-13,18-divinylbilin-3,7-dipropionic acid (formerly biliverdin IX $\beta$ )

or  
3,7-Bis(2-carboxyethyl)-21,24-dihydro-2,8,12,17-tetramethyl-13,18-divinylbilin-1,19-dione

2.

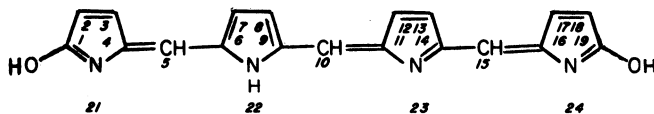


1,19,21,24-Tetrahydro-3,7,12,17-tetramethyl-1,19-dioxo-8,13-divinylbilin-2,18-dipropionic acid (formerly biliverdin IX $\gamma$ )

or  
2,18-Bis(2-carboxyethyl)-21,24-dihydro-3,7,12,17-tetramethyl-8,13-divinylbilin-1,19-dione

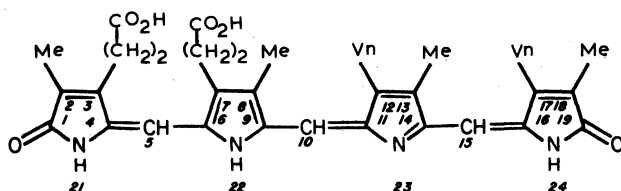
a. Common biochemical practice favors the expression of the ketone function as a suffix in contradistinction to the usual hierarchy of functions in systematic organic nomenclature which favors the expression of the acid function as a suffix. These names are included as an alternative in the examples that follow.

b. The linear tetrapyrrole structures shown in these examples are formally tautomeric with a correspondingly substituted 1,19-dihydroxybilin. However, present evidence indicates it is less likely to represent the predominant tautomeric form. Thus, most naturally occurring linear tetrapyrroles are named on the basis of the bislactam or keto tautomer.



1,19-Dihydroxybilin

3.

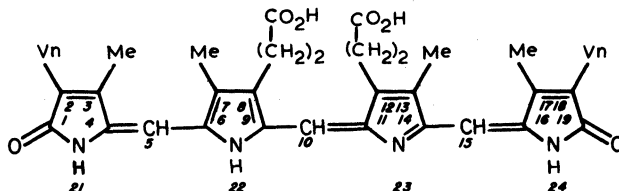


1,19,21,24-Tetrahydro-2,8,13,18-tetramethyl-1,19-dioxo-12,17-divinyl-bilin-3,7-dipropionic acid (formerly biliverdin IX $\delta$ )<sup>a</sup>

or

3,7-Bis(2-carboxyethyl)-21,24-dihydro-2,8,13,18-tetramethyl-12,17-divinylbilin-1,19-dione

4.

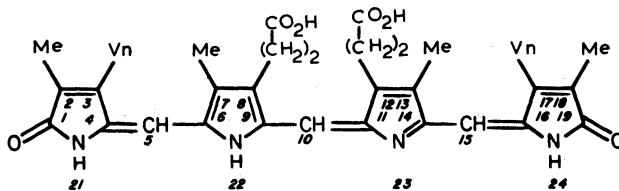


1,19,21,24-Tetrahydro-3,7,13,17-tetramethyl-1,19-dioxo-2,18-divinyl-bilin-8,12-dipropionic acid (formerly biliverdin III $\alpha$ )

or

8,12-Bis(2-carboxyethyl)-21,24-dihydro-3,7,12,17-tetramethyl-2,18-divinylbilin-1,19-dione

5.

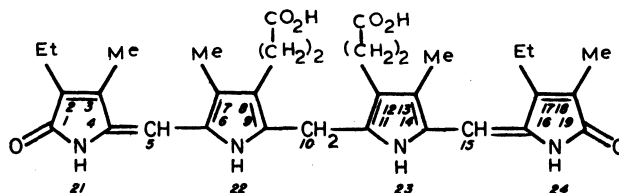


1,19,21,24-Tetrahydro-2,7,13,18-tetramethyl-1,19-dioxo-3,17-divinylbilin-8,12-dipropionic acid (formerly biliverdin XIII $\alpha$ )

or

8,12-Bis(2-carboxyethyl)-21,24-dihydro-2,7,13,18-tetramethyl-3,17-divinylbilin-1,19-dione

6.



2,17-Diethyl-1,10,19,21,23,24-hexahydro-3,7,13,18-tetramethyl-1,19-dioxobilin-8,12-dipropionic acid<sup>b</sup>

or

8,12-Bis(2-carboxyethyl)-2,17-diethyl-10,21,23,24-tetrahydro-3,7,13,18-tetramethylbilin-1,19-dione

a. Note that the systematic orientation and numbering differ from that established for this structure for its former name biliverdin IX $\delta$

b. Note that the systematic orientation and numbering differ from that accepted for the recommended trivial name, mesobilirubin, shown in Fig. 19 in TP-6.4.

TP-6.4. *Trivially Named Substituted Bilins*. Seven trivial names and associated locants are retained for naming the substituted bilin structures shown in Figs. 16 to 22.<sup>a</sup> The side chains may be numbered using the locant of the point of substitution on the bilin system with a following superscript numeral as for trivially named porphyrins in TP-2.1.

These recommended trivial names may be used to form semisystematic names for derivatives as directed in TP-6.5. However, positional isomers of these trivially named structures are named systematically according to TP-6.3.

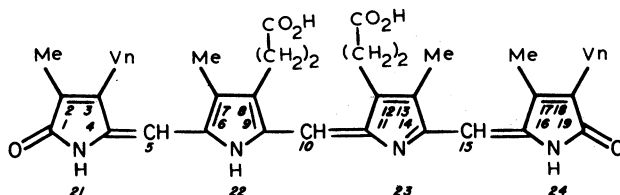


Fig. 16. Biliverdin (formerly biliverdin IX $\alpha$ ).

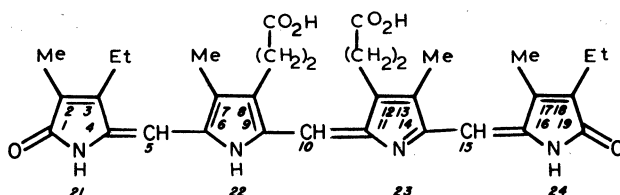


Fig. 17. Mesobiliverdin (formerly mesobiliverdin IX $\alpha$ ; glaucobilin IX $\alpha$ ).

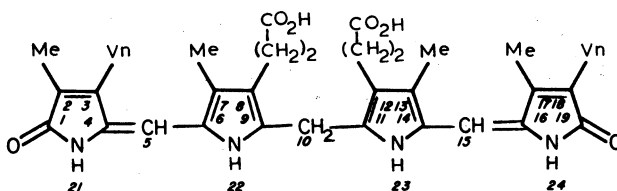


Fig. 18. Bilirubin (formerly bilirubin IX $\alpha$ ).<sup>b</sup>

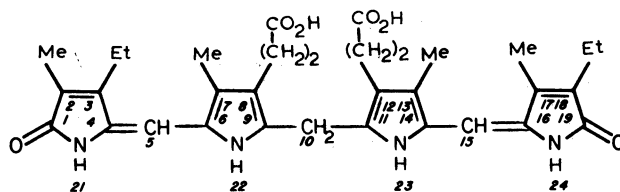
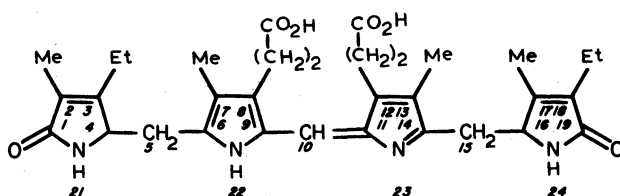
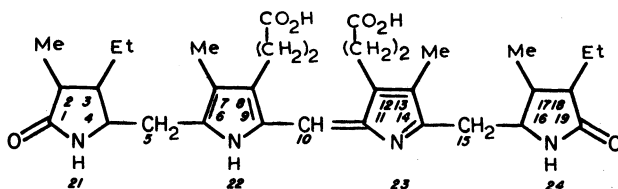
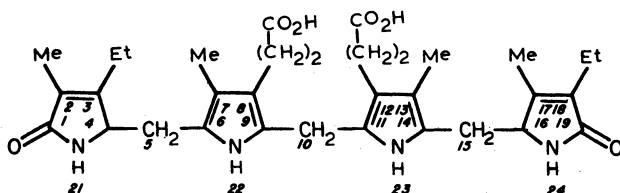


Fig. 19. Mesobilirubin (formerly mesobilirubin IX $\alpha$ ).

a. In the recommended nomenclature the Roman numeral and Greek letter (that in the Fischer system refer in a formal way to the substitution pattern and to the position of cleavage of the corresponding porphyrin respectively) have been dropped. Thus biliverdin was formerly biliverdin IX $\alpha$ . Because the vast majority of references are to this common substitution pattern, it has become common practice to drop the IX $\alpha$  designation.

b. X-ray crystallography has shown that the natural compound has the configuration (4Z.15Z). See R. Bonnett, J. E. Davies and M. B. Hursthouse, *Nature* 262, 326 (1976).

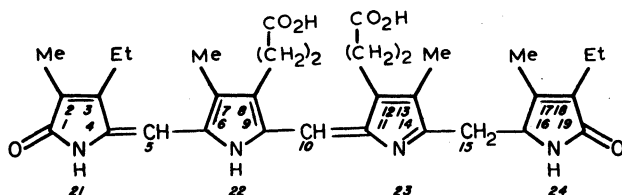


Fig. 20. Urobilin (formerly urobilin IX etc. [10]).<sup>a</sup>Fig. 21. Stercobilin (formerly stercobilin IX $\alpha$ ).<sup>a</sup>Fig. 22. Urobilinogen (formerly mesobilirubinogen IX $\alpha$ ; urobilinogen IX $\alpha$ ).<sup>a</sup>

TP-6.5. *Semisystematic Names.* As an alternative to the systematic nomenclature of TP-6.3, substituted bilins closely related to the trivially named bilin structures shown in Figs. 16 to 22, in which only a few substituents differ or that differ only in degree of saturation, may be conveniently named semisystematically on the basis of the recommended trivial names. The subtractive prefix "de," and the substitutive prefixes and suffixes may be used as for porphyrin derivatives in TP-3.1 through TP-3.3. When sites of saturation are known to be either one of two possible locations, the lowest possible locants are cited, followed in parentheses by the italic word "or" and the alternate locants.

Examples:

1.

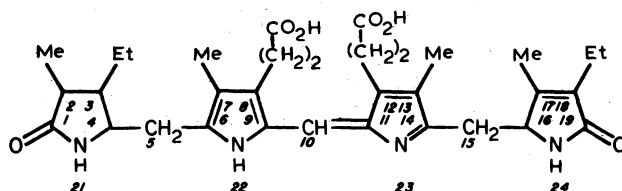
15,16-Dihydromesobiliverdin (formerly mesobiliviolin IX $\alpha$ )<sup>a,b,c</sup>

a. If it is necessary to indicate the absolute stereochemistry of any of the chiral centers, this should be indicated by *R* or *S* in accord with TP-0.3.

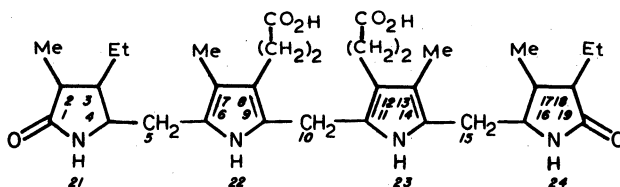
b. Where sites of saturation are indefinite, the name would be 4,5(*or* 15,16)-dihydromesobiliverdin

c. Note that, in many cases, the older trivial names do not distinguish between isomeric possibilities. "Mesobiliviolin IX $\alpha$ " may refer to two possible isomers [11].

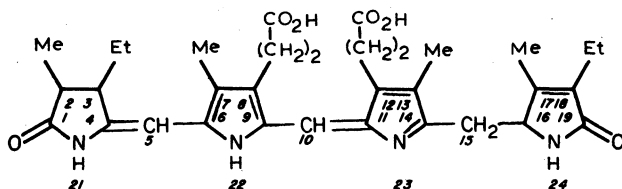
2.

2,3-Dihydrourobilin (formerly half-stereobilin IX $\alpha$ )<sup>a</sup>

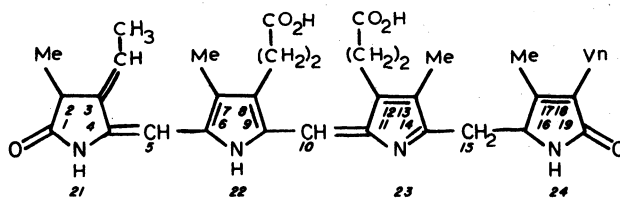
3.

10,23-Dihydrostercobilin (formerly stercobilinogen IX $\alpha$ )<sup>a</sup>

4.

2,3,15,16-Tetrahydromesobiliverdin (formerly mesobilirhodin IX $\alpha$ )<sup>a,b</sup>

5.

3,3<sup>1</sup>,18<sup>1</sup>,18<sup>2</sup>-Tetrahydro-2,3,15,16-tetrahydromesobiliverdin (formerly phycoerythrobilin; phycobiliviolin)<sup>a,c,d,e</sup>

a. If it is necessary to indicate the absolute stereochemistry of any of the chiral centers, this should be indicated by *R* or *S* in accord with TP-0.3.

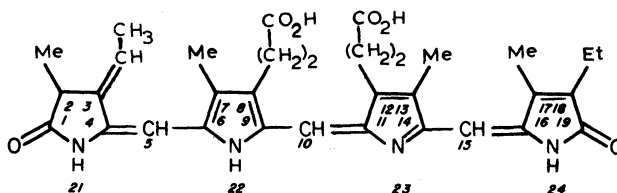
b. The name "mesobilirhodin IX $\alpha$ " may refer to two possible isomers [12].

c. Two sets of trivial names have arisen for the bilinoids derived from algal biliproteins. (W. Rüdiger, *Fortschritte der Chemie organischer Naturstoffe* 29, 60 (1971); D. J. Chapman, W. J. Cole, and H. W. Siegelman, *J. Am. Chem. Soc.* 89, 5976 (1967); H. L. Crespi, L. J. Boucher, G. D. Norman, J.J. Katz and R. C. Dougherty, *J. Am. Chem. Soc.* 89, 3642 (1967)). While the semisystematic names based on mesobiliverdin in examples 5 and 6 are preferred, if a trivial name is to be used, phycoerythrobilin and phycocyanobilin would be better choices than phycobiliviolin and phycobiliverdin because the violins are muted in these recommendations.

d. Aplysioviolin is the monomethyl ester of this structure, *Angew. Chem., Int. Ed.* 9, 473 (1970).

e. The stereochemistry of the 3(3<sup>1</sup>)-double bond may be indicated by *E* or *Z* in accord with TP-0.3.

6.



3,3'-Didehydro-2,3-dihydromesobiliverdin (formerly phycocyanobilin; phycobiliverdin)<sup>a,b</sup>

Rule Tetrapyrrole 7. Relatives of Linear Tetrapyrroles.

*TP-7.1. Linear Tripyrroles.* By analogy with the nomenclature of linear tetrapyrroles, the nomenclature of linear tripyrroles is based systematically on the most unsaturated system known, which is called tripyrrin and shown in Fig. 23.

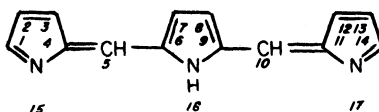
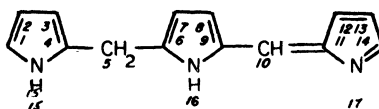


Fig. 23. 16*H*-Tripyrrin.

Reduced tripyrrins are named as dihydro, tetrahydro etc. derivatives:

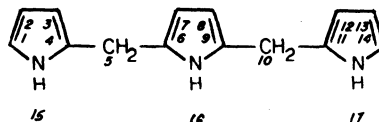
Examples:

1.



5,15-Dihydro-16*H*-tripyrrin

2.



5,10,15,17-Tetrahydro-16*H*-tripyrrin<sup>c</sup>

Rule Tetrapyrrole 8. Metal Coordination Complexes.

*TP-8.1. General Description.* The common structural pattern for metal coordination complexes in this series consists of a metal ion coordinated to a roughly planar tetrapyrrole, acting as a tetradentate dianionic ligand, and, possibly, to one or two axial ligands, as illustrated in Fig. 24.<sup>c</sup>

a. If it is necessary to indicate the absolute stereochemistry of any of the chiral centers, this should be indicated by *R* or *S*.

b. The stereochemistry of the 3(3')- double bond may be indicated by *E* or *Z* in accord with TP-03.

c. This structure is called tripyrrane in the Fischer system.

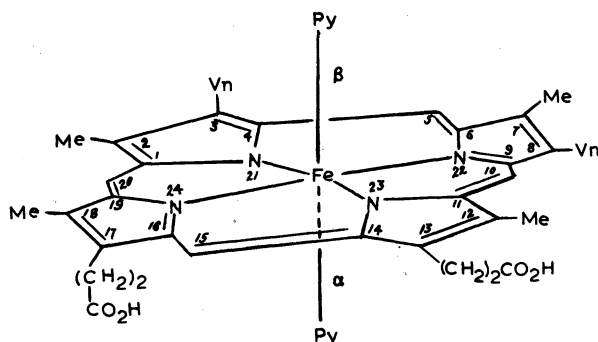


Fig. 24. A protoheme<sup>a</sup> as an example of a tetrapyrrole coordination complex containing a tetrapyrrole terradentate dianionic ligand and two pyridine molecules as axial ligands.

The tetrapyrrolic ligand is oriented with the numbering clockwise when seen from above (see TP-1.2, TP-1.7 and TP-2.1). The axial ligands above and below the plane are then designated by the use of  $\beta$  and  $\alpha$  respectively, in analogy with established custom for other groups of compounds.<sup>b,c,d</sup> For example, hemoglobin coordinates with oxygen on the  $\alpha$  face of the protoheme system.

Coordination of the four central nitrogen atoms (N-21, N-22, N-23, N-24) is the common structural pattern, and need not be specifically designated, but may be designated as instructed in Inorganic Rule 7.33 or D-2.38 if desired. When the charge on the tetrapyrrolic ligand is not specified it is understood that it carries a formal negative charge of two units. For systems that do not conform to the common structural pattern see TP-9.2.

*TP-8.2. Coordination Nomenclature.* The Rules for Coordination Compounds<sup>e</sup> are followed, except that stereochemical configuration of axial ligands, if any, may be designated, where known, by the use of  $\alpha$  and  $\beta$  as in TP-8.1, Fig. 24. The names of ligands precede the name of the metal, the ligands being cited in alphabetical order. Enclosing marks are employed as described in Inorganic Rule 7.3 and D-2.21 of the Rules for Coordination Compounds.<sup>f</sup>

For coordination complexes of the common structural pattern described in Rule TP-8.1 the macrocycle name takes the ending "ato".<sup>g</sup> Thus chlorin becomes chlorinato, porphyrin becomes porphyrinato, bilirubin becomes bilirubinato and mesoporphyrin diethyl ester becomes mesoporphyrinato diethyl ester. The name of the metal follows, and is itself followed by its oxidation number (Roman numeral in brackets), or its Ewens-Bassett number<sup>h</sup> to indicate the charge on the entire coordination complex (instead of an oxidation number) as recommended in Inorganic Rule 7.22 or Rule D-2.23.

a. See TP-8.42 for definition.

b. Because the assignment of  $\alpha$  and  $\beta$  is dependent on the direction of numbering of substituents, they are defined only in a relative sense. For example, the  $\alpha$  side of mesoporphyrin named systematically as 7,12-diethyl-3,8,13,17-tetramethylporphyrin-2,18-dipropionic acid is the  $\beta$  side of mesoporphyrin named and numbered according to the trivial system.

c. IUPAC-IUB Commission on Biochemical Nomenclature, "Nomenclature of Corrinoids, Rules Approved 1975". *Pure Appl. Chem.* **48**, 495-502 (1976).

d. IUPAC Commission on the Nomenclature of Organic Chemistry and IUPAC-IUB Commission on Biochemical Nomenclature. "1971 Definitive Rules for Nomenclature of Steroids." *Pure Appl. Chem.* **31**, 284-322 (1972).

e. IUPAC, "Nomenclature of Inorganic Chemistry. Definitive Rules 1970" 2nd ed. *Pure Appl. Chem.* **28**, 39 (1971) Section 7; and IUPAC, "Nomenclature of Organic Chemistry, Section D". *Inf. Bull. Append. Tentative Nomencl., Symb., Units, Stand.* (IUPAC) No. 31 August 1973, Section D-2.

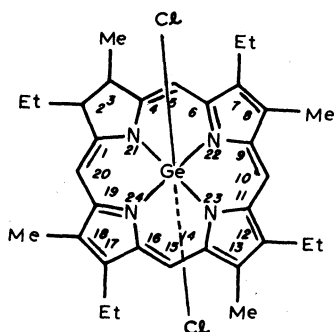
f. An essential result is that organic anions, including macrocyclic anions, are placed in brackets. The names of inorganic anions are not bracketed except in special cases [e.g. when the name contains a numerical prefix e.g. (triphosphato)]. When a neutral molecule is coordinated its name is used unchanged, and is bracketed, except, on both counts, for the following common neutral ligands: water (becomes aqua), ammonia (becomes ammine), nitric oxide (becomes nitrosyl), and carbon monoxide (becomes carbonyl).

g. The designation of the charge on the ligand such as (2-) is often not specified.

h. See Inorganic Rule 2.252 for definition.

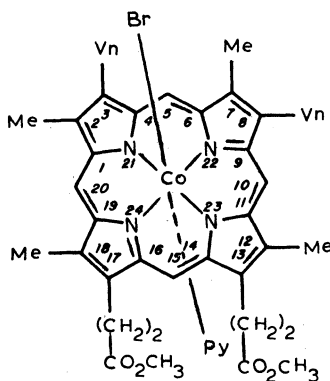
Examples: (Py = pyridine)

1.



Dichloro(2,7,12,17-tetraethyl-2,3-dihydro-3,8,13,18-tetramethyl porphyrinato)germanium(IV)

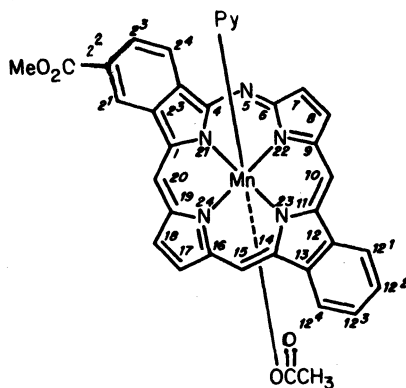
2.



$\beta$ -Bromo(protoporphyrinato dimethyl ester)- $\alpha$ -(pyridine)cobalt(III)

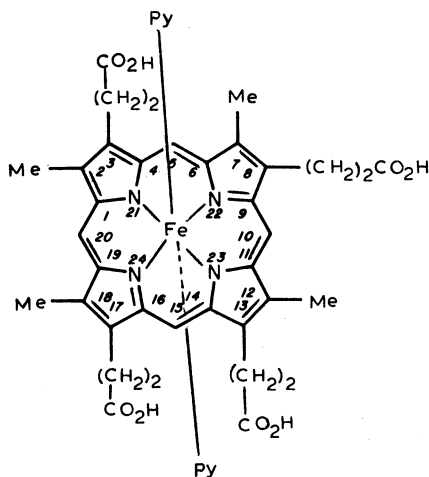
$\beta$ -Bromo[ dimethyl 3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionato(2-)]- $\alpha$ -(pyridine)cobalt(III)

3.



$\alpha$ -(Acetato)[ 2<sup>2</sup>-(methoxycarbonyl) dibenzo[ *b*, *l* ]-5-azaporphyrinato ]- $\beta$ -(pyridine)manganese(III)

4.

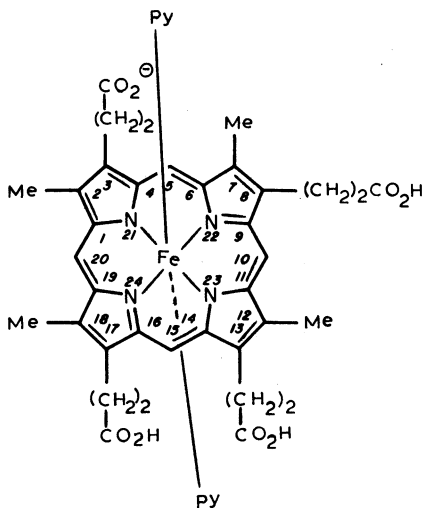


(Coproporphyrinato III)bis(pyridine)iron(II)<sup>a</sup>

or

Bis(pyridine)(3,8,13,17-tetramethylporphyrin-2,7,12,18-tetrapropionato)iron(II)

5.



[Coproporphyrinato(6-) III] bis(pyridine)iron(III)

or

Bis(pyridine)[3,8,13,17-tetramethylporphyrin-2,7,12,18-tetrapropionato-(3-)]iron(III)

a. Practice varies as to whether the protons of the acid groups are formally removed from the ligand or are retained in naming such coordination complexes. If they are retained for this coordination complex, the name is based on iron. If they are removed, a hexaanionic ligand results, and the precise name of the anion would be [coproporphyrinato(6-) III *N*<sup>21</sup>,*N*<sup>22</sup>,*N*<sup>23</sup>,*N*<sup>24</sup>] bis(pyridine)ferrate(4-).

TP-8.3. *Alternative Order of the Components of the Name:* (Alternative to TP-8.2). Since the macrocyclic name is frequently complex and unwieldy the alternative order of components: (axial ligands)-metal-tetrapyrrolic ligand is introduced here for use in naming tetrapyrrole metal coordination complexes. This form of name, although not encompassed by the established IUPAC coordination rules, has the additional advantage that confusion between axial ligands and substituents on the macrocyclic ligand cannot easily arise.

The axial ligands are cited in alphabetical order and with enclosing marks as before (Rule TP-8.2.). The name of the metal follows, and is itself followed by the oxidation number (Roman numeral in parentheses) or the Ewens Bassett number. After a space the name of the tetrapyrrole ligand is given, ending in "ate":<sup>a</sup> it is not bracketed.

The structures drawn in Rule TP-8.2. are named as follows on the basis of this alternative procedure:

1. Dichlorogermanium(IV) 2,7,12,17-tetraethyl-2,3-dihydro-3,8,13,18-tetramethylporphyrinate
2.  $\beta$ -Bromo- $\alpha$ -(pyridine)cobalt(III) protoporphyrinate dimethyl ester
3.  $\alpha$ -(Acetato)- $\beta$ -(pyridine)manganese(III) 2<sup>2</sup>-(methoxycarbonyl)dibenzo[*b*, *l*]-5-azaporphyrinate
4. Bis(pyridine)iron(II) coproporphyrinate III
5. Bis(pyridine)iron(III) coproporphyrinate(3-) III

TP-8.4. *Trivial Names.* Because of their natural occurrence the magnesium and iron coordination complexes are associated with an extensive trivial nomenclature.

TP-8.4.1. Nine trivial names may be used to name the chlorophyll structures as indicated in Figs. 25, 26, 27, and 28.

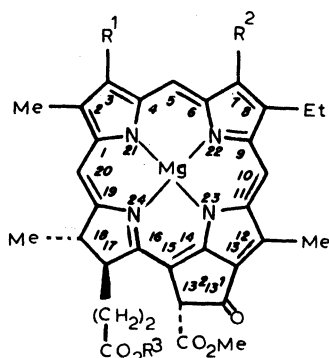
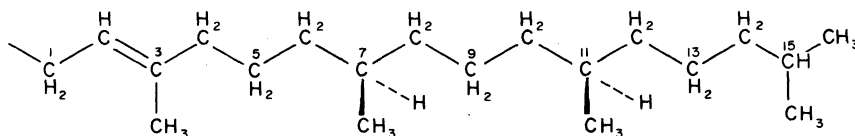


Fig. 25. Chlorophyll <i>a</i>	$R^1 = \text{Vn}$	$R^2 = \text{Me}$	$R^3 = \text{phytyl}^b$
Chlorophyll <i>b</i>	$R^1 = \text{Vn}$	$R^2 = -\text{CHO}$	$R^3 = \text{phytyl}$
Chlorophyll <i>d</i>	$R^1 = -\text{CHO}$ ,	$R^2 = \text{Me}$	$R^3 = \text{phytyl}$
Mesochlorophyll <i>a</i>	$R^1 = \text{Et}$	$R^2 = \text{Me}$	$R^3 = \text{phytyl}$
Chlorophyllide <i>a</i>	$R^1 = \text{Vn}$	$R^2 = \text{Me}$	$R^3 = -\text{H}$ .

a. The use of the "ate" ending here is not sanctioned by any current organic nomenclature rule in IUPAC Sections A,B,C,D or in the IUPAC inorganic rules. In the organic rules, "ate" refers to an anion derived by loss of a proton from a functional group (see IUPAC Rules C-84.1 and C-84.2). In the inorganic nomenclature rules "ate" denotes the loss of a proton from an acid group, or the presence of an anionic coordination center (see Inorganic Rule 3.223).

b. Phytlyl = (2*E*)-(7*R*,11*R*)-3,7,11,15-tetramethyl-2-hexadecenyl



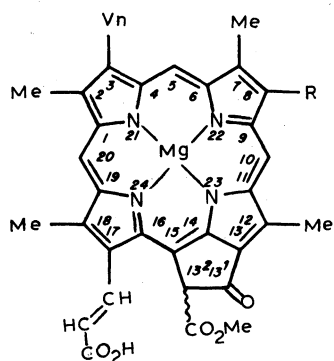


Fig. 26.<sup>a</sup> Chlorophyll  $c_1$      R = Et  
 Chlorophyll  $c_2$      R = Vn.

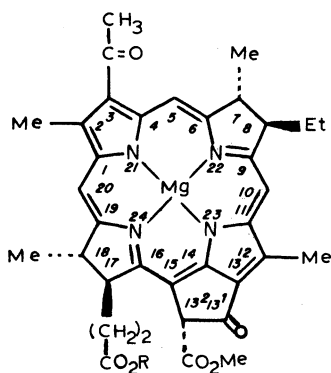


Fig. 27. Bacteriochlorophyll  $a^b$      R = phtyl.

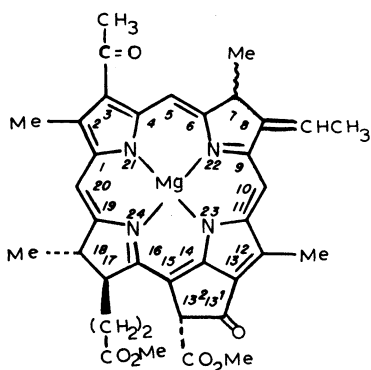


Fig. 28. Bacteriochlorophyll  $b^{c,d}$      R = phtyl.

a. The double bond at C-17<sup>1</sup> is *E* which is implied by these names. However, if the absolute configuration is known at C-13<sup>2</sup>, it may be expressed by *R* or *S* placed in front of these names. See TP-0.3.

b. Bacteriochlorophyllide *a* (*all-trans*)-geranylgeranyl ester has also been reported, and called bacteriochlorophyll *gg*: J. J. Katz, H. H. Strain, A. L. Harkness, M. H. Studier, W. A. Svec, T. R. Janson and B. T. Cope, *J. Am. Chem. Soc.* 94, 7938 (1972).

c. The stereochemistry of the 8(8<sup>1</sup>) double bond may be designated by *E* or *Z* in accord with TP-0.3.

d. The structure of bacteriochlorophyll *b* has been formulated by H. Scheer, W. A. Svec, B. T. Cope, M. H. Studier, R. G. Scott and J. J. Katz, *J. Am. Chem. Soc.* 96, 3714 (1974).



TP-8.4.2. Alternatively, the structures represented in Figs. 25, 27 and 28 may be named semisystematically as magnesium(II) coordination complexes of pheophytins, bacteriopheophytins or mesopheophytin, respectively.<sup>a,b</sup> Chlorophyll *c*<sub>1</sub> and *c*<sub>2</sub> may be named semisystematically as 3<sup>1</sup>,3<sup>2</sup>,17<sup>1</sup>,17<sup>2</sup>-tetrahydro-13<sup>2</sup>-(methoxycarbonylphytylporphyrinato) and 3<sup>1</sup>,3<sup>2</sup>,8<sup>1</sup>,8<sup>2</sup>,17<sup>1</sup>,17<sup>2</sup>-hexa-dehydro-13-(methoxycarbonyl)phytylporphyrinato magnesium(II) coordination complexes, respectively. Chlorophyll structures containing a free propionic acid residue at position C-17 are called chlorophyllides. They may be named semisystematically as magnesium(II) coordination complexes of pheophorbides.

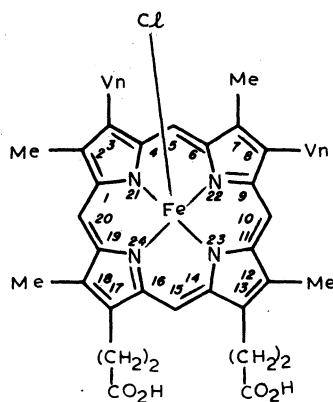
TP-8.4.3. Similarly terms for iron coordination complexes may be defined and interrelated as follows:

#### Iron Coordination Complexes

heme	:	an iron porphyrin coordination complex
ferroheme	:	an iron(II) porphyrin coordination complex
ferriheme	:	an iron(III) porphyrin coordination complex
hemochrome	:	a low-spin iron porphyrin coordination complex with one or more strong field axial ligands (e.g. pyridine)
ferrohemochrome:		an iron(II) hemochrome
ferrihemochrome:		an iron(III) hemochrome
hemin	:	a chloro(porphyrinato)iron(III) coordination complex. For example protohemin = chloro(protochlorophyrinato)iron(III) or chloroiron(III) protoporphyrinate
hematin	:	a hydroxo(porphyrinato)iron(III) coordination complex. <sup>c</sup>

#### Examples:

1.



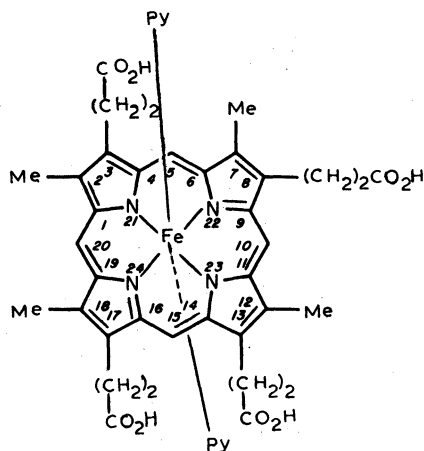
Protohemin  
or  
Chloro(protochlorophyrinato)iron(III)

a. See TP-4.3.2 for pheophytin and pheophorbide names.

b. See TP-2.1 Fig. 5 for phytylporphyrin structure.

c. Such compounds appear to be isolated as the  $\mu$ -oxo anhydro dimers ( $\mu$ -oxo dimers). Examples are given in Rule TP-9.5.

2.



Bis(pyridine)coproferrohemochrome III  
or  
(Coproporphyrinato III)bis(pyridine)iron(II)

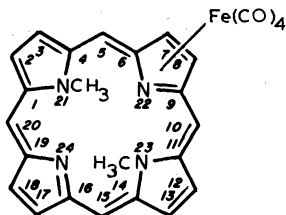
**Rule Tetrapyrrole 9. Metal Coordination Complexes - Less Common Structural Types.**

Although most of the metal coordination complexes in this series fall under Rule TP-8.1, other structural types do occur, and seem likely to increase. These are named using the Rules for Coordination Compounds<sup>a,b</sup> as illustrated below, where the number in brackets after the side heading refers to the appropriate part of those rules.

**TP-9.1. Coordination Complexes of Unknown Structure (Inorganic Rule 7.41).** Where the detail of structure is unknown the name, in the extended form "metal complex of free base" (e.g. the zinc coordination complex of bilirubin), indicates stoichiometric composition only.

**TP-9.2. Coordination other than at Central Nitrogen (Inorganic Rules 7.33, 7.34, 7.513 and D-2.38, D-2.39.).** All earlier examples assume coordination to central nitrogen atoms (Rule TP-8.1). Coordination to other sites must be specifically designated as shown below:

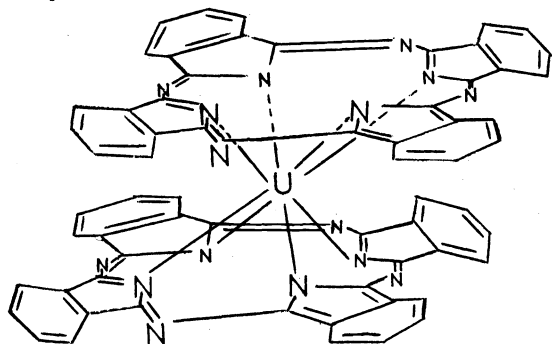
Example:



Tetracarbonyl[7-8-η-(21,23-dimethylporphyrin)] iron(0)  
(η is read as hapto)

**TP-9.3. Mononuclear Metal Coordination Complexes with Two Tetrapyrrolic Ligands**

Example:



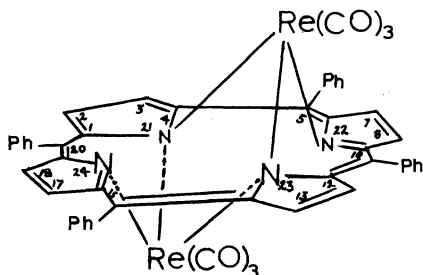
Bis(phthalocyaninato)uranium(IV)  
or  
Uranium(IV) bisphthalocyaninate

a. IUPAC, "Nomenclature of Inorganic Chemistry, Definitive Rules 1970" 2nd ed. Butterworths, London 1971 also published in *Pure Appl. Chem.* **28**, 39(1971), Section 7.

b. IUPAC, "Nomenclature of Organic Chemistry: Section D" *Inf. Bull. Append. Tentative Nomencl., Symb. Units, Stand. No. 31* August 1973, Section D-2.

TP-9.4. *Porphyrin as a Bridging Ligand (Inorganic Rule 7.6)*

The bridging ligand is given the prefix  $\mu$ , and if, in addition, certain atoms function as bridges, this symbol is repeated to indicate these, as shown in the following example:



$\mu$ -[5,10,15,20-Tetraphenylporphyrinato  
(2-)- $N^{22}, N^{24}, \mu-N^{21}, \mu-N^{23}$ ]-bis  
[tricarbonylrhenium(I)]

or

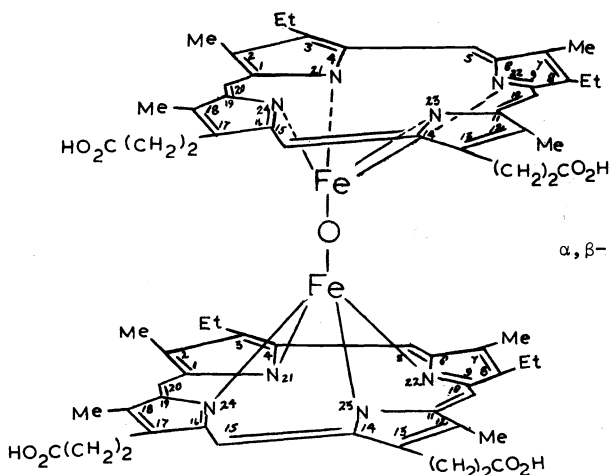
Bis[ tricarbonylrhenium(I)]  $\mu$ -[5,10,15,20-  
tetraphenylporphyrinato(2-)- $N^{22}, N^{24}, \mu-N^{21},$   
 $\mu-N^{23}$ ]

Less symmetrically substituted molecules of this type can be named by using the locant designators given in Inorganic Rules 7.613 and 7.614 to denote the position of ligands.

TF-9.5. *Axial Bridging Ligands.*

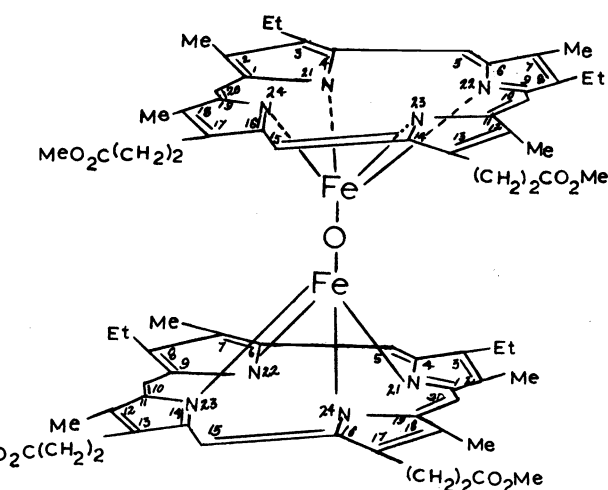
Examples:

1.



$\alpha, \beta$ -( $\mu$ -Oxo)-bis[ mesoporphyrinatoiron(III)]

2.



$\alpha, \alpha-(\mu\text{-Oxo})\text{-bis[ (mesoporphyrinato dimethyl ester) iron(III) ]}$

or

Bis[ dimethyl 7,12-diethyl-3,8,13,17-tetramethyl-2,18-porphyrindipropionato (2-)]- $\beta, \beta-(\mu\text{-oxo})\text{-diiron}^a$

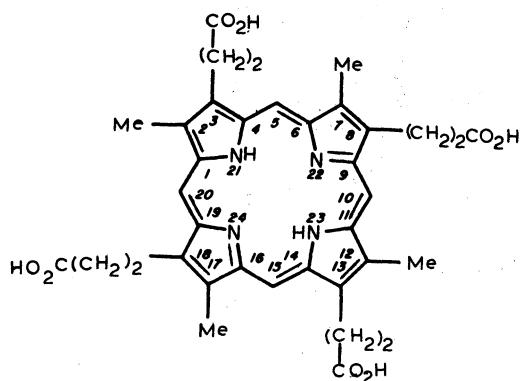
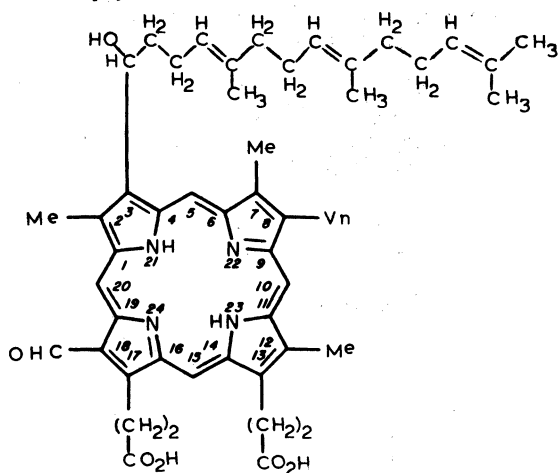
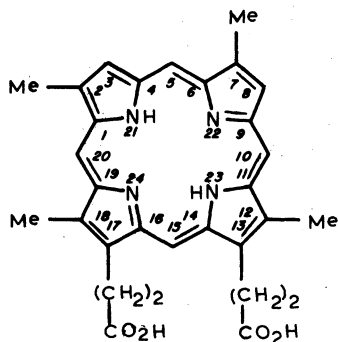
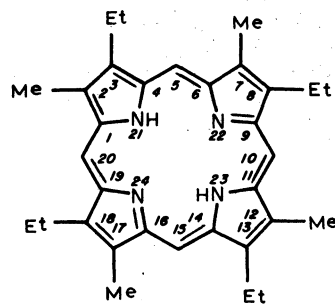
(Where the stereochemical configuration is unknown the stereochemical designators  $\alpha$  and  $\beta$  are omitted).

## REFERENCES

1. R. Bonnett, *Ann. N. Y. Acad. Sci.*, **206**, 745 (1973).
2. R. Bonnett, Proceeding of 9th Meeting of the European Association for the Study of Liver Diseases, Hemsedal (1974) p. 212.
3. H. Fischer and H. Orth, *Die Chemie des Pyrrols*, Volume II.1, Akademische Verlagsgesellschaft, Leipzig (1937).
4. H. Fischer and A. Stern, *Die Chemie des Pyrrols*, Volume II.2, Akademische Verlagsgesellschaft, Leipzig, (1940).
5. S. Sano, T. Shingu, J. M. French and E. Thonger, *Biochem. J.*, **97**, 250 (1965).
6. G. Y. Kennedy, A. H. Jackson, G. W. Kenner and C. J. Suckling, *FEBS Letters*, **6**, 9 (1970).
7. A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1620 (1965).
8. R. B. Woodward, Chemical Society Meeting on Aromaticity, Sheffield, 1966. M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc. Perkin Trans. 1*, 2111 (1972).
9. A. Eschenmoser, *Chem. Soc. Quarterly Rev.*, **24**, 366, (1970).
10. For a discussion of the confused earlier practices see T. K. With, "Bile Pigments", pp. 30-31, Academic Press, New York and London, 1968.
11. M. Stoll and C. H. Gray, *Biochem. J.*, **117**, 271 (1970).
12. P. O'Carra and S. D. Killilea, *Tetrahedron Letters*, 4211 (1970).

a. Because the assignment of  $\alpha$  and  $\beta$  is dependent on the direction of numbering of substituents, the  $\alpha$  side of the trivially named mesoporphyrin is the  $\beta$  side when named systematically.

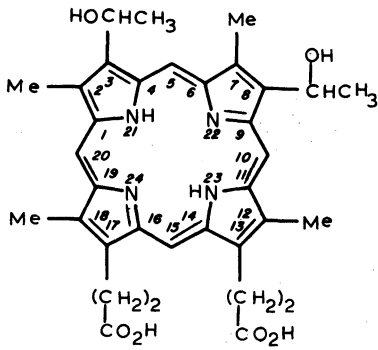
## APPENDIX 1.

A. Trivially Named Porphyrins<sup>a</sup>Coproporphyrin I<sup>b</sup>Cyttoporphyrin<sup>c</sup>Deuterioporphyrin<sup>c</sup>Etioporphyrin I<sup>b</sup>

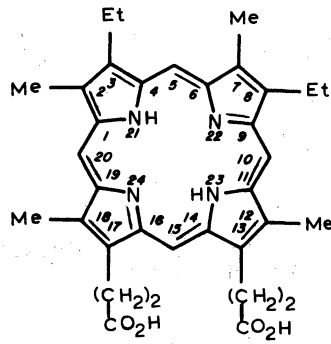
a. The trivial names apply to the tautomeric structures also. See TP-1.1.

b. Type I shown only. See TP-2.2 for "type nomenclature" using Roman numerals.

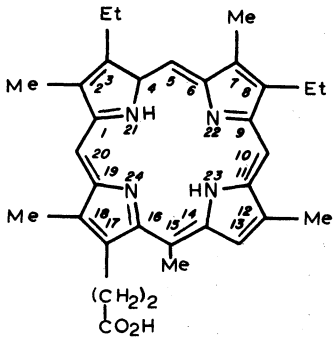
c. Not to be confused with the isotopically labeled compound deuterioporphyrin.



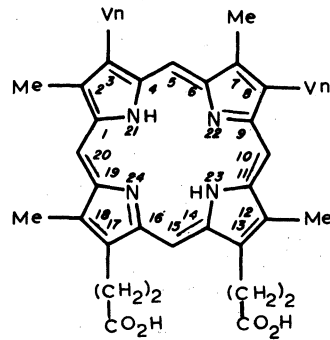
Hematoporphyrin



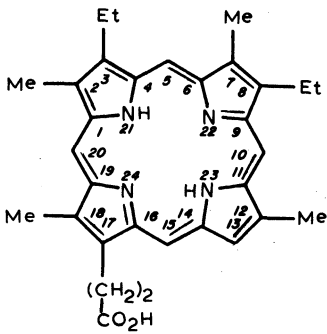
Mesoporphyrin



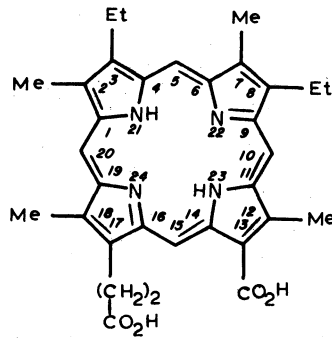
Phylloporphyrin



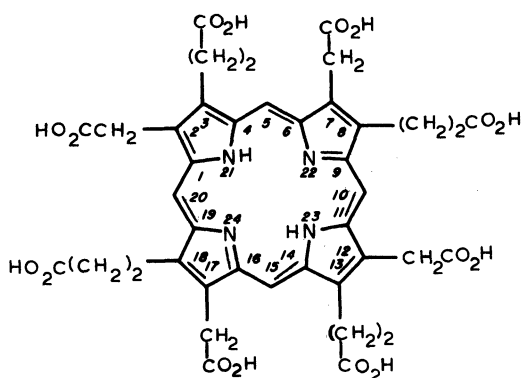
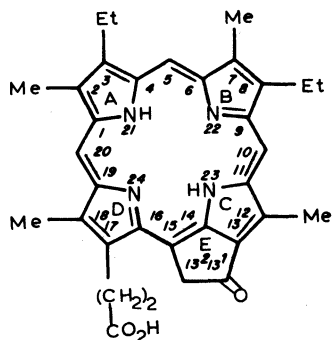
Protoporphyrin



Pyrroporphyrin

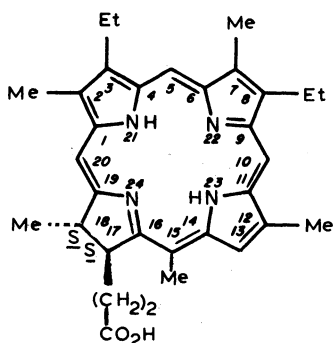
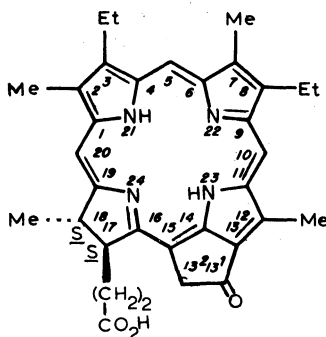


Rhodoporphyrin

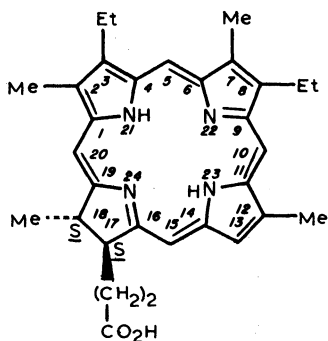
Uroporphyrin I<sup>a</sup>

Phytoporphylin

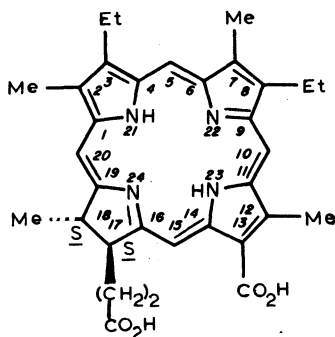
## B. Trivially Named Chlorins

Phyllochlorin<sup>b</sup>

Phytochlorin



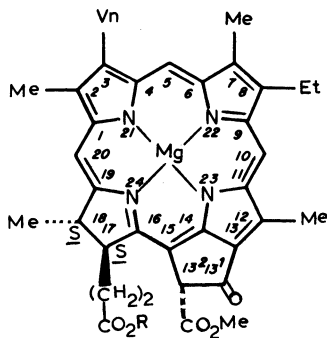
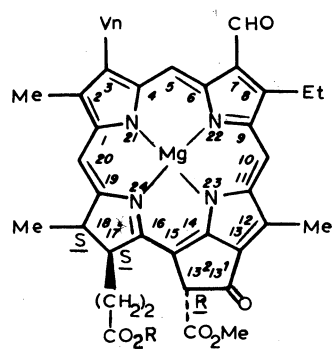
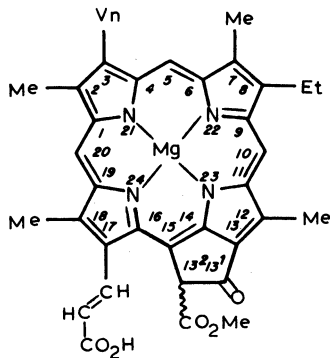
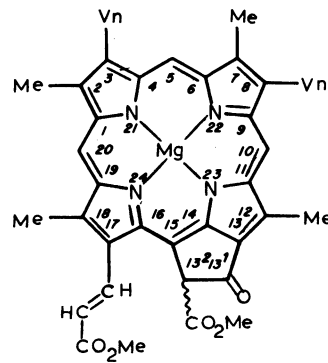
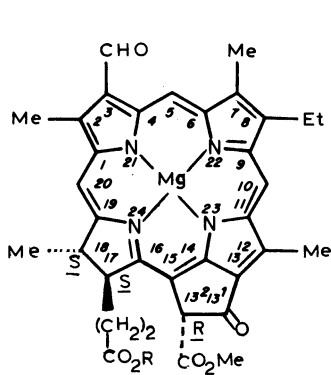
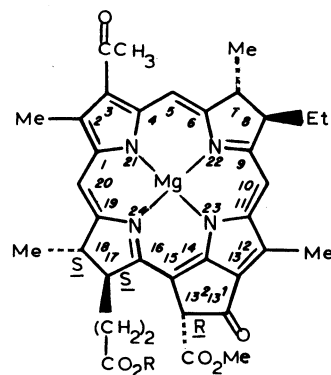
Pyrrochlorin

Rhodochlorin<sup>b</sup>

a. Type I shown only. See TP-2.2 for "type nomenclature" using Roman numerals.

b. Phyllochlorin and rhodochlorin have been redefined so that they are now 17,18-dihydro derivatives of the corresponding phylloporphyrin and rhodoporphyrin. These chlorin names have formerly been used in the literature to refer to the structure shown, but with vinyl groups in place of ethyl groups at position 3.

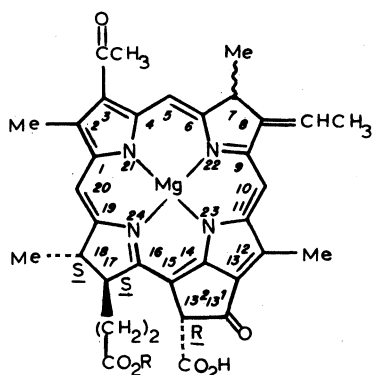
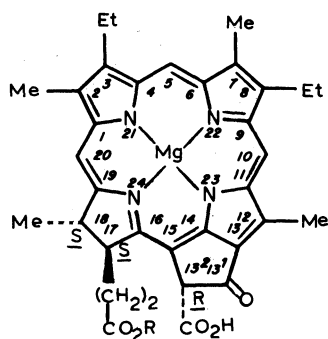
## C. Trivially Named Chlorophylls

Chlorophyll *a*Chlorophyll *b*Chlorophyll *c*<sub>1</sub><sup>a</sup>Chlorophyll *c*<sub>2</sub><sup>a</sup>Chlorophyll *d*Bacteriochlorophyll *a*

R = phytol

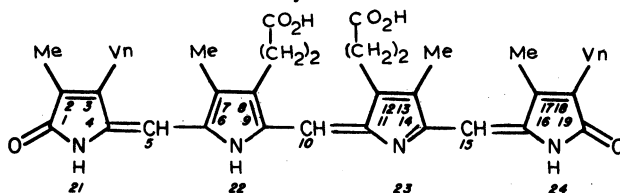
a. In contrast to the other chlorophyll structures, chlorophylls *c*<sub>1</sub> and *c*<sub>2</sub> are unsaturated at positions 17 and 18. Further they are free acids at position 17.



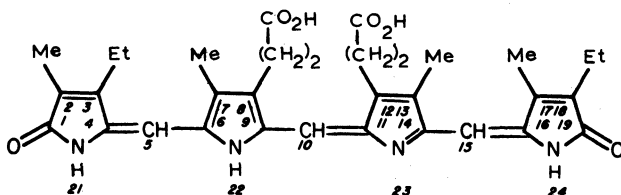
Bacteriochlorophyll *b*Mesochlorophyll *a*

R = phtyl

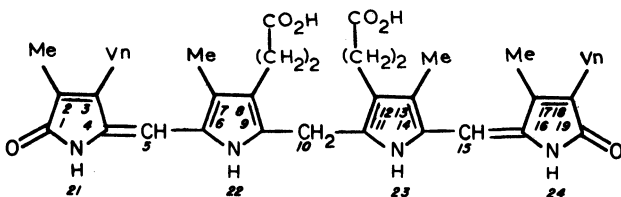
## D. Trivially Named Bilins



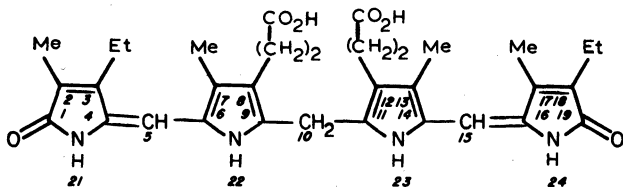
Biliverdin



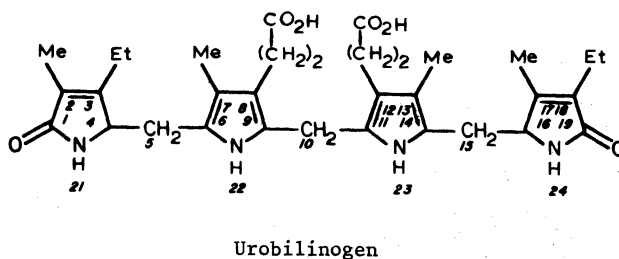
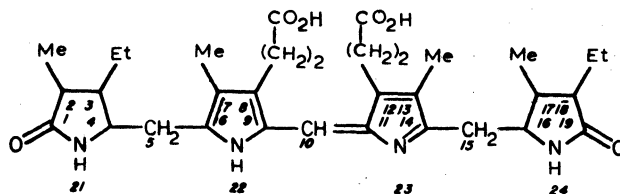
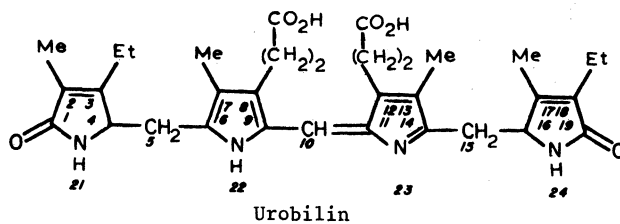
Mesobiliverdin



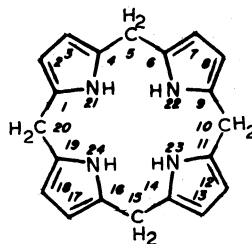
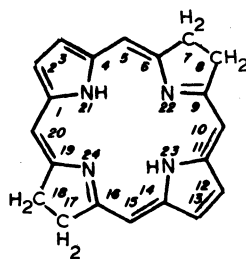
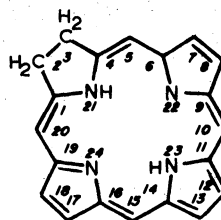
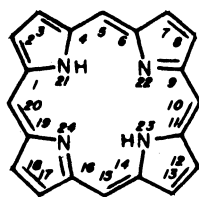
Bilirubin

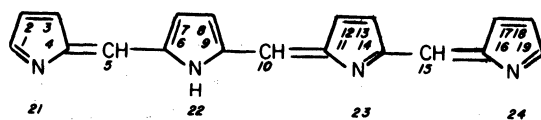


Mesobilirubin

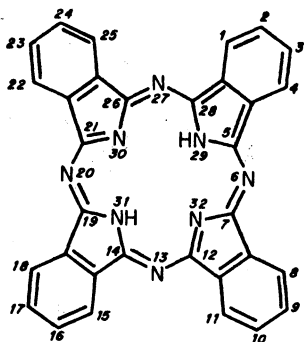


E. Fundamental Parents

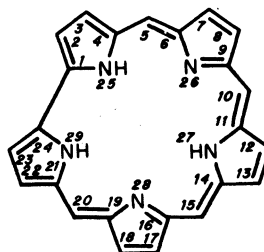




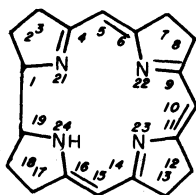
Bilin



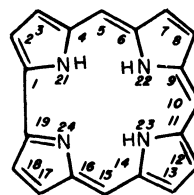
Phthalocyanine



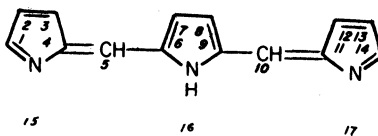
Sapphyrin



Corrin



Corrole



16H-Tripyrrin

## APPENDIX 2.

Comparison of the Numbering of the Trivially Named Porphyrins (TNP) With  
Numbering Based on CNOC/CAS Numbering Principles

TNP Trivial Name	Numbering Basis	2	3	7	8	12	13	15	17	18	20
1. Uroporphyrin I	TNP CNOC/CAS	Cm Cet	Cet Cm	Cm Cet	Cet Cm	Cm Cet	Cet Cm	-- --	Cm Cet	Cet Cm	-- --
2. Coproporphyrin II	TNP CNOC/CAS	Me Cet	Cet Me	Cet Me	Me Cet	Me Cet	Cet Me	-- --	Cet Me	Me Cet	-- --
3. Etioporphyrin I	TNP CNOC/CAS	Me Et	Et Me	Me Et	Et Me	Me Et	Et Me	-- --	Me Et	Et Me	-- --
4. Etioporphyrin II	TNP CNOC/CAS	Me Et	Et Me	Et Me	Me Et	Me Et	Et Me	-- --	Et Me	Me Et	-- --
5. Etioporphyrin III	TNP CNOC/CAS	Me Et	Et Me	Me Et	Et Me	Me Et	Et Me	-- --	Et Me	Me Et	-- --
6. Etioporphyrin IV	TNP CNOC/CAS	Me Et	Et Me	Me Et	Et Me	Et Me	Me Et	-- --	Et Me	Me Et	-- --
7. Cytoporphylin	TNP CNOC/CAS	Me Cet	R <sup>1</sup> CHOH Me	Me Vn	Vn Me	Me R <sup>1</sup> CHOH	Cet Me	-- --	Cet --CHO	--CHO Cet	-- --
8. Protoporphyrin	TNP CNOC/CAS	Me Cet	Vn Me	Me Vn	Vn Me	Me Vn	Cet Me	-- --	Cet Me	Me Cet	-- --
9. Mesoporphyrin	TNP CNOC/CAS	Me Cet	Et Me	Me Et	Et Me	Me Et	Cet Me	-- --	Cet Me	Me Cet	-- --
10. Hematoporphyrin	TNP CNOC/CAS	Me Cet	Me Me	Me CH <sub>3</sub> CHOH	Me Me	Me CH <sub>3</sub> CHOH	Cet Me	-- --	Cet Me	Me Cet	-- --

