The Enzyme List
Class 5 — Isomerases

Nomenclature Committee
of the
International Union of Biochemistry and Molecular Biology
(NC-IUBMB)

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Contents

EC 5.1 Racemases and epimerases

This subclass contains enzymes that catalyse either racemization or epimerization of a centre of chirality. Sub-subclasses are based on the substrate: amino acids and derivatives (EC 5.1.1), hydroxy acids and derivatives (EC 5.1.2), carbohydrates and derivatives (EC 5.1.3), or other compounds (EC 5.1.99).

EC 5.1.1 Acting on amino acids and derivatives

EC 5.1.1.1
Accepted name: alanine racemase
Reaction: L-alanine = D-alanine
Other name(s): L-alanine racemase
Systematic name: alanine racemase
Comments: A pyridoxal-phosphate protein.
References: [371, 637, 638]

[EC 5.1.1.1 created 1961]

EC 5.1.1.2
Accepted name: methionine racemase
Reaction: L-methionine = D-methionine
Systematic name: methionine racemase
Comments: A pyridoxal-phosphate protein.
References: [274]

[EC 5.1.1.2 created 1961]

EC 5.1.1.3
Accepted name: glutamate racemase
Reaction: L-glutamate = D-glutamate
Systematic name: glutamate racemase
Comments: A pyridoxal-phosphate protein.
References: [186]

[EC 5.1.1.3 created 1961]

EC 5.1.1.4
Accepted name: proline racemase
Reaction: L-proline = D-proline
Systematic name: proline racemase
References: [548]

[EC 5.1.1.4 created 1961]

EC 5.1.1.5
Accepted name: lysine racemase

Reaction: L-lysine = D-lysine
Systematic name: lysine racemase
Comments: The enzyme is involved in a lysine catabolic pathway.
References: [239, 238, 87, 284]

[EC 5.1.1.5 created 1961]

EC 5.1.1.6
Accepted name: threonine racemase
Reaction: L-threonine = D-threonine
Systematic name: threonine racemase
Comments: Inverts both chiral centres.
References: [18]

[EC 5.1.1.6 created 1961, modified 1981]

EC 5.1.1.7
Accepted name: diaminopimelate epimerase
Reaction: LL-2,6-diaminoheptanedioate = *meso*-diaminoheptanedioate
Systematic name: LL-2,6-diaminoheptanedioate 2-epimerase
References: [26]

[EC 5.1.1.7 created 1961]

EC 5.1.1.8
Accepted name: 4-hydroxyproline epimerase
Reaction: *trans*-4-hydroxy-L-proline = *cis*-4-hydroxy-D-proline
Other name(s): hydroxyproline epimerase; hydroxyproline 2-epimerase; L-hydroxyproline epimerase
Systematic name: 4-hydroxyproline 2-epimerase
Comments: Also interconverts *trans*-4-hydroxy-D-proline and *cis*-4-hydroxy-L-proline.
References: [6]

[EC 5.1.1.8 created 1965, modified 1983]

EC 5.1.1.9
Accepted name: arginine racemase
Reaction: L-arginine = D-arginine
Systematic name: arginine racemase
Comments: A pyridoxal-phosphate protein.
References: [659]

[EC 5.1.1.9 created 1972]

EC 5.1.1.10
Accepted name: amino-acid racemase
Reaction: an L-amino acid = a D-amino acid
Other name(s): L-amino acid racemase
Systematic name: amino-acid racemase
Comments: A pyridoxal-phosphate protein.
References: [541]

[EC 5.1.1.10 created 1972]

EC 5.1.1.11

Accepted name: phenylalanine racemase (ATP-hydrolysing)
Reaction: ATP + L-phenylalanine + H_2O = AMP + diphosphate + D-phenylalanine
Other name(s): phenylalanine racemase; phenylalanine racemase (adenosine triphosphate-hydrolysing); gramicidin S synthetase I
Systematic name: phenylalanine racemase (ATP-hydrolysing)
References: [650]

[EC 5.1.1.11 created 1972]

EC 5.1.1.12

Accepted name: ornithine racemase
Reaction: L-ornithine = D-ornithine
Systematic name: ornithine racemase
References: [86]

[EC 5.1.1.12 created 1972 as EC 5.4.3.1, transferred 1976 to EC 5.1.1.12]

EC 5.1.1.13

Accepted name: aspartate racemase
Reaction: L-aspartate = D-aspartate
Other name(s): D-aspartate racemase; McyF
Systematic name: aspartate racemase
Comments: Also acts, at half the rate, on L-alanine.
References: [329, 654, 350, 532, 653]

[EC 5.1.1.13 created 1976]

EC 5.1.1.14

Accepted name: nocardicin A epimerase
Reaction: (1) isonocardicin C = nocardicin C
(2) isonocardicin A = nocardicin A
Other name(s): isonocardicin A epimerase; *nocJ* (gene name)
Systematic name: nocardicin-C epimerase
Comments: Requires pyridoxal 5′-phosphate. The enzyme, characterized from the bacterium *Nocardia uniformis*, is involved in the biosynthesis of the monolactam antibiotic nocardicin A. It catalyses the epimerization of the amino group at position 9′ from (*S*)- configuration to (*R*)-. The enzyme can act on both isonocardicin A and isonocardicin C, but the *in vivo* substrate appears to be the latter [293].
References: [625, 292, 293]

[EC 5.1.1.14 created 1992, modified 2016]

EC 5.1.1.15

Accepted name: 2-aminohexano-6-lactam racemase
Reaction: (*S*)-2-aminohexano-6-lactam = (*R*)-2-aminohexano-6-lactam
Other name(s): α-amino-ε-caprolactam racemase
Systematic name: 2-aminohexano-6-lactam racemase
Comments: Contains pyridoxal 5′-phosphate. Also racemises 2-aminopentano-5-lactam (α-amino-δ-valerolactam) and 2-amino-4-thiahexano-6-lactam (where S replaces CH_2 of C-4). It does not catalyse the racemisation of α-amino acids but has some transaminase activity with them.
References: [8, 9, 438]

[EC 5.1.1.15 created 1999]

EC 5.1.1.16

Accepted name: protein-serine epimerase
Reaction: [protein]-L-serine = [protein]-D-serine
Other name(s): protein-serine racemase
Systematic name: [protein]-serine epimerase
Comments: The enzyme specifically interconverts the configuration of Ser-46 of the peptide ω-agatoxin-KT, found in the venom of the funnel web spider, *Agelenopsis aperta*, but not that of the other serine residue, Ser-28.
References: [526]

[EC 5.1.1.16 created 1999]

EC 5.1.1.17

Accepted name: isopenicillin-N epimerase
Reaction: isopenicillin N = penicillin N
Systematic name: penicillin-N 5-amino-5-carboxypentanoyl-epimerase
Comments: This enzyme contains pyridoxal phosphate. Epimerization at C-5 of the 5-amino-5-carboxypentanoyl group to form penicillin N is required to make a substrate for EC 1.14.20.1, deactoxycephalosporin-C synthase, to produce cephalosporins. Forms part of the penicillin biosynthesis pathway (for pathway, click here).
References: [598, 328, 74, 656]

[EC 5.1.1.17 created 2002]

EC 5.1.1.18

Accepted name: serine racemase
Reaction: L-serine = D-serine
Other name(s): SRR
Systematic name: serine racemase
Comments: A pyridoxal-phosphate protein that is highly selective for L-serine as substrate. D-Serine is found in type-II astrocytes in mammalian brain, where it appears to be an endogenous ligand of the glycine site of *N*-methyl-D-aspartate (NMDA) receptors [635, 636]. The reaction can also occur in the reverse direction but does so more slowly at physiological serine concentrations [164].
References: [635, 636, 400, 164]

[EC 5.1.1.18 created 2007]

EC 5.1.1.19

Accepted name: *O*-ureido-serine racemase
Reaction: *O*-ureido-L-serine = *O*-ureido-D-serine
Other name(s): *dcsC* (gene name)
Systematic name: (2*S*)-2-amino-3-[(carbamoylamino)oxy]propanoate 2-epimerase
Comments: The enzyme employs a two-base mechanism, with a thiolate-thiol pair in the active site. It participates in the biosynthetic pathway of D-cycloserine, an antibiotic substance produced by several *Streptomyces* species.
References: [319, 135]

[EC 5.1.1.19 created 2013]

EC 5.1.1.20

Accepted name: L-Ala-D/L-Glu epimerase
Reaction: L-alanyl-D-glutamate = L-alanyl-L-glutamate
Other name(s): YkfB; YcjG; AEE; AE epimerase

Systematic name: L-alanyl-D-glutamate epimerase
Comments: The enzyme, characterized from the bacteria *Escherichia coli* and *Bacillus subtilis*, is involved in the recycling of the murein peptide, of which L-Ala-D-Glu is a component. *In vitro* the enzyme from *Escherichia coli* epimerizes several L-Ala-L-X dipeptides with broader specificity than the enzyme from *Bacillus subtilis*.
References: [510, 199]

[EC 5.1.1.20 created 2015]

EC 5.1.1.21
Accepted name: isoleucine 2-epimerase
Reaction: L-isoleucine = D-*allo*-isoleucine
Other name(s): BCAA racemase
Systematic name: isoleucine 2-epimerase
Comments: A pyridoxal phosphate protein. The enzyme, characterized from the bacterium *Lactobacillus buchneri*, specifically catalyses racemization of nonpolar amino acids at the C-2 position.
References: [416]

[EC 5.1.1.21 created 2015]

EC 5.1.1.22
Accepted name: 4-hydroxyproline betaine 2-epimerase
Reaction: (1) *trans*-4-hydroxy-L-proline betaine = *cis*-4-hydroxy-D-proline betaine
(2) L-proline betaine = D-proline betaine
Other name(s): *hpbD* (gene name); Hyp-B 2-epimerase; (4*R*)-4-hydroxyproline betaine 2-epimerase
Systematic name: 4-hydroxyproline betaine 2-epimerase
Comments: The enzyme, characterized from the bacteria *Pelagibaca bermudensis* and *Paracoccus denitrificans*, specifically catalyses racemization of *trans*-4-hydroxy-L-proline betaine and L-proline betaine at the C-2 position.
References: [685, 320]

[EC 5.1.1.22 created 2017]

EC 5.1.1.23
Accepted name: UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate epimerase
Reaction: ATP + UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate + H_2O = AMP + diphosphate + UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-D-glutamate
Other name(s): *murL* (gene name); UDP-MurNAc-L-Ala-L-Glu epimerase
Systematic name: UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate L-glutamate-epimerase
Comments: The enzyme, characterized from the bacterium *Xanthomonas oryzae*, catalyses epimerization of the terminal L-glutamate in UDP-*N*-acetyl-α-D-muramoyl-L-alanyl-L-glutamate. The reaction proceeds only in one direction and involves an adenylated intermediate. The combined activity of this enzyme and EC 6.3.2.53, UDP-*N*-acetylmuramoyl-L-alanine—L-glutamate ligase, provides an alternative route for incorporating D-glutamate into peptidoglycan, replacing the more common combination of EC 5.1.1.3, glutamate racemase, and EC 6.3.2.9, UDP-*N*-acetylmuramoyl-L-alanine—D-glutamate ligase.
References: [155]

[EC 5.1.1.23 created 2018]

EC 5.1.2 Acting on hydroxy acids and derivatives

EC 5.1.2.1

Accepted name: lactate racemase
Reaction: (*S*)-lactate = (*R*)-lactate
Other name(s): lacticoracemase; hydroxyacid racemase; lactic acid racemase; *larA* (gene name)
Systematic name: lactate racemase
Comments: The enzyme has been characterized from the bacterium *Lactobacillus plantarum* and appears to be restricted to lactic acid bacteria. It contains a unique nickel-containing cofactor, pyridinium-3-thioamide-5-thiocarboxylate mononucleotide Ni pincer complex.
References: [241, 299, 189, 128, 129, 665]

[EC 5.1.2.1 created 1961]

EC 5.1.2.2

Accepted name: mandelate racemase
Reaction: (*S*)-mandelate = (*R*)-mandelate
Systematic name: mandelate racemase
References: [200]

[EC 5.1.2.2 created 1961]

EC 5.1.2.3

Accepted name: 3-hydroxybutyryl-CoA epimerase
Reaction: (*S*)-3-hydroxybutanoyl-CoA = (*R*)-3-hydroxybutanoyl-CoA
Other name(s): 3-hydroxybutyryl coenzyme A epimerase; 3-hydroxyacyl-CoA epimerase
Systematic name: 3-hydroxybutanoyl-CoA 3-epimerase
References: [551, 608]

[EC 5.1.2.3 created 1961]

EC 5.1.2.4

Accepted name: acetoin racemase
Reaction: (*S*)-acetoin = (*R*)-acetoin
Other name(s): acetylmethylcarbinol racemase
Systematic name: acetoin racemase
References: [576]

[EC 5.1.2.4 created 1972]

EC 5.1.2.5

Accepted name: tartrate epimerase
Reaction: (*R*,*R*)-tartrate = *meso*-tartrate
Other name(s): tartaric racemase
Systematic name: tartrate epimerase
References: [472]

[EC 5.1.2.5 created 1972]

EC 5.1.2.6

Accepted name: isocitrate epimerase
Reaction: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate = (1*S*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate
Systematic name: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate 1-epimerase
Comments: (1*R*,2*S*)-1-hydroxypropane-1,2,3-tricarboxylate is the commonly occurring isomer of isocitrate.
References: [234]

[EC 5.1.2.6 created 1984]

EC 5.1.2.7

Accepted name: tagaturonate epimerase
Reaction: D-tagaturonate = D-fructuronate
Other name(s): fructuronate epimerase; tagaturonate/fructuronate epimerase; UxaE
Systematic name: D-tagaturonate 3-epimerase
Comments: The enzyme, present in bacteria, is involved in a degradation pathway of D-galacturonate.
References: [491]

[EC 5.1.2.7 created 2017]

EC 5.1.3 Acting on carbohydrates and derivatives

EC 5.1.3.1

Accepted name: ribulose-phosphate 3-epimerase
Reaction: D-ribulose 5-phosphate = D-xylulose 5-phosphate
Other name(s): phosphoribulose epimerase; erythrose-4-phosphate isomerase; phosphoketopentose 3-epimerase; xylulose phosphate 3-epimerase; phosphoketopentose epimerase; ribulose 5-phosphate 3-epimerase; D-ribulose phosphate-3-epimerase; D-ribulose 5-phosphate epimerase; D-ribulose-5-P 3-epimerase; D-xylulose-5-phosphate 3-epimerase; pentose-5-phosphate 3-epimerase
Systematic name: D-ribulose-5-phosphate 3-epimerase
Comments: The enzyme also converts D-erythrose 4-phosphate into D-erythrulose 4-phosphate and D-threose 4-phosphate.
References: [31, 133, 244, 557, 578]

[EC 5.1.3.1 created 1961, modified 1989]

EC 5.1.3.2

Accepted name: UDP-glucose 4-epimerase
Reaction: UDP-α-D-glucose = UDP-α-D-galactose
Other name(s): UDP-galactose 4-epimerase; uridine diphosphoglucose epimerase; galactowaldenase; UDPG-4-epimerase; uridine diphosphate galactose 4-epimerase; uridine diphospho-galactose-4-epimerase; UDP-glucose epimerase; 4-epimerase; uridine diphosphoglucose 4-epimerase; uridine diphosphate glucose 4-epimerase; UDP-D-galactose 4-epimerase
Systematic name: UDP-α-D-glucose 4-epimerase
Comments: Requires NAD^+. Also acts on UDP-2-deoxyglucose.
References: [336, 383, 626]

[EC 5.1.3.2 created 1961]

EC 5.1.3.3

Accepted name: aldose 1-epimerase
Reaction: α-D-glucose = β-D-glucose
Other name(s): mutarotase; aldose mutarotase; galactose mutarotase; galactose 1-epimerase; D-galactose 1-epimerase
Systematic name: aldose 1-epimerase
Comments: Also acts on L-arabinose, D-xylose, D-galactose, maltose and lactose. This enzyme catalyses the first step in galactose metabolism by converting β-D-galactose into α-D-galactose, which is the substrate for EC 2.7.1.6, galactokinase [44, 582].
References: [51, 52, 291, 340, 44, 582, 581]

[EC 5.1.3.3 created 1961]

EC 5.1.3.4

Accepted name: L-ribulose-5-phosphate 4-epimerase
Reaction: L-ribulose 5-phosphate = D-xylulose 5-phosphate
Other name(s): phosphoribulose isomerase; ribulose phosphate 4-epimerase; L-ribulose-phosphate 4-epimerase; L-ribulose 5-phosphate 4-epimerase; AraD; L-Ru5P
Systematic name: L-ribulose-5-phosphate 4-epimerase
Comments: Requires a divalent cation for activity.
References: [71, 130, 333, 634, 22, 332, 502]

[EC 5.1.3.4 created 1965, modified 2005]

EC 5.1.3.5

Accepted name: UDP-arabinose 4-epimerase
Reaction: UDP-L-arabinose = UDP-D-xylose
Other name(s): uridine diphosphoarabinose epimerase; UDP arabinose epimerase; uridine 5′-diphosphate-D-xylose 4-epimerase; UDP-D-xylose 4-epimerase
Systematic name: UDP-L-arabinose 4-epimerase
References: [153]

[EC 5.1.3.5 created 1965]

EC 5.1.3.6

Accepted name: UDP-glucuronate 4-epimerase
Reaction: UDP-glucuronate = UDP-D-galacturonate
Other name(s): uridine diphospho-D-galacturonic acid; UDP glucuronic epimerase; uridine diphosphoglucuronic epimerase; UDP-galacturonate 4-epimerase; uridine diphosphoglucuronate epimerase; UDP-D-galacturonic acid 4-epimerase
Systematic name: UDP-glucuronate 4-epimerase
References: [153]

[EC 5.1.3.6 created 1965]

EC 5.1.3.7

Accepted name: UDP-*N*-acetylglucosamine 4-epimerase
Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-*N*-acetyl-α-D-galactosamine
Other name(s): UDP acetylglucosamine epimerase; uridine diphosphoacetylglucosamine epimerase; uridine diphosphate *N*-acetylglucosamine-4-epimerase; uridine 5′-diphospho-*N*-acetylglucosamine-4-epimerase; UDP-*N*-acetyl-D-glucosamine 4-epimerase
Systematic name: UDP-*N*-acetyl-α-D-glucosamine 4-epimerase
References: [185, 314]

[EC 5.1.3.7 created 1965]

EC 5.1.3.8

Accepted name: *N*-acylglucosamine 2-epimerase
Reaction: *N*-acyl-D-glucosamine = *N*-acyl-D-mannosamine
Other name(s): acylglucosamine 2-epimerase; *N*-acetylglucosamine 2-epimerase
Systematic name: *N*-acyl-D-glucosamine 2-epimerase
Comments: Requires catalytic amounts of ATP.
References: [183]

[EC 5.1.3.8 created 1972]

EC 5.1.3.9

Accepted name: *N*-acylglucosamine-6-phosphate 2-epimerase
Reaction: *N*-acyl-D-glucosamine 6-phosphate = *N*-acyl-D-mannosamine 6-phosphate
Other name(s): acylglucosamine-6-phosphate 2-epimerase; acylglucosamine phosphate 2-epimerase
Systematic name: *N*-acyl-D-glucosamine-6-phosphate 2-epimerase
References: [182]

[EC 5.1.3.9 created 1972]

EC 5.1.3.10

Accepted name: CDP-paratose 2-epimerase
Reaction: CDP-α-D-paratose = CDP-α-D-tyvelose
Other name(s): CDP-paratose epimerase; cytidine diphosphoabequose epimerase; cytidine diphosphodideoxyglucose epimerase; cytidine diphosphoparatose epimerase; cytidine diphosphate paratose-2-epimerase; CDP-abequose epimerase (incorrect); CDP-D-abequose 2-epimerase (incorrect); CDP-tyvelose 2-epimerase,
Systematic name: CDP-3,6-dideoxy-D-glucose 2-epimerase
Comments: Requires NAD^+.
References: [381, 349, 315]

[EC 5.1.3.10 created 1972, modified 2005]

EC 5.1.3.11

Accepted name: cellobiose epimerase
Reaction: cellobiose = 4-*O*-β-D-glucopyranosyl-D-mannose
Systematic name: cellobiose 2-epimerase
Comments: The enzyme catalyses the interconversion between D-glucose and D-mannose residues at the reducing end of β-1,4-linked disaccharides by epimerizing the hydroxyl group at the C-2 position of the glucose moiety.
References: [593, 252, 172]

[EC 5.1.3.11 created 1972]

EC 5.1.3.12

Accepted name: UDP-glucuronate 5′-epimerase
Reaction: UDP-α-D-glucuronate = UDP-β-L-iduronate
Other name(s): uridine diphosphoglucuronate 5′-epimerase; UDP-glucuronic acid 5′-epimerase; C-5-uronosyl epimerase
Systematic name: UDP-α-D-glucuronate 5′-epimerase
Comments: Requires NAD^+.
References: [256]

[EC 5.1.3.12 created 1972]

EC 5.1.3.13

Accepted name: dTDP-4-dehydrorhamnose 3,5-epimerase
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucose = dTDP-4-dehydro-β-L-rhamnose
Other name(s): dTDP-L-rhamnose synthetase; dTDP-L-rhamnose synthase; thymidine diphospho-4-ketorhamnose 3,5-epimerase; TDP-4-ketorhamnose 3,5-epimerase; dTDP-4-dehydro-6-deoxy-D-glucose 3,5-epimerase; TDP-4-keto-L-rhamnose-3,5-epimerase
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucose 3,5-epimerase
Comments: The enzyme occurs in a complex with EC 1.1.1.133 dTDP-4-dehydrorhamnose reductase.
References: [176, 391]

[EC 5.1.3.13 created 1972]

EC 5.1.3.14

Accepted name: UDP-*N*-acetylglucosamine 2-epimerase (non-hydrolysing)
Reaction: UDP-*N*-acetyl-α-D-glucosamine = UDP-*N*-acetyl-α-D-mannosamine
Other name(s): UDP-*N*-acetylglucosamine 2′-epimerase (ambiguous); uridine diphosphoacetylglucosamine 2′-epimerase (ambiguous); uridine diphospho-*N*-acetylglucosamine 2′-epimerase (ambiguous); uridine diphosphate-*N*-acetylglucosamine-2′-epimerase (ambiguous); *rffE* (gene name); *mnaA* (gene name); UDP-*N*-acetyl-D-glucosamine 2-epimerase
Systematic name: UDP-*N*-acetyl-α-D-glucosamine 2-epimerase
Comments: This bacterial enzyme catalyses the reversible interconversion of UDP-GlcNAc and UDP-ManNAc. The latter is used in a variety of bacterial polysaccharide biosyntheses. *cf.* EC 3.2.1.183, UDP-*N*-acetylglucosamine 2-epimerase (hydrolysing).
References: [288, 389, 406, 72, 503, 544]

[EC 5.1.3.14 created 1976, modified 2012]

EC 5.1.3.15

Accepted name: glucose-6-phosphate 1-epimerase
Reaction: α-D-glucose 6-phosphate = β-D-glucose 6-phosphate
Systematic name: D-glucose-6-phosphate 1-epimerase
References: [644]

[EC 5.1.3.15 created 1976]

EC 5.1.3.16

Accepted name: UDP-glucosamine 4-epimerase
Reaction: UDP-α-D-glucosamine = UDP-α-D-galactosamine
Systematic name: UDP-α-D-glucosamine 4-epimerase
References: [363, 533]

[EC 5.1.3.16 created 1984]

EC 5.1.3.17

Accepted name: heparosan-*N*-sulfate-glucuronate 5-epimerase
Reaction: Epimerization of D-glucuronate in heparosan-*N*-sulfate to L-iduronate.
Other name(s): heparosan epimerase; heparosan-*N*-sulfate-D-glucuronosyl 5-epimerase; C-5 uronosyl epimerase; polyglucuronate epimerase; D-glucuronyl C-5 epimerase; poly[(1,4)-β-D-glucuronosyl-(1,4)-*N*-sulfo-α-D-glucosaminyl] glucurono-5-epimerase
Systematic name: poly[(1→4)-β-D-glucuronosyl-(1→4)-*N*-sulfo-α-D-glucosaminyl] glucurono-5-epimerase
Comments: The enzyme acts on D-glucosyluronate residues in *N*-sulfated heparosan polymers, converting them to L-iduronate, thus modifying the polymer to heparan-*N*-sulfate. The enzyme requires that at least the *N*-acetylglucosamine residue linked to C-4 of the substrate has been deacetylated and *N*-sulfated, and activity is highest with fully *N*-sulfated substrate. It does not act on glucuronate residues that are *O*-sulfated or are adjacent to *N*-acetylglucosamine residues that are *O*-sulfated at the 6 position. Thus the epimerization from D-glucuronate to L-iduronate occurs after *N*-sulfation of glucosamine residues but before *O*-sulfation. Not identical with EC 5.1.3.19 chondroitin-glucuronate 5-epimerase or with EC 5.1.3.36, heparosan-glucuronate 5-epimerase.
References: [257, 258, 204]

[EC 5.1.3.17 created 1984, modified 2015]

EC 5.1.3.18

Accepted name: GDP-mannose 3,5-epimerase
Reaction: GDP-α-D-mannose = GDP-β-L-galactose
Other name(s): GDP-D-mannose:GDP-L-galactose epimerase; guanosine 5′-diphosphate D-mannose:guanosine 5′-diphosphate L-galactose epimerase
Systematic name: GDP-α-D-mannose 3,5-epimerase
References: [36, 221]

[EC 5.1.3.18 created 1986]

EC 5.1.3.19
Accepted name: chondroitin-glucuronate 5-epimerase
Reaction: chondroitin D-glucuronate = dermatan L-iduronate
Other name(s): polyglucuronate 5-epimerase; dermatan-sulfate 5-epimerase; urunosyl C-5 epimerase; chondroitin D-glucuronosyl 5-epimerase
Systematic name: chondroitin-D-glucuronate 5-epimerase
Comments: Not identical with EC 5.1.3.17 heparosan-*N*-sulfate-glucuronate 5-epimerase.
References: [364]

[EC 5.1.3.19 created 1986]

EC 5.1.3.20
Accepted name: ADP-*glyceromanno*-heptose 6-epimerase
Reaction: ADP-D-*glycero*-D-*manno*-heptose = ADP-L-*glycero*-D-*manno*-heptose
Systematic name: ADP-L-*glycero*-D-*manno*-heptose 6-epimerase
Comments: Requires NAD^+.
References: [136, 468]

[EC 5.1.3.20 created 1999]

EC 5.1.3.21
Accepted name: maltose epimerase
Reaction: α-maltose = β-maltose
Systematic name: maltose 1-epimerase
Comments: The enzyme catalyses the interconversion of α and β anomers of maltose more effectively than those of disaccharides such as lactose and cellobiose.
References: [530]

[EC 5.1.3.21 created 2002]

EC 5.1.3.22
Accepted name: L-ribulose-5-phosphate 3-epimerase
Reaction: L-ribulose 5-phosphate = L-xylulose 5-phosphate
Other name(s): L-xylulose 5-phosphate 3-epimerase; UlaE; SgaU
Systematic name: L-ribulose-5-phosphate 3-epimerase
Comments: Along with EC 4.1.1.85, 3-dehydro-L-gulonate-6-phosphate decarboxylase, this enzyme is involved in a pathway for the utilization of L-ascorbate by *Escherichia coli*.
References: [657]

[EC 5.1.3.22 created 2005]

EC 5.1.3.23
Accepted name: UDP-2,3-diacetamido-2,3-dideoxyglucuronic acid 2-epimerase

Reaction: UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucuronate = UDP-2,3-diacetamido-2,3-dideoxy-α-D-mannuronate
Other name(s): UDP-GlcNAc3NAcA 2-epimerase; UDP-α-D-GlcNAc3NAcA 2-epimerase; 2,3-diacetamido-2,3-dideoxy-α-D-glucuronic acid 2-epimerase; WbpI; WlbD
Systematic name: 2,3-diacetamido-2,3-dideoxy-α-D-glucuronate 2-epimerase
Comments: This enzyme participates in the biosynthetic pathway for UDP-α-D-ManNAc3NAcA (UDP-2,3-diacetamido-2,3-dideoxy-α-D-mannuronic acid), an important precursor of the B-band lipopolysaccharide of *Pseudomonas aeroginosa* serotype O5 and of the band-A trisaccharide of *Bordetella pertussis*, both important respiratory pathogens [617]. The enzyme is highly specific as UDP-α-D-GlcNAc, UDP-α-D-GlcNAcA (UDP-2-acetamido-2-deoxy-α-D-glucuronic acid) and UDP-α-D-GlcNAc3NAc (UDP-2,3-diacetamido-2,3-dideoxy-α-D-glucose) cannot act as substrates [617].
References: [617, 616, 278]

[EC 5.1.3.23 created 2007]

EC 5.1.3.24
Accepted name: *N*-acetylneuraminate epimerase
Reaction: *N*-acetyl-α-neuraminate = *N*-acetyl-β-neuraminate
Other name(s): sialic acid epimerase; *N*-acetylneuraminate mutarotase; YjhT
Systematic name: *N*-acetyl-α-neuraminate 2-epimerase
Comments: Sialoglycoconjugates present in vertebrates are linked exclusively by α-linkages and are released in α form during degradation. This enzyme accelerates maturotation to the β form (which also occurs as a slow spontaneous reaction), which is necessary for further metabolism by the bacteria.
References: [518]

[EC 5.1.3.24 created 2011]

EC 5.1.3.25
Accepted name: dTDP-L-rhamnose 4-epimerase
Reaction: dTDP-6-deoxy-β-L-talose = dTDP-β-L-rhamnose
Other name(s): dTDP-4-L-rhamnose 4-epimerase; *wbiB* (gene name)
Systematic name: dTDP-6-deoxy-β-L-talose 4-epimerase
Comments: The equilibrium is strongly towards dTDP-β-L-rhamnose.
References: [658]

[EC 5.1.3.25 created 2012]

EC 5.1.3.26
Accepted name: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol 4-epimerase
Reaction: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol = *N*-acetyl-α-D-galactosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol
Other name(s): GlcNAc-P-P-Und epimerase; GlcNAc-P-P-Und 4-epimerase; *gne* (gene name)
Systematic name: *N*-acetyl-α-D-glucosaminyl-diphospho-*ditrans*,*octacis*-undecaprenol 4-epimerase
Comments: The enzyme is involved in biosynthesis of the repeating tetrasaccharide unit of the O-antigen produced by some Gram-negative bacteria.
References: [497]

[EC 5.1.3.26 created 2013]

EC 5.1.3.27
Accepted name: dTDP-4-dehydro-6-deoxy-D-glucose 3-epimerase
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucose = dTDP-4-dehydro-6-deoxy-α-D-gulose

Other name(s): dTDP-deoxyglucose 3-epimerase; dTDP-4-keto-6-deoxy-D-glucose 3-epimerase; dTDP-4-keto-6-deoxyglucose 3-epimerase; *gerF* (gene name); *tylJ* (gene name); *chmJ* (gene name); *mydH* (gene name)
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucose 3-epimerase
Comments: The enzyme is involved in the biosynthetic pathway of dTDP-6-deoxy-α-D-allose, which is converted to mycinose after attachment to the aglycones of several macrolide antibiotics, including tylosin, chalcomycin, dihydrochalcomycin, and mycinamicin II.
References: [542, 584, 316]

[EC 5.1.3.27 created 2013]

EC 5.1.3.28
Accepted name: UDP-*N*-acetyl-L-fucosamine synthase
Reaction: UDP-2-acetamido-2,6-dideoxy-β-L-talose = UDP-*N*-acetyl-β-L-fucosamine
Other name(s): WbjD; Cap5G
Systematic name: UDP-2-acetamido-2,6-dideoxy-β-L-talose 2-epimerase
Comments: Isolated from the bacteria *Pseudomonas aeruginosa* and *Staphylococcus aureus*. Involved in bacterial polysaccharide biosynthesis.
References: [305, 414]

[EC 5.1.3.28 created 2014]

EC 5.1.3.29
Accepted name: L-fucose mutarotase
Reaction: α-L-fucopyranose = β-L-fucopyranose
Other name(s): FucU; fucose mutarotase; FucM
Systematic name: L-fucose 1-epimerase
Comments: This enzyme shows no 1-epimerase activity with D-glucose, L-rhamnose and D-fucose (*cf.* EC 5.1.3.3, aldose 1-epimerase) [499].
References: [499, 447]

[EC 5.1.3.29 created 2014]

EC 5.1.3.30
Accepted name: D-psicose 3-epimerase
Reaction: D-psicose = D-fructose
Other name(s): D-allulose 3-epimerase; DPEase (ambiguous)
Systematic name: D-psicose 3-epimerase
Comments: The enzyme is highly specific for D-psicose and shows very low activity with D-tagatose (*cf.* EC 5.1.3.31, D-tagatose 3-epimerase). The enzyme from the bacterium *Clostridium scindens* requires Mn^{2+} [411], whereas the enzymes from the bacteria *Clostridium cellulolyticum* [79, 412], *Clostridium* sp. BNL1100 [689], and *Clostridium bolteae* [682] require Co^{2+} as optimum cofactor. The enzyme from *Ruminococcus* sp. [262] is not dependent on the presence of metal ions, but its activity is enhanced by Mn^{2+}.
References: [411, 79, 689, 682, 412, 262]

[EC 5.1.3.30 created 2014]

EC 5.1.3.31
Accepted name: D-tagatose 3-epimerase
Reaction: (1) D-tagatose = D-sorbose
(2) D-psicose = D-fructose
Other name(s): L-ribulose 3-epimerase; ketose 3-epimerase

Systematic name: D-tagatose 3-epimerase
Comments: The enzymes isolated from the bacteria *Pseudomonas cichorii* [660], *Pseudomonas* sp. ST-24 [253], *Rhodobacter sphaeroides* [680] and *Mesorhizobium loti* [594] catalyse the epimerization of various ketoses at the C-3 position, interconverting D-fructose and D-psicose, D-tagatose and D-sorbose, D-ribulose and D-xylulose, and L-ribulose and L-xylulose. The specificity depends on the species. The enzymes from *Pseudomonas cichorii* and *Rhodobacter sphaeroides* require Mn^{2+} [660, 680].
References: [253, 660, 680, 594]

[EC 5.1.3.31 created 2014]

EC 5.1.3.32
Accepted name: L-rhamnose mutarotase
Reaction: α-L-rhamnopyranose = β-L-rhamnopyranose
Other name(s): rhamnose 1-epimerase; type-3 mutarotase; YiiL
Systematic name: L-rhamnopyranose 1-epimerase
Comments: The enzyme is specific for L-rhamnopyranose.
References: [499, 500]

[EC 5.1.3.32 created 2014]

EC 5.1.3.33
Accepted name: 2-*epi*-5-*epi*-valiolone epimerase
Reaction: 2-*epi*-5-*epi*-valiolone = 5-*epi*-valiolone
Other name(s): CetB; EVE
Systematic name: 2-*epi*-5-*epi*-valiolone 2-epimerase
Comments: The enzyme, characterized from the bacterium *Actinomyces* sp. Lu 9419, is involved in the biosynthesis of the antitumor agent cetoniacytone A.
References: [643]

[EC 5.1.3.33 created 2015]

EC 5.1.3.34
Accepted name: monoglucosyldiacylglycerol epimerase
Reaction: a 1,2-diacyl-3-*O*-(β-D-glucopyranosyl)-*sn*-glycerol = a 1,2-diacyl-3-*O*-(β-D-galactopyranosyl)-*sn*-glycerol
Other name(s): glucolipid epimerase; *mgdE* (gene name)
Systematic name: 1,2-diacyl-3-*O*-(β-D-glucopyranosyl)-*sn*-glycerol 4-epimerase
Comments: The enzyme, characterized from cyanobacteria, is involves in the biosynthesis of galactolipids found in their photosynthetic membranes.
References: [504, 33]

[EC 5.1.3.34 created 2015]

EC 5.1.3.35
Accepted name: 2-*epi*-5-*epi*-valiolone 7-phosphate 2-epimerase
Reaction: 2-*epi*-5-*epi*-valiolone 7-phosphate = 5-*epi*-valiolone 7-phosphate
Other name(s): AcbO
Systematic name: 2-*epi*-5-*epi*-valiolone-7-phosphate 2-epimerase
Comments: The enzyme, isolated from the bacterium *Actinoplanes* sp. SE 50/110, is involved in the biosynthesis of the α-glucosidase inhibitor acarbose.
References: [676]

[EC 5.1.3.35 created 2015]

EC 5.1.3.36

Accepted name: heparosan-glucuronate 5-epimerase
Reaction: [heparosan]-D-glucuronate = [acharan]-L-iduronate
Other name(s): HG-5epi
Systematic name: [heparosan]-D-glucuronate 5-epimerase
Comments: The enzyme, characterized from the giant African snail *Achatina fulica*, participates in the biosynthetic pathway of acharan sulfate. Unlike EC 5.1.3.17, heparosan-*N*-sulfate-glucuronate 5-epimerase, it shows no activity with D-glucuronate residues in heparosan-*N*-sulfate.
References: [401]

[EC 5.1.3.36 created 2015]

EC 5.1.3.37

Accepted name: mannuronan 5-epimerase
Reaction: [mannuronan]-β-D-mannuronate = [alginate]-α-L-guluronate
Other name(s): *algG* (gene name); alginate epimerase; C^5-mannuronan epimerase; mannuronan C-5-epimerase
Systematic name: [mannuronan]-β-D-mannuronate 5-epimerase
Comments: The enzyme epimerizes the C-5 bond in some β-D-mannuronate residues in mannuronan, converting them to α-L-guluronate residues, and thus modifying the mannuronan into alginate. It is found in brown algae and alginate-producing bacterial species from the *Pseudomonas* and *Azotobacter* genera.
References: [166, 405, 435, 259, 139, 633]

[EC 5.1.3.37 created 2015]

EC 5.1.3.38

Accepted name: D-erythrulose 1-phosphate 3-epimerase
Reaction: D-erythrulose 1-phosphate = L-erythrulose 1-phosphate
Other name(s): *eryC* (gene name)
Systematic name: D-erythrulose-1-phosphate 3-epimerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [37]

[EC 5.1.3.38 created 2016]

[5.1.3.39 Deleted entry. L-erythrulose 4-phosphate epimerase. The activity has been shown not to take place.]

[EC 5.1.3.39 created 2016, deleted 2018]

EC 5.1.3.40

Accepted name: D-tagatose 6-phosphate 4-epimerase
Reaction: D-tagatose 6-phosphate = D-fructose 6-phosphate
Systematic name: D-tagatose 6-phosphate 4-epimerase
Comments: The enzyme from *Agrobacterium fabrum* C58 is part of D-altritol and galactitol degradation pathways.
References: [623]

[EC 5.1.3.40 created 2017]

EC 5.1.3.41

Accepted name: fructoselysine 3-epimerase
Reaction: N^6-(D-fructosyl)-L-lysine = N^6-(D-psicosyl)-L-lysine
Other name(s): *frlC* (gene name)
Systematic name: D-fructosyl-L-lysine 3-epimerase

Comments: The enzyme, characterized from the bacterium *Escherichia coli*, is involved in the catabolism of fructoseamines, amino acid sugar complexes that are formed non-enzymically.
References: [622]

[EC 5.1.3.41 created 2017]

EC 5.1.3.42
Accepted name: D-glucosamine-6-phosphate 4-epimerase
Reaction: D-glucosamine 6-phosphate = D-galactosamine 6-phosphate
Other name(s): ST2245 (locus name)
Systematic name: D-glucosamine 6-phosphate 4-epimerase
Comments: The enzyme, characterized from the archaeon *Sulfolobus tokodaii*, participates in a pathway for the biosynthesis of UDP-*N*-acetyl-α-D-galactosamine.
References: [117]

[EC 5.1.3.42 created 2018]

EC 5.1.99 Acting on other compounds

EC 5.1.99.1
Accepted name: methylmalonyl-CoA epimerase
Reaction: (*R*)-methylmalonyl-CoA = (*S*)-methylmalonyl-CoA
Other name(s): methylmalonyl-CoA racemase; methylmalonyl coenzyme A racemase; DL-methylmalonyl-CoA racemase; 2-methyl-3-oxopropanoyl-CoA 2-epimerase [incorrect]
Systematic name: methylmalonyl-CoA 2-epimerase
References: [384, 444]

[EC 5.1.99.1 created 1965, modified 1981]

EC 5.1.99.2
Accepted name: 16-hydroxysteroid epimerase
Reaction: 16α-hydroxysteroid = 16β-hydroxysteroid
Systematic name: 16-hydroxysteroid 16-epimerase
References: [119]

[EC 5.1.99.2 created 1972]

EC 5.1.99.3
Accepted name: allantoin racemase
Reaction: (*S*)(+)-allantoin = (*R*)(-)-allantoin
Systematic name: allantoin racemase
References: [602]

[EC 5.1.99.3 created 1976]

EC 5.1.99.4
Accepted name: α-methylacyl-CoA racemase
Reaction: (2*S*)-2-methylacyl-CoA = (2*R*)-2-methylacyl-CoA
Systematic name: 2-methylacyl-CoA 2-epimerase
Comments: α-methyl-branched acyl-CoA derivatives with chain lengths of more than C_{10} are substrates. Also active towards some aromatic compounds (e.g. ibuprofen) and bile acid intermediates, such as trihydroxycoprostanoyl-CoA. Not active towards free acids

References: [512]

[EC 5.1.99.4 created 1999]

EC 5.1.99.5

Accepted name: hydantoin racemase
Reaction: D-5-monosubstituted hydantoin = L-5-monosubstituted hydantoin
Other name(s): 5′-monosubstituted-hydantoin racemase; HyuA; HyuE
Systematic name: D-5-monosubstituted-hydantoin racemase
Comments: This enzyme, along with *N*-carbamoylase (EC 3.5.1.77 and EC 3.5.1.87) and hydantoinase, forms part of the reaction cascade known as the "hydantoinase process", which allows the total conversion of D,L-5-monosubstituted hydantoins into optically pure D- or L-amino acids [17]. The enzyme from *Pseudomonas* sp. (HyuE) has a preference for hydantoins with aliphatic substituents, e.g. D- and L-5-[2-(methylsulfanyl)ethyl]hydantoin, whereas that from *Arthrobacter aurescens* shows highest activity with arylalkyl substituents, especially 5-benzylhydantoin, at the 5-position [624]. In the enzyme from *Sinorhizobium meliloti*, Cys^{76} is responsible for recognition and proton retrieval of D-isomers, while Cys^{181} is responsible for L-isomer recognition and racemization [375].
References: [614, 624, 377, 376, 568, 375, 17]

[EC 5.1.99.5 created 2008]

EC 5.1.99.6

Accepted name: NAD(P)H-hydrate epimerase
Reaction: (1) (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide = (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide
(2) (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate = (6*S*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide phosphate
Other name(s): NAD(P)HX epimerase
Systematic name: (6*R*)-6β-hydroxy-1,4,5,6-tetrahydronicotinamide-adenine dinucleotide 6-epimerase
Comments: The enzyme can use either (*R*)-NADH-hydrate or (*R*)-NADPH-hydrate as a substrate. Its physiological role is to convert the (*R*) forms to the (*S*) forms, which could then be restored to active dinucleotides by EC 4.2.1.93, ATP-dependent NAD(P)H-hydrate dehydratase.
References: [366]

[EC 5.1.99.6 created 2012]

EC 5.1.99.7

Accepted name: dihydroneopterin triphosphate 2′-epimerase
Reaction: 7,8-dihydroneopterin 3′-triphosphate = 7,8-dihydromonapterin 3′-triphosphate
Other name(s): D-*erythro*-7,8-dihydroneopterin triphosphate epimerase; *folX* (gene name)
Systematic name: 7,8-dihydroneopterin 3′-triphosphate 2′-epimerase
Comments: The enzyme, found in gammaproteobacteria, has almost no activity with 7,8-dihydroneopterin [214].
References: [10, 214]

[EC 5.1.99.7 created 2015]

EC 5.1.99.8

Accepted name: 7,8-dihydroneopterin epimerase
Reaction: 7,8-dihydroneopterin = 7,8-dihydromonapterin
Systematic name: 7,8-dihydroneopterin 2′-epimerase
Comments: The enzyme, which has been characterized in bacteria and plants, also has the activity of EC 4.1.2.25, dihydroneopterin aldolase. The enzyme from the bacterium *Mycobacterium tuberculosis* has an additional oxygenase function (EC 1.13.11.81, 7,8-dihydroneopterin oxygenase) [57].
References: [214, 192, 116, 57]

[EC 5.1.99.8 created 2015]

EC 5.2 *cis-trans*-Isomerases

This subclass contains a single sub-subclass for enzymes that rearrange the geometry at double bonds (*cis-trans* isomerases; EC 5.2.1).

EC 5.2.1 *cis-trans* Isomerases (only sub-subclass identified to date)

EC 5.2.1.1
Accepted name: maleate isomerase
Reaction: maleate = fumarate
Systematic name: maleate *cis-trans*-isomerase
References: [48]

[EC 5.2.1.1 created 1961]

EC 5.2.1.2
Accepted name: maleylacetoacetate isomerase
Reaction: 4-maleylacetoacetate = 4-fumarylacetoacetate
Other name(s): maleylacetoacetic isomerase; maleylacetone isomerase; maleylacetone *cis-trans*-isomerase
Systematic name: 4-maleylacetoacetate *cis-trans*-isomerase
Comments: Also acts on maleylpyruvate.
References: [142, 326, 517]

[EC 5.2.1.2 created 1961]

[5.2.1.3 Deleted entry. retinal isomerase. Now known to be catalysed by a pathway involving EC 1.1.1.300, NADP-retinol dehydrogenase; EC 2.3.1.135, phosphatidylcholineretinol O-acyltransferase; EC 3.1.1.64, retinoid isomerohydrolase; and EC 1.1.1.315, 11-cis-retinol dehydrogenase.]

[EC 5.2.1.3 created 1961, modified 1976, deleted 2011]

EC 5.2.1.4
Accepted name: maleylpyruvate isomerase
Reaction: 3-maleylpyruvate = 3-fumarylpyruvate
Systematic name: 3-maleylpyruvate *cis-trans*-isomerase
References: [326]

[EC 5.2.1.4 created 1965]

EC 5.2.1.5
Accepted name: linoleate isomerase
Reaction: 9-*cis*,12-*cis*-octadecadienoate = 9-*cis*,11-*trans*-octadecadienoate
Other name(s): linoleic acid isomerase
Systematic name: linoleate Δ^{12}-*cis*-Δ^{11}-*trans*-isomerase
References: [295]

[EC 5.2.1.5 created 1972]

EC 5.2.1.6

Accepted name: furylfuramide isomerase
Reaction: (*E*)-2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide = (*Z*)-2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide
Systematic name: 2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide *cis-trans*-isomerase
Comments: Requires NADH.
References: [586]

[EC 5.2.1.6 created 1978]

[5.2.1.7 Transferred entry. retinol isomerase. Transferred to EC 3.1.1.64, retinoid isomerohydrolase.]

[EC 5.2.1.7 created 1989, deleted 2011]

EC 5.2.1.8
Accepted name: peptidylprolyl isomerase
Reaction: peptidylproline (ω=180) = peptidylproline (ω=0)
Other name(s): PPIase; cyclophilin [misleading, see comments]; peptide bond isomerase; peptidyl-prolyl *cis-trans* isomerase
Systematic name: peptidylproline *cis-trans*-isomerase
Comments: The first type of this enzyme found [161] proved to be the protein cyclophilin, which binds the immunosuppressant cyclosporin A. Other distinct families of the enzyme exist, one being FK-506 binding proteins (FKBP) and another that includes parvulin from *Escherichia coli*. The three families are structurally unrelated and can be distinguished by being inhibited by cyclosporin A, FK-506 and 5-hydroxy-1,4-naphthoquinone, respectively.
References: [161, 162, 163, 569, 224, 160, 210, 145]

[EC 5.2.1.8 created 1989, modified 2002]

EC 5.2.1.9
Accepted name: farnesol 2-isomerase
Reaction: (2*E*,6*E*)-farnesol = (2*Z*,6*E*)-farnesol
Other name(s): farnesol isomerase
Systematic name: (2*E*,6*E*)-farnesol 2-*cis-trans*-isomerase
References: [19]

[EC 5.2.1.9 created 1989]

EC 5.2.1.10
Accepted name: 2-chloro-4-carboxymethylenebut-2-en-1,4-olide isomerase
Reaction: *cis*-2-chloro-4-carboxymethylenebut-2-en-1,4-olide = *trans*-2-chloro-4-carboxymethylenebut-2-en-1,4-olide
Other name(s): 2-chlorocarboxymethylenebutenolide isomerase; chlorodienelactone isomerase
Systematic name: 2-chloro-4-carboxymethylenebut-2-en-1,4-olide *cis-trans*-isomerase
References: [513]

[EC 5.2.1.10 created 1992]

[5.2.1.11 Deleted entry. 4-hydroxyphenylacetaldehyde-oxime isomerase. The existence of this enzyme has been called into question by one of the authors of the reference cited]

[EC 5.2.1.11 created 1992, deleted 2005]

EC 5.2.1.12
Accepted name: ζ-carotene isomerase
Reaction: 9,15,9′-*tricis*-ζ-carotene = 9,9′-*dicis*-ζ-carotene

Other name(s): Z-ISO; 15-*cis*-ζ-carotene isomerase
Systematic name: 9,15,9′-*tricis*-ζ-carotene *cis-trans*-isomerase
Comments: The enzyme catalyses the *cis-trans* isomerization of the 15-15′ carbon-carbon double bond in 9,15,9′-*tricis*-ζ-carotene, which is required for biosynthesis of all plant carotenoids. Requires heme *b*.
References: [91, 341, 49]

[EC 5.2.1.12 created 2011]

EC 5.2.1.13
Accepted name: prolycopene isomerase
Reaction: 7,9,7′,9′-*tetracis*-lycopene = *all-trans*-lycopene
Other name(s): CRTISO; carotene *cis-trans* isomerase; ZEBRA2 (gene name); carotene isomerase; carotenoid isomerase
Systematic name: 7,9,7′,9′-*tetracis*-lycopene *cis-trans*-isomerase
Comments: Requires $FADH_2$ [666]. The enzyme is involved in carotenoid biosynthesis.
References: [666, 342, 249, 77]

[EC 5.2.1.13 created 2011]

EC 5.2.1.14
Accepted name: β-carotene isomerase
Reaction: *all-trans*-β-carotene = 9-*cis*-β-carotene
Other name(s): DWARF27 (gene name)
Systematic name: β-carotene 9-*cis*-*all-trans* isomerase
Comments: The enzyme participates in a pathway leading to biosynthesis of strigolactones, plant hormones involved in promotion of symbiotic associations known as arbuscular mycorrhiza.
References: [348, 13]

[EC 5.2.1.14 created 2012]

EC 5.3 Intramolecular oxidoreductases

These enzymes bring about the oxidation of one part of a molecule with a corresponding reduction of another part. They include the enzymes interconverting, in the sugar series, aldoses and ketoses, and related compounds (sugar isomerases, EC 5.3.1), enzymes catalysing a keto-enol equilibrium (tautomerases, EC 5.3.2), enzymes shifting a carbon-carbon double bond from one position to another (EC 5.3.3), enzymes transposing S-S bonds (EC 5.3.4), and a group of miscellaneous enzymes (EC 5.3.99).

EC 5.3.1 Interconverting aldoses and ketoses, and related compounds

EC 5.3.1.1
Accepted name: triose-phosphate isomerase
Reaction: D-glyceraldehyde 3-phosphate = glycerone phosphate
Other name(s): phosphotriose isomerase; triose phosphoisomerase; triose phosphate mutase; D-glyceraldehyde-3-phosphate ketol-isomerase
Systematic name: D-glyceraldehyde-3-phosphate aldose-ketose-isomerase
References: [397, 398]

[EC 5.3.1.1 created 1961]

[5.3.1.2 Deleted entry. erythrose isomerase]

[EC 5.3.1.2 created 1961, deleted 1976]

EC 5.3.1.3

Accepted name: D-arabinose isomerase
Reaction: D-arabinose = D-ribulose
Other name(s): D-arabinose(L-fucose) isomerase; L-fucose isomerase; D-arabinose ketol-isomerase; arabinose isomerase (misleading)
Systematic name: D-arabinose aldose-ketose-isomerase
Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}). The enzyme binds the closed form of the sugar and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [514]. The enzyme catalyses the aldose-ketose isomerization of several sugars. Most enzymes also catalyse the reaction of EC 5.3.1.25, L-fucose isomerase [514]. The enzyme from the bacterium *Falsibacillus pallidus* also converts D-altrose to D-psicose [570]. *cf.* EC 5.3.1.4, L-arabinose isomerase.
References: [94, 194, 514, 570]

[EC 5.3.1.3 created 1961, modified 2013]

EC 5.3.1.4

Accepted name: L-arabinose isomerase
Reaction: L-arabinose = L-ribulose
Other name(s): L-arabinose ketol-isomerase; *araA* (gene name)
Systematic name: L-arabinose aldose-ketose-isomerase
Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}) [453]. The enzyme binds the closed form of the sugar and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [35]. The enzyme can also convert D-galactose to D-tagatose with lower efficiency [85].
References: [220, 453, 423, 85, 35, 365]

[EC 5.3.1.4 created 1961]

EC 5.3.1.5

Accepted name: xylose isomerase
Reaction: D-xylopyranose = D-xylulose
Other name(s): D-xylose isomerase; D-xylose ketoisomerase; D-xylose ketol-isomerase
Systematic name: D-xylose aldose-ketose-isomerase
Comments: Contains two divalent metal ions, preferably magnesium, located at different metal-binding sites within the active site. The enzyme catalyses the interconversion of aldose and ketose sugars with broad substrate specificity. The enzyme binds the closed form of its sugar substrate (in the case of glucose, only the α anomer) and catalyses ring opening to generate a form of open-chain conformation that is coordinated to one of the metal sites. Isomerization proceeds via a hydride-shift mechanism.
References: [230, 539, 652, 76, 95, 618, 16]

[EC 5.3.1.5 created 1961 (EC 5.3.1.18 created 1972, part incorporated 1978)]

EC 5.3.1.6

Accepted name: ribose-5-phosphate isomerase
Reaction: D-ribose 5-phosphate = D-ribulose 5-phosphate
Other name(s): phosphopentosisomerase; phosphoriboisomerase; ribose phosphate isomerase; 5-phosphoribose isomerase; D-ribose 5-phosphate isomerase; D-ribose-5-phosphate ketol-isomerase
Systematic name: D-ribose-5-phosphate aldose-ketose-isomerase
Comments: Also acts on D-ribose 5-diphosphate and D-ribose 5-triphosphate.
References: [133, 232, 245]

[EC 5.3.1.6 created 1961]

EC 5.3.1.7

Accepted name: mannose isomerase
Reaction: D-mannose = D-fructose
Other name(s): D-mannose isomerase; D-mannose ketol-isomerase
Systematic name: D-mannose aldose-ketose-isomerase
Comments: Also acts on D-lyxose and D-rhamnose.
References: [445]

[EC 5.3.1.7 created 1961]

EC 5.3.1.8

Accepted name: mannose-6-phosphate isomerase
Reaction: D-mannose 6-phosphate = D-fructose 6-phosphate
Other name(s): phosphomannose isomerase; phosphohexomutase; phosphohexoisomerase; mannose phosphate isomerase; phosphomannoisomerase; D-mannose-6-phosphate ketol-isomerase
Systematic name: D-mannose-6-phosphate aldose-ketose-isomerase
Comments: A zinc protein.
References: [70, 193, 538]

[EC 5.3.1.8 created 1961, modified 1976]

EC 5.3.1.9

Accepted name: glucose-6-phosphate isomerase
Reaction: D-glucose 6-phosphate = D-fructose 6-phosphate
Other name(s): phosphohexose isomerase; phosphohexomutase; oxoisomerase; hexosephosphate isomerase; phosphosaccharomutase; phosphoglucoisomerase; phosphohexoisomerase; phosphoglucose isomerase; glucose phosphate isomerase; hexose phosphate isomerase; D-glucose-6-phosphate ketol-isomerase
Systematic name: D-glucose-6-phosphate aldose-ketose-isomerase
Comments: Also catalyses the anomerization of D-glucose 6-phosphate.
References: [34, 422, 430, 431, 471, 590]

[EC 5.3.1.9 created 1961, modified 1976 (EC 5.3.1.18 created part 1972, incorporated 1978)]

[5.3.1.10 Transferred entry. glucosamine-6-phosphate isomerase. Now EC 3.5.99.6, glucosamine-6-phosphate deaminase]

[EC 5.3.1.10 created 1961, deleted 2000]

[5.3.1.11 Deleted entry. acetylglucosaminephosphate isomerase]

[EC 5.3.1.11 created 1961, deleted 1978]

EC 5.3.1.12

Accepted name: glucuronate isomerase
Reaction: D-glucuronate = D-fructuronate
Other name(s): uronic isomerase; uronate isomerase; D-glucuronate isomerase; uronic acid isomerase; D-glucuronate ketol-isomerase
Systematic name: D-glucuronate aldose-ketose-isomerase
Comments: Also converts D-galacturonate to D-tagaturonate.
References: [32, 296]

[EC 5.3.1.12 created 1961]

EC 5.3.1.13

Accepted name: arabinose-5-phosphate isomerase
Reaction: D-arabinose 5-phosphate = D-ribulose 5-phosphate
Other name(s): *kdsD* (gene name); *gutQ* (gene name); arabinose phosphate isomerase; phosphoarabinoisomerase; D-arabinose-5-phosphate ketol-isomerase
Systematic name: D-arabinose-5-phosphate aldose-ketose-isomerase
Comments: The enzyme is involved in the pathway for synthesis of 3-deoxy-D-*manno*-octulosonate (Kdo), a component of bacterial lipopolysaccharides and plant call walls.
References: [606, 347, 394, 191, 92]

[EC 5.3.1.13 created 1965]

EC 5.3.1.14

Accepted name: L-rhamnose isomerase
Reaction: L-rhamnopyranose = L-rhamnulose
Other name(s): rhamnose isomerase; L-rhamnose ketol-isomerase
Systematic name: L-rhamnose aldose-ketose-isomerase
Comments: Contains two divalent metal ions located at different metal-binding sites within the active site. The enzyme binds the closed ring form of the substrate and catalyses ring opening to generate a form of open-chain conformation that is coordinated to one of the metal sites. Isomerization proceeds via a hydride-shift mechanism. While the enzyme from the bacterium *Escherichia coli* is specific for L-rhamnose, the enzyme from the bacterium *Pseudomonas stutzeri* has broad substrate specificity and catalyses the interconversion of L-mannose and L-fructose, L-lyxose and L-xylulose, D-ribose and D-ribulose, and D-allose and D-psicose [330].
References: [137, 330, 313, 661]

[EC 5.3.1.14 created 1965]

EC 5.3.1.15

Accepted name: D-lyxose ketol-isomerase
Reaction: D-lyxose = D-xylulose
Other name(s): D-lyxose isomerase; D-lyxose ketol-isomerase
Systematic name: D-lyxose aldose-ketose-isomerase
References: [21]

[EC 5.3.1.15 created 1972]

EC 5.3.1.16

Accepted name: 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide isomerase
Reaction: 1-(5-phospho-β-D-ribosyl)-5-[(5-phospho-β-D-ribosylamino)methylideneamino]imidazole-4-carboxamide = 5-[(5-phospho-1-deoxy-D-ribulos-1-ylamino)methylideneamino]-1-(5-phospho-β-D-ribosyl)imidazole-4-carboxamide
Other name(s): *N*-(5′-phospho-D-ribosylformimino)-5-amino-1-(5″-phosphoribosyl)-4-imidazolecarboxamide isomerase; phosphoribosylformiminoaminophosphoribosylimidazolecarboxamide isomerase; *N*-(phosphoribosylformimino) aminophosphoribosylimidazolecarboxamide isomerase; 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide ketol-isomerase; 1-(5-phosphoribosyl)-5-[(5-phosphoribosylamino)methylideneamino]imidazole-4-carboxamide aldose-ketose-isomerase
Systematic name: 1-(5-phospho-β-D-ribosyl)-5-[(5-phospho-β-D-ribosylamino)methylideneamino]imidazole-4-carboxamide aldose-ketose-isomerase
Comments: Involved in histidine biosynthesis.
References: [368]

[EC 5.3.1.16 created 1972, modified 2000]

EC 5.3.1.17

Accepted name: 5-dehydro-4-deoxy-D-glucuronate isomerase
Reaction: 5-dehydro-4-deoxy-D-glucuronate = 3-deoxy-D-*glycero*-2,5-hexodiulosonate
Other name(s): 4-deoxy-L-*threo*-5-hexulose uronate isomerase; 4-deoxy-L-*threo*-5-hexosulose-uronate ketol-isomerase; *kduI* (gene name)
Systematic name: 5-dehydro-4-deoxy-D-glucuronate aldose-ketose-isomerase
Comments: The enzyme is involved in the degradation of polygalacturonate, a later stage in the degradation of pectin by many microorganisms.
References: [466, 96, 140, 112]

[EC 5.3.1.17 created 1972, modified 2012]

[5.3.1.18 Deleted entry. glucose isomerase. Reaction is due to EC 5.3.1.9 glucose-6-phosphate isomerase, in the presence of arsenate, or EC 5.3.1.5 xylose isomerase]

[EC 5.3.1.18 created 1972, deleted 1978]

[5.3.1.19 Transferred entry. glucosaminephosphate isomerase. Now EC 2.6.1.16, glutamine—fructose-6-phosphate transaminase (isomerizing)]

[EC 5.3.1.19 created 1972, deleted 1984]

EC 5.3.1.20

Accepted name: ribose isomerase
Reaction: D-ribose = D-ribulose
Other name(s): D-ribose isomerase; D-ribose ketol-isomerase
Systematic name: D-ribose aldose-ketose-isomerase
Comments: Also acts on L-lyxose and L-rhamnose.
References: [255]

[EC 5.3.1.20 created 1978]

EC 5.3.1.21

Accepted name: corticosteroid side-chain-isomerase
Reaction: 11-deoxycorticosterone = 20-hydroxy-3-oxopregn-4-en-21-al
Systematic name: 11-deoxycorticosterone aldose-ketose-isomerase
Comments: An epimerization at C-20 and C-21 is probably catalysed by the same enzyme.
References: [373, 403]

[EC 5.3.1.21 created 1983]

EC 5.3.1.22

Accepted name: hydroxypyruvate isomerase
Reaction: hydroxypyruvate = 2-hydroxy-3-oxopropanoate
Systematic name: hydroxypyruvate aldose-ketose-isomerase
References: [628]

[EC 5.3.1.22 created 1983]

EC 5.3.1.23

Accepted name: *S*-methyl-5-thioribose-1-phosphate isomerase
Reaction: *S*-methyl-5-thio-α-D-ribose 1-phosphate = *S*-methyl-5-thio-D-ribulose 1-phosphate

Other name(s): methylthioribose 1-phosphate isomerase; 1-PMTR isomerase; 5-methylthio-5-deoxy-D-ribose-1-phosphate ketol-isomerase; *S*-methyl-5-thio-5-deoxy-D-ribose-1-phosphate ketol-isomerase; *S*-methyl-5-thio-5-deoxy-D-ribose-1-phosphate aldose-ketose-isomerase; 1-phospho-5′-*S*-methylthioribose isomerase; *S*-methyl-5-thio-D-ribose-1-phosphate aldose-ketose-isomerase
Systematic name: *S*-methyl-5-thio-α-D-ribose-1-phosphate aldose-ketose-isomerase
References: [181, 588, 173]

[EC 5.3.1.23 created 1989]

EC 5.3.1.24

Accepted name: phosphoribosylanthranilate isomerase
Reaction: *N*-(5-phospho-β-D-ribosyl)anthranilate = 1-(2-carboxyphenylamino)-1-deoxy-D-ribulose 5-phosphate
Other name(s): PRA isomerase; PRAI; IGPS:PRAI (indole-3-glycerol-phosphate synthetase/*N*-5′-phosphoribosylanthranilate isomerase complex); *N*-(5-phospho-β-D-ribosyl)anthranilate ketol-isomerase
Systematic name: *N*-(5-phospho-β-D-ribosyl)anthranilate aldose-ketose-isomerase
Comments: In some organisms, this enzyme is part of a multifunctional protein, together with one or more other components of the system for the biosynthesis of tryptophan [EC 2.4.2.18 (anthranilate phosphoribosyltransferase), EC 4.1.1.48 (indole-3-glycerol-phosphate synthase), EC 4.1.3.27 (anthranilate synthase) and EC 4.2.1.20 (tryptophan synthase)].
References: [64, 103, 247]

[EC 5.3.1.24 created 1990]

EC 5.3.1.25

Accepted name: L-fucose isomerase
Reaction: L-fucopyranose = L-fuculose
Systematic name: L-fucose aldose-ketose-isomerase
Comments: Requires a divalent metal ion (the enzyme from the bacterium *Escherichia coli* prefers Mn^{2+}). The enzyme binds the closed form of the sugar and catalyses ring opening to generate a form of open-chain conformation that facilitates the isomerization reaction, which proceeds via an ene-diol mechanism [514]. The enzyme from *Escherichia coli* can also convert D-arabinose to D-ribulose [194]. The enzyme from the thermophilic bacterium *Caldicellulosiruptor saccharolyticus* also converts D-altrose to D-psicose and L-galactose to L-tagatose [270].
References: [194, 357, 514, 270]

[EC 5.3.1.25 created 1999]

EC 5.3.1.26

Accepted name: galactose-6-phosphate isomerase
Reaction: D-galactose 6-phosphate = D-tagatose 6-phosphate
Systematic name: D-galactose-6-phosphate aldose-ketose-isomerase
Comments: Involved in the tagatose 6-phosphate pathway of lactose catabolism in bacteria.
References: [607, 493]

[EC 5.3.1.26 created 1999]

EC 5.3.1.27

Accepted name: 6-phospho-3-hexuloisomerase
Reaction: D-*arabino*-hex-3-ulose 6-phosphate = D-fructose 6-phosphate
Other name(s): 3-hexulose-6-phosphate isomerase; phospho-3-hexuloisomerase; PHI; 6-phospho-3-hexulose isomerase; YckF
Systematic name: D-*arabino*-hex-3-ulose-6-phosphate isomerase

Comments: This enzyme, along with EC 4.1.2.43, 3-hexulose-6-phosphate synthase, plays a key role in the ribulose-monophosphate cycle of formaldehyde fixation, which is present in many microorganisms that are capable of utilizing C1-compounds [156]. The hyperthermophilic and anaerobic archaeon *Pyrococcus horikoshii* OT3 constitutively produces a bifunctional enzyme that sequentially catalyses the reactions of EC 4.1.2.43 (3-hexulose-6-phosphate synthase) and this enzyme [439].
References: [156, 673, 283, 439, 374, 575]

[EC 5.3.1.27 created 2008]

EC 5.3.1.28
Accepted name: D-sedoheptulose 7-phosphate isomerase
Reaction: D-sedoheptulose 7-phosphate = D-*glycero*-D-*manno*-heptose 7-phosphate
Other name(s): sedoheptulose-7-phosphate isomerase; phosphoheptose isomerase; *gmhA* (gene name); *lpcA* (gene name)
Systematic name: D-*glycero*-D-*manno*-heptose 7-phosphate aldose-ketose-isomerase
Comments: In Gram-negative bacteria the enzyme is involved in biosynthesis of ADP-L-*glycero*-β-D-*manno*-heptose, which is utilized for assembly of the lipopolysaccharide inner core. In Gram-positive bacteria the enzyme is involved in biosynthesis of GDP-D-*glycero*-α-D-*manno*-heptose, which is required for assembly of S-layer glycoprotein.
References: [304, 303, 601, 297, 577]

[EC 5.3.1.28 created 2010]

EC 5.3.1.29
Accepted name: ribose 1,5-bisphosphate isomerase
Reaction: α-D-ribose 1,5-bisphosphate = D-ribulose 1,5-bisphosphate
Other name(s): R15P isomerase; ribulose 1,5-bisphosphate synthase; RuBP synthase
Systematic name: α-D-ribose 1,5-bisphosphate aldose-ketose-isomerase
Comments: This archaeal enzyme is involved in AMP metabolism and CO_2 fixation through type III RubisCO enzymes. The enzyme is activated by cAMP [27].
References: [505, 27, 424]

[EC 5.3.1.29 created 2013]

EC 5.3.1.30
Accepted name: 5-deoxy-glucuronate isomerase
Reaction: 5-deoxy-D-glucuronate = 5-dehydro-2-deoxy-D-gluconate
Other name(s): 5DG isomerase; IolB
Systematic name: 5-deoxy-D-glucuronate aldose-ketose-isomerase
Comments: The enzyme, found in the bacterium *Bacillus subtilis*, is part of a *myo*-inositol degradation pathway leading to acetyl-CoA.
References: [663]

[EC 5.3.1.30 created 2014]

EC 5.3.1.31
Accepted name: sulfoquinovose isomerase
Reaction: sulfoquinovose = 6-deoxy-6-sulfo-D-fructose
Other name(s): *yihS* (gene name)
Systematic name: 6-deoxy-6-sulfo-D-glucopyranose aldose-ketose-isomerase
Comments: The enzyme, characterized from the bacterium *Escherichia coli*, is involved in the degradation pathway of sulfoquinovose, the polar headgroup of sulfolipids found in the photosynthetic membranes of all higher plants, mosses, ferns, algae, and most photosynthetic bacteria, as well as the surface layer of some archaea.

References: [127]

[EC 5.3.1.31 created 2014]

EC 5.3.1.32

Accepted name: (4*S*)-4-hydroxy-5-phosphonooxypentane-2,3-dione isomerase
Reaction: (4*S*)-4-hydroxy-5-phosphooxypentane-2,3-dione = 3-hydroxy-5-phosphooxypentane-2,4-dione
Other name(s): *lsrG* (gene name); phospho-AI-2 isomerase; (4*S*)-4-hydroxy-5-phosphonooxypentane-2,3-dione aldose-ketose-isomerase
Systematic name: (4*S*)-4-hydroxy-5-phosphooxypentane-2,3-dione aldose-ketose-isomerase
Comments: The enzyme participates in a degradation pathway of the bacterial quorum-sensing autoinducer molecule AI-2.
References: [645, 370]

[EC 5.3.1.32 created 2015]

EC 5.3.1.33

Accepted name: L-erythrulose 1-phosphate isomerase
Reaction: L-erythrulose 1-phosphate = D-erythrulose 4-phosphate
Other name(s): *eryH* (gene name)
Systematic name: L-erythrulose-1-phosphate isomerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [37]

[EC 5.3.1.33 created 2016]

EC 5.3.1.34

Accepted name: D-erythrulose 4-phosphate isomerase
Reaction: D-erythrulose 4-phosphate = D-erythrose 4-phosphate
Other name(s): *eryI* (gene name)
Systematic name: D-erythrulose-4-phosphate ketose-aldose isomerase
Comments: The enzyme, characterized from the pathogenic bacterium *Brucella abortus*, which causes brucellosis in livestock, participates in erythritol catabolism.
References: [37]

[EC 5.3.1.34 created 2016]

EC 5.3.1.35

Accepted name: 2-dehydrotetronate isomerase
Reaction: (1) 2-dehydro-L-erythronate = 3-dehydro-L-erythronate
(2) 2-dehydro-D-erythronate = 3-dehydro-D-erythronate
Other name(s): *otnI* (gene name)
Systematic name: 2-dehydrotetronate isomerase
Comments: The enzyme, characterized from bacteria, is involved in D-erythronate and L-threonate catabolism.
References: [683]

[EC 5.3.1.35 created 2017]

EC 5.3.2 Interconverting keto- and enol-groups

EC 5.3.2.1

Accepted name: phenylpyruvate tautomerase
Reaction: *keto*-phenylpyruvate = *enol*-phenylpyruvate
Other name(s): phenylpyruvic keto-enol isomerase
Systematic name: phenylpyruvate *keto—enol*-isomerase
Comments: Also acts on other arylpyruvates.
References: [56, 306, 307]

[EC 5.3.2.1 created 1961]

EC 5.3.2.2

Accepted name: oxaloacetate tautomerase
Reaction: *keto*-oxaloacetate = *enol*-oxaloacetate
Other name(s): oxalacetic keto-enol isomerase
Systematic name: oxaloacetate *keto—enol*-isomerase
References: [23]

[EC 5.3.2.2 created 1972]

EC 5.3.2.3

Accepted name: TDP-4-oxo-6-deoxy-α-D-glucose-3,4-oxoisomerase (dTDP-3-dehydro-6-deoxy-α-D-galactopyranose-forming)
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-3-dehydro-6-deoxy-α-D-galactopyranose
Other name(s): dTDP-6-deoxy-hex-4-ulose isomerase; TDP-6-deoxy-hex-4-ulose isomerase; FdtA
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose:dTDP-3-dehydro-6-deoxy-α-D-galactopyranose isomerase
Comments: The enzyme is involved in the biosynthesis of dTDP-3-acetamido-3,6-dideoxy-α-D-galactose. Four moieties of α-D-rhamnose and two moities of 3-acetamido-3,6-dideoxy-α-D-galactose form the repeating unit of the glycan chain in the S-layer of the bacterium *Aneurinibacillus thermoaerophilus*.
References: [461, 124]

[EC 5.3.2.3 created 2011]

EC 5.3.2.4

Accepted name: TDP-4-oxo-6-deoxy-α-D-glucose-3,4-oxoisomerase (dTDP-3-dehydro-6-deoxy-α-D-glucopyranose-forming)
Reaction: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose = dTDP-3-dehydro-6-deoxy-α-D-glucopyranose
Other name(s): TDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase (ambiguous); Tyl1a; dTDP-4-keto-6-deoxy-D-glucose-3,4-ketoisomerase (ambiguous)
Systematic name: dTDP-4-dehydro-6-deoxy-α-D-glucopyranose:dTDP-3-dehydro-6-deoxy-α-D-glucopyranose isomerase
Comments: The enzyme is involved in biosynthesis of D-mycaminose.
References: [390]

[EC 5.3.2.4 created 2011]

EC 5.3.2.5

Accepted name: 2,3-diketo-5-methylthiopentyl-1-phosphate enolase
Reaction: 5-(methylsulfanyl)-2,3-dioxopentyl phosphate = 2-hydroxy-5-(methylsulfanyl)-3-oxopent-1-enyl phosphate
Other name(s): DK-MTP-1-*P* enolase; MtnW; YkrW; RuBisCO-like protein; RLP; 2,3-diketo-5-methylthiopentyl-1-phosphate *keto—enol*-isomerase
Systematic name: 5-(methylsulfanyl)-2,3-dioxopentyl phosphate *keto—enol*-isomerase

Comments: The enzyme participates in the methionine salvage pathway in *Bacillus subtilis* [30].In some species a single bifunctional enzyme, EC 3.1.3.77, acireductone synthase, catalyses both this reaction and EC 3.1.3.87, 2-hydroxy-3-keto-5-methylthiopentenyl-1-phosphate phosphatase [417].
References: [417, 30]

[EC 5.3.2.5 created 2012]

EC 5.3.2.6
Accepted name: 2-hydroxymuconate tautomerase
Reaction: (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate = (3*E*)-2-oxohex-3-enedioate
Other name(s): 4-oxalocrotonate tautomerase (misleading); 4-oxalocrotonate isomerase (misleading); *cnbG* (gene name); *praC* (gene name); *xylH* (gene name)
Systematic name: (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate *keto—enol* isomerase
Comments: Involved in the *meta*-cleavage pathway for the degradation of phenols, modified phenols and catechols. The enol form (2*Z*,4*E*)-2-hydroxyhexa-2,4-dienedioate is produced as part of this pathway and is converted to the keto form (3*E*)-2-oxohex-3-enedioate by the enzyme [280]. Another keto form, (4*E*)-2-oxohex-4-enedioate (4-oxalocrotonate), was originally thought to be produced by the enzyme [619, 620] but later shown to be produced non-enzymically [610].
References: [619, 620, 560, 553, 610, 280]

[EC 5.3.2.6 created 2012]

EC 5.3.2.7
Accepted name: ascopyrone tautomerase
Reaction: 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose = 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose
Other name(s): ascopyrone isomerase; ascopyrone intramolecular oxidoreductase; 1,5-anhydro-D-*glycero*-hex-3-en-2-ulose tautomerase; APM tautomerase; ascopyrone P tautomerase; APTM
Systematic name: 1,5-anhydro-4-deoxy-D-*glycero*-hex-3-en-2-ulose Δ^3-Δ^1-isomerase
Comments: This enzyme catalyses one of the steps in the anhydrofructose pathway, which leads to the degradation of glycogen and starch via 1,5-anhydro-D-fructose [669, 668]. The other enzymes involved in this pathway are EC 4.2.1.110 (aldos-2-ulose dehydratase), EC 4.2.1.111 (1,5-anhydro-D-fructose dehydratase) and EC 4.2.2.13 [exo-(1→4)-α-D-glucan lyase]. Ascopyrone P is an anti-oxidant [668].
References: [669, 668]

[EC 5.3.2.7 created 2006 as EC 5.3.3.15, transferred 2012 to EC 5.3.2.7]

EC 5.3.2.8
Accepted name: 4-oxalomesaconate tautomerase
Reaction: (1*E*)-4-oxobut-1-ene-1,2,4-tricarboxylate = (1*E*,3*E*)-4-hydroxybuta-1,3-diene-1,2,4-tricarboxylate
Other name(s): GalD
Systematic name: 4-oxalomesaconate *keto—enol*-isomerase
Comments: This enzyme has been characterized from the bacterium *Pseudomonas putida* KT2440 and is involved in the degradation pathway of syringate and 3,4,5-trihydroxybenzoate. It catalyses the interconversion of two of the tautomers of 4-oxalomesaconate, a reaction that can also occur spontaneously.
References: [429]

[EC 5.3.2.8 created 2011 as EC 5.3.3.16, modified 2011, transferred 2012 to EC 5.3.2.8]

EC 5.3.3 Transposing C=C bonds

EC 5.3.3.1
Accepted name: steroid Δ-isomerase

Reaction: a 3-oxo-Δ^5-steroid = a 3-oxo-Δ^4-steroid
Other name(s): hydroxysteroid isomerase; steroid isomerase; Δ^5-ketosteroid isomerase; Δ^5(or Δ^4)-3-keto steroid isomerase; Δ^5-steroid isomerase; 3-oxosteroid isomerase; Δ^5-3-keto steroid isomerase; Δ^5-3-oxosteroid isomerase
Systematic name: 3-oxosteroid Δ^5-Δ^4-isomerase
Comments: This activity is catalysed by several distinct enzymes (*cf.* EC 1.1.3.6, cholesterol oxidase and EC 1.1.1.145, 3-hydroxy-5-steroid dehydrogenase).
References: [150, 286, 571, 361]

[EC 5.3.3.1 created 1961]

EC 5.3.3.2
Accepted name: isopentenyl-diphosphate Δ-isomerase
Reaction: isopentenyl diphosphate = dimethylallyl diphosphate
Other name(s): isopentenylpyrophosphate Δ-isomerase; methylbutenylpyrophosphate isomerase; isopentenylpyrophosphate isomerase
Systematic name: isopentenyl-diphosphate Δ^3-Δ^2-isomerase
Comments: The enzyme from *Streptomyces* sp. strain CL190 requires FMN and NAD(P)H as cofactors. Activity is reduced if FMN is replaced by FAD, but the enzyme becomes inactive when NAD(P)H is replaced by NAD^+ or $NADP^+$. That enzyme also requires Mg^{2+}, Mn^{2+} or Ca^{2+} for activity.
References: [277, 54, 7]

[EC 5.3.3.2 created 1961, modified 2002]

EC 5.3.3.3
Accepted name: vinylacetyl-CoA Δ-isomerase
Reaction: vinylacetyl-CoA = (*E*)-but-2-enoyl-CoA
Other name(s): vinylacetyl coenzyme A Δ-isomerase; vinylacetyl coenzyme A isomerase; Δ^3-*cis*-Δ^2-*trans*-enoyl-CoA isomerase
Systematic name: vinylacetyl-CoA Δ^3-Δ^2-isomerase
Comments: Also acts on 3-methyl-vinylacetyl-CoA.
References: [360, 489]

[EC 5.3.3.3 created 1961, modified 2011]

EC 5.3.3.4
Accepted name: muconolactone Δ-isomerase
Reaction: (+)-muconolactone = (4,5-dihydro-5-oxofuran-2-yl)-acetate
Other name(s): muconolactone isomerase; 5-oxo-4,5-dihydrofuran-2-acetate Δ^3-Δ^2-isomerase
Systematic name: (+)-muconolactone Δ^3-Δ^2-isomerase
References: [440, 442]

[EC 5.3.3.4 created 1961 as EC 3.1.1.16, part transferred 1972 to EC 5.3.3.4 rest to EC 5.3.3.4]

EC 5.3.3.5
Accepted name: cholestenol Δ-isomerase
Reaction: 5α-cholest-7-en-3β-ol = 5α-cholest-8-en-3β-ol
Systematic name: Δ^7-cholestenol Δ^7-Δ^8-isomerase
References: [627]

[EC 5.3.3.5 created 1972]

EC 5.3.3.6

Accepted name: methylitaconate Δ-isomerase
Reaction: methylitaconate = 2,3-dimethylmaleate
Other name(s): methylitaconate isomerase
Systematic name: methylitaconate Δ^2-Δ^3-isomerase
References: [322]

[EC 5.3.3.6 created 1972]

EC 5.3.3.7

Accepted name: aconitate Δ-isomerase
Reaction: *trans*-aconitate = *cis*-aconitate
Other name(s): aconitate isomerase
Systematic name: aconitate Δ^2-Δ^3-isomerase
Comments: *cis*-Aconitate is used to designate the isomer (*Z*)-prop-1-ene-1,2,3-tricarboxylate. This isomerization could take place either in a direct *cis-trans* interconversion or by an allylic rearrangement; the enzyme has been shown to catalyse the latter change.
References: [302, 301]

[EC 5.3.3.7 created 1972]

EC 5.3.3.8

Accepted name: Δ^3-Δ^2-enoyl-CoA isomerase
Reaction: (1) a (3*Z*)-alk-3-enoyl-CoA = a (2*E*)-alk-2-enoyl-CoA
(2) a (3*E*)-alk-3-enoyl-CoA = a (2*E*)-alk-2-enoyl-CoA
Other name(s): ECI (gene name); dodecenoyl-CoA isomerase; dodecenoyl-CoA Δ-isomerase; Δ^3-*cis*-Δ^2-*trans*-enoyl-CoA isomerase; acetylene-allene isomerase; dodecenoyl-CoA Δ^3-*cis*-Δ^2-*trans*-isomerase; dodecenoyl-CoA (3*Z*)-(2*E*)-isomerase
Systematic name: (3*Z*/3*E*)-alk-3-enoyl-CoA (2*E*)-isomerase
Comments: The enzyme participates in the β-oxidation of fatty acids with double bonds at an odd position. Processing of these substrates via the β-oxidation system results in intermediates with a *cis*- or *trans*-double bond at position C_3, which cannot be processed further by the regular enzymes of the β-oxidation system. This enzyme isomerizes the bond to a *trans* bond at position C_2, which can be processed further. The reaction rate is ten times higher for the (3*Z*) isomers than for (3*E*) isomers. The enzyme can also catalyse the isomerization of 3-acetylenic fatty acyl thioesters to 2,3-dienoyl fatty acyl thioesters.
References: [554, 555, 556, 399, 147, 179, 678, 188]

[EC 5.3.3.8 created 1978, modified 1980, modified 2018]

EC 5.3.3.9

Accepted name: prostaglandin-A_1 Δ-isomerase
Reaction: (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-10,13-dienoate = (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-11,13-dienoate
Other name(s): prostaglandin A isomerase
Systematic name: (13*E*)-(15*S*)-15-hydroxy-9-oxoprosta-10,13-dienoate Δ^{10}-Δ^{11}-isomerase
Comments: Interconverts prostaglandin A_1 and prostaglandin C_1.
References: [203]

[EC 5.3.3.9 created 1978]

EC 5.3.3.10

Accepted name: 5-carboxymethyl-2-hydroxymuconate Δ-isomerase

Reaction: 5-carboxymethyl-2-hydroxymuconate = (3*E*,5*R*)-5-carboxy-2-oxohept-3-enedioate
Other name(s): CHM isomerase; 5-carboxymethyl-2-hydroxymuconic acid isomerase
Systematic name: 5-carboxymethyl-2-hydroxymuconate Δ^2,Δ^4-2-oxo,Δ^3-isomerase
Comments: Part of the homoprotocatechuate degradation pathway in *Escherichia coli C*.
References: [174, 264]

[EC 5.3.3.10 created 1984]

EC 5.3.3.11
Accepted name: isopiperitenone Δ-isomerase
Reaction: isopiperitenone = piperitenone
Systematic name: isopiperitenone Δ^8-Δ^4-isomerase
Comments: Involved in the biosynthesis of menthol and related monoterpenes in peppermint (*Mentha piperita*) leaves.
References: [300]

[EC 5.3.3.11 created 1989]

EC 5.3.3.12
Accepted name: L-dopachrome isomerase
Reaction: L-dopachrome = 5,6-dihydroxyindole-2-carboxylate
Other name(s): dopachrome tautomerase; tyrosinase-related protein 2; TRP-1; TRP2; TRP-2; tyrosinase-related protein-2; dopachrome Δ^7,Δ^2-isomerase; dopachrome Δ-isomerase; dopachrome conversion factor; dopachrome isomerase; dopachrome oxidoreductase; dopachrome-rearranging enzyme; DCF; DCT; dopachrome keto-enol isomerase; L-dopachrome-methyl ester tautomerase
Systematic name: L-dopachrome keto-enol isomerase
Comments: A zinc enzyme. Stereospecific for L-dopachrome. Dopachrome methyl ester is a substrate, but dopaminochrome (2,3-dihydroindole-5,6-quinone) is not (see also EC 4.1.1.84, D-dopachrome decarboxylase).
References: [543, 454, 456]

[EC 5.3.3.12 created 1992, modified 1999, modified 2005]

EC 5.3.3.13
Accepted name: polyenoic fatty acid isomerase
Reaction: (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-icosapentaenoate = (5*Z*,7*E*,9*E*,14*Z*,17*Z*)-icosapentaenoate
Other name(s): PFI; eicosapentaenoate *cis*-$\Delta^{5,8,11,14,17}$-eicosapentaenoate *cis*-Δ^5-*trans*-$\Delta^{7,9}$-*cis*-$\Delta^{14,17}$ isomerase; (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-eicosapentaenoate $\Delta^{8,11}$-$\Delta^{7,8}$-isomerase (incorrect); (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-eicosapentaenoate $\Delta^{8,11}$-$\Delta^{7,9}$-isomerase (*trans*-double-bond-forming)
Systematic name: (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-icosapentaenoate $\Delta^{8,11}$-$\Delta^{7,9}$-isomerase (*trans*-double-bond-forming)
Comments: The enzyme from the red alga *Ptilota filicina* catalyses the isomerization of skip dienes (methylene-interrupted double bonds) in a broad range of fatty acids and fatty-acid analogues, such as arachidonate and γ-linolenate, to yield a conjugated triene.
References: [629, 632, 630, 687]

[EC 5.3.3.13 created 2004]

EC 5.3.3.14
Accepted name: *trans*-2-decenoyl-[acyl-carrier protein] isomerase
Reaction: a *trans*-dec-2-enoyl-[acyl-carrier protein] = a *cis*-dec-3-enoyl-[acyl-carrier protein]
Other name(s): β-hydroxydecanoyl thioester dehydrase; *trans*-2-*cis*-3-decenoyl-ACP isomerase; *trans*-2,*cis*-3-decenoyl-ACP isomerase; *trans*-2-decenoyl-ACP isomerase; FabM; decenoyl-[acyl-carrier-protein] Δ^2-*trans*-Δ^3-*cis*-isomerase

Systematic name: decenoyl-[acyl-carrier protein] Δ^2-*trans*-Δ^3-*cis*-isomerase
Comments: While the enzyme from *Escherichia coli* is highly specific for the 10-carbon enoyl-ACP, the enzyme from *Streptococcus pneumoniae* can also use the 12-carbon enoyl-ACP as substrate in vitro but not 14- or 16-carbon enoyl-ACPs [372]. ACP can be replaced by either CoA or *N*-acetylcysteamine thioesters. The *cis*-3-enoyl product is required to form unsaturated fatty acids, such as palmitoleic acid and *cis*-vaccenic acid, in dissociated (or type II) fatty-acid biosynthesis.
References: [66, 58, 372, 104]

[EC 5.3.3.14 created 2006]

[5.3.3.15 Transferred entry. ascopyrone tautomerase. Now EC 5.3.2.7, ascopyrone tautomerase]

[EC 5.3.3.15 created 2006, deleted 2013]

[5.3.3.16 Transferred entry. 4-oxalomesaconate tautomerase. Now EC 5.3.2.8, 4-oxalomesaconate tautomerase]

[EC 5.3.3.16 created 2011, modified 2011, deleted 2013]

EC 5.3.3.17
Accepted name: *trans*-2,3-dihydro-3-hydroxyanthranilate isomerase
Reaction: (5*S*,6*S*)-6-amino-5-hydroxycyclohexa-1,3-diene-1-carboxyate = (1*R*,6*S*)-6-amino-5-oxocyclohex-2-ene-1-carboxylate
Other name(s): *phzF* (gene name); (5*S*,6*S*)-6-amino-5-hydroxycyclohexane-1,3-diene-1-carboxyate isomerase (incorrect)
Systematic name: (5*S*,6*S*)-6-amino-5-hydroxycyclohexa-1,3-diene-1-carboxyate isomerase
Comments: The enzyme is involved in phenazine biosynthesis. The product probably spontaneously dimerises to 1,4,5a,6,9,10a-hexahydrophenazine-1,6-dicarboxylate
References: [451, 55, 450, 382, 11]

[EC 5.3.3.17 created 2011]

EC 5.3.3.18
Accepted name: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA isomerase
Reaction: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA = 2-oxepin-2(3*H*)-ylideneacetyl-CoA
Other name(s): *paaG* (gene name); 1,2-epoxyphenylacetyl-CoA isomerase (misleading)
Systematic name: 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA isomerase
Comments: The enzyme catalyses the reversible isomerization of 2-(1,2-epoxy-1,2-dihydrophenyl)acetyl-CoA to the unusual unsaturated, oxygen-containing, seven-member heterocyclic enol ether 2-oxepin-2(3*H*)-ylideneacetyl-CoA, as part of an aerobic phenylacetate degradation pathway.
References: [250, 579]

[EC 5.3.3.18 created 2011]

EC 5.3.3.19
Accepted name: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate isomerase
Reaction: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate = 3-[(1*E*,4*R*)-4-hydroxycyclohex-2-en-1-ylidene]-2-oxopropanoate
Other name(s): BacB
Systematic name: 3-[(4*R*)-4-hydroxycyclohexa-1,5-dien-1-yl]-2-oxopropanoate isomerase
Comments: The enzyme, characterized from the bacterium *Bacillus subtilis*, is involved in the biosynthesis of the nonribosomally synthesized dipeptide antibiotic bacilysin, composed of L-alanine and L-anticapsin. The enzyme can interconvert the (*E*) isomer formed in the reaction into the (*Z*) isomer [448], although this isomerization is not part of the pathway leading to bacilysin [449].
References: [362, 448, 449]

[EC 5.3.3.19 created 2015]

[5.3.3.20 Transferred entry. 2-hydroxyisobutanoyl-CoA mutase. Now EC 5.4.99.64, 2-hydroxyisobutanoyl-CoA mutase]

[EC 5.3.3.20 created 2016, deleted 2017]

EC 5.3.3.21

Accepted name: $\Delta^{3,5}$-$\Delta^{2,4}$-dienoyl-CoA isomerase
Reaction: a (3*E*,5*Z*)-alka-3,5-dienoyl-CoA = a (2*E*,4*E*)-alka-2,4-dienoyl-CoA
Other name(s): 3,5-tetradecadienoyl-CoA isomerase; DCI1 (gene name)
Systematic name: (3*E*,5*Z*)-alka-3,5-dienoyl-CoA $\Delta^{3,5}$-$\Delta^{2,4}$ isomerase
Comments: The enzyme participates in an alternative degradation route of fatty acids with *cis*-double bonds on odd-number carbons such as oleate and linoleate. The main physiological substrate is (3*E*,5*Z*)-tetradeca-3,5-dienoyl-CoA, but other (3*E*,5*Z*)-dienoyl-CoAs with varying carbon chain lengths are also substrates.
References: [157, 402, 178, 202, 677, 187]

[EC 5.3.3.21 created 2018]

EC 5.3.3.22

Accepted name: lutein isomerase
Reaction: lutein = *meso*-zeaxanthin
Other name(s): RPE65 (gene name); *meso*-zeaxanthin isomerase
Systematic name: lutein Δ^{4}-Δ^{5}-isomerase
Comments: The enzyme is found in the retinal pigment epithelium (RPE) of vertebrates. It also has the activity of EC 3.1.1.64, retinoid isomerohydrolase.
References: [531]

[EC 5.3.3.22 created 2018]

EC 5.3.4 Transposing S-S bonds

EC 5.3.4.1

Accepted name: protein disulfide-isomerase
Reaction: Catalyses the rearrangement of -S-S- bonds in proteins
Other name(s): S-S rearrangase
Systematic name: protein disulfide-isomerase
Comments: Needs reducing agents or partly reduced enzyme; the reaction depends on sulfhydryl-disulfide interchange.
References: [356, 170]

[EC 5.3.4.1 created 1972]

EC 5.3.99 Other intramolecular oxidoreductases

[5.3.99.1 Deleted entry. hydroperoxide isomerase. Reaction due to combined action of EC 4.2.1.92 (hydroperoxide dehydratase) and EC 5.3.99.6 (allene-oxide cyclase)]

[EC 5.3.99.1 created 1972, deleted 1992]

EC 5.3.99.2

Accepted name: prostaglandin-D synthase

Reaction: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*,15*S*)-9α,15-dihydroxy-11-oxoprosta-5,13-dienoate
Other name(s): prostaglandin-H_2 Δ-isomerase; prostaglandin-R-prostaglandin D isomerase; PGH-PGD isomerase(5,13)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate Δ-isomerase (incorrect); (5,13)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate D-isomerase; prostaglandin endoperoxide Δ-isomerase; prostaglandin D synthetase
Systematic name: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate D-isomerase
Comments: Brings about the opening of the epidioxy bridge. Some enzymes require glutathione.
References: [93, 527]

[EC 5.3.99.2 created 1976, modified 1990]

EC 5.3.99.3

Accepted name: prostaglandin-E synthase
Reaction: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*)-(15*S*)-11α,15-dihydroxy-9-oxoprosta-5,13-dienoate
Other name(s): prostaglandin-H_2 E-isomerase; endoperoxide isomerase; endoperoxide isomerase; prostaglandin *R*-prostaglandin E isomerase; prostaglandin endoperoxide E isomerase; PGE isomerase; PGH-PGE isomerase; PGE_2 isomerase; prostaglandin endoperoxide E_2 isomerase; prostaglandin H-E isomerase
Systematic name: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate E-isomerase
Comments: Brings about the opening of the epidioxy bridge. Requires glutathione.
References: [436, 572]

[EC 5.3.99.3 created 1976, modified 1990]

EC 5.3.99.4

Accepted name: prostaglandin-I synthase
Reaction: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*,15*S*)-6,9α-epoxy-11α,15-dihydroxyprosta-5,13-dienoate
Other name(s): prostacyclin synthase; prostacycline synthetase; prostagladin I2 synthetase; PGI_2 synthase; PGI_2 synthetase; (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate 6-isomerase
Systematic name: (5*Z*,13*E*,15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate 6-isomerase
Comments: A cytochrome *P*-450 heme-thiolate enzyme. Converts prostaglandin H_2 into prostaglandin I_2 (prostacyclin).
References: [131, 595]

[EC 5.3.99.4 created 1984, modified 1990]

EC 5.3.99.5

Accepted name: thromboxane-A synthase
Reaction: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate = (5*Z*,13*E*)-(15*S*)-9α,11α-epoxy-15-hydroxythromboxa-5,13-dienoate
Other name(s): thromboxane synthase; (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate thromboxane-A_2-isomerase
Systematic name: (5*Z*,13*E*)-(15*S*)-9α,11α-epidioxy-15-hydroxyprosta-5,13-dienoate isomerase
Comments: A cytochrome *P*-450 heme-thiolate enzyme. Converts prostaglandin H_2 into thromboxane A_2.
References: [519, 596]

[EC 5.3.99.5 created 1984, modified 1990]

EC 5.3.99.6

Accepted name: allene-oxide cyclase
Reaction: (9*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate = (15*Z*)-12-oxophyto-10,15-dienoate

Systematic name: (9*Z*)-(13*S*)-12,13-epoxyoctadeca-9,11,15-trienoate isomerase (cyclizing)
Comments: Allene oxides formed by the action of EC 4.2.1.92 hydroperoxide dehydratase, are converted into cyclopentenone derivatives.
References: [206]

[EC 5.3.99.6 created 1992]

EC 5.3.99.7
Accepted name: styrene-oxide isomerase
Reaction: styrene oxide = phenylacetaldehyde
Other name(s): SOI
Systematic name: styrene-oxide isomerase (epoxide-cleaving)
Comments: Highly specific.
References: [212]

[EC 5.3.99.7 created 1992]

EC 5.3.99.8
Accepted name: capsanthin/capsorubin synthase
Reaction: (1) violaxanthin = capsorubin
(2) antheraxanthin = capsanthin
Other name(s): CCS; ketoxanthophyll synthase; capsanthin-capsorubin synthase
Systematic name: violaxanthin—capsorubin isomerase (ketone-forming)
Comments: This multifunctional enzyme is induced during chromoplast differentiation in plants [61]. Isomerization of the epoxide ring of violaxanthin gives the cyclopentyl-ketone of capsorubin or capsanthin.
References: [61, 335, 647]

[EC 5.3.99.8 created 2005]

EC 5.3.99.9
Accepted name: neoxanthin synthase
Reaction: violaxanthin = neoxanthin
Other name(s): NSY
Systematic name: violaxanthin—neoxanthin isomerase (epoxide-opening)
Comments: The opening of the epoxide ring of violaxanthin generates a chiral allene. Neoxanthin is a precursor of the plant hormone abscisic acid and the last product of carotenoid synthesis in green plants [60].
References: [12, 60]

[EC 5.3.99.9 created 2005]

EC 5.3.99.10
Accepted name: thiazole tautomerase
Reaction: 2-[(2*R*,5*Z*)-2-carboxy-4-methylthiazol-5(2*H*)-ylidene]ethyl phosphate = 2-(2-carboxy-4-methylthiazol-5-yl)ethyl phosphate
Other name(s): *tenI* (gene name)
Systematic name: 2-(2-carboxy-4-methylthiazol-5-yl)ethyl phosphate isomerase
Comments: The enzyme catalyses the irreversible aromatization of the thiazole moiety of 2-[(2*R*,5*Z*)-2-carboxy-4-methylthiazol-5(2*H*)-ylidene]ethyl phosphate.
References: [218]

[EC 5.3.99.10 created 2012]

EC 5.3.99.11

Accepted name: 2-keto-*myo*-inositol isomerase
Reaction: 2,4,6/3,5-pentahydroxycyclohexanone = 2D-2,3,5/4,6-pentahydroxycyclohexanone
Other name(s): IolI; inosose isomerase; 2KMI isomerase.
Systematic name: 2,4,6/3,5-pentahydroxycyclohexanone 2-isomerase
Comments: Requires a divalent metal ion for activity. Mn^{2+}, Fe^{2+} and Co^{2+} can be used. The enzyme, found in the bacterium *Bacillus subtilis*, is part of the *myo*-inositol/D-*chiro*-inositol degradation pathway leading to acetyl-CoA.
References: [681, 662]

[EC 5.3.99.11 created 2014]

EC 5.4 Intramolecular transferases

This subclass contains enzymes that transfer a group from one position to another within a molecule. Sub-subclasses are based on the group transferred: acyl group (EC 5.4.1), phospho group (EC 5.4.2), amino group (EC 5.4.3), hydroxy group (EC 5.4.4), or some other group (EC 5.4.99).

EC 5.4.1 Transferring acyl groups

EC 5.4.1.1

Accepted name: lysolecithin acylmutase
Reaction: 2-lysolecithin = 3-lysolecithin
Other name(s): lysolecithin migratase
Systematic name: lysolecithin 2,3-acylmutase
References: [599]

[EC 5.4.1.1 created 1961]

[5.4.1.2 Transferred entry. precorrin-8X methylmutase. Now EC 5.4.99.61, precorrin-8X methylmutase]

[EC 5.4.1.2 created 1999, deleted 2014]

EC 5.4.1.3

Accepted name: 2-methylfumaryl-CoA isomerase
Reaction: 2-methylfumaryl-CoA = 3-methylfumaryl-CoA
Other name(s): mesaconyl-CoA C_1-C_4 CoA transferase; Mct
Systematic name: 2-methylfumaryl-CoA 1,4-CoA-mutase
Comments: The enzyme, purified from the bacterium *Chloroflexus aurantiacus*, acts as an intramolecular CoA transferase and does not transfer CoA to free mesaconate. It is part of the 3-hydroxypropanoate cycle for carbon assimilation.
References: [675]

[EC 5.4.1.3 created 2014]

EC 5.4.1.4

Accepted name: D-galactarolactone isomerase
Reaction: D-galactaro-1,5-lactone = D-galactaro-1,4-lactone
Other name(s): GLI
Systematic name: D-galactaro-1,5-lactone isomerase (D-galactaro-1,4-lactone-forming)
Comments: The enzyme, characterized from the bacterium *Agrobacterium fabrum* strain C58, belongs to the amidohydrolase superfamily. It participates in the degradation of D-galacturonate.
References: [62]

[EC 5.4.1.4 created 2015]

EC 5.4.2 Phosphotransferases (phosphomutases)

Most of these enzymes were previously listed as sub-subclass EC 2.7.5, under the heading: 'Phosphotransferases with regeneration of donors, apparently catalysing intramolecular transfers'. The reaction for these enzymes was written in the form:¡p¿

X-(*P*)2 + A*P* = B*P* + X-(*P*)$_2$.

In fact, since phosphorylation of the acceptor produces a bisphosphate that is identical to the donor, the overall reaction is an isomerization of AP into BP, with the bisphosphate acting catalytically. It has been shown in some cases that the enzyme has a functional phosphate group, which can act as the donor. Phosphate is transferred to the substrate, forming the intermediate bisphosphate; the other phosphate group is subsequently transferred to the enzyme:¡p¿

E-*P* + A*P* = E + X-(*P*)$_2$¡p¿

X-(*P*)$_2$ + E = B*P* + E-*P*.

The bisphosphate may be firmly attached to the enzyme during the catalytic cycle, or, in other cases, may be released so that free bisphosphate is required as an activator. Under these circumstances, it was agreed in 1983 that all of these enzymes should be listed together in this sub-subclass based on the overall isomerase reaction.

[5.4.2.1 Transferred entry. phosphoglycerate mutase. Now recognized as two separate enzymes EC 5.4.2.11, phosphoglycerate mutase (2,3-diphosphoglycerate-dependent) and EC 5.4.2.12, phosphoglycerate mutase (2,3-diphosphoglycerate-independent)]

[EC 5.4.2.1 created 1961 (EC 2.7.5.3 created 1961, incorporated 1984), deleted 2013]

EC 5.4.2.2

Accepted name: phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent)
Reaction: α-D-glucose 1-phosphate = D-glucose 6-phosphate
Other name(s): glucose phosphomutase; phosphoglucose mutase
Systematic name: α-D-glucose 1,6-phosphomutase
Comments: Maximum activity is only obtained in the presence of α-D-glucose 1,6-bisphosphate. This bisphosphate is an intermediate in the reaction, being formed by transfer of a phosphate residue from the enzyme to the substrate, but the dissociation of bisphosphate from the enzyme complex is much slower than the overall isomerization. The enzyme also catalyses (more slowly) the interconversion of 1-phosphate and 6-phosphate isomers of many other α-D-hexoses, and the interconversion of α-D-ribose 1-phosphate and 5-phosphate. *cf.* EC 5.4.2.5, phosphoglucomutase (glucose-cofactor).
References: [268, 418, 478, 477, 567]

[EC 5.4.2.2 created 1961 as EC 2.7.5.1, transferred 1984 to EC 5.4.2.2]

EC 5.4.2.3

Accepted name: phosphoacetylglucosamine mutase
Reaction: *N*-acetyl-α-D-glucosamine 1-phosphate = *N*-acetyl-D-glucosamine 6-phosphate
Other name(s): acetylglucosamine phosphomutase; acetylglucosamine phosphomutase; acetylaminodeoxyglucose phosphomutase; phospho-*N*-acetylglucosamine mutase; *N*-acetyl-D-glucosamine 1,6-phosphomutase
Systematic name: *N*-acetyl-α-D-glucosamine 1,6-phosphomutase
Comments: The enzyme is activated by *N*-acetyl-α-D-glucosamine 1,6-bisphosphate.
References: [75, 337, 477, 483]

[EC 5.4.2.3 created 1961 as EC 2.7.5.2, transferred 1984 to EC 5.4.2.3]

EC 5.4.2.4

Accepted name: bisphosphoglycerate mutase
Reaction: 3-phospho-D-glyceroyl phosphate = 2,3-bisphospho-D-glycerate

Other name(s): diphosphoglycerate mutase; glycerate phosphomutase; bisphosphoglycerate synthase; bisphosphoglyceromutase; biphosphoglycerate synthase; diphosphoglyceric mutase; 2,3-diphosphoglycerate mutase; phosphoglyceromutase; 2,3-diphosphoglycerate synthase; DPGM; 2,3-bisphosphoglycerate mutase; BPGM; diphosphoglyceromutase; 2,3-diphosphoglyceromutase
Systematic name: 3-phospho-D-glycerate 1,2-phosphomutase
Comments: In the direction shown, this enzyme is phosphorylated by 3-phosphoglyceroyl phosphate, to give phosphoenzyme and 3-phosphoglycerate. The latter is rephosphorylated by the enzyme to yield 2,3-bisphosphoglycerate, but this reaction is slowed by dissociation of 3-phosphoglycerate from the enzyme, which is therefore more active in the presence of added 3-phosphoglycerate. This enzyme also catalyses, slowly, the reaction of EC 5.4.2.11 [phosphoglycerate mutase (2,3-diphosphoglycerate-dependent)] and EC 5.4.2.12 [phosphoglycerate mutase (2,3-diphosphoglycerate-independent)].
References: [477, 494, 495]

[EC 5.4.2.4 created 1961 as EC 2.7.5.4, transferred 1984 to EC 5.4.2.4]

EC 5.4.2.5

Accepted name: phosphoglucomutase (glucose-cofactor)
Reaction: α-D-glucose 1-phosphate = D-glucose 6-phosphate
Other name(s): glucose phosphomutase; glucose-1-phosphate phosphotransferase
Systematic name: α-D-glucose 1,6-phosphomutase (glucose-cofactor)
Comments: The enzyme is activated by D-glucose, which probably acts as an acceptor for a phosphate residue from the substrate, thus being itself converted into the product. *cf.* EC 5.4.2.2, phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent).
References: [171, 477]

[EC 5.4.2.5 created 1972 as EC 2.7.5.5, transferred 1984 to EC 5.4.2.5]

EC 5.4.2.6

Accepted name: β-phosphoglucomutase
Reaction: β-D-glucose 1-phosphate = β-D-glucose 6-phosphate
Other name(s): β-*pgm* (gene name)
Systematic name: β-D-glucose 1,6-phosphomutase
Comments: The enzyme requires Mg^{2+} and phosphorylation of an aspartate residue at the active site. The enzyme is able to autophosphorylate itself with its substrate β-D-glucose 1-phosphate. Although this is a slow reaction, only a single turnover is required for activation. Once the phosphorylated enzyme is formed, it generates the reaction intermediate β-D-glucose 1,6-bisphosphate, which can be used to phosphorylate the enzyme in subsequent cycles [120]. *cf.* EC 5.4.2.2, phosphoglucomutase (α-D-glucose-1,6-bisphosphate-dependent).
References: [50, 477, 327, 120]

[EC 5.4.2.6 created 1984]

EC 5.4.2.7

Accepted name: phosphopentomutase
Reaction: α-D-ribose 1-phosphate = D-ribose 5-phosphate
Other name(s): phosphodeoxyribomutase; deoxyribose phosphomutase; deoxyribomutase; phosphoribomutase; α-D-glucose-1,6-bisphosphate:deoxy-D-ribose-1-phosphate phosphotransferase; D-ribose 1,5-phosphomutase
Systematic name: α-D-ribose 1,5-phosphomutase
Comments: Also converts 2-deoxy-α-D-ribose 1-phosphate into 2-deoxy-D-ribose 5-phosphate. α-D-Ribose 1,5-bisphosphate, 2-deoxy-α-D-ribose 1,5-bisphosphate, or α-D-glucose 1,6-bisphosphate can act as cofactor.
References: [208, 275, 477]

[EC 5.4.2.7 created 1972 as EC 2.7.5.6, transferred 1984 to EC 5.4.2.7]

EC 5.4.2.8

Accepted name: phosphomannomutase
Reaction: α-D-mannose 1-phosphate = D-mannose 6-phosphate
Other name(s): mannose phosphomutase; phosphomannose mutase; D-mannose 1,6-phosphomutase
Systematic name: α-D-mannose 1,6-phosphomutase
Comments: α-D-Mannose 1,6-bisphosphate or α-D-glucose 1,6-bisphosphate can act as cofactor.
References: [540]

[EC 5.4.2.8 created 1981 as EC 2.7.5.7, transferred 1984 to EC 5.4.2.8]

EC 5.4.2.9

Accepted name: phospho*enol*pyruvate mutase
Reaction: phospho*enol*pyruvate = 3-phosphonopyruvate
Other name(s): phospho*enol*pyruvate-phosphonopyruvate phosphomutase; PEP phosphomutase; phospho*enol*pyruvate phosphomutase; PEPPM; PEP phosphomutase
Systematic name: phospho*enol*pyruvate 2,3-phosphonomutase
Comments: Involved in the biosynthesis of the C-P bond, although the equilibrium greatly favours phospho*enol*pyruvate.
References: [63, 227, 516]

[EC 5.4.2.9 created 1990]

EC 5.4.2.10

Accepted name: phosphoglucosamine mutase
Reaction: α-D-glucosamine 1-phosphate = D-glucosamine 6-phosphate
Systematic name: α-D-glucosamine 1,6-phosphomutase
Comments: The enzyme is involved in the pathway for bacterial cell-wall peptidoglycan and lipopolysaccharide biosyntheses, being an essential step in the pathway for UDP-*N*-acetylglucosamine biosynthesis. The enzyme from *Escherichia coli* is activated by phosphorylation and can be autophosphorylated in vitro by α-D-glucosamine 1,6-bisphosphate, which is an intermediate in the reaction, α-D-glucose 1,6-bisphosphate or ATP. It can also catalyse the interconversion of α-D-glucose 1-phosphate and glucose 6-phosphate, although at a much lower rate.
References: [392, 125, 267, 265, 266]

[EC 5.4.2.10 created 2001]

EC 5.4.2.11

Accepted name: phosphoglycerate mutase (2,3-diphosphoglycerate-dependent)
Reaction: 2-phospho-D-glycerate = 3-phospho-D-glycerate (overall reaction)
(1a) [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate = [enzyme]-N^{τ}-phospho-L-histidine + 2/3-phospho-D-glycerate
(1b) [enzyme]-N^{τ}-phospho-L-histidine + 2-phospho-D-glycerate = [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate
(1c) [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate = [enzyme]-N^{τ}-phospho-L-histidine + 3-phospho-D-glycerate
(1d) [enzyme]-N^{τ}-phospho-L-histidine + 2/3-bisphospho-D-glycerate = [enzyme]-L-histidine + 2,3-bisphospho-D-glycerate
Other name(s): glycerate phosphomutase (diphosphoglycerate cofactor); 2,3-diphosphoglycerate dependent phosphoglycerate mutase; cofactor dependent phosphoglycerate mutase; phosphoglycerate phosphomutase (ambiguous); phosphoglyceromutase (ambiguous); monophosphoglycerate mutase (ambiguous); monophosphoglyceromutase (ambiguous); GriP mutase (ambiguous); PGA mutase (ambiguous); MPGM; PGAM; PGAM-d; PGM; dPGM

Systematic name: D-phosphoglycerate 2,3-phosphomutase (2,3-diphosphoglycerate-dependent)
Comments: The enzymes from vertebrates, platyhelminths, mollusks, annelids, crustaceans, insects, algae, some fungi and some bacteria (particularly Gram-negative) require 2,3-bisphospho-D-glycerate as a cofactor. The enzyme is activated by 2,3-bisphospho-D-glycerate by transferring a phosphate to histidine (His^{10} in man and *Escherichia coli*, His^{8} in *Saccharomyces cerevisiae*). This phosphate can be transferred to the free OH of 2-phospho-D-glycerate, followed by transfer of the phosphate already on the phosphoglycerate back to the histidine. *cf.* EC 5.4.2.12 phosphoglycerate mutase. The enzyme has no requirement for metal ions. This enzyme also catalyse, slowly, the reactions of EC 5.4.2.4 bisphosphoglycerate mutase.
References: [196, 477, 495, 488, 59, 487, 486]

[EC 5.4.2.11 created 1961 as EC 5.4.2.1 (EC 2.7.5.3 created 1961, incorporated 1984) transferred 2013 to EC 5.4.2.11, modified 2014]

EC 5.4.2.12
Accepted name: phosphoglycerate mutase (2,3-diphosphoglycerate-independent)
Reaction: 2-phospho-D-glycerate = 3-phospho-D-glycerate
Other name(s): cofactor independent phosphoglycerate mutase; 2,3-diphosphoglycerate-independent phosphoglycerate mutase; phosphoglycerate phosphomutase (ambiguous); phosphoglyceromutase (ambiguous); monophosphoglycerate mutase (ambiguous); monophosphoglyceromutase (ambiguous); GriP mutase (ambiguous); PGA mutase (ambiguous); iPGM; iPGAM; PGAM-i
Systematic name: D-phosphoglycerate 2,3-phosphomutase (2,3-diphosphoglycerate-independent)
Comments: The enzymes from higher plants, algae, some fungi, nematodes, sponges, coelenterates, myriapods, arachnids, echinoderms, archaea and some bacteria (particularly Gram-positive) have maximum activity in the absence of 2,3-bisphospho-D-glycerate. *cf.* EC 5.4.2.11 phosphoglycerate mutase (2,3-diphosphoglycerate-dependent). The enzyme contains two Mn^{2+} (or in some species two Co^{2+} ions). The reaction involves a phosphotransferase reaction to serine followed by transfer back to the glycerate at the other position. Both metal ions are involved in the reaction.
References: [260, 485, 684, 433, 432, 393]

[EC 5.4.2.12 created 2013]

EC 5.4.2.13
Accepted name: phosphogalactosamine mutase
Reaction: D-galactosamine 6-phosphate = α-D-galactosamine-1-phosphate
Other name(s): ST0242 (locus name)
Systematic name: α-D-galactosamine 1,6-phosphomutase
Comments: The enzyme, characterized from the archaeon *Sulfolobus tokodaii*, is also active toward D-glucosamine 6-phosphate (*cf.* EC 5.4.2.10, phosphoglucosamine mutase).
References: [117]

[EC 5.4.2.13 created 2018]

EC 5.4.3 Transferring amino groups

[5.4.3.1 Deleted entry. ornithine 4,5-aminomutase. This reaction was due to a mixture of EC 5.1.1.12 (ornithine racemase) and EC 5.4.3.5 (D-ornithine 4,5-aminomutase)]

[EC 5.4.3.1 created 1972, deleted 1976]

EC 5.4.3.2
Accepted name: lysine 2,3-aminomutase
Reaction: L-lysine = (3*S*)-3,6-diaminohexanoate
Systematic name: L-lysine 2,3-aminomutase

Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It contains pyridoxal phosphate and a [4Fe-4S] cluster and binds an exchangeable *S*-adenosyl-L-methionine molecule. Activity *in vitro* requires a strong reductant such as dithionite and strictly anaerobic conditions. A 5′-deoxyadenosyl radical is generated during the reaction cycle by reductive cleavage of *S*-adenosyl-L-methionine, mediated by the iron-sulfur cluster. *S*-adenosyl-L-methionine is regenerated at the end of the reaction.
References: [674, 4, 168, 346, 338, 169]

[EC 5.4.3.2 created 1972]

EC 5.4.3.3
Accepted name: lysine 5,6-aminomutase
Reaction: (1) (3*S*)-3,6-diaminohexanoate = (3*S*,5*S*)-3,5-diaminohexanoate
(2) D-lysine = (2*R*,5*S*)-2,5-diaminohexanoate
Other name(s): β-lysine 5,6-aminomutase; β-lysine mutase; L-β-lysine 5,6-aminomutase; D-lysine 5,6-aminomutase; D-α-lysine mutase; adenosylcobalamin-dependent D-lysine 5,6-aminomutase
Systematic name: (3*S*)-3,6-diaminohexanoate 5,6-aminomutase
Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It requires pyridoxal 5′-phosphate and adenosylcobalamin for activity. A 5′-deoxyadenosyl radical is generated during the reaction cycle by reductive cleavage of adenosylcobalamin, which is regenerated at the end of the reaction.
References: [550, 549, 409, 484, 81, 573, 574, 53]

[EC 5.4.3.3 created 1972 (EC 5.4.3.4 created 1972, incorporated 2017), modified 2017]

[5.4.3.4 Transferred entry. D-lysine 5,6-aminomutase. Now included in EC 5.4.3.3, lysine 5,6-aminomutase]

[EC 5.4.3.4 created 1972, modified 2003, deleted 2017]

EC 5.4.3.5
Accepted name: D-ornithine 4,5-aminomutase
Reaction: D-ornithine = (2*R*,4*S*)-2,4-diaminopentanoate
Other name(s): D-α-ornithine 5,4-aminomutase; D-ornithine aminomutase
Systematic name: D-ornithine 4,5-aminomutase
Comments: A pyridoxal-phosphate protein that requires a cobamide coenzyme for activity.
References: [545]

[EC 5.4.3.5 created 1972 as EC 5.4.3.1, transferred 1976 to EC 5.4.3.5, modified 2003]

EC 5.4.3.6
Accepted name: tyrosine 2,3-aminomutase
Reaction: L-tyrosine = 3-amino-3-(4-hydroxyphenyl)propanoate
Other name(s): tyrosine α,β-mutase
Systematic name: L-tyrosine 2,3-aminomutase
Comments: Requires ATP.
References: [324]

[EC 5.4.3.6 created 1976]

EC 5.4.3.7
Accepted name: leucine 2,3-aminomutase
Reaction: (2*S*)-α-leucine = (3*R*)-β-leucine
Systematic name: (2*S*)-α-leucine 2,3-aminomutase
Comments: Requires a cobamide coenzyme.

References: [167, 465, 464]

[EC 5.4.3.7 created 1982]

EC 5.4.3.8

Accepted name: glutamate-1-semialdehyde 2,1-aminomutase
Reaction: L-glutamate 1-semialdehyde = 5-aminolevulinate
Other name(s): glutamate-1-semialdehyde aminotransferase
Systematic name: (*S*)-4-amino-5-oxopentanoate 4,5-aminomutase
Comments: Requires pyridoxal phosphate.
References: [190]

[EC 5.4.3.8 created 1983]

EC 5.4.3.9

Accepted name: glutamate 2,3-aminomutase
Reaction: L-glutamate = 3-aminopentanedioate
Systematic name: L-glutamate 2,3-aminomutase
Comments: This enzyme is a member of the 'AdoMet radical' (radical SAM) family. It contains pyridoxal phosphate and a [4Fe-4S] cluster, which is coordinated by 3 cysteines and binds an exchangeable *S*-adenosyl-L-methionine molecule. During the reaction cycle, the AdoMet forms a 5′-deoxyadenosyl radical, which is regenerated at the end of the reaction.
References: [498]

[EC 5.4.3.9 created 2012]

EC 5.4.3.10

Accepted name: phenylalanine aminomutase (L-β-phenylalanine forming)
Reaction: L-phenylalanine = L-β-phenylalanine
Systematic name: L-phenylalanine 2,3-aminomutase [(*R*)-3-amino-3-phenylpropanoate forming]
Comments: The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO). This unique cofactor is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine. *cf.* EC 5.4.3.11, phenylalanine aminomutase (D-β-phenylalanine forming).
References: [154]

[EC 5.4.3.10 created 2013]

EC 5.4.3.11

Accepted name: phenylalanine aminomutase (D-β-phenylalanine forming)
Reaction: L-phenylalanine = D-β-phenylalanine
Other name(s): *admH* (gene name); L-phenylalanine 2,3-aminomutase [(*S*)-3-amino-3-phenylpropanoate]
Systematic name: L-phenylalanine 2,3-aminomutase [(*S*)-3-amino-3-phenylpropanoate-forming]
Comments: The enzyme from the bacterium *Pantoea agglomerans* produces D-β-phenylalanine, an intermediate in the biosynthesis of the polyketide non-ribosomal antibiotic andrimid. The enzyme contains the cofactor 3,5-dihydro-5-methylidene-4*H*-imidazol-4-one (MIO), which is formed autocatalytically by cyclization and dehydration of the three amino-acid residues alanine, serine and glycine. *cf.* EC 5.4.3.10, phenylalanine aminomutase (L-β-phenylalanine forming).
References: [475]

[EC 5.4.3.11 created 2013]

EC 5.4.4 Transferring hydroxy groups

EC 5.4.4.1

Accepted name: (hydroxyamino)benzene mutase
Reaction: (hydroxyamino)benzene = 2-aminophenol
Other name(s): HAB mutase; hydroxylaminobenzene hydroxymutase; hydroxylaminobenzene mutase
Systematic name: (hydroxyamino)benzene hydroxymutase
References: [219, 123]

[EC 5.4.4.1 created 2003]

EC 5.4.4.2

Accepted name: isochorismate synthase
Reaction: chorismate = isochorismate
Other name(s): MenF
Systematic name: isochorismate hydroxymutase
Comments: Requires Mg^{2+}. The reaction is reversible.
References: [664, 604, 118, 122]

[EC 5.4.4.2 created 1972 as EC 5.4.99.6, transferred 2003 to EC 5.4.4.2]

EC 5.4.4.3

Accepted name: 3-(hydroxyamino)phenol mutase
Reaction: 3-hydroxyaminophenol = aminohydroquinone
Other name(s): 3-hydroxylaminophenol mutase; 3*H*AP mutase
Systematic name: 3-(hydroxyamino)phenol hydroxymutase
References: [509]

[EC 5.4.4.3 created 2003]

EC 5.4.4.4

Accepted name: geraniol isomerase
Reaction: geraniol = (3*S*)-linalool
Systematic name: geraniol hydroxymutase
Comments: In absence of oxygen the bifunctional linalool dehydratase-isomerase can catalyse *in vitro* two reactions, the isomerization of (3*S*)-linalool to geraniol and the hydration of myrcene to (3*S*)-linalool, the latter activity being classified as EC 4.2.1.127, linalool dehydratase.
References: [68, 359]

[EC 5.4.4.4 created 2011, modified 2012]

EC 5.4.4.5

Accepted name: 9,12-octadecadienoate 8-hydroperoxide 8*R*-isomerase
Reaction: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate = (5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate
Other name(s): 5,8-LDS (bifunctional enzyme); 5,8-linoleate diol synthase (bifunctional enzyme); 8-hydroperoxide isomerase; (8*R*,9*Z*,12*Z*)-8-hydroperoxy-9,12-octadecadienoate mutase ((5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxy-9,12-octadecadienoate-forming); PpoA
Systematic name: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate hydroxymutase [(5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate-forming]

Comments: The enzyme contains heme [67]. The bifunctional enzyme from *Aspergillus nidulans* uses different heme domains to catalyse two separate reactions. Linoleic acid is oxidized within the N-terminal heme peroxidase domain to (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate (*cf.* EC 1.13.11.60, linoleate 8*R*-lipoxygenase), which is subsequently isomerized to (5*S*,8*R*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate within the C-terminal *P*-450 heme thiolate domain [67].
References: [231, 261, 67]

[EC 5.4.4.5 created 2011]

EC 5.4.4.6
Accepted name: 9,12-octadecadienoate 8-hydroperoxide 8*S*-isomerase
Reaction: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate = (7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxyoctadeca-9,12-dienoate
Other name(s): 8-hydroperoxide isomerase (ambiguous); (8*R*,9*Z*,12*Z*)-8-hydroperoxy-9,12-octadecadienoate mutase ((7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxy-9,12-octadecadienoate-forming)
Systematic name: (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate hydroxymutase [(7*S*,8*S*,9*Z*,12*Z*)-7,8-dihydroxyoctadeca-9,12-dienoate-forming]
Comments: The enzyme contains heme. The bifunctional enzyme from *Gaeumannomyces graminis* catalyses the oxidation of linoleic acid to (8*R*,9*Z*,12*Z*)-8-hydroperoxyoctadeca-9,12-dienoate (*cf.* EC 1.13.11.60, linoleate 8*R*-lipoxygenase), which is then isomerized to (7*S*,8*S*,9*Z*,12*Z*)-5,8-dihydroxyoctadeca-9,12-dienoate [558].
References: [207, 559, 558]

[EC 5.4.4.6 created 2011]

EC 5.4.4.7
Accepted name: hydroperoxy icosatetraenoate isomerase
Reaction: a hydroperoxyicosatetraenoate = a hydroxyepoxyicosatrienoate
Other name(s): epidermal lipoxygenase-3 (ambiguous); eLOX3 (ambiguous)
Systematic name: hydroperoxyicosatetraenoate hydroxymutase
Comments: Binds Fe^{2+}. The enzyme from mammals accepts a range of hydroperoxyicosatetraenoates producing one or several different hydroxyepoxyicosatrienoates. The human enzyme has highest activity with (12*R*)-HPETE producing (5*Z*,8*R*,9*E*,11*R*,12*R*,14*Z*)-8-hydroxy-11,12-epoxyicosa-5,9,14-trienoate, followed by (12*S*)-HPETE producing (5*Z*,8*Z*,10*R*,11*S*,12*S*,14*Z*)-10-hydroxy-11,12-epoxyicosa-5,8,14-trienoate and (5*Z*,8*R*,9*E*,11*S*,12*S*,14*Z*)-8-hydroxy-11,12-epoxyicosa-5,9,14-trienoate [671]. The mouse enzyme has highest activity with (8*S*)-HPETE, producing (5*Z*,8*S*,9*S*,10*R*,11*Z*,14*Z*)-10-hydroxy-8,9-epoxyicosa-5,11,14-trienoate [670]. The enzymes also have the activity of EC 4.2.1.152, hydroperoxy icosatetraenoate dehydratase.
References: [671, 670, 688]

[EC 5.4.4.7 created 2014]

EC 5.4.4.8
Accepted name: linalool isomerase
Reaction: (*RS*)-linalool = geraniol
Other name(s): 3,1-hydroxyl-Δ^1-Δ^2-mutase (linalool isomerase)
Systematic name: (*RS*)-linalool hydroxymutase
Comments: Isolated from the bacterium *Thauera linaloolentis* grown on (*RS*)-linalool as the sole source of carbon. Unlike EC 5.4.4.4, geraniol isomerase, which only acts on (*S*)-linalool, this enzyme acts equally well on both enantiomers.
References: [369]

[EC 5.4.4.8 created 2017]

EC 5.4.99 Transferring other groups

EC 5.4.99.1

Accepted name: methylaspartate mutase
Reaction: L-*threo*-3-methylaspartate = L-glutamate
Other name(s): glutamate mutase; glutamic mutase; glutamic isomerase; glutamic acid mutase; glutamic acid isomerase; methylaspartic acid mutase; β-methylaspartate-glutamate mutase; glutamate isomerase
Systematic name: L-*threo*-3-methylaspartate carboxy-aminomethylmutase
Comments: Requires a cobamide coenzyme.
References: [39, 615]

[EC 5.4.99.1 created 1961]

EC 5.4.99.2

Accepted name: methylmalonyl-CoA mutase
Reaction: (*R*)-methylmalonyl-CoA = succinyl-CoA
Other name(s): methylmalonyl-CoA CoA-carbonyl mutase; methylmalonyl coenzyme A mutase; methylmalonyl coenzyme A carbonylmutase; (*S*)-methylmalonyl-CoA mutase; (*R*)-2-methyl-3-oxopropanoyl-CoA CoA-carbonylmutase [incorrect]
Systematic name: (*R*)-methylmalonyl-CoA CoA-carbonylmutase
Comments: Requires a cobamide coenzyme.
References: [38]

[EC 5.4.99.2 created 1961, modified 1983]

EC 5.4.99.3

Accepted name: 2-acetolactate mutase
Reaction: 2-acetolactate = 3-hydroxy-3-methyl-2-oxobutanoate
Other name(s): acetolactate mutase; acetohydroxy acid isomerase
Systematic name: 2-acetolactate methylmutase
Comments: Requires ascorbic acid; also converts 2-aceto-2-hydroxybutanoate to 3-hydroxy-3-methyl-2-oxopentanoate.
References: [15]

[EC 5.4.99.3 created 1972]

EC 5.4.99.4

Accepted name: 2-methyleneglutarate mutase
Reaction: 2-methyleneglutarate = 2-methylene-3-methylsuccinate
Other name(s): α-methyleneglutarate mutase
Systematic name: 2-methyleneglutarate carboxy-methylenemethylmutase
Comments: Requires a cobamide coenzyme.
References: [321, 322]

[EC 5.4.99.4 created 1972]

EC 5.4.99.5

Accepted name: chorismate mutase
Reaction: chorismate = prephenate
Other name(s): hydroxyphenylpyruvate synthase
Systematic name: chorismate pyruvatemutase
References: [100, 355, 547, 639]

[EC 5.4.99.5 created 1972]

[5.4.99.6 Transferred entry. isochorismate synthase. Now EC 5.4.4.2, isochorismate synthase]

[EC 5.4.99.6 created 1972, deleted 2003]

EC 5.4.99.7

Accepted name: lanosterol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = lanosterol
Other name(s): 2,3-epoxysqualene lanosterol cyclase; squalene-2,3-oxide-lanosterol cyclase; lanosterol 2,3-oxidosqualene cyclase; squalene 2,3-epoxide:lanosterol cyclase; 2,3-oxidosqualene sterol cyclase; oxidosqualene cyclase; 2,3-oxidosqualene cyclase; 2,3-oxidosqualene-lanosterol cyclase; oxidosqualene-lanosterol cyclase; squalene epoxidase-cyclase; (*S*)-2,3-epoxysqualene mutase (cyclizing, lanosterol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, lanosterol-forming)
References: [126]

[EC 5.4.99.7 created 1961 as EC 1.99.1.13, transferred 1965 to EC 1.14.1.3, part transferred 1972 to EC 5.4.99.7 rest to EC 1.14.99.7]

EC 5.4.99.8

Accepted name: cycloartenol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = cycloartenol
Other name(s): 2,3-epoxysqualene cycloartenol-cyclase; squalene-2,3-epoxide-cycloartenol cyclase; 2,3-epoxysqualene-cycloartenol cyclase; 2,3-oxidosqualene-cycloartenol cyclase; (*S*)-2,3-epoxysqualene mutase (cyclizing, cycloartenol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, cycloartenol-forming)
References: [481]

[EC 5.4.99.8 created 1972]

EC 5.4.99.9

Accepted name: UDP-galactopyranose mutase
Reaction: UDP-α-D-galactopyranose = UDP-α-D-galactofuranose
Other name(s): UGM; UDP-D-galactopyranose furanomutase
Systematic name: UDP-α-D-galactopyranose furanomutase
Comments: A flavoenzyme which generates UDP-α-D-glactofuranose required for cell wall formation in bacteria, fungi, and protozoa.
References: [589, 452, 132, 603]

[EC 5.4.99.9 created 1984, modified 2012]

[5.4.99.10 Deleted entry. isomaltulose synthetase. Now included with EC 5.4.99.11, isomaltulose synthase]

[EC 5.4.99.10 created 1984, deleted 1992]

EC 5.4.99.11

Accepted name: isomaltulose synthase
Reaction: sucrose = 6-*O*-α-D-glucopyranosyl-D-fructofuranose
Other name(s): isomaltulose synthetase; sucrose α-glucosyltransferase; trehalulose synthase
Systematic name: sucrose glucosylmutase
Comments: The enzyme simultaneously produces isomaltulose (6-*O*-α-D-glucopyranosyl-D-fructose) and smaller amounts of trehalulose (1-*O*-α-D-glucopyranosyl-β-D-fructose) from sucrose.
References: [83, 84]

[EC 5.4.99.11 created 1989 (EC 5.4.99.10 created 1984, incorporated 1992)]

EC 5.4.99.12

Accepted name: tRNA pseudouridine$^{38-40}$ synthase
Reaction: tRNA uridine$^{38-40}$ = tRNA pseudouridine$^{38-40}$
Other name(s): TruA; tRNA pseudouridine synthase I; PSUI; *hisT* (gene name)
Systematic name: tRNA-uridine$^{38-40}$ uracil mutase
Comments: The uridylate residues at positions 38, 39 and 40 of nearly all tRNAs are isomerized to pseudouridine. TruA specifically modifies uridines at positions 38, 39, and/or 40 in the anticodon stem loop of tRNAs with highly divergent sequences and structures [243].
References: [243, 240, 276, 591, 686, 165, 138, 29]

[EC 5.4.99.12 created 1990, modified 2011]

EC 5.4.99.13

Accepted name: isobutyryl-CoA mutase
Reaction: 2-methylpropanoyl-CoA = butanoyl-CoA
Other name(s): isobutyryl coenzyme A mutase; butyryl-CoA:isobutyryl-CoA mutase; *icmA* (gene name); *icmB* (gene name); *icmF* (gene name)
Systematic name: 2-methylpropanoyl-CoA CoA-carbonylmutase
Comments: This bacterial enzyme utilizes 5′-deoxyadenosylcobalamin as a cofactor. Following substrate binding, the enzyme catalyses the homolytic cleavage of the cobalt-carbon bond of AdoCbl, yielding cob(II)alamin and a 5′-deoxyadenosyl radical, which initiates the the carbon skeleton rearrangement reaction by hydrogen atom abstraction from the substrate. At the end of each catalytic cycle the 5′-deoxyadenosyl radical and cob(II)alamin recombine, regenerating the resting form of the cofactor. The enzyme is prone to inactivation resulting from occassional loss of the 5′-deoxyadenosyl molecule. Inactivated enzymes are repaired by the action of EC 2.5.1.17, cob(I)yrinic acid *a*,*c*-diamide adenosyltransferase, and a G-protein chaperone, which restore cob(II)alamin (which is first reduced to cob(I)alamin by an unidentified reductase) to 5′-deoxyadenosylcobalamin and load it back on the mutase. Some mutases are fused with their G-protein chaperone. These enzyme can also catalyse the interconversion of isovaleryl-CoA with pivalyl-CoA.
References: [65, 474, 102, 101, 269, 345]

[EC 5.4.99.13 created 1992, revised 2017]

EC 5.4.99.14

Accepted name: 4-carboxymethyl-4-methylbutenolide mutase
Reaction: 4-carboxymethyl-4-methylbut-2-en-1,4-olide = 4-carboxymethyl-3-methylbut-2-en-1,4-olide
Other name(s): 4-methyl-2-enelactone isomerase; 4-methylmuconolactone methylisomerase; 4-methyl-3-enelactone methyl isomerase
Systematic name: 4-carboxymethyl-4-methylbut-2-en-1,4-olide methylmutase
References: [69]

[EC 5.4.99.14 created 1992]

EC 5.4.99.15

Accepted name: (1→4)-α-D-glucan 1-α-D-glucosylmutase
Reaction: 4-[(1→4)-α-D-glucosyl]$_{n-1}$-D-glucose = 1-α-D-[(1→4)-α-D-glucosyl]$_{n-1}$-α-D-glucopyranoside
Other name(s): malto-oligosyltrehalose synthase; maltodextrin α-D-glucosyltransferase
Systematic name: (1→4)-α-D-glucan 1-α-D-glucosylmutase
Comments: The enzyme from *Arthrobacter sp.*, *Sulfolobus acidocaldarius* acts on (1→4)-α-D-glucans containing three or more (1→4)-α-linked D-glucose units. Not active towards maltose.
References: [378, 420, 419]

[EC 5.4.99.15 created 1999]

EC 5.4.99.16

Accepted name: maltose α-D-glucosyltransferase
Reaction: maltose = α,α-trehalose
Other name(s): trehalose synthase; maltose glucosylmutase
Systematic name: maltose α-D-glucosylmutase
References: [427, 428]

[EC 5.4.99.16 created 1999]

EC 5.4.99.17

Accepted name: squalene—hopene cyclase
Reaction: squalene = hop-22(29)-ene
Systematic name: squalene mutase (cyclizing, hop-22(29)-ene-forming)
Comments: The enzyme also produces the cyclization product hopan-22-ol by addition of water (*cf.* EC 4.2.1.129, squalenehopanol cyclase). Hopene and hopanol are formed at a constant ratio of 5:1.
References: [236, 235, 506, 482]

[EC 5.4.99.17 created 2002, modified 2011]

EC 5.4.99.18

Accepted name: 5-(carboxyamino)imidazole ribonucleotide mutase
Reaction: 5-carboxyamino-1-(5-phospho-D-ribosyl)imidazole = 5-amino-1-(5-phospho-D-ribosyl)imidazole-4-carboxylate
Other name(s): N^5-CAIR mutase; PurE; N^5-carboxyaminoimidazole ribonucleotide mutase; class I PurE
Systematic name: 5-carboxyamino-1-(5-phospho-D-ribosyl)imidazole carboxymutase
Comments: In eubacteria, fungi and plants, this enzyme, along with EC 6.3.4.18, 5-(carboxyamino)imidazole ribonucleotide synthase, is required to carry out the single reaction catalysed by EC 4.1.1.21, phosphoribosylaminoimidazole carboxylase, in vertebrates [158]. In the absence of EC 6.3.2.6, phosphoribosylaminoimidazolesuccinocarboxamide synthase, the reaction is reversible [395]. The substrate is readily converted into 5-amino-1-(5-phospho-D-ribosyl)imidazole by non-enzymic decarboxylation [395].
References: [396, 413, 395, 380, 159, 158]

[EC 5.4.99.18 created 2006]

EC 5.4.99.19

Accepted name: 16S rRNA pseudouridine^{516} synthase
Reaction: 16S rRNA uridine^{516} = 16S rRNA pseudouridine^{516}
Other name(s): 16S RNA pseudouridine^{516} synthase; 16S PsiI516 synthase; 16S RNA Ψ^{516} synthase; RNA pseudouridine synthase RsuA; RsuA; 16S RNA pseudouridine 516 synthase
Systematic name: 16S rRNA-uridine^{516} uracil mutase
Comments: The enzyme is specific for uridine^{516} in 16S rRNA. *In vitro*, the enzyme does not modify free 16S rRNA. The preferred substrate is a 5′-terminal fragment of 16S rRNA complexed with 30S ribosomal proteins [640].
References: [640, 97, 537]

[EC 5.4.99.19 created 2011]

EC 5.4.99.20

Accepted name: 23S rRNA pseudouridine^{2457} synthase

Reaction: 23S rRNA uridine^{2457} = 23S rRNA pseudouridine^{2457}
Other name(s): RluE; YmfC
Systematic name: 23S rRNA-uridine^{2457} uracil mutase
Comments: The enzyme modifies uridine^{2457} in a stem of 23S RNA in *Escherichia coli*.
References: [73, 446]

[EC 5.4.99.20 created 2011]

EC 5.4.99.21
Accepted name: 23S rRNA pseudouridine^{2604} synthase
Reaction: 23S rRNA uridine^{2604} = 23S rRNA pseudouridine^{2604}
Other name(s): RluF; YjbC
Systematic name: 23S rRNA-uridine^{2604} uracil mutase
Comments: The enzyme is not completely specific for uridine^{2604} and can, to a small extent, also react with uridine^{2605} [73].
References: [73, 14, 566]

[EC 5.4.99.21 created 2011]

EC 5.4.99.22
Accepted name: 23S rRNA pseudouridine^{2605} synthase
Reaction: 23S rRNA uridine^{2605} = 23S rRNA pseudouridine^{2605}
Other name(s): RluB; YciL
Systematic name: 23S rRNA-uridine^{2605} uracil mutase
Comments: Pseudouridine synthase RluB converts uridine^{2605} of 23S rRNA to pseudouridine.
References: [73, 263]

[EC 5.4.99.22 created 2011]

EC 5.4.99.23
Accepted name: 23S rRNA pseudouridine$^{1911/1915/1917}$ synthase
Reaction: 23S rRNA uridine^{1911}/uridine^{1915}/uridine^{1917} = 23S rRNA pseudouridine^{1911}/pseudouridine^{1915}/pseudouridine^{1917}
Other name(s): RluD; pseudouridine synthase RluD
Systematic name: 23S rRNA-uridine$^{1911/1915/1917}$ uracil mutase
Comments: Pseudouridine synthase RluD converts uridines at positions 1911, 1915, and 1917 of 23S rRNA to pseudouridines. These nucleotides are located in the functionally important helix-loop 69 of 23S rRNA [339].
References: [339, 146, 536, 641]

[EC 5.4.99.23 created 2011]

EC 5.4.99.24
Accepted name: 23S rRNA pseudouridine$^{955/2504/2580}$ synthase
Reaction: 23S rRNA uridine^{955}/uridine^{2504}/uridine^{2580} = 23S rRNA pseudouridine^{955}/pseudouridine^{2504}/pseudouridine^{2580}
Other name(s): RluC; pseudouridine synthase RluC
Systematic name: 23S rRNA-uridine$^{955/2504/2580}$ uracil mutase
Comments: The enzyme converts uridines at position 955, 2504 and 2580 of 23S rRNA to pseudouridines.
References: [263, 98, 99, 585]

[EC 5.4.99.24 created 2011]

EC 5.4.99.25

Accepted name: tRNA pseudouridine^{55} synthase
Reaction: tRNA uridine^{55} = tRNA pseudouridine^{55}
Other name(s): TruB; aCbf5; Pus4; YNL292w (gene name); Ψ^{55} tRNA pseudouridine synthase; tRNA:Ψ^{55}-synthase; tRNA pseudouridine 55 synthase; tRNA:pseudouridine-55 synthase; Ψ^{55} synthase; tRNA Ψ^{55} synthase; tRNA:Ψ^{55} synthase; tRNA-uridine^{55} uracil mutase; Pus10; tRNA-uridine$^{54/55}$ uracil mutase
Systematic name: tRNA-uridine^{55} uracil mutase
Comments: Pseudouridine synthase TruB from *Escherichia coli* specifically modifies uridine^{55} in tRNA molecules [434]. The bifunctional archaeal enzyme also catalyses the pseudouridylation of uridine^{54} [201]. It is not known whether the enzyme from *Escherichia coli* can also act on position 54 *in vitro*, since this position is occupied in *Escherichia coli* tRNAs by thymine.
References: [434, 43, 462, 82, 229, 201]

[EC 5.4.99.25 created 2011, modified 2011]

EC 5.4.99.26

Accepted name: tRNA pseudouridine^{65} synthase
Reaction: tRNA uridine^{65} = tRNA pseudouridine^{65}
Other name(s): TruC; YqcB
Systematic name: tRNA-uridine^{65} uracil mutase
Comments: TruC specifically modifies uridines at positions 65 in tRNA.
References: [73]

[EC 5.4.99.26 created 2011]

EC 5.4.99.27

Accepted name: tRNA pseudouridine^{13} synthase
Reaction: tRNA uridine^{13} = tRNA pseudouridine^{13}
Other name(s): TruD; YgbO; tRNA PSI13 synthase; RNA:PSI-synthase Pus7p; Pus7p; RNA:pseudouridine-synthase Pus7p; Pus7 protein
Systematic name: tRNA-uridine^{13} uracil mutase
Comments: Pseudouridine synthase TruD from *Escherichia coli* specifically acts on uridine^{13} in tRNA [78, 289]. The Pus7 protein from *Saccharomyces cerevisiae* is a multisite-multisubstrate pseudouridine synthase that is able to modify uridine^{13} in several yeast tRNAs, uridine^{35} in the pre-tRNA^{Tyr}, uridine^{35} in U2 small nuclear RNA, and uridine^{50} in 5S rRNA [597].
References: [149, 78, 289, 47, 597]

[EC 5.4.99.27 created 2011]

EC 5.4.99.28

Accepted name: tRNA pseudouridine^{32} synthase
Reaction: tRNA uridine^{32} = tRNA pseudouridine^{32}
Other name(s): RluA (ambiguous); pseudouridine synthase RluA (ambiguous); Pus9p; Rib$_2$/Pus8p
Systematic name: tRNA-uridine^{32} uracil mutase
Comments: The dual-specificity enzyme from *Escherichia coli* also catalyses the formation of pseudouridine^{746} in 23S rRNA [642]. *cf.* EC 5.4.99.29 (23S rRNA pseudouridine^{746} synthase).
References: [228, 546, 479, 470, 642, 46]

[EC 5.4.99.28 created 2011, modified 2011]

EC 5.4.99.29

Accepted name: 23S rRNA pseudouridine^{746} synthase
Reaction: 23S rRNA uridine^{746} = 23S rRNA pseudouridine^{746}

Other name(s): RluA (ambiguous); 23S RNA PSI746 synthase; 23S rRNA pseudouridine synthase; pseudouridine synthase RluA (ambiguous)
Systematic name: 23S rRNA-uridine^{746} uracil mutase
Comments: RluA is the sole protein responsible for the *in vivo* formation of 23S RNA pseudouridine^{746} [479]. The dual-specificity enzyme also catalyses the formation of uridine^{32} in tRNA [642]. *cf.* EC 5.4.99.28 (tRNA pseudouridine^{32} synthase).
References: [228, 479, 642]

[EC 5.4.99.29 created 2011]

EC 5.4.99.30
Accepted name: UDP-arabinopyranose mutase
Reaction: UDP-β-L-arabinofuranose = UDP-β-L-arabinopyranose
Other name(s): Os03g40270 protein; UAM1; UAM3; RGP1; RGP3; OsUAM1; OsUAM2; Os03g0599800 protein; Os07g41360 protein
Systematic name: UDP-arabinopyranose pyranomutase
Comments: The reaction is reversible and at thermodynamic equilibrium the pyranose form is favored over the furanose form (90:10) [312].
References: [312, 311, 310]

[EC 5.4.99.30 created 2011]

EC 5.4.99.31
Accepted name: thalianol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = thalianol
Other name(s): (*S*)-2,3-epoxysqualene mutase (cyclizing, thalianol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, thalianol-forming)
References: [152]

[EC 5.4.99.31 created 2011]

EC 5.4.99.32
Accepted name: protostadienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = (17*Z*)-protosta-17(20),24-dien-3β-ol
Other name(s): PdsA; (*S*)-2,3-epoxysqualene mutase [cyclizing, (17*Z*)-protosta-17(20),24-dien-3β-ol-forming]
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase [cyclizing, (17*Z*)-protosta-17(20),24-dien-3β-ol-forming]
Comments: (17*Z*)-Protosta-17(20),24-dien-3β-ol is a precursor of the steroidal antibiotic helvolic acid.
References: [353]

[EC 5.4.99.32 created 2011]

EC 5.4.99.33
Accepted name: cucurbitadienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = cucurbitadienol
Other name(s): CPQ (gene name); (*S*)-2,3-epoxysqualene mutase (cyclizing, cucurbitadienol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, cucurbitadienol-forming)
References: [522]

[EC 5.4.99.33 created 2011]

EC 5.4.99.34
Accepted name: germanicol synthase

Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = germanicol
Other name(s): RsM1; (*S*)-2,3-epoxysqualene mutase (cyclizing, germanicol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualenee mutase (cyclizing, germanicol-forming)
Comments: The enzyme produces germanicol, β-amyrin and lupeol in the ratio 63:33:4.
References: [42]

[EC 5.4.99.34 created 2011]

EC 5.4.99.35
Accepted name: taraxerol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = taraxerol
Other name(s): RsM2; (*S*)-2,3-epoxysqualene mutase (cyclizing, taraxerol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, taraxerol-forming)
Comments: The enzyme gives taraxerol, β-amyrin and lupeol in the ratio 70:17:13.
References: [42]

[EC 5.4.99.35 created 2011]

EC 5.4.99.36
Accepted name: isomultiflorenol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = isomultiflorenol
Other name(s): LcIMS1; (*S*)-2,3-epoxysqualene mutase (cyclizing, isomultiflorenol-forming)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualenee mutase (cyclizing, isomultiflorenol-forming)
References: [215]

[EC 5.4.99.36 created 2011]

EC 5.4.99.37
Accepted name: dammaradiene synthase
Reaction: squalene = dammara-20,24-diene
Systematic name: squalene mutase (cyclizing, dammara-20,24-diene-forming)
References: [528]

[EC 5.4.99.37 created 2011]

EC 5.4.99.38
Accepted name: camelliol C synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = camelliol C
Other name(s): CAMS1; LUP3 (gene name)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, camelliol-C-forming)
Comments: The product is 97% camelliol, 2% achilleol A and 0.2% β-amyrin. Achilleol is an isomer of camelliol C with a 4-methylenecyclohexanol ring system. This enzyme probably evolved from EC 5.4.99.39, β-amyrin synthase.
References: [308]

[EC 5.4.99.38 created 2011]

EC 5.4.99.39
Accepted name: β-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = β-amyrin
Other name(s): 2,3-oxidosqualene β-amyrin cyclase; AsbAS1; BPY; EtAS; GgbAS1; LjAMY1; MtAMY1; PNY; BgbAS

Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, β-amyrin-forming)
Comments: Some organism possess a monofunctional β-amyrin synthase [3,4,6-11], other have a multifunctional enzyme that also catalyses the synthesis of α-amyrin (EC 5.4.99.40) [246] or lupeol (EC 5.4.99.41) [254].
References: [2, 3, 325, 216, 246, 254, 679, 217, 272, 42, 351]

[EC 5.4.99.39 created 2011]

EC 5.4.99.40
Accepted name: α-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = α-amyrin
Other name(s): 2,3-oxidosqualene α-amyrin cyclase; mixed amyrin synthase
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, α-amyrin-forming)
Comments: A multifunctional enzyme which produces both α- and β-amyrin (see EC 5.4.99.39, β-amyrin synthase).
References: [407]

[EC 5.4.99.40 created 2011]

EC 5.4.99.41
Accepted name: lupeol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = lupeol
Other name(s): LUPI; BPW; *RcLUS*
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, lupeol-forming)
Comments: Also forms some β-amyrin. The recombinant enzyme from *Arabidopsis thaliana* [515] gives a 1:1 mixture of lupeol and lupan-3β,20-diol with small amounts of β-amyrin, germanicol, taraxasterol and ψ-taraxasterol. See EC 4.2.1.128 (lupan-3β,20-diol synthase).
References: [226, 525, 515, 679, 217, 198, 42]

[EC 5.4.99.41 created 2011]

EC 5.4.99.42
Accepted name: tRNA pseudouridine^{31} synthase
Reaction: tRNA uridine^{31} = tRNA pseudouridine^{31}
Other name(s): Pus6p
Systematic name: tRNA-uridine^{31} uracil mutase
Comments: The enzyme specifically acts on uridine^{31} in tRNA.
References: [25]

[EC 5.4.99.42 created 2011]

EC 5.4.99.43
Accepted name: 21S rRNA pseudouridine^{2819} synthase
Reaction: 21S rRNA uridine^{2819} = 21S rRNA pseudouridine^{2819}
Other name(s): Pus5p
Systematic name: 21S rRNA-uridine^{2819} uracil mutase
Comments: The enzyme specifically acts on uridine^{2819} in 21S rRNA.
References: [24]

[EC 5.4.99.43 created 2011]

EC 5.4.99.44

Accepted name: mitochondrial tRNA pseudouridine$^{27/28}$ synthase
Reaction: mitochondrial tRNA uridine$^{27/28}$ = mitochondrial tRNA pseudouridine$^{27/28}$

Other name(s): Pus2; Pus2p; RNA:pseudouridine synthases 2
Systematic name: mitochondrial tRNA-uridine$^{27/28}$ uracil mutase
Comments: The mitochondrial enzyme Pus2p is specific for position 27 or 28 in mitochondrial tRNA [45].
References: [45]

[EC 5.4.99.44 created 2011]

EC 5.4.99.45
Accepted name: tRNA pseudouridine$^{38/39}$ synthase
Reaction: tRNA uridine$^{38/39}$ = tRNA pseudouridine$^{38/39}$
Other name(s): Deg1; Pus3p; pseudouridine synthase 3
Systematic name: tRNA-uridine$^{38/39}$ uracil mutase
Comments: The enzyme from *Saccharomyces cerevisiae* is active only towards uridine^{38} and uridine^{39}, and shows no activity with uridine^{40} (*cf.* EC 5.4.99.12, tRNA pseudouridine$^{38-40}$ synthase) [331]. *In vitro* the enzyme from mouse is active on uridine^{39} and very slightly on uridine^{38} (human tRNA^{Leu}) [88].
References: [331, 88]

[EC 5.4.99.45 created 2011]

EC 5.4.99.46
Accepted name: shionone synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = shionone
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, shionone-forming)
Comments: The enzyme gives traces of four other triterpenoids
References: [508]

[EC 5.4.99.46 created 2011]

EC 5.4.99.47
Accepted name: parkeol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = parkeol
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, parkeol-forming)
Comments: The enzyme from rice (*Oryza sativa*) produces parkeol as a single product [251].
References: [251]

[EC 5.4.99.47 created 2011]

EC 5.4.99.48
Accepted name: achilleol B synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = achilleol B
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, achilleol-B-forming)
Comments: Achilleol B is probably formed by cleavage of the 8-14 and 9-10 bonds of (3*S*)-2,3-epoxy-2,3-dihydrosqualene as part of the cyclization reaction, after formation of the oleanane skeleton.
References: [251]

[EC 5.4.99.48 created 2011]

EC 5.4.99.49
Accepted name: glutinol synthase

Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = glutinol
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, glutinol-forming)
Comments: The enzyme from *Kalanchoe daigremontiana* also gives traces of other triterpenoids.
References: [613]

[EC 5.4.99.49 created 2011]

EC 5.4.99.50
Accepted name: friedelin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = friedelin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, friedelin-forming)
Comments: The enzyme from *Kalanchoe daigremontiana* also gives traces of other triterpenoids.
References: [613]

[EC 5.4.99.50 created 2011]

EC 5.4.99.51
Accepted name: baccharis oxide synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = baccharis oxide
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, baccharis-oxide-forming)
Comments: The enzyme from *Stevia rebaudiana* also gives traces of other triterpenoids.
References: [523]

[EC 5.4.99.51 created 2011]

EC 5.4.99.52
Accepted name: α-seco-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = α-seco-amyrin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, α-seco-amyrin-forming)
Comments: The enzyme from *Arabidopsis thaliana* is multifunctional and produces about equal amounts of α- and β-seco-amyrin. See EC 5.4.99.54, β-seco-amyrin synthase.
References: [524]

[EC 5.4.99.52 created 2011]

EC 5.4.99.53
Accepted name: marneral synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = marneral
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, marneral-forming)
Comments: Marneral is a triterpenoid formed by Grob fragmentation of the A ring of 2,3-epoxy-2,3-dihydrosqualene during cyclization.
References: [646]

[EC 5.4.99.53 created 2011]

EC 5.4.99.54
Accepted name: β-seco-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = β-seco-amyrin
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, β-seco-amyrin-forming)
Comments: The enzyme from *Arabidopsis thaliana* is multifunctional and produces about equal amounts of α- and β-seco-amyrin. See EC 5.4.99.52, α-seco-amyrin synthase.
References: [524]

[EC 5.4.99.54 created 2011]

EC 5.4.99.55

Accepted name: δ-amyrin synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = δ-amyrin
Other name(s): SlTTS2 (gene name)
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, δ-amyrin-forming)
Comments: The enzyme from tomato (*Solanum lycopersicum*) gives 48% δ-amyrin, 18% α-amyrin, 13% β-amyrin and traces of three or four other triterpenoid alcohols [612]. See also EC 5.4.99.40, α-amyrin synthase and EC 5.4.99.39, β-amyrin synthase.
References: [612]

[EC 5.4.99.55 created 2011]

EC 5.4.99.56

Accepted name: tirucalladienol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = tirucalla-7,24-dien-3β-ol
Other name(s): PEN3
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, tirucalla-7,24-dien-3β-ol-forming)
Comments: The product from *Arabidopsis thaliana* is 85% tirucalla-7,24-dien-3β-ol with trace amounts of other triterpenoids.
References: [408]

[EC 5.4.99.56 created 2011]

EC 5.4.99.57

Accepted name: baruol synthase
Reaction: (3*S*)-2,3-epoxy-2,3-dihydrosqualene = baruol
Other name(s): BARS1
Systematic name: (3*S*)-2,3-epoxy-2,3-dihydrosqualene mutase (cyclizing, baruol-forming)
Comments: The enzyme from *Arabidopsis thaliana* also produces traces of 22 other triterpenoids.
References: [354]

[EC 5.4.99.57 created 2012]

EC 5.4.99.58

Accepted name: methylornithine synthase
Reaction: L-lysine = (3*R*)-3-methyl-D-ornithine
Other name(s): PylB
Systematic name: L-lysine carboxy-aminomethylmutase
Comments: The enzyme is a member of the superfamily of *S*-adenosyl-L-methionine-dependent radical (radical AdoMet) enzymes. Binds a [4Fe-4S] cluster that is coordinated by 3 cysteines and an exchangeable *S*-adenosyl-L-methionine molecule. The reaction is part of the biosynthesis pathway of pyrrolysine, a naturally occurring amino acid found in some archaeal methyltransferases.
References: [175, 467]

[EC 5.4.99.58 created 2012]

EC 5.4.99.59

Accepted name: dTDP-fucopyranose mutase
Reaction: dTDP-α-D-fucopyranose = dTDP-α-D-fucofuranose
Other name(s): Fcf2

Systematic name: dTDP-α-D-fucopyranose furanomutase
Comments: The enzyme is involved in the biosynthesis of the *Escherichia coli* O52 O antigen.
References: [609]

[EC 5.4.99.59 created 2013]

EC 5.4.99.60
Accepted name: cobalt-precorrin-8 methylmutase
Reaction: cobalt-precorrin-8 = cobyrinate
Other name(s): *cbiC* (gene name)
Systematic name: precorrin-8 11,12-methylmutase
Comments: The enzyme catalyses the the conversion of cobalt-precorrin-8 to cobyrinate by methyl rearrangement, a step in the anaerobic (early cobalt insertion) pathway of adenosylcobalamin biosynthesis. The equivalent enzyme in the aerobic pathway is EC 5.4.99.61, precorrin-8X methylmutase.
References: [492, 496, 649, 404]

[EC 5.4.99.60 created 2014]

EC 5.4.99.61
Accepted name: precorrin-8X methylmutase
Reaction: precorrin-8X = hydrogenobyrinate
Other name(s): precorrin isomerase; hydrogenobyrinic acid-binding protein; *cobH* (gene name)
Systematic name: precorrin-8X 11,12-methylmutase
Comments: The enzyme catalyses the the conversion of precorrin-8X to hydrogenobyrinate by methyl rearrangement, a step in the aerobic (late cobalt insertion) pathway of adenosylcobalamin biosynthesis. The equivalent enzyme in the anaerobic pathway is EC 5.4.99.60, precorrin-8 methylmutase.
References: [580, 111, 529]

[EC 5.4.99.61 created 1999 as EC 5.4.1.2, transferred 2014 to EC 5.4.99.61]

EC 5.4.99.62
Accepted name: D-ribose pyranase
Reaction: β-D-ribopyranose = β-D-ribofuranose
Other name(s): RbsD
Systematic name: D-ribopyranose furanomutase
Comments: The enzyme also catalyses the conversion between β-allopyranose and β-allofuranose.
References: [298, 499]

[EC 5.4.99.62 created 2014]

EC 5.4.99.63
Accepted name: ethylmalonyl-CoA mutase
Reaction: (2*R*)-ethylmalonyl-CoA = (2*S*)-methylsuccinyl-CoA
Other name(s): Ecm
Systematic name: (2*R*)-ethylmalonyl-CoA CoA-carbonylmutase
Comments: The enzyme, characterized from the bacterium *Rhodobacter sphaeroides*, is involved in the ethylmalonyl-CoA pathway for acetyl-CoA assimilation. Requires coenzyme B_{12} for activity.
References: [148]

[EC 5.4.99.63 created 2015]

EC 5.4.99.64

Accepted name: 2-hydroxyisobutanoyl-CoA mutase
Reaction: 2-hydroxy-2-methylpropanoyl-CoA = (*S*)-3-hydroxybutanoyl-CoA
Other name(s): *hcmAB* (gene names)
Systematic name: 2-hydroxy-2-methylpropanoyl-CoA mutase
Comments: The enzyme, characterized from the bacterium *Aquincola tertiaricarbonis*, uses radical chemistry to rearrange the positions of both a methyl group and a hydroxyl group. It consists of two subunits, the smaller one containing a cobalamin cofactor. It plays a central role in the degradation of assorted substrates containing a *tert*-butyl moiety.
References: [655, 323]

[EC 5.4.99.64 created 2016 as EC 5.3.3.20, transferred 2017 to EC 5.4.99.64]

EC 5.4.99.65
Accepted name: pre-α-onocerin synthase
Reaction: (3*S*,22*S*)-2,3:22,23-diepoxy-2,3,22,23-tetrahydrosqualene = pre-α-onocerin
Other name(s): LCC
Systematic name: (3*S*,22*S*)-2,3:22,23-diepoxy-2,3,22,23-tetrahydrosqualene mutase (cyclizing, pre-α-onocerin-forming)
Comments: Isolated from the plant *Lycopodium clavatum*. The enzyme does not act on (3*S*)-2,3-epoxy-2,3-dihydrosqualene and does not form any α-onocerin.
References: [28]

[EC 5.4.99.65 created 2017]

EC 5.4.99.66
Accepted name: α-onocerin synthase
Reaction: pre-α-onocerin = α-onocerin
Other name(s): LCD
Systematic name: pre-α-onocerin mutase (cyclizing, α-onocerin-forming)
Comments: Isolated from the plant *Lycopodium clavatum*.
References: [28]

[EC 5.4.99.66 created 2017]

EC 5.5 Intramolecular lyases

This subclass contains a single sub-subclass for enzymes that catalyse reactions in which a group can be regarded as being eliminated from one part of a molecule, leaving a double bond, while remaining covalently attached to the molecule (intramolecular lyases; EC 5.5.1).

EC 5.5.1 Intramolecular lyases (only sub-subclass identified to date)

EC 5.5.1.1
Accepted name: muconate cycloisomerase
Reaction: (+)-muconolactone = *cis*,*cis*-muconate
Other name(s): muconate cycloisomerase I; *cis*,*cis*-muconate-lactonizing enzyme; *cis*,*cis*-muconate cycloisomerase; muconate lactonizing enzyme; 4-carboxymethyl-4-hydroxyisocrotonolactone lyase (decyclizing); CatB; MCI; 2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing); 2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Systematic name: (+)-muconolactone lyase (ring-opening)
Comments: Requires Mn^{2+}. Also acts (in the reverse reaction) on 3-methyl-*cis*,*cis*-muconate and, very slowly, on *cis*,*trans*-muconate. Not identical with EC 5.5.1.7 (chloromuconate cycloisomerase) or EC 5.5.1.11 (dichloromuconate cycloisomerase).

References: [440, 442, 535]

[EC 5.5.1.1 created 1961]

EC 5.5.1.2

Accepted name: 3-carboxy-*cis*,*cis*-muconate cycloisomerase
Reaction: 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate = *cis*,*cis*-butadiene-1,2,4-tricarboxylate
Other name(s): β-carboxymuconate lactonizing enzyme; 3-carboxymuconolactone hydrolase; 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 2-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
References: [441, 442]

[EC 5.5.1.2 created 1972]

EC 5.5.1.3

Accepted name: tetrahydroxypteridine cycloisomerase
Reaction: tetrahydroxypteridine = xanthine-8-carboxylate
Systematic name: tetrahydroxypteridine lyase (isomerizing)
References: [388]

[EC 5.5.1.3 created 1972]

EC 5.5.1.4

Accepted name: inositol-3-phosphate synthase
Reaction: D-glucose 6-phosphate = 1D-*myo*-inositol 3-phosphate
Other name(s): *myo*-inositol-1-phosphate synthase; D-glucose 6-phosphate cycloaldolase; inositol 1-phosphate synthatase; glucose 6-phosphate cyclase; inositol 1-phosphate synthetase; glucose-6-phosphate inositol monophosphate cycloaldolase; glucocycloaldolase; 1L-*myo*-inositol-1-phosphate lyase (isomerizing)
Systematic name: 1D-*myo*-inositol-3-phosphate lyase (isomerizing)
Comments: Requires NAD^+, which dehydrogenates the -CHOH- group to -CO- at C-5 of the glucose 6-phosphate, making C-6 into an active methylene, able to condense with the -CHO at C-1. Finally, the enzyme-bound NADH reconverts C-5 into the -CHOH- form.
References: [144, 521, 40, 41]

[EC 5.5.1.4 created 1972, modified 2001]

EC 5.5.1.5

Accepted name: carboxy-*cis*,*cis*-muconate cyclase
Reaction: 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate = 3-carboxy-*cis*,*cis*-muconate
Other name(s): 3-carboxymuconate cyclase; 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 3-carboxy-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
References: [197]

[EC 5.5.1.5 created 1972]

EC 5.5.1.6

Accepted name: chalcone isomerase
Reaction: a chalcone = a flavanone
Other name(s): chalcone-flavanone isomerase; flavanone lyase (decyclizing)
Systematic name: flavanone lyase (ring-opening)
References: [410]

[EC 5.5.1.6 created 1972]

EC 5.5.1.7

Accepted name: chloromuconate cycloisomerase
Reaction: (2*R*)-2-chloro-2,5-dihydro-5-oxofuran-2-acetate = 3-chloro-*cis*,*cis*-muconate
Other name(s): muconate cycloisomerase II; 2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing); 2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Systematic name: (2*R*)-2-chloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Comments: Requires Mn^{2+}. The product of cycloisomerization of 3-chloro-*cis*,*cis*-muconate spontaneously eliminates chloride to produce *cis*-4-carboxymethylenebut-2-en-4-olide. Also acts on 2-chloro-*cis*,*cis*-muconate. Not identical with EC 5.5.1.1 (muconate cycloisomerase) or EC 5.5.1.11 (dichloromuconate cycloisomerase).
References: [511, 285, 271]

[EC 5.5.1.7 created 1983]

EC 5.5.1.8

Accepted name: (+)-bornyl diphosphate synthase
Reaction: geranyl diphosphate = (+)-bornyl diphosphate
Other name(s): bornyl pyrophosphate synthase (ambiguous); bornyl pyrophosphate synthetase (ambiguous); (+)-bornylpyrophosphate cyclase; geranyl-diphosphate cyclase (ambiguous); (+)-bornyl-diphosphate lyase (decyclizing)
Systematic name: (+)-bornyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. The enzyme from *Salvia officinalis* (sage) can also use (3*R*)-linalyl diphosphate or more slowly neryl diphosphate *in vitro* [108]. The reaction proceeds via isomeration of geranyl diphosphate to (3*R*)-linalyl diphosphate. The oxygen and phosphorus originally linked to C-1 of geranyl diphosphate end up linked to C-2 of (+)-bornyl diphosphate [108]. *cf.* EC 5.5.1.22 [(–)-bornyl diphosphate synthase].
References: [107, 106, 108, 105, 110, 386, 631, 621, 459]

[EC 5.5.1.8 created 1984, modified 2012]

EC 5.5.1.9

Accepted name: cycloeucalenol cycloisomerase
Reaction: cycloeucalenol = obtusifoliol
Other name(s): cycloeucalenol—obtusifoliol isomerase; cycloeucalenol lyase (cyclopropane-decyclizing)
Systematic name: cycloeucalenol lyase (cyclopropane-ring opening)
Comments: Opens the cyclopropane ring of a number of related 4α-methyl-9β-19-cyclosterols, but not those with a 4β-methyl group, with formation of an 8(9) double bond. Involved in the synthesis of plant sterols.
References: [222, 469]

[EC 5.5.1.9 created 1986]

EC 5.5.1.10

Accepted name: α-pinene-oxide decyclase
Reaction: α-pinene oxide = (*Z*)-2-methyl-5-isopropylhexa-2,5-dienal
Other name(s): α-pinene oxide lyase; α-pinene-oxide lyase (decyclizing)
Systematic name: α-pinene-oxide lyase (ring-opening)
Comments: Both rings of pinene are cleaved in the reaction.
References: [195]

[EC 5.5.1.10 created 1990]

EC 5.5.1.11

Accepted name: dichloromuconate cycloisomerase
Reaction: 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate = 2,4-dichloro-*cis*,*cis*-muconate
Other name(s): 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate lyase (decyclizing)
Systematic name: 2,4-dichloro-2,5-dihydro-5-oxofuran-2-acetate lyase (ring-opening)
Comments: Requires Mn^{2+}. The product of cycloisomerization of dichloro-*cis*,*cis*-muconate spontaneously eliminates chloride to produce *cis*-4-carboxymethylene-3-chlorobut-2-en-4-olide. Also acts, in the reverse direction, on *cis*,*cis*-muconate and its monochloro-derivatives, but with lower affinity. Not identical with EC 5.5.1.1 (muconate cycloisomerase) or EC 5.5.1.7 (chloromuconate cycloisomerase).
References: [317]

[EC 5.5.1.11 created 1992]

EC 5.5.1.12

Accepted name: copalyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (+)-copalyl diphosphate
Other name(s): (+)-copalyl-diphosphate lyase (decyclizing)
Systematic name: (+)-copalyl-diphosphate lyase (ring-opening)
Comments: In some plants, such as *Salvia miltiorrhiza*, this enzyme is monofunctional. In other plants this activity is often a part of a bifunctional enzyme. For example, in *Selaginella moellendorffii* this activity is catalysed by a bifunctional enzyme that also catalyses EC 4.2.3.131, miltiradiene synthase, while in the tree *Abies grandis* (grand fir) it is catalysed by a bifunctional enzyme that also catalyses EC 4.2.3.18, abietadiene synthase.
References: [460, 561, 458, 476, 457]

[EC 5.5.1.12 created 2002, modified 2012]

EC 5.5.1.13

Accepted name: *ent*-copalyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = *ent*-copalyl diphosphate
Other name(s): *ent*-kaurene synthase A; *ent*-kaurene synthetase A; *ent*-CDP synthase; *ent*-copalyl-diphosphate lyase (decyclizing)
Systematic name: *ent*-copalyl-diphosphate lyase (ring-opening)
Comments: Part of a bifunctional enzyme involved in the biosynthesis of kaurene. See also EC 4.2.3.19 (*ent*-kaurene synthase)
References: [151, 565, 287, 587]

[EC 5.5.1.13 created 2002]

EC 5.5.1.14

Accepted name: *syn*-copalyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = 9α-copalyl diphosphate
Other name(s): OsCyc1; OsCPSsyn; *syn*-CPP synthase; *syn*-copalyl diphosphate synthase; 9α-copalyl-diphosphate lyase (decyclizing)
Systematic name: 9α-copalyl-diphosphate lyase (ring-opening)
Comments: Requires a divalent metal ion, preferably Mg^{2+}, for activity. This class II terpene synthase produces *syn*-copalyl diphosphate, a precursor of several rice phytoalexins, including oryzalexin S and momilactones A and B. Phytoalexins are diterpenoid secondary metabolites that are involved in the defense mechanism of the plant, and are produced in response to pathogen attack through the perception of elicitor signal molecules such as chitin oligosaccharide, or after exposure to UV irradiation. The enzyme is constitutively expressed in the roots of plants where one of its products, momilactone B, acts as an allelochemical (a molecule released into the environment to suppress the growth of neighbouring plants). In other tissues the enzyme is upregulated by conditions that stimulate the biosynthesis of phytoalexins.

References: [443, 648]

[EC 5.5.1.14 created 2008]

EC 5.5.1.15

Accepted name: terpentedienyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = terpentedienyl diphosphate
Other name(s): terpentedienol diphosphate synthase; Cyc1; clerodadienyl diphosphate synthase; terpentedienyl-diphosphate lyase (decyclizing)
Systematic name: terpentedienyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. Contains a DXDD motif, which is a characteristic of diterpene cylases whose reactions are initiated by protonation at the 14,15-double bond of geranylgeranyl diphosphate (GGDP) [205]. The triggering proton is lost at the end of the cyclization reaction [143]. The product of the reaction, terpentedienyl diphosphate, is the substrate for EC 4.2.3.36, terpentetriene synthase and is a precursor of the diterpenoid antibiotic terpentecin.
References: [121, 205, 143]

[EC 5.5.1.15 created 2008]

EC 5.5.1.16

Accepted name: halimadienyl-diphosphate synthase
Reaction: geranylgeranyl diphosphate = tuberculosinyl diphosphate
Other name(s): Rv3377c; halimadienyl diphosphate synthase; tuberculosinol diphosphate synthase; halima-5(6),13-dien-15-yl-diphosphate lyase (cyclizing); halima-5,13-dien-15-yl-diphosphate lyase (decyclizing)
Systematic name: halima-5,13-dien-15-yl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+} for activity. This enzyme is found in pathogenic prokaryotes such as *Mycobacterium tuberculosis* but not in non-pathogens such as *Mycobacterium smegmatis* so may play a role in pathogenicity. The product of the reaction is subsequently dephosphorylated yielding tuberculosinol (halima-5,13-dien-15-ol).
References: [425]

[EC 5.5.1.16 created 2008, modified 2012]

EC 5.5.1.17

Accepted name: (*S*)-β-macrocarpene synthase
Reaction: (*S*)-β-bisabolene = (*S*)-β-macrocarpene
Other name(s): TPS6; TPS11; (*S*)-β-macrocarpene lyase (decyclizing)
Systematic name: (*S*)-β-macrocarpene lyase (ring-opening)
Comments: The synthesis of (*S*)-β-macrocarpene from (2*E*,6*E*)-farnesyl diphosphate proceeds in two steps. The first step is the cyclization to (*S*)-β-bisabolene (*cf.* EC 4.2.3.55, (*S*)-β-bisabolene synthase). The second step is the isomerization to (*S*)-β-macrocarpene.
References: [309]

[EC 5.5.1.17 created 2011]

EC 5.5.1.18

Accepted name: lycopene ε-cyclase
Reaction: carotenoid ψ-end group = carotenoid ε-end group
Other name(s): CrtL-e; LCYe; carotenoid ψ-end group lyase (decyclizing)
Systematic name: carotenoid ψ-end group lyase (ring-opening)
Comments: The carotenoid lycopene has the ψ-end group at both ends. When acting on one end, this enzyme forms δ-carotene. When acting on both ends, it forms ε-carotene.
References: [114, 552]

[EC 5.5.1.18 created 2011]

EC 5.5.1.19

Accepted name: lycopene β-cyclase
Reaction: carotenoid ψ-end group = carotenoid β-end group
Other name(s): CrtL; CrtL-b; CrtY; LCYb; carotenoid β-end group lyase (decyclizing)
Systematic name: carotenoid β-end group lyase (ring-opening)
Comments: The enzyme is a non-redox flavoprotein, containing $FADH_2$ that is used for stabilization of a transition state. Lycopene has a ψ-end group at both ends. When acting on one end, the enzyme forms γ-carotene. When acting on both ends it forms β-carotene. It also acts on neurosporene to give β-zeacarotene.
References: [113, 115, 242, 455, 233, 367, 667]

[EC 5.5.1.19 created 2011]

EC 5.5.1.20

Accepted name: prosolanapyrone-III cycloisomerase
Reaction: prosolanapyrone III = (–)-solanapyrone A
Other name(s): Sol5 (ambiguous); SPS (ambiguous); solanapyrone synthase (bifunctional enzyme: prosolanapyrone II oxidase/prosolanapyrone III cyclosiomerase)
Systematic name: prosolanapyrone-III:(–)-solanapyrone A isomerase
Comments: The enzyme is involved in the biosynthesis of the phytotoxin solanapyrone in some fungi. The bifunctional enzyme catalyses the oxidation of prosolanapyrone II and the subsequent Diels Alder cycloisomerization of the product prosolanapyrone III to (–)-solanapyrone A (*cf.* EC 1.1.3.42, prosolanapyrone II oxidase).
References: [279, 282, 281]

[EC 5.5.1.20 created 2011]

[5.5.1.21 Transferred entry. copal-8-ol diphosphate synthase. The enzyme was discovered at the public-review stage to have been misclassified and so was withdrawn. See EC 4.2.1.133, copal-8-ol diphosphate hydratase]

[EC 5.5.1.21 created 2012, deleted 2012]

EC 5.5.1.22

Accepted name: (–)-bornyl diphosphate synthase
Reaction: geranyl diphosphate = (–)-bornyl diphosphate
Other name(s): bornyl pyrophosphate synthase (ambiguous); bornyl pyrophosphate synthetase (ambiguous); (–)-bornyl pyrophosphate cyclase; bornyl diphosphate synthase; geranyl-diphosphate cyclase (ambiguous); (–)-bornyl-diphosphate lyase (decyclizing)
Systematic name: (–)-bornyl-diphosphate lyase (ring-opening)
Comments: Requires Mg^{2+}. The enzyme from *Tanacetum vulgare* (tansy) can also use (3*S*)-linalyl diphosphate or more slowly neryl diphosphate *in vitro*. The reaction proceeds via isomeration of geranyl diphosphate to (3*S*)-linalyl diphosphate [105]. The oxygen and phosphorus originally linked to C-1 of geranyl diphosphate end up linked to C-2 of (–)-bornyl diphosphate [110]. *cf.* EC 5.5.1.8 (+)-bornyl diphosphate synthase.
References: [106, 109, 105, 110, 5]

[EC 5.5.1.22 created 2012]

EC 5.5.1.23

Accepted name: aklanonic acid methyl ester cyclase
Reaction: aklaviketone = methyl aklanonate

Other name(s): *dauD* (gene name); *aknH* (gene name); *dnrD* (gene name); methyl aklanonate cyclase; methyl aklanonate-aklaviketone isomerase (cyclizing); aklaviketone lyase (decyclizing)
Systematic name: aklaviketone lyase (ring-opening)
Comments: The enzyme is involved in the biosynthesis of aklaviketone, an intermediate in the biosynthetic pathways leading to formation of several anthracycline antibiotics, including aclacinomycin, daunorubicin and doxorubicin.
References: [134, 294, 273]

[EC 5.5.1.23 created 2013, modified 2014]

EC 5.5.1.24
Accepted name: tocopherol cyclase
Reaction: (1) δ-tocopherol = 2-methyl-6-phytylbenzene-1,4-diol
(2) γ-tocopherol = 2,3-dimethyl-6-phytylbenzene-1,4-diol
(3) δ-tocotrienol = 6-geranylgeranyl-2-methylbenzene-1,4-diol
(4) γ-tocotrienol = 6-geranylgeranyl-2,3-dimethylbenzene-1,4-diol
Other name(s): VTE1 (gene name); SXD1 (gene name); δ/γ-tocopherol lyase (decyclizing)
Systematic name: δ/γ-tocopherol lyase (ring-opening)
Comments: The enzyme has been described from plants and cyanobacteria. It has similar activity with all four listed benzoquinol substrates. Involved in the biosynthesis of vitamin E (tocopherols and tocotrienols).
References: [463, 507]

[EC 5.5.1.24 created 2013]

EC 5.5.1.25
Accepted name: 3,6-anhydro-L-galactonate cycloisomerase
Reaction: 3,6-anhydro-L-galactonate = 2-dehydro-3-deoxy-L-galactonate
Other name(s): 3,6-anhydro-α-L-galactonate lyase (ring-opening); 3,6-anhydro-α-L-galactonate cycloisomerase
Systematic name: 3,6-anhydro-L-galactonate lyase (ring-opening)
Comments: The enzyme, characterized from the marine bacteria *Vibrio* sp. EJY3 and *Postechiella marina* M091, is involved in a degradation pathway for 3,6-anhydro-α-L-galactopyranose, a major component of the polysaccharides of red macroalgae.
References: [672, 334]

[EC 5.5.1.25 created 2014, modified 2015]

EC 5.5.1.26
Accepted name: nogalonic acid methyl ester cyclase
Reaction: nogalaviketone = methyl nogalonate
Other name(s): methyl nogalonate cyclase; SnoaL (gene name); methyl nogalonate lyase (cyclizing)
Systematic name: nogalaviketone lyase (ring-opening)
Comments: The enzyme, characterized from the bacterium *Streptomyces nogalater*, is involved in the biosynthesis of the aromatic polyketide nogalamycin.
References: [563, 562]

[EC 5.5.1.26 created 2015]

EC 5.5.1.27
Accepted name: D-galactarolactone cycloisomerase
Reaction: (1) D-galactaro-1,4-lactone = 5-dehydro-4-deoxy-D-glucarate
(2) D-glucaro-1,4-lactone = 5-dehydro-4-deoxy-D-glucarate
Other name(s): GCI

Systematic name: D-galactaro-1,4-lactone lyase (ring-opening)
Comments: The enzyme, characterized from the bacterium *Agrobacterium fabrum* strain C58, is involved in degradation of D-galacturonate and D-glucuronate. Activity with D-galactaro-1,4-lactone is 4-fold higher than with D-glucaro-1,4-lactone.
References: [20, 62]

[EC 5.5.1.27 created 2015]

EC 5.5.1.28
Accepted name: (–)-kolavenyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (–)-kolavenyl diphosphate
Other name(s): SdKPS; TwTPS14; TwTPS10/KPS; SdCPS2; clerodienyl diphosphate synthase; CLPP
Systematic name: (–)-kolavenyl diphosphate lyase (ring-opening)
Comments: Isolated from the hallucinogenic plant *Salvia divinorum* (seer's sage) and the medicinal plant *Tripterygium wilfordii* (thunder god vine).
References: [209, 90]

[EC 5.5.1.28 created 2017]

EC 5.5.1.29
Accepted name: (+)-kolavenyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (+)-kolavenyl diphosphate
Systematic name: (+)-kolavenyl-diphosphate lyase (ring-opening)
Comments: Isolated from the bacterium *Herpetosiphon aurantiacus*.
References: [426]

[EC 5.5.1.29 created 2017]

EC 5.5.1.30
Accepted name: labda-7,13-dienyl diphosphate synthase
Reaction: geranylgeranyl diphosphate = (13*E*)-labda-7,13-dien-15-yl diphosphate
Other name(s): SCLAV_p0490
Systematic name: (13*E*)-labda-7,13-dien-15-yl-diphosphate lyase (ring-opening)
Comments: Isolated from the bacterium *Streptomyces clavuligerus*.
References: [651]

[EC 5.5.1.30 created 2017]

EC 5.5.1.31
Accepted name: hapalindole H synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = hapalindole H
Other name(s): *famC*2 (gene name); *famC*3 (gene name)
Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (hapalindole H-forming)
Comments: The enzyme, characterized from the cyanobacterium *Fischerella ambigua* UTEX 1903, forms the core structure of the hapalindole family of alkaloids. The enzyme is a heterodimeric complex.
References: [343]

[EC 5.5.1.31 created 2018]

EC 5.5.1.32
Accepted name: 12-*epi*-hapalindole U synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = 12-*epi*-hapalindole U

Other name(s): *famC*1 (gene name); HpiC1 (gene name)
Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (12-*epi*-hapalindole U-forming)
Comments: The enzyme, characterized from the cyanobacterium *Fischerella ambigua* UTEX 1903, forms the core structure of the 12-*epi*-hapalindole family of alkaloids.
References: [344]

[EC 5.5.1.32 created 2018]

EC 5.5.1.33
Accepted name: 12-*epi*-fischerindole U synthase
Reaction: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole = 12-*epi*-fischerindole U
Other name(s): *fisC* (gene name); *fimC*5 (gene name)
Systematic name: 3-geranyl-3-[(*Z*)-2-isocyanoethenyl]-1*H*-indole cyclase (12-*epi*-fischerindole U-forming)
Comments: The enzyme, characterized from multiple species of the cyanobacterial genus *Fischerella*, participates in the biosynthesis of the terpenoid indole alkaloids 12-*epi*-fischerindoles.
References: [343]

[EC 5.5.1.33 created 2018]

EC 5.6 Isomerases altering macromolecular conformation

These enzyme catalyse changes to the conformations of macromolecules.

EC 5.6.1 Enzymes altering polypeptide conformation or assembly

EC 5.6.1.1
Accepted name: microtubule-severing ATPase
Reaction: ***n*** ATP + ***n*** H_2O + a microtubule = ***n*** ADP + ***n*** phosphate + (***n*+1**) α/β tubulin heterodimers
Other name(s): katanin
Systematic name: ATP phosphohydrolase (tubulin-dimerizing)
Comments: A member of the AAA-ATPase family, active in splitting microtubules into tubulin dimers in the centrosome.
References: [387, 211]

[EC 5.6.1.1 created 2000 as 3.6.4.3, transferred 2018 to EC 5.6.1.1]

EC 5.6.1.2
Accepted name: dynein ATPase
Reaction: ATP + H_2O + a dynein associated with a microtubule at position *n* = ADP + phosphate + a dynein associated with a microtubule at position *n*-1 (toward the minus end)
Other name(s): dynein adenosine 5′-triphosphatase
Systematic name: ATP phosphohydrolase (tubulin-translocating)
Comments: A multisubunit protein complex associated with microtubules. Hydrolysis of ATP provides energy for the movement of organelles (endosomes, lysosomes, mitochondria) along microtubules to the centrosome towards the microtubule's minus end. It also functions in the movement of eukaryotic flagella and cilia. It consists of two heavy chains (about 500 kDa), three-four intermediate chains (about 70 kDa) and four light chains (about 50 kDa).
References: [564, 184, 177]

[EC 5.6.1.2 created 1984 as EC 3.6.1.33, transferred 2000 to EC 3.6.4.2, transferred 2018 to EC 5.6.1.2]

EC 5.6.1.3

Accepted name: plus-end-directed kinesin ATPase
Reaction: ATP + H_2O + a kinesin associated with a microtubule at position *n* = ADP + phosphate a kinesin associated with a microtubule at position *n*+1 (toward the plus end)
Other name(s): kinesin
Systematic name: kinesin ATP phosphohydrolase (plus-end-directed)
Comments: Kinesins are a family of motor proteins that move unidirectionally along microtubules as they hydrolyse ATP. The enzymes described here move towards the plus end of the microtubule, in contrast to EC 5.6.1.2, dynein ATPase and EC 5.6.1.4, minus-end-directed kinesin ATPase. They are involved in organelle movement in mitosis and meiosis, and also power vesicular trafficking toward the synapse in neurons. The motor domain, which contains the ATP- and microtubule-binding activities, is located at the N-terminus while the C-terminus links to the cargo being transported.
References: [600, 318, 237, 421, 534, 611]

[EC 5.6.1.3 created 2000 as 3.6.4.4, transferred 2018 to EC 5.6.1.3]

EC 5.6.1.4

Accepted name: minus-end-directed kinesin ATPase
Reaction: ATP + H_2O + a kinesin associated with a microtubule at position *n* = ADP + phosphate + a kinesin associated with a microtubule at position *n*-1 (toward the minus end)
Other name(s): non-claret disjunctional; *ncd* (gene name)
Systematic name: kinesin ATP phosphohydrolase (minus-end-directed)
Comments: Kinesins are a family of motor proteins that move unidirectionally along microtubules as they hydrolyse ATP and are involved in organelle movement. This enzyme is similar to EC 5.6.1.3, plus-end-directed kinesin ATPase, but the organization of the different domains differs, resulting in movement in the opposite direction along the microtubules.
References: [385, 80, 352, 225, 501]

[EC 5.6.1.4 created 2000, as 3.6.4.5, transferred 2018 to EC 5.6.1.4]

EC 5.6.1.5

Accepted name: proteasome ATPase
Reaction: ATP + H_2O + polypeptide = ADP + phosphate + unfolded polypeptide
Systematic name: ATP phosphohydrolase (polypeptide-degrading)
Comments: Belongs to the AAA-type superfamily and, like EC 5.6.1.4 (minus-end-directed kinesin ATPase), is involved in channel gating and polypeptide unfolding before proteolysis in the proteasome. Six ATPase subunits are present in the regulatory particle (RP) of 26*S* proteasome.
References: [490, 379]

[EC 5.6.1.5 created 2000 as 3.6.4.8, transferred 2018 to EC 5.6.1.5]

EC 5.6.1.6

Accepted name: channel-conductance-controlling ATPase
Reaction: ATP + H_2O + closed Cl^- channel = ADP + phosphate + open Cl^- channel
Other name(s): cystic fibrosis transmembrane conductance regulator; CFTR (gene name)
Systematic name: ATP phosphohydrolase (channel-conductance-controlling)
Comments: ABC-type (ATP-binding cassette-type) ATPase, characterized by the presence of two similar ATP-binding domains. The enzyme is found in animals, and in humans its absence brings about cystic fibrosis. Unlike most of the ABC transporters, chloride pumping is not directly coupled to ATP hydrolysis. Instead, the passive flow of anions through the channel is gated by cycles of ATP binding and hydrolysis by the ATP-binding domains. The enzyme is also involved in the functioning of other transmembrane channels.
References: [89, 592, 520, 248]

[EC 5.6.1.6 created 2000 as EC 3.6.3.49, transferred 2018 to EC 5.6.1.6]

EC 5.6.1.7

Accepted name: chaperonin ATPase
Reaction: ATP + H_2O + a folded polypeptide = ADP + phosphate + an unfolded polypeptide
Other name(s): chaperonin
Systematic name: ATP phosphohydrolase (polypeptide-unfolding)
Comments: Multisubunit proteins with 2x7 (Type I, in most cells) or 2x8 (Type II, in Archaea) ATP-binding sites involved in maintaining an unfolded polypeptide structure before folding or entry into mitochondria and chloroplasts. Molecular masses of subunits ranges from 10-90 kDa. They are a subclass of molecular chaperones that are related to EC 5.6.1.5 (proteasome ATPase).
References: [223, 358, 1, 473]

[EC 5.6.1.7 created 2000 as EC 3.6.4.9, transferred 2018 to EC 5.6.1.7]

EC 5.6.1.8

Accepted name: myosin ATPase
Reaction: ATP + H_2O + myosin bound to actin filament at position *n* = ADP + phosphate + myosin bound to actin filament at position *n*+1
Systematic name: ATP phosphohydrolase (actin-translocating)
Comments: Proteins of the contractile apparatus of muscle and nonmuscle cells; myosin molecule consists of two heavy chains (about 200 kDa) and two pairs of light chains (15–27 kDa). The head region of the heavy chain contains actin- and ATP-binding sites. ATP hydrolysis provides energy for actomyosin contraction.
References: [480, 213, 415]

[EC 5.6.1.8 created 1984 as EC 3.6.1.32, transferred 2000 to EC 3.6.4.1, transferred 2018 to EC 5.6.1.8]

EC 5.6.2 Enzymes altering nucleic acid conformation

EC 5.6.2.1

Accepted name: DNA topoisomerase
Reaction: ATP-independent breakage of single-stranded DNA, followed by passage and rejoining
Other name(s): type I DNA topoisomerase; untwisting enzyme; relaxing enzyme; nicking-closing enzyme; swivelase; ω-protein; deoxyribonucleate topoisomerase; topoisomerase
Systematic name: DNA topoisomerase
Comments: These enzymes bring about the conversion of one topological isomer of DNA into another, e.g., the relaxation of superhelical turns in DNA, the interconversion of simple and knotted rings of single-stranded DNA, and the intertwisting of single-stranded rings of complementary sequences, *cf.* EC 5.6.2.2 DNA topoisomerase (ATP-hydrolysing).
References: [180]

[EC 5.6.2.1 created 1984 as 5.99.1.2 transferred 2019 to EC 5.6.2.1]

EC 5.6.2.2

Accepted name: DNA topoisomerase (ATP-hydrolysing)
Reaction: ATP-dependent breakage, passage and rejoining of double-stranded DNA
Other name(s): type II DNA topoisomerase; DNA-gyrase; deoxyribonucleate topoisomerase; deoxyribonucleic topoisomerase; topoisomerase; DNA topoisomerase II
Systematic name: DNA topoisomerase (ATP-hydrolysing)
Comments: The enzyme can introduce negative superhelical turns into double-stranded circular DNA. One unit has nicking-closing activity, and another catalyses super-twisting and hydrolysis of ATP (*cf.* EC 5.6.2.1 DNA topoisomerase).

References: [180]

[EC 5.6.2.2 created 1984 as 5.99.1.3, transferred 2019 to EC 5.6.2.2]

EC 5.99 Other isomerases

This subclass contains miscellaneous enzymes in a single sub-subclass (EC 5.99.1).

EC 5.99.1 Sole sub-subclass for isomerases that do not belong in the other subclasses

EC 5.99.1.1
Accepted name: thiocyanate isomerase
Reaction: benzyl isothiocyanate = benzyl thiocyanate
Other name(s): isothiocyanate isomerase
Systematic name: benzyl-thiocyanate isomerase
References: [605]

[EC 5.99.1.1 created 1965]

[5.99.1.2 Transferred entry. DNA topoisomerase. Now EC 5.6.2.1, DNA topoisomerase]

[EC 5.99.1.2 created 1984, deleted 2018]

[5.99.1.3 Transferred entry. DNA topoisomerase (ATP-hydrolysing). Now EC 5.6.2.2, DNA topoisomerase (ATP-hydrolysing)]

[EC 5.99.1.3 created 1984, deleted 2018]

EC 5.99.1.4
Accepted name: 2-hydroxychromene-2-carboxylate isomerase
Reaction: 2-hydroxy-2*H*-chromene-2-carboxylate = (3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate
Other name(s): HCCA isomerase; 2HC2CA isomerase; 2-hydroxychromene-2-carboxylic acid isomerase
Systematic name: 2-hydroxy-2*H*-chromene-2-carboxylate—(3*E*)-4-(2-hydroxyphenyl)-2-oxobut-3-enoate isomerase
Comments: This enzyme is involved in naphthalene degradation.
References: [437, 290, 141, 583]

[EC 5.99.1.4 created 2010]

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