Example:

L-arabinose, L-Ara

(6) **Positional numerals and anomeric prefixes.**—These are added at the appropriate places, the former being separated by arrows pointing from the glycosyl group to the hydroxyl group which is substituted thereby.

(7) **Joining of symbols.**—Symbols formed as above are joined by hyphens.

(8) **Arrays.**—Polydirectional arrays may be used.

Examples:

Xylan

β-D-Xyl*p*-(1 → 4)-(β-D-Xyl*p*)$_x$-(1 → 4)-β-D-Xyl*p*-(β-D-Xyl*p*)$_y$-
3
↑
1
β-D-Xyl*p*-(1 → 4)-(β-D-Xyl*p*)$_z$
(1 → 4)-β-D-Xyl*p*

Inulin

D-Fru*f*-(2 → 1)-(D-Fru*f*)$_{35x}$-(2 → 3)-D-G*p*-
(1 → 1)-(D-Fru*f*)$_x$-(2 → 1)-D-G*p*

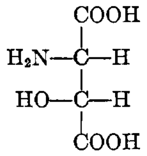
ADDENDUM TO "DEFINITIVE RULES FOR THE NOMENCLATURE OF NATURAL AMINO ACIDS AND RELATED SUBSTANCES"[1]

This rule was proposed by Dr. H. B. Vickery who was largely responsible for the original report. The rule has been approved by the Committee on Nomenclature, Spelling, and Pronunciation of The American Chemical Society and by the Council of The American Chemical Society in March, 1962, on a tentative basis for at least one year. It was previously approved by the National Research Council Subcommittee on Biochemical Nomenclature and informally approved by the National Research Council Committee on Nomenclature and by the Division Committee on Carbohydrate Nomenclature of The American Chemical Society.

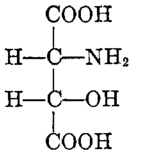
AA-11. A Rule for Naming α-Amino Acids which Have Two or More Centers of Asymmetry

Names of α-amino acids which have two or more centers of asymmetry and in which a hydrogen atom is attached to each asymmetric carbon atom may be formed with use of the prefixes of carbohydrate nomenclature to define the configurational relationships. The small capital letter prefixes L$_s$ or D$_s$ are placed immediately before the name of the parent α-amino acid or its radical. The subscripts must invariably be inserted in order to show that the capital letter prefix refers to the configuration of the α-carbon atom (carbon atom 2). The carbohydrate name prefix is italicized in print.

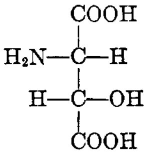
Examples: The four optically active 3-hydroxyaspartic acids may be formulated according to the Fischer conventions and named as follows:



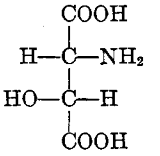
erythro-3-Hydroxy-L$_s$-aspartic acid (related to *meso*-tartaric acid)



erythro-3-Hydroxy-D$_s$-aspartic acid (related to *meso*-tartaric acid)



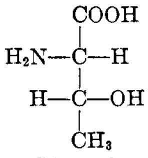
threo-3-Hydroxy-L$_s$-aspartic acid [related to (−)-tartaric acid]



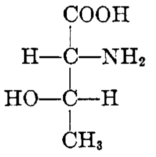
threo-3-Hydroxy-D$_s$-aspartic acid [related to (+)-tartaric acid]

L$_s$-Threonine was so named in order to define the configurational relationships of both asymmetric centers. Its diastereomer hitherto called L$_s$-allothreonine may accordingly be named L$_s$-erythronine.

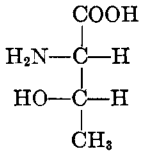
The formulas of the two pairs of enantiomorphs are as follows:



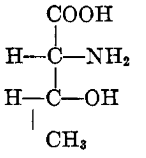
L$_s$-Threonine (derived from proteins)



D$_s$-Threonine

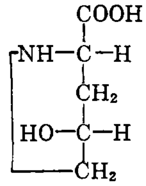


L$_s$-Erythronine (otherwise L$_s$-allothreonine)

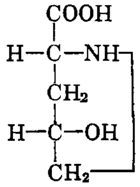


D$_s$-Erythronine

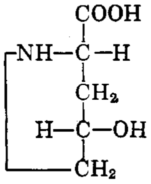
Since the configurational relationships of both asymmetric centers of hydroxyproline are known,[2] the isomers may be formulated and named as follows:



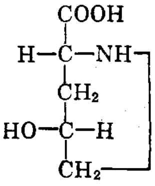
erythro-4-Hydroxy-L$_s$-proline (derived from proteins)



erythro-4-Hydroxy-D$_s$-proline

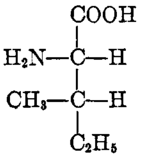


threo-4-Hydroxy-L$_s$-proline (otherwise allohydroxy-L-proline)

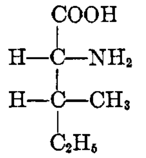


threo-4-Hydroxy-D$_s$-proline

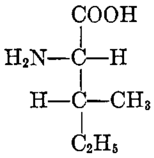
Similarly for the four isomers of isoleucine[3]:



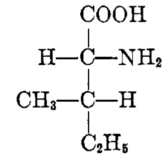
erythro-L$_s$-Isoleucine (derived from proteins[2])



erythro-D$_s$-Isoleucine



threo-L$_s$-Isoleucine (otherwise L-alloisoleucine)



threo-D$_s$-Isoleucine

Note that these formulations imply the acceptability of a precedence convention according to which a smaller alkyl group is preferred to a larger. Alternatively, the formulas may be regarded as being written with the longest possible hydrocarbon chain.

The configurational relationships of the hydroxylysines have not at present been confirmed,[4] but the isomers may be formulated and named as follows:

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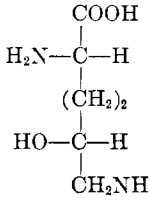
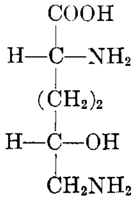
[1] *J. Am. Chem. Soc.*, **82**, 5575 (1960).

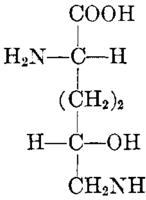
[2] The formulation is based upon the assignment of configuration by A. Neuberger [*J. Chem. Soc.*, 429 (1945)] and by L. Benoiton, M. Winitz, S. M. Birnbaum, and J. P. Greenstein [*J. Am. Chem. Soc.*, **79**, 6192 (1957)], and recently confirmed by the studies of E. Adams and A. Goldstone [*J. Biol. Chem.*, **235**, 3504 (1960)].

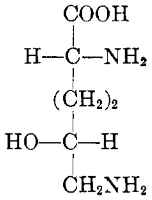
[3] The formulation is based upon the assignment of the absolute configuration by J. Trommel and J. M. Bijvoet [*Acta Cryst.*, **7**, 703 (1954)] who employed X-ray crystallographic methods, and also upon the studies of J. P. Greenstein, L. Levintow, C. G. Baker, and J. White [*J. Biol. Chem.*, **188**, 647 (1951)] and of W. S. Fones [*J. Am. Chem. Soc.*, **76**, 1377 (1954)].

[4] B. Witkop [*Experientia*, **12**, 372 (1956)] assigns the structure *erythro*-5-hydroxy-L$_s$-lysine to the amino acid from proteins, but this assignment has not been confirmed by other investigators.

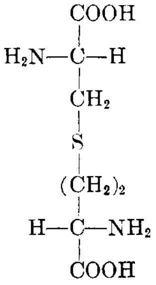

erythro-5-Hydroxy-L_s-lysine (probably the form derived from proteins)

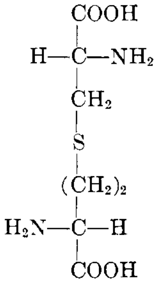

erythro-5-Hydroxy-D_s-lysine

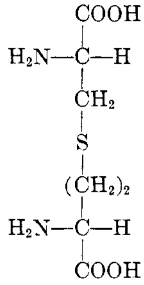

threo-5-Hydroxy-L_s-lysine (probably allohydroxy-L-lysine

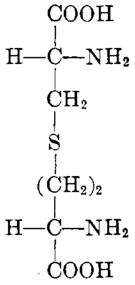

threo-5-Hydroxy-D_s-lysine

The four cystathionines may be formulated and named as follows:


threo-L_s-Cystathionine (related to L-cysteine and L-homocysteine; otherwise L-cystathionine)

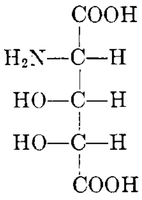

threo-D_s-Cystathionine

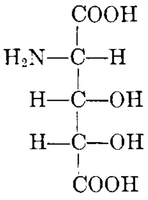

erythro-L_s-Cystathionine (related to L-cysteine and D-homocysteine; otherwise L-allocystathionine)

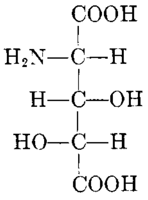

erythro-D_s-Cystathionine

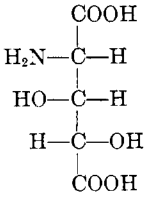
Note that the α-amino groups are written *trans* to each other for L-cystathionine, but that the formula must be rotated through 180° in the plane of the paper in order to interpret the configuration of the longer chain.

α-Amino acids which have three centers of asymmetry may be formulated and named as illustrated for the four possible 3,4-dihydroxy-L-glutamic acids. One of the racemic diastereomers of this substance has been prepared by Touster and Carter[5] and an amino acid of this composition has been detected in a number of higher plants by Virtanen and Ettala.[6]


ribo-3,4-Dihydroxy-L.-glutamic acid

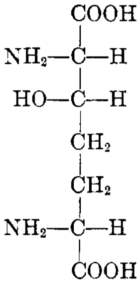

arabino-3,4-Dihydroxy-L_s-glutamic acid

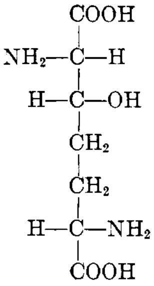

xylo-3,4-Dihydroxy-L_s-glutamic acid

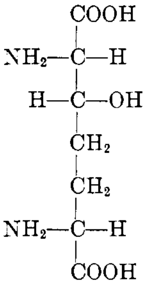

lyxo-3,4-Dihydroxy-L_s-glutamic acid

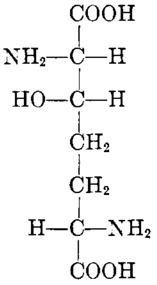
Of these substances, the first and third belong to the L_g series, the second and fourth to the D_g series. Note that the carbon atom that bears the amino group is in position two and in the L_s-compounds the amino group is written to the left. The relative positions of the hydroxyl groups in positions three and four of the L_s-isomers are then written as in the sugars of corresponding names in which the hydroxyl group in position two is written to the left.

The 2,6-diamino-3-hydroxypimelic acids of the L_s-series may be formulated and named as follows. The racemic diastereomers of this substance have been synthesized by Stewart[7] and their configurational relationships established.


ribo-L_s-2,6-diamino-3-hydroxypimelic acid (isomer A of Stewart)


arabino-L_s-2,6-diamino-3-hydroxypimelic acid (isomer C of Stewart)


xylo-L_s-2,6-diamino-3-hydroxypimelic acid (isomer B of Stewart)


lyxo-L_s-2,6-diamino-3-hydroxypimelic acid (isomer D of Stewart)

COMMENT ON RULE AA-11

This is a permissive rule and is suggested in order to provide useful and easily apprehended specific names for the increasing number of α-amino acids with more than one center of asymmetry for which the configurational relationships have been established. Names formed on the principle of this rule have been used by a number of investigators and especially by Greenstein and Winitz.[8]

Hitherto it has been customary to employ the prefix allo in naming the diastereomers of such common acids as threonine and isoleucine, but many instances have already been noted among novel synthetic amino acids (the hydroxyaspartic acids are an example) where it is difficult, if not impossible, to select under Rule AA-6 for the nomenclature of amino acids the form to which the prefix allo should be applied. Once the relationship of all of the asymmetric centers of such novel amino acids to substances of known configuration has been established, it should be possible to assign specific names with carbohydrate prefixes to convey full information regarding structure. In conformity with custom in carbohydrate nomenclature, the prefix is italicized and is written without a capital even at the beginning of a sentence.

Application of the rule is for the present necessarily restricted to the naming of α-amino acids in which a hydrogen atom constitutes one of the four radicals attached to each of the asymmetric carbon atoms. Although a few diastereomeric α-amino acids are known in which the hydrogen atom attached to the second asymmetric center is replaced by another radical, for example, 3-hydroxy-3-methylaspartic acid,[9] techniques and conventions for the assignment of the configurational relationships of all such centers to glyceraldehyde or serine remain to be fully developed.

Nevertheless, the rule represents a compromise. At about the time that the official International Union of Pure and Applied Chemistry rules for naming amino

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(5) O. Touster and H. E. Carter, *J. Am. Chem. Soc.*, **73**, 54 (1951).

(6) A. I. Virtanen and T. Ettala, *Acta Chem. Scand.*, **11**, 182 (1957).

(7) J. M. Stewart, *J. Am. Chem. Soc.*, **83**, 435 (1961).

(8) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 213.

(9) L. Benoiton, M. Winitz, R. F. Colman, S. M. Birnbaum, and J. P. Greenstein, *J. Am. Chem. Soc.*, **81**, 1726 (1959).

acids,[10,1] were being developed, several completely general systems for the naming of substances with more than one asymmetric center were put forward. Of these, that of Cahn and Ingold,[11] although it has occasionally been used in the literature, was not found to be completely acceptable. The use of the carbohydrate prefixes in the special field of amino acids was considered, but appeared to be inapplicable since at that time the committee working on the carbohydrate rules restricted the use of these prefixes to the names of substances containing adjacent asymmetric centers. However, a recent draft of the rules of carbohydrate nomenclature does not make this restriction. Accordingly, the prefixes may now be applied even when one or more methylene groups separate the asymmetric centers. It thus becomes possible to use these prefixes in naming amino acids such as hydroxyproline and hydroxylysine.

When the carbohydrate prefixes are so used, it is essential to specify with great care the significance of the capital letter prefix. In carbohydrate nomenclature, this prefix denotes the configuration of the highest numbered asymmetric center. In amino acid nomenclature, it denotes the configuration of the α-amino group, that is, the *lowest* numbered asymmetric center. Accordingly, the subscript s (for serine) to the L or D prefix must invariably be shown when naming amino acids with carbohydrate prefixes since without the subscript the center to which the capital letter prefix applies is left uncertain. The prefix is placed immediately before the trivial name of the parent amino acid since it refers only to the configuration of the α-carbon atom in the parent acid however substituted elsewhere.

Although the use of the carbohydrate prefixes is restricted under the rules of carbohydrate nomenclature to the naming of substances which contain asymmetric centers in which hydroxyl, methoxyl, acetoxyl, or amino groups occur, the use of the capital letter prefixes to denote configuration has been extended in recent years to other classes of substances in which configurational relationships have been established. This is notably the case for a number of substances that contain branched hydrocarbon chains. Inasmuch as the methyl group of isoleucine has been shown by Trommel and Bijvoet[3] to be in the *cis* position to the amino group, it is possible to suggest specific names with carbohydrate prefixes for the diastereomers of this substance. The extention of the rule to the naming of homologs and analogs of established configuration may require the development of a convention for the precedence of radicals.

It is not proposed that names devised under this Rule should replace the commonly used names for these amino acids. The Rule has been suggested to meet the situation where exact definition of the configurational relationships has become essential as, for example, in papers that deal with such relationships. Furthermore, as more and more complex amino acids are found in nature or are prepared in the laboratory, it is obvious that substances will be encountered which approach ever closer in structure to the acids derived from the amino sugars. At some level of complexity it will be necessary to draw the line between the use of a nomenclature based upon the rules for naming amino acids and the rules for naming carbohydrate derivatives. This point has been dealt with by Rule AA-3.2 of the Definitive Rules for the Nomenclature of Natural Amino Acids and Related Substances[1] and was also discussed in the Comment on the rules for amino acid nomenclature published in 1952.[10] It was there stated that such substances as mannosaminic acid should be named according to the custom in carbohydrate nomenclature, for example $\mathrm{D_g}$-mannosaminic acid (2-amino-2-deoxy-$\mathrm{D_g}$-mannonic acid), the subscript g (for glyceraldehyde) being written when any possibility occurs of confusion between the meaning of the capital letter prefix as used in carbohydrate nomenclature and in amino acid nomenclature. It is obvious that good judgment must be employed in applying Rule AA-11 for the naming of complex amino acids.

THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION
NEW HAVEN, CONNECTICUT
H. B. VICKERY

(10) *Chem. Eng. News*, **30**, 4522 (1952).

(11) R. S. Cahn and C. K. Ingold, *J. Chem. Soc.*, 612 (1951).

The Structure of Isojervine[1]

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Received September 7, 1962

When the veratrum alkaloid jervine is allowed to react with ethanolic hydrochloric acid, it is isomerized into isojervine. This new isomer possesses structure II resulting from the opening of the 17,23-oxide with concomitant migration of the 13,17a-double bond to the 17,17a-position and the introduction of a new double bond at the 8,9-position. The ultraviolet spectral features of this new isomer are analogous to those found with 2,5-dihydroacetophenone.

In the course of the elucidation of the structure of the veratrum alkaloid jervine (I), particular attention was paid to the transformations induced by acids. Depending on the conditions employed, a variety of products were isolated[2–4] and the structures of most of the transformations products were established. It is of interest to note, however, that the first acid transformation product ever reported in this series has received little attention and its structure has not been determined.

In 1944, Jacobs and Craig[5] reported that when jervine was allowed to react with ethanolic hydrochloric acid, it was transformed into an isomeric substance

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(1) This work was supported in part by the National Science Foundation, grant no. G-14526.

(2) O. Wintersteiner and M. Moore, *J. Am. Chem. Soc.*, **75**, 4938 (1953).

(3) J. Fried and A. Klingsberg, *ibid.*, **75**, 4929 (1953).

(4) O. Wintersteiner and M. Moore, *ibid.*, **78**, 6193 (1956).

(5) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **155**, 565 (1944).