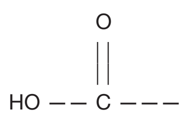
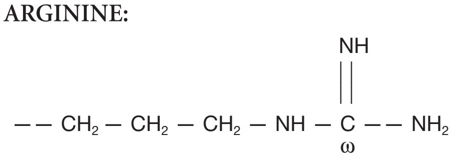
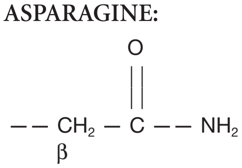
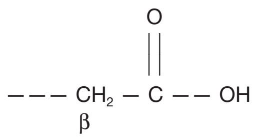
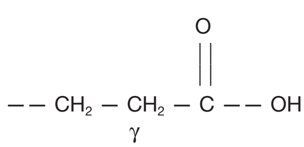
Some properties of posttranslational derivatives

Derivative	Derived from[a]	Delta mass[b]	Stability[c]	
THE AMINO TERMINUS:				
				
N-Pyrrolidone carboxyl- (3)	**Gln**	–17	A–, B–	
N-α-Ketoacyl- (4)	**Ser**	–16	A–, B–	
N-Methyl- (5)		14	A+	P+
N-Formyl- (6)		28	A–, B–	
N-Acetyl- (7)		42	A–, B–	
N-Glucosyl- (8)		162	A+ (after BH_4^-)	
N-Lauroyl- (9)		182	A–, B–	
N-Tetradeca (mono and di)enoyl- (9)		208, 206	A–, B–	
N-Myristoyl-[d] (10)		210	A–, B–	
THE CARBOXYL TERMINUS:				
				
-Amide (11)		–1	A–, B–	
O-Methyl- (12)		14	A–, B–	
-(N^{α}-Tyr) (13)		163	A+	P+
O-(ADP-ribosyl)- (14)		541	A–, B–	
O-(*N*-Ethanolamine-glycan-phosphoinositides)[d] (15)		>1907[d]	A–, B–	
ARGININE:				
				
Ornithine (16)		–42	A+, B+	P+
Citrulline (17)		1	A+	
N^{ω}-Methyl- (18)		14	A+, B–	
N^{ω}-Dimethyl-; N^{ω}, $N^{\omega'}$, -dimethyl- (18)		28	A+, B–	
Pentosidine (19)	Arg, Lys, (Ribose)	59	A±	
N^{ω}-(ADP-ribosyl)- (20)		541	A–, B–	
ASPARAGINE:				
				
$N^{\varepsilon(-(}$β-Aspartyl)-lysine (21)	Asn, Lys	–17	A–, B–	
Aspartate (22)		1	(A+, B+)	P+
N-Methyl- (23)		14	A–, B–	
N-(ADP-ribosyl)- (24)		541	A–, B–	
N-Glycosyl-[d] (25)		(892–2770)[d]	A–, B–	

Some properties of posttranslational derivatives (*Continued*)

Derivative	Derived from[a]	Delta mass[b]	Stability[c]	
ASPARTATE:				
				
O-Methyl- (26)		14	A–, B–	**P+**
Erythro-β-hydroxy- (27)		16	A+	
β-Carboxy- (28)		44	A–, B+	
O-Phosphoryl- (29)		80	A–, B–	
CYSTEINE:				
—— CH_2 — SH				
Dehydroalanine (30)		–34	A–, B–	
Lysinoalanine (30)	Cys, Lys	–34	A+, B+	
Lanthionine (30)	2 Cys	–34	A+, B+	
S-γ-Glutamyl- (31)	Cys, Glu	–18	A–, B–	
Cystine (32)	2 Cys	–2	A–, B–	
S-(2-Histidyl)- (33)	Cys, His	–2	A–	
S-(*3*-Tyr) (34)	Cys, Tyr	–2	A–	
S-(*sn*-1-Glyceryl)- (35)		74	A±	
S-Farnesyl- (36)		206	A±, B+	
S-Palmitoyl- (37)		238	A–, B–	
S-*p*-Coumaroyl (38)		249	A–, B–	
S-Geranylgeranyl- (36)		276	A±, B+	
S-(*sn*-1-Dipalmitoyl-glyceryl)-[d] (39)		524	A±, B+	
S-(ADP-ribosyl)- 40		541	A–	
S-Phycocyanobilin[d] (41)		587	A±	
S-Haem[d] (40)		617	A±	
S-(*sn*-1-Di-*O*-[3´,7´,11´,15´-tetramethyl-hexadecyl]-glyceryl)- (43)		623	A±	
S-(8α-Flavin [FAD]) (44)		784	A–, B–	
GLUTAMATE:				
				
O-Methyl- (6,45)		14	A–, B–	
γ-Carboxy- (46)		44	A–, B±	
O-(ADP-ribosyl)- (20)		541	A–, B–	
N^{α}-(γ-Glutamyl)-$Glu_{1\text{-}5}$ (47)		129–645	A–, B–	
N^{α}-(γ-Glutamyl)-$Gly_{3\text{-}34}$ (48)		171–1936	A–, B–	

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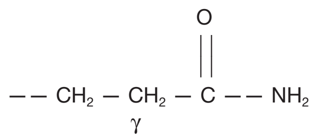
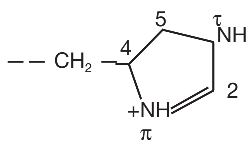
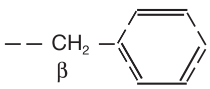
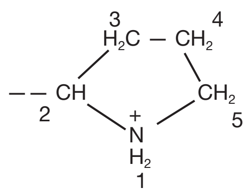
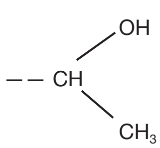
Some properties of posttranslational derivatives (*Continued*)

Derivative	Derived from[a]	Delta mass[b]	Stability[c]	
GLUTAMINE:				
				
N^{ε}-(γ-Glutamyl)-lysine (40)	Gln, Lys	–17	A–, B–	
Glutamate (22)		1	(A+, B+)	<u>**P+**</u>
N^{5}-Methyl- (50)		14	A–, B–	
HISTIDINE:				
				
N^{π} -Methyl- (51)		14	A+	
N-Phosphoryl- (52)		80	A–, B–	
Diphthamide (53)		107	A±	
4-Lodo- and diido- (54)		128 and 256	A–	
N^{τ} -(ADP-ribosyl) diphthamide (55)		648	A–, B–	
N^{τ} - and N^{π} -(8α-Flavin [FAD]) (44)		784	A–	
LYSINE:				
$—— CH_2 — CH_2 — \underset{\delta}{CH_2} — \underset{\varepsilon}{CH_2} — NH_2$				
Desmosine (56)	4 Lys	–58	A±	
Lysylpyridinoline (57)	3 Lys	–39	A±	
Merodesmosine (56)	3 Lys	–36	A±	
Aldol-histidine (57)	2 Lys, His	–20	A±, B+	
Lysinonorleucine (57)	2 Lys	–14	A+, B+	
Aldol (57)	2 Lys	–2	A+, B+	
Allysine (58)		–1	A–, B–	
Syndesine (59)	2 Lys	14	A+, B+	
δ-Hydroxyallysine (60)		15	A–, B–	
δ-Hydroxy- (60)		16	A+, B+	<u>**P+**</u>
N^{ε}-Acetyl- (61)		42	A–, B–	
N^{ε}-Lipoyl- (62)		188	A–, B–	
N^{ε}-Biotinyl- (63)		226	A–, B–	
N^{ε}-Ubiquitinyl-[d] (64)		$(8566)_n$	A–, B–	
N^{ε}-Glycosyl- (65)		162	A±	
N^{ε}-Mono, di, trimethyl- (66)		14,28,42	A+	
Hypusine: N^{ε}- (4-amino, 2-hydroxybutyl)- (67)		87	A+	
δ-Hexosyloxy-[d] (68)		177	A–, B±	
METHIONINE:				
$—— CH_2 — CH_2 — S —— CH_3$				
Sulfoxide (69, 70)		16	A–	

Some properties of posttranslational derivatives (*Continued*)

Derivative	Derived from[a]	Delta mass[b]	Stability[c]	
PHENYLALANINE:				
				
β-Glycosyloxy-[d] (71)		177	A–	
PROLINE:				
				
3-Hydroxy- (72)		16	A±, B±	**P+**
4-Hydroxy- (73)		16	A+, B+	P+
3,4-Dihydroxy- (74)		32	A+, B+	
4-Arabinosyloxy-[d] (75)		157	A–, B±	
O^4-Hexosyloxy-[d] (75)		177	A–, B±	
SERINE:				
—— CH_2 — OH				
Dehydroalanine (76)		–18		**A–**
Lanthionine (77)	Ser, Cys	–18		A+
Alanino (τ- or π-histidine) (76)	Ser, His	–18		A+
O-Methyl- (78)		14	A+	
O-Acetyl- (79)		42	A–, B–	
Selenocysteine (80)		64	A–	
O-Phosphoryl- (81)		80	A±	
O-(GlcNAc-1-phosphoryl)- (82)		268	A–, B–	
O-Pantetheinephosphoryl- (83)		324	A±	
O-Glycosyl-[d] (84)		≥162	A–, B–	
THREONINE:				
				
O-Methyl- (78)		14	A+	
β-Methyl-lanthionine (77)	Thr, Cys	18	A+	

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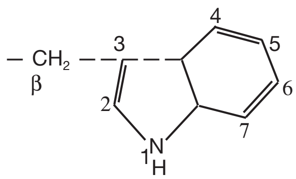
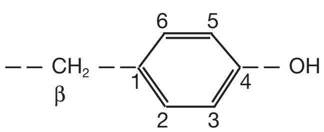
Some properties of posttranslational derivatives (*Continued*)

Derivative	Derived from[a]	Delta mass[b]	Stability[c]
TRYPTOPHAN:			
			
2,4´-BisTrp-6´,7´-dione (85)	2 Trp	28	A–
C2-Aldohexopyranosyl- (86)		162	A–
TYROSINE:			
			
3,3´-Bityr (87)		–2	A+
IsodiTyr (88)		–2	A+
3,4-Dihydroxy-Phe (DOPA) (89)		16	A±
3,4,6-Trihydroxyl-Phe (TOPA) (85)		32	A–
Halogenated derivatives[e] (90)			
3-chloro-		34,36	A+
3,5-dichloro-		68,70,72	A+
3-bromo-		78,80	A+
O-Phosphate (91)		80	A±, B±
O-Sulfate (92)		80	A–, B±
3-iodo-		126	A+
3,5-dibromo-[e]		156,158,160	A+
3,5-diido-		252	A+
O-Uridylyl- (93)		306	A–
O-Adenylyl- (93)		329	A–
Triiodo-thyronine (94)		470	A±, B±
Tetraiodo-thyronine (94)		596	A±, B±
O-(8a-Flavin [FAD]) (44)		783	A–

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[a]In the case of cross-linking derivatives, all the amino acid precursors have been identified; for the others, the precursor is identified as the primary amino acid under which the derivative is listed. It is essential to know the identity of the parent amino acid in defining the mass changes; dehydroalanine has a delta mass of –34 if it is derived from Cys, and –18 if derived from Ser.

[b]The delta mass values represent the changes in mass that would be observed if the primary amino acid has been converted to the specific derivative identified (e.g., Asn [radical mass 144]→Man_3Glc-NAC_2Asn [radical mass 1006], delta mass 892; Cys [103] + Ser [87]→lanthionine (172), delta mass –18).

[c]The chemical stability is recorded very broadly in terms of the standard hydrolysis conditions (*A*, 6 M HCl, 110°C, 20–24 hr; *B*, 5 M NaOH, 110°C, 5–20 hr). + indicates that a significant quantity of the derivative will survive these conditions; – indicates that the derivative will be destroyed; and ± indicates that it is possible to modify the acid or base hydrolysis conditions to allow some of the derivative to remain after all or most of the peptide bonds have been cleaved. P+ indicates that the PTH derivative can be observed and analyzed directly by the standard sequencing conditions.

[d]Several different derivatives are possible in this group. In the case of the glycosylated derivatives, the main saccharides and their radical masses are pentose, 132; deoxyhexose, 146; hexose, 162; Nac-hexosamine, 203; sialic acid, 291. For derivatives involving fatty acids, acids different from those provided will give different masses. Some derivatives such as haem and phycocyanobilins have closely related isomers; ubiquitin, a polypeptide with radical mass 8566, could add different masses according to the number of ubiquitin chains that are involved in a given derivative.

[e]For Cl and Br, both of the most abundant masses (^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br) must be considered in estimating the mass of the halogenated derivatives.