The first naturally occurring form of vitamin B6 was isolated in 1938. It has the structure, confirmed by chemical synthesis (1939), of 3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine (I; \( R = -\text{CH}_{2}\text{OH} \)). The trivial name "pyridoxine," proposed for this compound by P. György, came into general use as a synonym for "vitamin B6." Two other natural compounds possessing vitamin B6 activity, detected in 1944 and recognized as the aldehyde, or 4-formyl analogue (I; \( R = -\text{CHO} \)), and the corresponding amine, or 4-aminomethyl analogue (I; \( R = -\text{CH}_{2}\text{NH}_{2} \)), were designated "pyridoxal" and "pyridoxamine," respectively.

Within the next few years, I. C. Gunsalus, E. E. Snell, A. E. Braunstein, and others demonstrated that a phosphorylated derivative of pyridoxal, later identified as pyridoxal 5'-phosphate (II; \( R = -\text{CHO} \)), is the coenzyme of a large group of specific enzymes catalyzing reactions of amino group transfer, decarboxylation, and other metabolic transformations of individual amino acids. In the course of enzyme transamination, pyridoxal 5'-phosphate undergoes reversible conversion into pyridoxamine 5'-phosphate (II; \( R = -\text{CH}_{2}\text{NH}_{2} \)), which has coenzyme activity for the aminotransferases (EC 2.6.1.1), but not for other types of vitamin B6-dependent enzymes.

In the IUPAC-IBU Tentative Rules of 1966 (1) for the nomenclature of vitamins and related compounds (Rule M-7.l), it was suggested that the latter compound should be designated "pyridoxal" or "pyridoxamine." One regrettable consequence of these conflicting recommendations, giving rise to justified criticism, is the continuing use of the word "pyridoxine" in two different meanings—as a generic name for substances with vitamin B6 activity, and as the trivial name of a definite chemical compound (which, incidentally, is one of the less abundant among the naturally occurring forms of vitamin B6).

An extensive literature has accumulated on the chemistry and biochemistry of the B6 vitamins and coenzymes, of their metabolites, and of many related synthetic compounds that often exhibit biological activity as substitutes for or as antagonists of the corresponding natural products. A number of trivial and semitrivial names, sometimes incorrect or ambiguous, have been coined for vitamin B6 derivatives and analogues, and several forms of abbreviated designations for these compounds have been introduced. For example, the abbreviations pyridoxal-P, P-pyridoxal, TP (the symbol used most frequently), PALP, PalP, PALPO are in use for pyridoxal 5'-phosphate, and similar abbreviated forms have been used for other members of the group and their derivatives.

The IUPAC-IUB Commission on Biochemical Nomenclature (CBN), at its meeting in June 1968, decided to publish a special document, extending Section M-7 of the 1966 Rules (1), to put in order the nomenclature of the vitamin B6 field and to unify relevant abbreviations for use in situations in which this is essential. The present Tentative Rules are based on a draft prepared by A. E. Braunstein and E. E. Snell after consultation with other active workers in the field.

RULES (REPLACING SECTION M-7 OF REFERENCE 1)

The term vitamin B6 should be used as the generic descriptor for all 2-methylpyridine derivatives exhibiting qualitatively the biological activity of pyridoxine. This term should be used in derived terms such as vitamin B6 deficiency, vitamin B6 activity, vitamin B6 antagonists (5, 6).

7.1. Compound I (\( R = -\text{CH}_{2}\text{OH} \)), 3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine, should be designated pyridoxine or pyridoxal. The alkyl residue formed by removal of the 4'-OH group is named pyridoxyl (e.g. in compounds such as N\(^4\)-pyridoxyl-L-lysine and the like).

7.2. Compound I (\( R = -\text{CHO} \)), 3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine, should be designated pyridoxine or pyridoxal. The bivalent radical formed by removal of the CHO group is named pyridoxyl (e.g. in compounds such as N\(^4\)-pyridoxyl-L-lysine and the like).

**Comment**—"Pyridoxine" should not be used as a generic name synonymous with "vitamin B6." (5, 6).

7.3. Compound I (\( R = -\text{CH}_{2}\text{NH}_{2} \)) should be designated pyridoxamine.
7.4. The commonly occurring oxidized metabolites of pyridoxal, namely, 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxylic acid (III) and the corresponding lactone (IV) should be designated 3-pyridoxic acid and 3-pyridoxolactone, respectively. (Three less commonly occurring metabolites of pyridoxine, formed by oxidation at position 5', have also been detected, namely, the aldehyde, the carboxylic acid, and its lactone; they have been designated by the trivial names "isopyridoxal," "5-pyridoxic acid," and "5-pyridoxolactone," respectively.)

7.5. The 5'-phosphoric esters of pyridoxine, pyridoxal, and pyridoxamine (II; R = -CH,OH, -CHO, -CH,NH,) should be designated pyridoxine 5'-phosphate (or pyridoxine-5'-P), pyridoxal 5'-phosphate (or pyridoxal-5'-P), and pyridoxamine 5'-phosphate (or pyridoxamine-5'-P), respectively. The positional numeral, 5', may be omitted when no ambiguity arises (in biochemical papers, etc.); e.g. pyridoxal 5'-phosphate may be abbreviated pyridoxal-P.

For convenience (for example, in names of derived compounds), it is admissible to use the symbol P (for "phosphoric ester") as a prefix, for example: NG-(5'-P-pyridoxyl)n-lysine, P-pyridoxylideneimines.

7.6. From the trivial names already indicated, semitrivial names for various derivatives and analogues of the B₆ vitamins and their phosphoric esters (coenzyme analogues) can be constructed according to the conventional rules of organic nomenclature (see also 7.9).

Examples:
5'-Deoxypyridoxal
2-Demethylpyridoxal or 2-norpyridoxal
2-Propyl-2-norpyridoxal
6-Methylpyridoxal (Compound V)
4'-Deoxypyridoxine 5'-phosphate
5'-Methylpyridoxal-5'-P (Compound VI)
Pyridoxal N-oxide 5'-phosphate

7.7. As noted in the "Introduction," many abbreviations have been used in the past to represent the three principal forms of vitamin B₆, their phosphoric esters, and analogues in the text of papers. Those listed in Column 2 of Table I have achieved prominence as the favored forms. Their use in text in place of the approved trivial names (Column 1), which are sufficiently short, is not recommended. It is admissible to use these abbreviations, with ad hoc definition in each paper (and with the consent of the editors concerned), when necessary in cases of space restriction, e.g. in tables, figures, and extensive lists of derivatives and their reactions.

Use of Symbols in Designation of Derivatives and Analologues

7.8. Pyridoxyl (7.1) and pyridoxylidene (7.2) groups and similar residues of vitamin B₆ phosphates and analogues (7.5, 7.6) frequently occur in natural substances (B₆-dependent enzymes) and in modified or synthetic products (e.g. enzymes reconstituted with coenzyme analogues or reduced with borohydride or both), in combination with aminoacyl or peptidyl residues.

To represent such derivatives in condensed forms similar to those recommended for substituted polypeptides, it is suggested that the following symbols be used:

\[ \text{Pxy}^- \] (having a single bond) for the pyridoxyl group;
\[ \text{Pxd}^- \] (having a double bond) for the pyridoxylidene group.

The corresponding 5'-phosphorylated residues may be designated by adding the symbol P as a hyphenated prefix or suffix, and common alkyl or acyl substituents by prefixes in parentheses, composed from the recommended symbols and their locants (7-9).

Examples:
\[ \text{Pxy}^- \text{Lys}^- \text{or } \text{Pxy} \text{Lys}^- \] for the \( N^t \)-pyridoxyl-L-lysyl residue
\[ \text{P-Pxy}^- \text{Lys}^- \text{or } \text{P-Pxy} \text{Lys}^- \text{or } \text{Lys}^- \text{P-Pxy}^- \] for the corresponding \( N^t \)-pyridoxyl-L-lysyl residue
\[ \text{Pxd}^- \text{Lys}^- \] etc., \[ \text{P-Pxd}^- \text{Lys}^- \] etc., for the \( N^t \)-pyridoxylidene-L-lysyl residue and its phosphoric ester

\[^3\] The latter two symbols are more suitable for use in sequences (see last three examples).
Pxy-²-Lys-, or Pxy-Val-, etc., for N^2-pyridoxyl-L-lysyl and other N^2-pyridoxyl-L-aminoacyl residues

P-Pxy-²-Lys-, P-Pxy-Val-, etc., for the corresponding N^2-(P-pyridoxyl)-L-aminoacyl residues

P-Pxd=Val-, P-Pxd=Val-, etc., for N^2-pyridoxylidene-L-aminoacyl residues and the corresponding phosphoric esters

P-(3-deoxy)Pxd=²-Lys-, for the N^2-(3-deoxy-5'-P-pyridoxylidene)-L-lysyl residue

(3Me-2nor)Pxy—P

....Leu-Lys—Gly—...., for an N^4-(3-O-methyl-2-nor-5'-P) pyridoxyl-L-lysyl residue in a peptide sequence

(3Me)Pxd

....Leu-Lys—Gly—...., for an N^4-(α-methylpyridoxylidene)-L-lysyl residue in a peptide sequence

Pyridoxal-P

....Gly—Ser—Val—...., for a hypothetical pyridoxal-5'-P-3-O-L-seryl (phosphodiester) residue in a peptide sequence

Isotopic Replacement

7.9. Isotopic replacement in B6 vitamins, coenzymes, and derivatives can be designated by the conventional notations.

4 In NH₂-terminal position.

Examples:

[3-¹⁸O]pyridoxal-P, for pyridoxal 5'-phosphate labeled with ¹⁸O at O-3

[6'-H, 5-³²P]6-methylpyridoxamine-P, for 6-methylpyridoxamine 5'-phosphate with tritium at C-6' and ³²P in the phosphate group

[2'-¹³C]Pxd

....Leu-Lys—Ser—...., for a peptide sequence with an N^ε-pyridoxylidene-L-lysyl residue labeled with ¹³C at C-2'.

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