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The Nomenclature of Lipids*

Preface

The nomenclature of lipids is the concern both of organic chemists and of biochemists. The systematic names of individual lipids can always be derived by the general rules of organic nomenclature; however, such names are often complex and need to be supplemented by alternative "semisystematic" names (as has been done, e.g., for steroids and corrinoids). Another problem is that of names for groups of related and homologous compounds (including mixtures); such names are hardly ever needed by the pure organic chemist, but are very necessary in biochemical work.

Several attempts have been made in the past to

standardize nomenclature in the lipid field, notably by the United States NAS-NRC Subcommittee on the Nomenclature of Biochemistry under the Chairmanship of W. E. M. Lands (Ann Arbor, Mich.) in 1962. At about the same time, proposals were made for names for groups of lipids by a German group (see *Biochem. Z. 335*, 423 (1962)).

The Biological Nomenclature Commission of IUPAC and the Commission of Editors of Biochemical Journals of IUB decided, in 1963, to set up an international Subcommittee on Lipid Nomenclature under the Chairmanship of H. Hirschmann (Cleveland, Ohio); this group discussed and, with the advice of interested colleagues, modified some of the material embodied in the two earlier proposals. The IUPAC-IUB Subcommittee, which later became responsible to the Combined Commission on Biochemical Nomenclature of IUPAC and IUB (CBN), when this was formed in Jan 1964, has consisted of the following: H. Hirschmann (Chairman, U. S. A.), A. Gottschalk (Australia), F. D. Gunstone (U. K.), M. L. Karnovsky (U. S. A.), E. Klenk (Germany), W. E. M. Lands (U. S. A.), J. Polonovski (France), and L. L. M. Van Deenen (The Netherlands). Their discussions were carried out largely by correspondence and resulted in draft proposals that were considered by CBN at its meetings in Paris (1965) and in Gothenburg (1966) and by correspondence between the meetings. The present proposals are the

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Comments on these proposals may be sent to any member of CBN: O. Hoffmann-Ostenhof (Chairman), W. E. Cohn (Secretary), A. E. Braunstein, J. S. Fruton, B. Keil, W. Klyne, C. Liébecq, B. Malmström, R. Schwyzer, E. C. Slater, or corresponding member, N. Tamiya.

Reprints of these proposals may be obtained from W. E. Cohn, Director, NAS-NRC Office of Biochemical Nomenclature, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

product of these events, and are published for the consideration of interested colleagues. It is hoped that discussion will shortly lead to the formulation of Tentative Rules acceptable to chemists in the field of lipids.

CBN is greatly indebted to the members of the Subcommittee on Lipid Nomenclature for their labors. The Introduction, prepared by the Subcommittee, explains the need for a rather novel departure in nomenclature, that of *stereospecific numbering*, which we believe to be worthy of detailed trial and consideration in the special circumstances that obtain in the lipid field.

Introduction

The most complex problem faced by the Subcommittee on the Nomenclature of Lipids concerned the distinguishing of stereoisomers. In the case of glycerol, at least four different systems of designations have been proposed and have been adopted by various authors. All of these proposals possess advantages and disadvantages and none is ideal for all purposes. In view of this situation, it seems desirable to set forth the principal considerations that prompted the selection made by the Subcommittee.

All assignments of configuration in this area rest on the pioneering work of E. Baer and H. O. L. Fischer and, if priority and widest use were the sole criteria, the system first proposed by these workers (J. Biol. Chem. 128, 475 (1939)) would have to be chosen. This system provided that "an α -monoglyceride is to be put in the same category with that glyceraldehyde into which it could be transformed by oxidation without any alteration or removal of substituents" and "since we can without constraint consider the α glycerophosphoric acids as monoglycerides, their coordination is subject to the same points of discussion." A serious limitation of this nomenclature was stated in the original publication: "An optical classification similar to that which we have suggested for the α -monoglycerides seems to be impossible for the triglycerides."

This nomenclature was later extended (E. Baer and D. Buchnea, J. Am. Chem. Soc. 81, 1758 (1959)) to compounds that could not be named under the original rule, such as "L- α -(dioleoyl)-cephalin," but as yet no extension has been proposed for the designation of the antipodal forms of, e.g., triacylglycerols or of isotopically labeled glycerols. The system has been criticized by D. M. Brown, B. F. C. Clark, and R. Letters (J. Chem. Soc., 3774 (1961)) who stated that "confusion can, and does, arise from whether α refers to the 1 or the 3 position" and by J. Baddiley, J. G. Buchanan, and B. Carss (J. Chem. Soc. 1869 (1957)): "The correct name for the naturally occurring L- α -glycerophosphate (I), according to standard rules of nomenclature, is D-glycerol 1-phosphate (II) (equivalent to L-glycerol 3-phosphate)." A more conventional nomenclature, which also employs D/L prefixes, using numerals as locators and (usually) giving the substituted primary

$$\begin{array}{cccc} CH_2OH & CH_2OPO_3H_2\\ \vdots & & \vdots\\ HO - C - H & \equiv & H - C - OH\\ \vdots & & \vdots\\ CH_2OPO_3H_2 & CH_2OH\\ I & II & \end{array}$$

carbinol group the lower number (M. L. Karnovsky, G. Hauser, and D. Elwyn J. Biol. Chem. 226, 881 (1957); A. A. Benson and B. Maruo, Biochim. Biophys. Acta 27, 189 (1958)) therefore came into use. This system is readily applicable to triacylglycerols, labeled glycerol, etc. Unfortunately, the coexistence of two systems that usually employ antipodal configurational prefixes for the same substance is a potential source of confusion and ambiguity that can be avoided only if the sole outward sign indicating which convention is being followed (the use of Greek letters or numbers as locators, respectively) is always shown and recognized.

This difficulty is avoided if the R/S system (R. S. Cahn, C. K. Ingold, and V. Prelog, Angew. Chem. Intern, Ed. Engl. 5, 385 (1966)) is adopted. Its universal character and its freedom from ambiguity have everything to recommend it as the general system and, therefore, the one to be used for information retrieval. However, like the two D/L systems, when applied to glycerol derivatives, it does not bring to the fore important structural and biochemical relationships and therefore does not always provide a convenient terminology for the formulation of significant generalizations. Only a few examples are given. A large part of the chemical and biochemical reactions in the field of glycerol derivatives involves the formation and cleavage of ester and ether linkages. Although these transformations do not affect any of the four bonds that extend from the C-2 of glycerol, the description of these processes under the rules of the R/S or D/Lsystem requires frequent changes of the configurational prefixes. For example, the phosphorylation of (S)-1,2diacylglycerol (III) gives an (R)-phosphatidic acid (IV).

The corresponding transformation under the Baer-Fischer system is D- α , β -diacylglycerol (III) \rightarrow diacyl-L- α -glycerophosphoric acid (IV). Under the conventional D/L system the precursor (III) is L-1,2-diacylglycerol and the product might be formulated and named as either L-1,2-diacylglycerol 3-phosphate (IV) or as D-2,3-diacylglycerol 1-phosphate (V) [III \rightarrow (IV \equiv V)]. If the former is chosen, the formal inversion is avoided, but it would be required in describing the removal of the acyl groups since the product can be properly named only as D-glycerol 1-phosphate (II) [(IV \equiv V) \rightarrow (I \equiv II)]. Furthermore, the enzyme

$$\begin{array}{cccc} CH_2O_2CR^1 & CH_2OPO_3H_2 \\ \vdots & \vdots & \vdots \\ R^2CO_2 - C - H & \equiv & H - C - O_2CR^2 \\ \vdots & \vdots & \vdots \\ CH_2OPO_3H_2 & CH_2O_2CR^1 \\ IV & V \end{array}$$

phospholipase A (EC 3.1.1.4) differentiates between two ester linkages in optically active (and inactive) 1,3-diacylglycero-2-phosphorylcholines (VI) (G. H.

De Haas and L. L. M. Van Deenen, *Biochim. Biophys. Acta 84*, 469 (1964)), but this stereospecificity cannot be expressed by the configuration of the substrate in either D/L or R/S terms. Still another problem arises if one reports observations demonstrating that the distribution of fatty acids attached to the primary carbinol groups in triacylglycerols is not random. The use of the traditional configurational symbols (D/L or R/S) for the description of the asymmetry of such complex mixtures seems quite inappropriate.

These diverse matters present no problem if the stereochemistry of glycerol derivatives is expressed by a fourth system (stereospecific numbering, H. Hirschmann, J. Biol. Chem. 235, 2762 (1960)), which takes recognition of the fact that the two primary carbinol groups of the parent substance, glycerol, are not identical in their reactions with dissymmetric structures, which include nearly all biochemical processes (A. G. Ogston, Nature 162, 963 (1948)) and that they therefore should be distinguished in nomenclature. On this basis, the numbers 1 and 3 should not be used interchangeably for the same primary carbinol group. The system proposed for deciding which carbinol group is to receive the lower number is a general one and is based on the priorities of the R/S system of Cahn et al. (loc. cit.). Its application to glycerol (VII) is

VII, glycerol (sn numbering to right)

particularly simple: if the secondary hydroxyl group is

shown to the left of C-2 in a Fischer projection, the carbon atom above C-2 is called C-1, the one below C-3; the use of this stereospecific numbering is indicated by the prefix "sn" before the stem name of the compound. With such a terminology for distinguishing the two primary carbinol groups of free glycerol, it seemed a logical extension to describe the stereochemistry of derivatives by indicating the carbon atoms that are substituted. This additional step was first taken by R. Stjernholm and H. G. Wood (J. Biol. Chem. 235, 2757 (1960)), who spoke of glycerol 3-phosphate. (This would become "sn-glycerol 3-phosphate" in the nomenclature proposed here; cf. I). Under this system, there can be no formal inversions as long as the four bonds of C-2 remain intact; a given primary carbinol group will always have the same number no matter what the Osubstituent on this or the other primary carbinol may be. Therefore, identity of configuration is obvious at a glance; e.g., under the sn system, the phosphorylation mentioned above is the conversion of a 1,2-diacyl-snglycerol (III) to a 1,2-diacyl-sn-glycerol 3-phosphate (IV).

Similarly, the specificity of the action of phospholipase A can be expressed by stating that it acts on the ester linkage at C-1 (indicated by the arrow) of 2-sn-phosphatidylcholine (VI). The nonrandom distribution of fatty acid residues might conveniently be expressed by such statements as "the 1 position contained most of the saturated fatty acids in the triacyl-sn-glycerols of rat liver" (W. E. M. Lands, R. A. Pieringer, P. M. Slakey, and A. Zschocke, Lipids 1, 444 (1966)).

The main disadvantage of the *sn* system of specifying configurations lies in the fact that it does not express *chirality* in the usual manner by configurational prefixes. This innovation is not altogether without precedent since L. Maquenne (Les Sucres et leur Principaux Dérivés, Gauthier-Villars (also G. Carré et C. Naud), Paris, 1900) used numbering in a stereospecific sense to specify the configurations of the inositols. Although the use of D and L or of R and S shows more clearly an antipodal relationship, the fact that C-1 and C-3 lie across a plane of symmetry of glycerol should be sufficient to show that *sn*-glycero-1-phosphoric acid (VIII) and *sn*-glycero-3-phosphoric acid (I) are optical antipodes.

Proposed Rules

1. Lipids Containing Glycerol

A. INDIVIDUAL COMPOUNDS

1.1. In designating esters, ethers, and other *O*-derivatives of glycerol, rules 10 and 11 of the Rules of

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Carbohydrate Nomenclature (*J. Org. Chem. 28*, 281 (1963)) are followed. These rules provide that: (a) if the hydrogen atom of an alcoholic hydroxyl group is replaced by another atom or group, the name of the parent compound may be retained as the root of the substituted compound and that, in such names, the prefix (denoting the substituent) is attached directly to the root; (b) an ester may be named by placing after the unchanged name of the parent compound, and separated therefrom by a space, the appropriate numeral (indicating position) and a hyphen, as prefix to the name of the anionic group derived from an acid.

If the substitution is on the carbon atom, the compound is designated by its systematic name and not as a derivative of glycerol. It is permissible, therefore, to omit the symbol "O" if the substitution is on the oxygen atoms of glycerol.

Examples

glycerol tristearate or tristearoylglycerol or tri-O-stearoylglycerol; 1,3-benzylideneglycerol or 1,3-O-benzylideneglycerol; glycerol 2-(dihydrogen phosphate) (a permissible alternative to this term is "glycero-2-phosphoric acid")

1.2. In order to designate the stereochemistry of glycerol derivatives, the carbon atoms of glycerol are numbered stereospecifically. The carbon atom that appears on top in that Fischer projection that shows a vertical carbon chain with the secondary hydroxyl group to the left is designated as C-1. To differentiate such numbering from conventional numbering conveying no steric information, the prefix "sn" (for stereospecifically numbered) is used. This term is printed in lower case italics, even at the beginning of a sentence, and it immediately precedes the term signifying glycerol and is separated from it by a hyphen. The prefix "rac-" (for racemo) precedes the full name if the product is an equal mixture of both antipodes, and the prefix "X-" if the configuration of the compound is either unknown or unspecified.

Examples

sn-glycerol 3-(dihydrogen phosphate) or sn-glycero-3-phosphoric acid for the stereoisomer previously known as either L- α -glycerophosphoric acid (E. Baer and H. O. L. Fischer, J. Biol. Chem. 128, 491 (1939)) or as D-glycerol 1-phosphate (A. A. Benson and B. Maruo, Biochim. Biophys. Acta 27, 189 (1958))

rac-1-hexadecylglycerol *X*-glycerol 1,2-dipalmitate 3-stearate

B. GENERIC TERMS

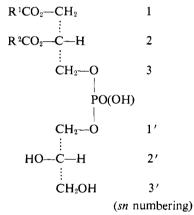
1.3. The term "phosphoglyceride" signifies any derivative of glycerophosphoric acid that contains at least one *O*-acyl, or *O*-alkyl, or *O*-alk-1'-en-1'-yl group attached to the glycerol residue. If the other ester component of a phosphoglyceride is known, it can be stated in a word that precedes the generic term.

Example choline phosphoglyceride

- 1.4 The term "phosphatidic acid" signifies a derivative of glycerophosphoric acid in which both remaining hydroxyl groups of glycerol are esterified with fatty acids.
- 1.5. The term "lecithin" is permitted but not recommended to designate a 1,2-diacyl-sn-glycero-3-phosphorylcholine. The recommended generic term for such compounds is 3-sn-phosphatidylcholine.
- 1.6. Other generic terms may be coined as needed. These should be patterned after the names of individual compounds (see 1A) and should indicate the type of substituent of glycerol by such prefixes as acyl, alkyl or alkenyl (for alk-1'-en-1'-yl, *i.e.*, RCH=CH-). If the nature of these substituents cannot be specified, the prefix "radyl" may be used.

Examples for rules 1.4 and 1.6 phosphatidic ester 1-alkenyl-2-acyl-sn-glycerophosphoric ester O-(diradylglycerophosphoryl)-L-serine O-(1-acyl-sn-glycero-3-phosphoryl)ethanolamine triacylglycerol

diacyl-sn-glycero-3-phosphoryl-1'-sn-glycerol or 3-sn-phosphatidyl-1'-sn-glycerol for structure (IX)



IX, 3-sn-phosphatidyl-1'-sn-glycerol

Comment: The terms triacylglycerol, diacylglycerol are preferred for neutral fats, not only for consistency, but mainly because strict interpretation of the traditional (optional) terms triglyceride, diglyceride does not convey the intended meaning.

2. Sphingolipids

A. INDIVIDUAL COMPOUNDS

The discovery of many compounds structurally related to sphingosine makes it desirable to develop a semisystematic nomenclature affording more concise names than the general rules of organic chemical nomenclature.

- 2.1. The compound previously known as dihydrosphingosine [2*D*-aminoöctadecane-1,3*D*-diol or *D*-erythro-2-aminoöctadecane-1,3-diol or (2*S*,3*R*)-2-aminoöctadecane-1,3-diol] is called sphinganine.
- 2.2. This name may be modified by prefixes to indicate additional substituents or higher or lower

homologs. The prefixes to designate homologs should be derived by deleting the terminal "ne" from the systematic names of the hydrocarbons (IUPAC, Nomenclature of Organic Chemistry, *J. Am. Chem. Soc.* 82, 5545 (1960), Rule A-1) that have the same number of carbon atoms as the long-chain bases.

2.3. The configuration of additional substituents should be specified by the prefixes "D-" or "L-" (italic capitals; cf. J. A. Mills and W. Klyne, Progr. Stereochem. I, 181 (1954)) following the number that indicates the position of the substituted carbon atom. The configurations at C-2 and C-3 should be specified in the same manner, but only if they differ from those in sphinganine. In every case, the prefixes D or L refer to the orientation of the functional groups to the right or left, respectively, of the carbon chain written vertically in a Fischer projection with C-1 on top. If the configuration is unknown, the prefix "X-" should be used. In the case of racemic mixtures, the term "rac-" should be used as a prefix to the name.

Comment: The semisystematic nomenclature for the long-chain bases is significantly shorter than fully systematic names only if the terms chosen imply not only substituents but also their configurations. The configurations usually encountered have identical configurational prefixes only if a D/L but not if the R/S system is used; e.g., C-3 is D and R in sphingosine and D and S in the compound previously known as phytosphingosine. Therefore, the rule that configurations at C-2 and C-3 are to be specified only if they differ from those in sphinganine is unambiguous only if the D/L system is used. Whenever it is desired to use the R/S system (R. S. Cahn, C. K. Ingold, and V. Prelog, Angew. Chem. Intern. Ed. Engl. 5, 385 (1966)), the fully systematic names should be used with specification of configuration at every center (and, when applicable, of the geometry at the double bond).

2.4. Names for partly unsaturated compounds are derived from the names of the corresponding saturated compounds by terminations denoting unsaturation, namely "ene," "diene," "yne," etc. A double bond is presumed to have the *trans* orientation of the carbon chain unless *cis* or unknown geometry is specified by the terms "*cis*-" or "x-" preceding the number that indicates the position of the double bond.

Examples for rules 2.1 to 2.4:

4D-hydroxysphinganine for phytosphingosine

4X-hydroxy-2X,3X-eicosasphinganine for the cerebrin base described by M. Prostenik and N. Z. Stanačev (*Chem. Ber. 91*, 961 (1958))

4-sphingenine for sphingosine

cis-4-sphingenine for the geometric isomer of sphingosine

2L-sphinganine for the C-2 epimer of sphinganine

2.5. The trivial name "sphingosine" may be retained. If trivial names other than sphingosine are used, they should be defined in each paper in terms of this nomenclature or of the general nomenclature of organic chemistry.

B. GENERIC TERMS

Definition: The term "long-chain base" as used in section 2 refers to sphinganine, to its homologs and stereoisomers, and to the hydroxy and unsaturated derivatives of these compounds.

2.6. The following generic terms may be used for the following groups of compounds:

sphingolipid, for any lipid containing a long-chain

glycosphingolipid, for any lipid containing a longchain base and one or more sugars

ceramide, for an *N*-acyl long-chain base cerebroside, for a monoglycosylceramide

ganglioside, for a glycosphingolipid containing neuraminic acid (see section 3)

sphingomyelin, for a ceramide 1-phosphorylcholine

2.7. If further structural details can be specified, appropriate prefixes should be used. These prefixes signify substitution and not definition or modification of a component already implied in the root name.

Examples

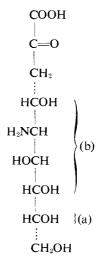
1-O-D-galactosylceramide, but not galactosecerebroside

N-acyl-1-*O*-D-galactosyl-4-sphingenine, if the structure of the long-chain base can also be specified

1-triglycosylceramide oligoglycosylceramide

3. Neuraminic Acid

3.1. The compound 5-amino-3,5-dideoxy-D-*glycero*-D-*galacto*-nonulosonic acid is neuraminic acid (X).



X, neuraminic acid [5-amino-3,5-dideoxy-D-*glycero*-D-*galacto*-nonulosonic acid] (a) (b)

- 3.2. The term "sialic acid" signifies the *N*-acylneuraminic acids and their esters and other derivatives of the alcoholic hydroxyl groups.
- 3.3. The radicals resulting from the deletion of a hydroxyl group of neuraminic acid or sialic acid are designated as neuraminoyl or sialoyl, respectively, if

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the hydroxyl is deleted from the carboxyl group, and as neuraminosyl and sialosyl, respectively, if the hydroxyl group is removed from the anomeric carbon atom of the cyclic structure.

4. Other Components of Lipids.

4.1. Fatty acids and their radicals should be named according to the IUPAC rules for the Nomenclature of Organic Chemistry (*Pure Appl. Chem. 11*, No. 1–2 (1965), Rule C-4). Fatty acids should always be numbered with the carboxyl group as C-1.

Comment: Regularities, such as the position of double bonds in some naturally occurring fatty acids, that are not apparent if numbering is done in this manner, can be indicated without violation of this principle of numbering if the position of the double bond is stated in the form (n-x) where n indicates the number of carbon atoms in the chain. The positions of the double bonds of linoleic acid, e.g., may be given as (n-9) and (n-6) but not as $\omega 9$, $\omega 6$.

4.2. Long-chain alcohols and the radicals derived from them should be designated according to systematic nomenclature (*Pure Appl. Chem. 11*, No. 1–2 (1965), Rule C-201; also *J. Am. Chem. Soc. 82*, 5545 (1960), Rule A-1 *et seq.*) but not by trivial names that are derived from those of fatty acids.

Example

1-hexadecanol and 1-hexadecyl, but not palmityl alcohol and palmityl

- 4.3. Other components of lipids, such as amino acids and sugars, should be named according to the internationally adopted conventions for these groups of compounds.
- 4.4. All trivial names or abbreviations that are not defined in the rules of sections 1–4 or the other rules cited should be defined in each paper.

5. Other Generic Terms

- 5.1. The term "phospholipid" may be used for any lipid containing a radical derived from phosphoric acid.
- 5.2. The term "phosphoinositide" may be used for any lipid containing radicals derived from inositol and phosphoric acid.
- 5.3. Synonyms for the generic terms defined in these rules should not be used, but other terms may be employed if they apply to different groups of lipids. Such nonofficial generic terms should be defined in each paper and should be so constructed that prefixes denote substituting groups rather than define components already implied in the root name.