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Nomenclature of Cyclic Peptides

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Nomenclature of Cyclic Peptides
(Recommendations 2004)

Prepared for publication by

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Summary

These recommendations extend rule 3AA-19.5 of the Nomenclature and Symbolism for Amino Acids and Peptides (Recommendations 1983) to cover all classes of cyclic peptides. They include rings generated from an acyclic peptide by formation of a peptide or ester bond; by a disulfide link; or by a new carbon-carbon, carbon-nitrogen, nitrogen-oxygen or carbon-sulfur bond (not esters or amides). These new bonds are indicated by the prefix anhydro, cyclo or epoxy, or combinations of them. The inclusion of modified standard amino acids or amino acids not related to standard amino acids is considered. Any stereochemistry generated by ring formation is indicated using standard organic conventions.

For Peer Review Only

Nomenclature of Cyclic Peptides

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Introduction

Cyclic peptides are briefly considered in the Nomenclature and Symbolism for Amino Acids and Peptides (recommendations 1983) [1] in part 2 under symbolism (see 3AA-19.5). There are no recommendations on naming these peptides. This deficiency is rectified by these recommendations which are based on the established procedures for naming peptides [1] and recommendation RF-4.3 in Revised Section F: Natural Products and Related Compounds (IUPAC Recommendations 1999) [3], rule C-44.1 and C-212.2 of the *IUPAC Nomenclature of Organic Chemistry* (1979) [4], R-1.2.6.1 and R-5.5.4.4 of *A Guide to IUPAC Nomenclature of Organic Chemistry* (1993) [5] and rule 2-Carb-26 of the Nomenclature of Carbohydrate [6].

CP-1 Ring Closure by Elimination of Water (the Prefix Anhydro)

Ring closure of a peptide with the formation of a new eupeptide, isopeptide (see 3AA-11 [1]) or ester bond involves the loss of the elements of water. By analogy with names for intramolecular anhydrides of carbohydrates (see rule 2-Carb-26 [6], also rule C-44.1 [4]) this process is indicated by the prefix anhydro placed in front of the name of the acyclic peptide in brackets (see also peptide use [7]). The peptide chain is numbered from the N-terminus and the numbers of the residues involved in ring formation are cited in residue number order in front of the prefix anhydro. Examples of the use of anhydro are given in CP-5 to CP-7 and CP-11 to CP-14.

The prefixes dianhydro, trianhydro, *etc.* are used if more than one ring is generated by this process (see examples in CP-6 and CP-12). The relevant residue numbers are cited in pairs separated by colons. If necessary the locant of the relevant group is cited as well as the residue number; 3AA-13.4 describes the citation of residue and atom numbers, 3AA-22.5 gives examples, and by these recommendations [1] atom C-3 of residue 5 is C-3.5.

CP-2 Ring Closure by Elimination of Hydrogen (the Prefix Cyclo)

Ring closure of a peptide by formation of a new bond between two atoms with the elimination of two atoms of hydrogen is indicated by the prefix cyclo (see rule RF-4.3 for general use of cyclo with natural products [3] and R-1.2.6.1 [5]) in front of the name of the peptide in brackets. The atoms involved in formation of the new bond are indicated by the appropriate element symbols in italics (underlined type) each with the residue number and (if relevant) the locant of the atom within the residue (see 3AA-13.4 and examples in 3AA-22.5 for citation of residue and atom numbers [1]). The residue number (and locant) are cited as superscripts after the element symbol, and these symbols are quoted in residue number order in front of the prefix cyclo. Examples of the use of cyclo are given in CP-8 to CP-10 and CP-12 to CP-14. If it is necessary to cite stereochemistry generated through cyclisation see CP-14.

If there is more than one ring generated by this process, the number of rings is indicated by dicyclo, tricyclo, *etc* (see examples in CP-9 and CP-14). The relevant residue numbers (and atom numbers if necessary) are cited in pairs separated by colons.

Ring closure within a residue may also require the prefix cyclo (see capreomycin IIA, example 2 in CP-13) In these cases the modified residue is named using cyclo (see rule RF-4.3 [3]) in the normal way *i.e.* parentheses are not required.

CP-3 Oxygen Bridge (the prefix epoxy)

Ring closure of a peptide by linking two atoms by an oxygen bridge is indicated by the prefix epoxy (see rule C-212.2 [4] and R-5.5.4.4 [5] for the general use of epoxy) in front of the name of the peptide in brackets. The atoms involved at either end of the bridge are indicated by the appropriate locants and residue numbers (see 3AA-13.4 and examples in 3AA-22.5 for citation of residue and atom numbers [1]). Examples of the use of epoxy are given in CP-10.

Note This procedure is only used if the oxygen atom cannot be cited as part of the residue *e.g.* O⁴ of tyrosine.

CP-4 Other Bridges

As an extension to the use of epoxy (see CP-3) as a bridging prefix in natural products, other bridging prefixes (see FR-8.3 [9]) can be used to express ring closure by an atom or group of atoms linking two atoms of the peptide chain. The atoms at either end of the bridge are indicated by the appropriate locants cited in the order of that implied by the name of the bridge. The bridging prefix and locants are placed in front of the name of the peptide in brackets. Examples are given in CP-10.

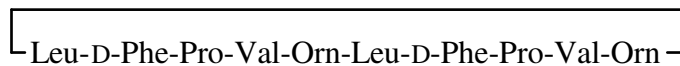
CP-5 Homodetic Cyclic Peptides

Cyclic peptides in which the ring consists solely of amino acid residues with eupeptide linkages may be called homodetic cyclic peptides. The acyclic peptide selected for naming the cyclic form using anhydro (see CP-1) is the one which would be cited first in an alphabetic list of possible names. This order ignores the prefix D or L unless a preferred acyclic form can only be decided using them (*i.e.* after selection of the preferred acyclic form from the residue names only). Note that the symbolic representation of a cyclic peptide may be shown starting with any residue {see 3AA-19.5.1 alternatives (ii) or (iii) [1]. To avoid confusion over the use of the term cyclo, the representation (i) of 3AA-19.5.1 is not recommended}.

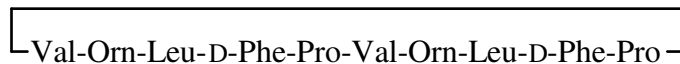
Examples:



1,5-anhydro(L-aspartyl-L-valyl-L-seryl-L-lysylglycine)
see CP-5 example 1-3 and CP-6 example 1 & 2 for other isomers



or



Both represent Gramicidin S and other representations are shown in 3AA-19.5.1 (ii) and (iii).

These are all named as:

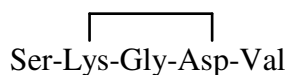
1,10-anhydro(L-leucyl-D-phenylalanyl-L-prolyl-L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-L-prolyl-L-valyl-L-ornithine)

The residue numbers should always be included to prevent confusion with an incompletely specified heterodetic cyclic peptide.

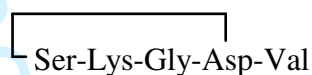
CP-6 Heterodetic Cyclic Peptides with an Isopeptide Bond

Cyclic peptides in which the linkages forming the ring are not solely eupeptide bonds may be called heterodetic cyclic peptides. If the ring is generated by an isopeptide bond the prefix anhydro (see CP-1) is used with the name of the acyclic peptide corresponding to the compound without the isopeptide bond.

Examples:



2,4-anhydro(L-seryl-L-lysylglycyl-L-aspartyl-L-valine)



2.1,4-anhydro(L-seryl-L-lysylglycyl-L-aspartyl-L-valine)

Note It is necessary to specify the amino group at carbon-2 of residue 1, serine (*cf.* example 1 of CP-7).

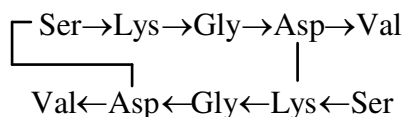


2,5-anhydro(L-seryl-L-lysylglycyl-L-aspartyl-L-valine)

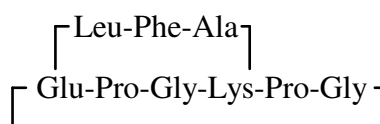
See CP-5 example 1 and CP-7 examples 1 & 2 for other isomers

If two peptide chains are joined by two isopeptide linkages to create a ring, the two chains are distinguished by the letters A and B. Each chain is then cited in parentheses with the A chain first and square brackets are used around the two chains. If the two chains differ, the designation A is allotted to the one first in alphabetical order. If the two chains are identical then the A chain is selected so that the lower residue number involved in ring formation is cited first.

Examples:



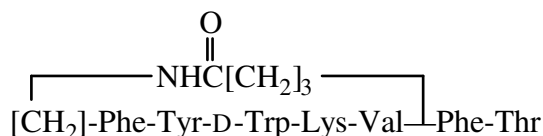
2.A1,B4:A4,B2-dianhydro[(L-seryl-L-lysylglycyl-L-aspartyl-L-valine)(L-seryl-L-lysylglycyl-L-aspartyl-L-valine)]



2.A1,A6:5.A1,B1:A4,B3-trianhydro[(L-glutamyl-L-prolylglycyl-L-lysyl-L-prolylglycine)(L-leucyl-L-phenylalanyl-L-alanine)]

In the following example the isopeptide bond involves the substituents of modified residues.

Example:

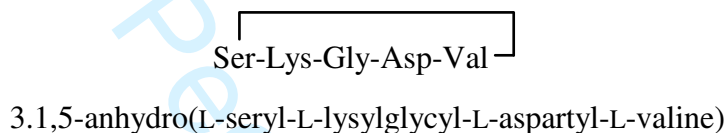
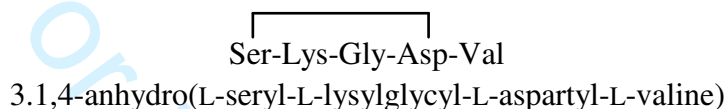


1,6-anhydro[*N*-(2-aminoethyl)-*L*-phenylalanyl-*L*-tyrosyl-*D*-tryptophyl-*L*-lysyl-*L*-valyl-*N*-(3-carboxypropyl)-*L*-phenylalanyl-*L*-threonine]
(somatostatin analogue)

CP-7 Heterodetic Cyclic Peptides with an Ester Bond

If the ring of a heterodetic cyclic peptide is generated by an ester bond the prefix anhydro (see CP-1) is used with the name of the acyclic peptide corresponding to the compound without the ester bond.

Examples:



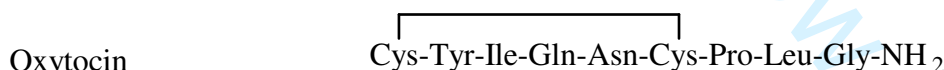
Note It is necessary to specify the alcohol group at carbon-3 of residue 1, serine (*cf* CP-5 example 1 and CP-6 examples 1-3 for isomers).

An alternative way of naming compounds of this type with a cyclic ester bond (*i.e.* lactones) was proposed in 3AA-13.4 [1].

CP-8 Heterodetic Cyclic Peptides with a Disulfide Bond

If the ring of a heterodetic cyclic peptide is generated by a disulfide bond the prefix cyclo (see CP-2) is used with the name of the acyclic peptide corresponding to the compound without the disulfide bond.

Example:

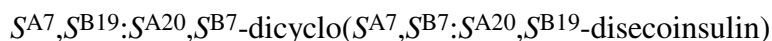


S^1, S^6 -cyclo(L-cysteinyl-*L*-tyrosyl-*L*-isoleucyl-*L*-glutaminyl-*L*-asparaginyl-*L*-cysteinyl-*L*-prolyl-*L*-leucylglycinamide)

CP-9 Heterodetic Cyclic Peptides Isomeric to a named Peptide

In the synthesis of polycyclic peptides it is often difficult to control the formation of disulfide bonds and so isomers of the intended product are formed. If the required product has a trivial name, it is convenient to relate the isomer to it by indicating which disulfide bonds have been broken and which new disulfide bonds have been formed. Cleavage of a bond with the addition of a hydrogen atom at each terminal group thus created is indicated by *seco* (see rule RF-4.4.1 [3]). The new disulfide bonds can then be indicated as in CP-8.

Example:

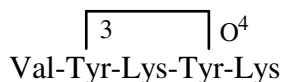


Note An alternative use of *seco* was recommended [8] in 1986 to indicate hydrolysis of a eupeptide bond of a cyclic peptide. This usage does not conform to the usual meaning as the elements of water are added in this cleavage. The different style of usage (*e.g.* [seco-3/4]oxytocin) should prevent confusion with the use above.

CP-10 Heterodetic Cyclic Peptides formed by Carbon-Carbon, Carbon-Nitrogen, Carbon-Oxygen or Carbon-Sulfur Bonds (not esters or amides)

Heterodetic cyclic peptides may arise from various reactions other than ester, amide or disulfide bond formation. For example the peptide shown below has undergone phenol oxidation between two tyrosine residues. This additional ring may be indicated by the prefix *cyclo* (CP-2). Additional examples are given in CP-13 and CP-14. In the symbolic representation of this type of cyclisation the atoms at each end of the new bond are indicated alongside the bond (see 3AA-16.4.1, 3AA-17.2 [1])

Example:

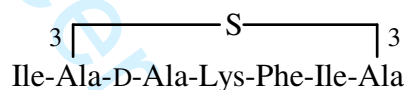


$C^{3,2},O^{4,4}$ -cyclo(L-valyl-L-tyrosyl-L-lysyl-L-tyrosyl-L-lysine)
(part sequence of extensin)

Note The new bond is between residues 2 (position 3 of ring) and 4 (phenolic oxygen) hence the order of citation.

In the example below there is a single sulfur atom linking residues 2 and 7 [*i.e.* the di(α -amino acid) *meso*-lanthionine]. In the symbolic form explicit representation of the single sulfur atom is less likely to be misinterpreted. For naming the peptide it is more convenient to use cysteine at residue 7.

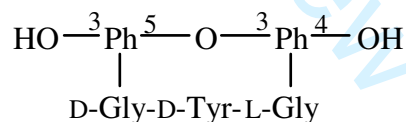
Example:



$C^{3,2},S^7$ -cyclo(L-isoleucyl-L-alanyl-D-alanyl-L-lysyl-L-phenylalanyl-L-isoleucyl-L-cysteine)
(part of the sequence of epidermine)

In the next example phenol oxidation has presumably occurred between a (3,5-dihydroxyphenyl)glycine residue 1 and (4-hydroxyphenyl)glycine residue 3. However the bridging oxygen is better expressed as an epoxy bridge as it is no longer a phenolic hydroxy group.

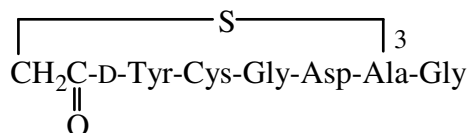
Example:



5.1,3.3-epoxy[D-(3-hydroxyphenyl)glycyl-D-tyrosyl-L-(4-hydroxyphenyl)glycine]
(part structure of ardacin)

The following two examples are acyl derivatives of the N-terminal residue which have been cyclised to an adjacent cysteine residue. Although named using cysteine, alanine is used for the symbolic representation so as to clarify how many sulfur atoms are present.

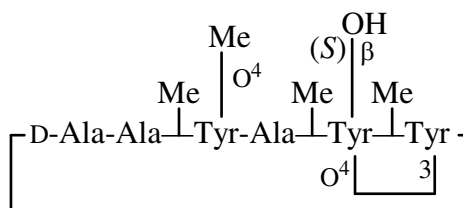
Example:



N^1,S^5 -(1-oxoethano)[D-tyrosyl-L-cysteinylglycyl-L-aspartyl-L-cysteinylglycine]
(part structure of the INN apcitide)

Example (see CP-14 for stereochemistry):

Bouvardin

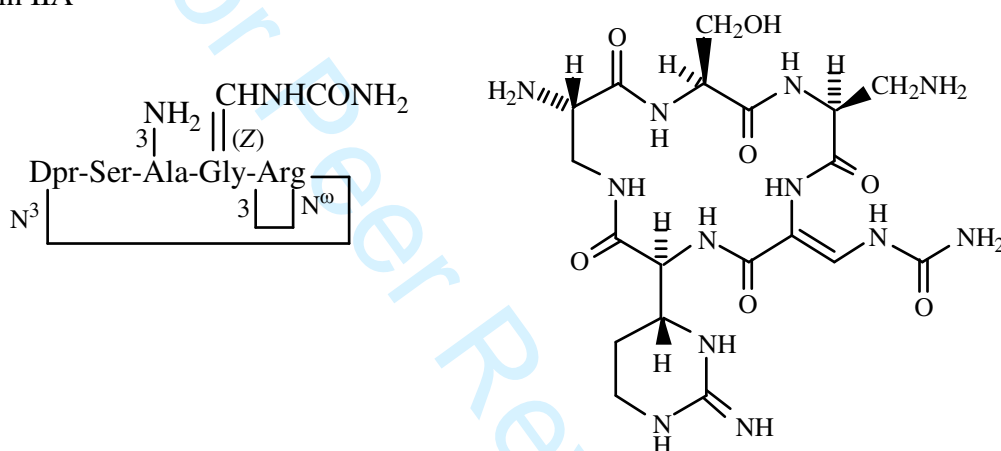


1,6-anhydro- $O^{4,5}$, $C^{3,6}$ -cyclo(D-alanyl-L-alanyl-*N,O*-dimethyl-L-tyrosyl-L-alanyl-(*S*)- β -hydroxy-*N*-methyl-L-tyrosyl-*N*-methyl-L-tyrosine)

More complex modifications may require consideration of the appropriate parent amino acid. If there is a choice the largest unmodified amino acid is selected for substitution.

Examples (see CP-14 for stereochemistry):

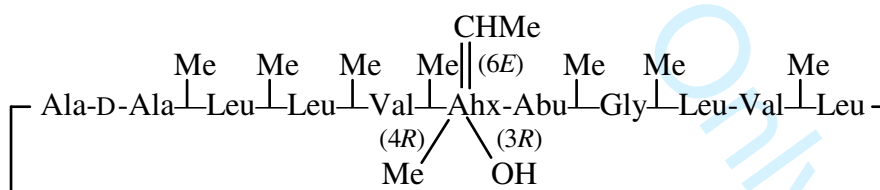
Capreomycin IIA



3.1,5-anhydro(3-amino-L-alanyl-L-seryl-3-amino-L-alanyl-(*Z*)-2,3-didehydro-3-ureido-L-alanyl-(*R*)- N^{ω} ,3-cyclo-L-arginine)

This example might be named as a derivative of (*S*)-2-amino- β -alanine. Dpr represents L-2,3-diaminopropanoic acid (see 3AA-15.2.5)

Cyclosporin A



1,11-cyclo[L-alanyl-D-alanyl-*N*-methyl-L-leucyl-*N*-methyl-L-leucyl-*N*-methyl-L-valyl-(*E*)-(2*S*,3*R*,4*R*)-2-amino-3-hydroxy-*N*,4-dimethyloct-6-enoyl-L-2-aminobutanoyl-*N*-methylglycyl-*N*-methyl-L-leucyl-L-valyl-*N*-methyl-L-leucine]

2-Aminohexanoic acid (Ahx, see 3AA-15.2.5 [1]) is preferred as a parent to leucine as the stereochemistry at C-4 is more clearly shown. As an alternative a separate symbol may be defined for this amino acid (e.g. MeBmt). If this is done the symbol must be defined somewhere in the paper.

CP-14 Stereochemistry

If the ring forming bond generates a new element of stereochemistry then this is indicated using the *R,S*-convention [10, 11] in front of the name. Vancomycin has three rings that arise from phenol oxidation; they generate an axially chiral biphenyl unit and two planar chiral chlorophenyl units.

L-*lyxo*-hexopyranosyl)- β -D-glucopyranosyl]oxy}phenyl)glycyl-D-2-(4-hydroxyphenyl)-glycyl-3-chloro-(*R*)- β -hydroxy-L-tyrosyl-L-2-(3,5-dihydroxyphenyl)glycine]

- Notes
1. In the symbolic representation the convention of 3AA-16.4 [1] is extended to substitute hydrogen atoms of the phenyl group. Thus the Ph group C₆H₅ of residues 4, 5 and 7 become C₆H₂, C₆H₃ and C₆H₂ respectively.
 2. The disaccharide substituent is named following carbohydrate nomenclature [6] and that for branched chain monosaccharides [12]. The symbolic representation follows the recommendations for glycopeptides [13].
 3. The order of nesting of brackets *i.e.* [({[()])}] follows the common practice of organic chemistry (see R-0.1.5.3 [5] and examples for rule C-54.2 and D-5.0 [4]).
 4. The new bonds are given in residue number order; thus the bond involving residue 2 is cited before that involving residue 4 and that involving residue 5 is quoted last.
 5. The new chiral units are quoted in residue number order.
 6. To emphasise the axial and planar chirality involved the subscript *a* or *p* has been added [14] *i.e.* (2.2*S_p*,3.5*S_a*,2.6*S_p*)... The latter should not be confused with the subscript P used to indicate chirality at phosphorus.
 7. The alternative systematic name [4] for vancomycin is (3*S*,6*R*,7*R*,11*R*,23*S*,26*S*,30*aS*,36*R*,38*aR*)-44-{[2-*O*-(3-amino-2,3,6-trideoxy-3-*C*-methyl- α -L-*lyxo*-hexopyranosyl)- β -D-glucopyranosyl]oxy}-3-(carbamoylmethyl)-10,19-dichloro-2,3,4,5,6,7,23,24,25,-26,36,37,38,38a-tetradecahydro-7,22,28,30,32-pentahydroxy-6-(*N*-methyl-D-leucyl)-2,5,24,38,39-pentaoxo-1*H*,22*H*-23,36-(epiminomethano)-8,11:18,21-dietheno-13,16:31,35-di(metheno)[1,6,9]oxadiazacyclohexadecino[4,5-*m*][10,2,16]benzoxadiazacyclotetracosine-26-carboxylic acid. When vancomycin is converted into CDP-I the L-asparagine residue is changed to a β -linked L-aspartic residue. This change in ring size changes the fused ring system and hence changes nearly all locants used with the systematic name.

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