Abstract: Most of the fungi from the *Fusarium* genus are pathogenic to cereals, vegetables, and fruits and the products of their secondary metabolism mycotoxins may accumulate in foods and feeds. Non-ribosomal cyclodepsipeptides are one of the main mycotoxin groups and include beauvericins (BEAs), enniatins (ENNs), and beauvenniatins (BEAEs). When ingested, even small amounts of these metabolites significantly affect human and animal health. On the other hand, in view of their antimicrobial activities and cytotoxicity, they may be used as components in drug discovery and processing and are considered as suitable candidates for anti-cancer drugs. Therefore, it is crucial to expand the existing knowledge about cyclodepsipeptides and to search for new analogues of these compounds. The present manuscript aimed to highlight the extensive variability of cyclodepsipeptides by describing chemistry, biosynthesis, and occurrence of BEAs, ENNs, and BEAEs in foods and feeds. Moreover, the co-occurrence of *Fusarium* species was compared to the amounts of toxins in crops, vegetables, and fruits from different regions of the world.

Keywords: phytopathogens; *Fusarium*; mycotoxin contamination; secondary metabolism; beauvericin; enniatin

Key Contribution: This article highlights the variability of cyclodepsipeptides mycotoxins such as BEAs; ENNs and BEAEs; produced by *Fusarium* species and the characteristics of the genes involved in the biosynthesis of these mycotoxins.

1. Introduction

Fungi belonging to the *Fusarium* genus produce a wide range of secondary metabolites, including the non-ribosomal depsipeptide mycotoxins, such as beauvericins (BEAs), beauvenniatins (BEAEs), enniatins (ENNs), and their analogues [1–4]. BEAs, BEAEs, and ENNs were included in the cyclodepsipeptide group of compounds, often found in high concentrations in grains, crops, vegetables, fruits, and even eggs, as a result of fungal infection [5–9]. They are involved in plant-pathogen interaction and may lead to many plants’ diseases, which can be very dangerous for animals’ health, including humans [10–14]. For example, ENNs produced by *Fusarium* species may act synergistically as a phytotoxin complex, which causes wilt and necrosis of plant tissue [15]. Moreover, ENN B affects mouse embryo development by inducing the dosage-related apoptosis or necrosis in mouse blastocyes [16]. On the other hand, BEA demonstrated neurotoxic properties in mice. In higher concentrations (7.5 and 10 μM), it affected the skeletal muscle fibers [17].

Additionally, BEA has a harmful influence on the reproductive system. The progesterone synthesis in cumulus cells was decreased when exposed to BEA [18]. Moreover, BEA inhibited estradiol and progesterone synthesis in bovine granulosa cells [19]. Also, ENN B reduced progesterone, testosterone,
and cortisol secretion in human adrenocortical carcinoma cells and modulated the expression of genes involved in steroidogenesis [20]. The cytotoxicity of cyclodepsipeptides (BEAs, BEAEs, ENNs) is related to their ionophoric properties [21–23]. Even at low concentrations, they possess the capacity of perforation of the cell membrane, which is associated with the induction of apoptotic cell death and disruption of extracellular regulated protein kinase (ERK) activity [24–27]. However, this ability does not exclude the capability of promoting the transport of cations such as K^+, Na^+, Mg^{2+}, and Ca^{2+} through the membranes, which leads to the disturbance of cellular ionic homeostasis [28]. This cytotoxic effect on various human cancer cell lines also suggests the potential use of cyclodepsipeptides as anti-cancer drugs [22,29–32]. All cyclodepsipeptides (BEAs, BEAEs, ENNs) have been shown as compounds exhibiting numerous biological activities, such as antimicrobial, insecticidal, and antibiotic activity, towards Mycobacterium tuberculosis and Plasmodium falciparum (human malaria parasite) because of their potential to inhibit the cholesterol acyltransferase of microbial origin [30,33]. Furthermore, BEA can be used as a co-drug for fungal infections in humans because the combination of BEA and ketoconazole (an anti-fungal drug) enhances its antifungal activities [29,33–35]. BEA has been reported as a growth inhibitor of human-pathogenic bacteria, such as Escherichia coli, Enterococcus faecium, Salmonella enterica, Shigella dysenteriae, Listeria monocytogenes, Yersinia enterocolitica, Clostridium perfringens, and Pseudomonas aeruginosa. The chemical properties of cyclodepsipeptides may allow for the emergence of new pharmaceutical products with anti-inflammatory and antibiotic properties [33,36,37]. The studies have shown the divergent impact of cyclodepsipeptides on human health; still, further studies are needed to indicate the potential effects of BEAs, BEAEs, and ENNs on human health. Moreover, it is imperative to study new compounds of the cyclodepsipeptide group, along with their analogues, to better understand the relationships between their structure, diversity, and toxicity.

The aim of the review article was to highlight the diversity among Fusarium species with regard to biosynthesis of BEAs, BEAEs, and ENNs and the characteristics of the multi-domain non-ribosomal peptide synthase (NRPS), which catalyses the synthesis of cyclodepsipeptides mycotoxins.

2. Chemistry

BEAs, ENNs, BEAEs, and allobauvericins (ALLOBEAs) represent a family of regular cyclodepsipeptides, consisting of three N-methyl amino acids and three hydroxy acid groups [4,38–41]. Characterization of all cyclodepsipeptides produced by Fusarium fungi, their elemental composition, molecular weights (used for their identification), and chemical structures are presented in Table 1 and Figure 1. Most of the BEAs contain three groups of N-methyl-phenylalanine, except for BEAs J, K, and L, which contain one, two, or three groups of N-methyl-tyrosine, respectively [2,26]. However, BEA D and E have demethylated amino acids-phenylalanine and leucine in their structures [42]. Moreover, BEAs differ in hydroxy acids possession. BEA and BEA D, E, J, K, and L possess D-2-hydroxyisovaleric acid (D-Hiv) (Figure 2a) and BEA A/F, B, and C possess D-2-hydroxy-3-methylpentanoic acid (D-Hmp) (Figure 2b), whereas BEA G_1 and G_2 possess D-2-hydroxybytyric acid (D-Hbu) (Figure 2c) [2,3,31,33,42]. ALLOBEAs A, B, and C are diastereomeric to BEAs A, B, and C, respectively. These compounds differ in the D-Hmp groups’ configuration [33]. Some of the BEAs, such as BEA B, C, J, K, L, G_1, G_2, and all ALLOBEAs, were known from previous publications as precursor-directed compounds, detected inside in vitro cultures of fungi belonging to Beauveria, Acremonium, and Paecilomyces genera [26,31,33]. It was proven that phytopathogenic fungi from the Fusarium genus naturally produce all BEAs and ALLOBEAs [2,3,42]. The structures of BEAs have been described in many articles, where they were determined by a variety of chemical methods, including liquid chromatography–mass spectrometry (LC-MS) and nuclear magnetic resonance (NMR).

ENNs are typically composed of N-methyl-leucine, N-methyl-isoleucine and/or N-methyl-valine [1,10,41]. However, two of the ENNs: ENN P_1 and P_2 also possess N-methyl-tyrosine in their structures [21]. ENN J_1, J_2, and J_3 are another group of ENNs that differ from the common ENNs. These cyclodepsipeptides consist of one N-methyl-isoleucine, one N-methyl-valine, and N-methyl-alanine [43]. Most ENNs contain three groups of D-2-hydroxyisovaleric acid (D-Hiv) and only three ENNs: ENN H, I, and MK 1688,
containing one, two, or three groups of D-2-hydroxy-3-methylpentanoic acid (D-Hmp), respectively [44]. Some of the reported ENNs are isomers, with the same amino acid composition but in different positions, e.g., ENN J₁, J₂, J₃ or ENN A and F [39,43,45]. On the other hand, even though the ENNs are not isomers, they share the same molecular weight. Therefore, the MS/MS technique with acid hydrolysis or NMR is sometimes necessary during the detection of cyclodepsipeptides for their correct identification.

BEAEs possess hybrid structures between the aliphatic (enniatin-type) and aromatic (beauvericin-type) cyclodepsipeptides [2,3,26,30]. Moieties of N-methyl-phenylalanine, N-methyl-leucine, and/or N-methyl-valine are the parts of BEAEs’ structures. BEAE A contains one N-methyl-valine, whereas BEAE B, G₁, G₂, and G₃ have two. BEAE L has one N-methyl-leucine in its structure. Apart from the D-2-hydroxyisovaleric acid (D-Hiv) group, three of the BEAE isomers, namely BEAE G₁, G₂, and G₃, contain two D-2-hydroxy-3-methylpentanoic acid (D-Hmp) groups in different combinations. At first, all BEAEs were described as cyclodepsipeptides from *Acremonium* sp., however further research revealed that *Fusarium* species are also able to produce these compounds [2,3,26,30].

**Table 1.** Elemental composition and molecular weights of beauvericins, enniatins, and their analogues.

| Compound                  | MW (2) | MW + NH₄⁺ (18) | MW + Na⁺ (23) | MW + K⁺ (39) | Elemental Composition | References |
|---------------------------|--------|----------------|----------------|---------------|-----------------------|------------|
| Beauvericin               | 783    | 801            | 806            | 822           | C₄₆H₅₀N₀O₀         | [2,26]     |
| Beauvericin A/F          | 797    | 815            | 820            | 836           | C₄₆H₅₀N₀O₀         | [2,33,42]  |
| Beauvericin B            | 811    | 829            | 834            | 850           | C₄₇H₅₁N₀O₀         | [3,33]     |
| Beauvericin C/Allobeauvericin B | 825 | 843            | 848            | 864           | C₄₈H₅₂N₀O₀         | [2,33]     |
| Beauvericin D            | 769    | 787            | 792            | 808           | C₄₅H₄₉N₀O₀         | [2,42]     |
| Beauvericin E            | 735    | 753            | 758            | 774           | C₄₃H₴₇N₀O₀         | [3,42]     |
| Beauvericin G₁           | 769    | 787            | 792            | 808           | C₄₅H₴₉N₀O₀         | [3,31]     |
| Beauvericin G₂           | 755    | 773            | 778            | 794           | C₄₃H₴₇N₀O₀         | [3,31]     |
| Beauvericin J            | 799    | 817            | 822            | 838           | C₄₆H₵₀N₀O₁₀        | [2,26]     |
| Beauvericin K            | 815    | 833            | 838            | 854           | C₄₆H₵₀N₁O₁         | [2]        |
| Beauvericin L            | 831    | 849            | 854            | 870           | C₄₆H₵₀N₁O₁₂        | [2]        |
| Beauvenniatin A          | 735    | 753            | 758            | 774           | C₄₃H₴₇N₀O₀         | [2,26]     |
| Beauvenniatin B          | 687    | 705            | 710            | 726           | C₃₇H₴₇N₀O₃         | [2,26,30]  |
| Beauvenniatin G₁/G₂/G₃   | 715    | 733            | 738            | 754           | C₃₉H₴₈N₀O₃         | [3,30]     |
| Beauvenniatin L          | 749    | 767            | 772            | 788           | C₄₂H₵₀N₀O₃         | [2]        |
| Enniatin A/F/MK 1688     | 681    | 699            | 704            | 720           | C₃₆H₴₉N₀O₃         | [25,39,44,45] |
| Enniatin A₃/I            | 667    | 685            | 690            | 706           | C₃₅H₴₈N₀O₃         | [25,39,44,45] |
| Enniatin A₂              | 681    | 699            | 704            | 720           | C₃₆H₴₉N₁O₃         | [25]       |
| Enniatin B               | 639    | 657            | 662            | 678           | C₃₉H₴₈N₀O₃         | [25,39]    |
| Enniatin B₆/B₇/D/H       | 653    | 671            | 676            | 692           | C₃₄H₴₉N₀O₃         | [25,39,44,45] |
| Enniatin B₉/J₃/K₄        | 625    | 643            | 648            | 664           | C₃₂H₴₈N₀O₃         | [25,43]    |
| Enniatin B₉/J₁           | 611    | 629            | 634            | 650           | C₃₁H₴₇N₀O₃         | [25,43,47] |
| Enniatin P₁              | 641    | 659            | 664            | 680           | C₃₁H₴₇N₀O₁₀        | [21]       |
| Enniatin P₂              | 655    | 673            | 678            | 694           | C₃₄H₴₉N₀O₁₀        | [21]       |
| Compound         | R₁       | R₂       | R₃       | R₄       | R₅       | R₆       | R₇       | R₈       | R₉       | R₁₀      | R₁₁      | R₁₂      |
|------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Beauvericin A/F  | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin B    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin C    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin D    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin E    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin J    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₁   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₂   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₃   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₄   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₅   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₆   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₇   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₈   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |
| Beauvericin G₉   | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    | CH₃H₃    |

Figure 1. Cont.
Figure 1. Chemical structures of beauvericin, enniatin, allobeauvericin, and beauvenniatin analogues produced by *Fusarium* species.
3. Biosynthesis

Cyclodepsipeptides are biosynthesized by a multi-domain non-ribosomal peptide synthase (NRPS) that is composed of enzymatic modules used to elongate the proteinogenic and non-proteinogenic amino acids, as well as carboxyl and hydroxy acids [48,49]. The modules respond to the order and number of the precursors incorporated into the chain. Separate NRPS modules are required to assemble the product and a minimal module consists of the three core domains: adenylation (A) domain, thiolation or peptidyl-carrier protein (T or PCP) domain, and condensation (C) domain. Moreover, each module and each active site domain is used only once for the recognition and activation of the precursors through adenylation with ATP (A: adenylation domain), covalent thioester tethering (T: thiolation or PCP: peptidyl carrier protein domain), which tethers the activated precursor to a 4′-phosphopantetheine (PP) cofactor through a thioester bond and transport substrates to the active sites of the domains, and condensation (C domain) of the precursors via catalyzing the peptide bond (C-N) formation between the elongated chain and the activated amino acid. The main domains may be supported by additional domains of the NRPS, such as the epimerization (E) domain, which catalyzes the transformation of an L-amino acid into a D-amino acid or the dual epimerization (E/C) domains, which catalyze the epimerization and condensation. NRPSs contain an additional reductase (R) domain, which is responsible for reducing the final peptide, the methylation (MT) domain, which catalyzes N-methylation of the amino acid substrate, the cyclization (Cy) domain that catalyzes the formation of oxazoline or thiazoline rings by internal cyclization of cysteine, serine, or threonine residues, and the oxidation (Ox) domain, which catalyzes the formation of an aromatic thiazol through oxidation of a thiazoline ring. The last domains (TE–thioesterase domains), mostly located at the final NRPS module, are responsible for releasing the full-length NRPS product from the enzyme through cyclization or hydrolysis [48–52].

Enniatin biosynthesis is catalyzed by the 347 kDa multienzyme enniatin synthase (ESYN1) purified for the first time from Fusarium oxysporum and further characterized by Zocher and coworkers [53]. Extensive molecular research revealed the basis of cyclic oligopeptide biosynthesis and allowed us to identify esyn1, a gene encoding enniatin synthase, as the essential enzyme of the metabolic pathway [39,54–57]. The biochemical characterization revealed that the enzyme possesses two substrate activation modules EA and EB, composed of approximately 420 amino acid residues. The EA module
activates and participates in binding the α-D-hydroxy acids, while the EB module activates the amino acids. These two modules consist of a conserved 4-phosphopantetheine binding site at the C-terminus, with a highly conserved serine residue. An additional 4-phosphopantetheine group and N-methyltransferase domain M are present in the EB module. Also, a putative condensation (C) domain exists between the EA and EB modules. The M domain is highly conserved among N-methyl peptide synthases of prokaryotic and eukaryotic origin, thus it represents only local sequence similarities to the structural elements of other AdoMet-dependent methyltransferases. A dipeptidol unit is formed due to the interaction between the EA and EB modules and later, it is transferred and condensed into a thiol group. Three such successive condensations of the enzyme-bound dipeptidols are followed by the ring’s closure into the enniatin (ENN) molecule [4,58–61] (Figure 3A,B).

The primary precursors of the ENNs are valine, leucine or isoleucine, D-2-hydroxyisovaleric acid, and S-adenosylmethionine and their synthesis is entirely dependent on the cyclization reaction of linear hexadepsipeptide. The amino acid specificity of ESYN1 contributes to the chemical diversity of ENNs and this is why different types of ENNs are produced by Fusarium scirpi, F. lateritium, and F. sambucinum. The Esyn domains activating L-valine in F. scirpi and preferably activating L-isoleucine in F. sambucinum are nearly identical, with an exception of the three regions showing significant differences in their structure.

![Figure 3. Mechanism of enniatin B formation according to Hornbogen et al. [4]. (A) Scheme of partial reactions leading to the formation of ENN B, P1, P2, P3 = 4’-phosphopantetheine. (B) Model of arrangement of catalytic sites in enniatin synthase; Cy: cyclization cavity; EA: D-Hiv-activation module; EB: L-valine-activation module; M: N-methyltransferase domain.](image-url)
structures. This difference in the activation can be accredited to the mutations that eventually occurred in the amino acid recognition sites of various enniatin synthases. In spite of the variability in amino acid units, certain ENNs can only be isolated from specific Fusarium strains, in which the enniatin synthase prefers some amino acids over others during biosynthesis [4,53,62–65].

BEAs are also formed as cyclic trimers assembled from three D-Hiv-N-methyl-L-amino acid dipeptidol monomers (Figure 4A) [50,51]. Similarly, they are also produced by a thiol template mechanism and synthesized by beauvericin synthase (BEAS) enzyme, which consists of a single polypeptide chain of about 351 kD [41,50]. For the first time, the 250 kDa BEAS enzyme was characterized by Peeters et al. [66] from the entomopathogenic fungus Beauveria bassiana, although Xu et al. [50], who conducted a more in-depth analysis, described a 33,475 bp beauvericin gene cluster including a 9570 bp bbBeas gene. Five years later, Zhang and coworkers [51] cloned and characterized 9413 bp beauvericin synthase gene (fpBeas) from Fusarium proliferatum.

The C_1, A_1, and T_1 domains within the first module of FpBEAS and ESYN (EA module) synthases have the same role in cyclodepsipeptide formation [51]. Nevertheless, the two depsipeptide synthases differ in A_2 domain substrate specificity within module 2 (ESYN EB module), i.e., apart from that of enniatin synthase, beauvericin synthase preferably accepts N-methyl-L-phenylalanine and some other aliphatic hydrophobic amino acids (e.g., leucine or isoleucine) [50]. Furthermore, their incorporation efficiency reduces with the length of side chains, where ortho-, meta-, and para-fluoro-substituted phenylalanine derivatives and N-methyl-L-leucine, N-methyl-L-norleucine, and N-methyl-L-isoleucine residues could replace N-methyl-L-phenylalanine. Domains C_2, T_{2ab}, M_2, and C_3 within module 2 of BEAS and ESYN play the same role in both synthases (Figure 4B) [50,66].

The depsipeptides, including BEAs, have a common 2-hydroxycarboxylic acid ingredient–D-2-hydroxyisovalerate (D-Hiv) that is formed from 2-ketoisovalerate (2-Kiv) by a highly specific chiral reduction reaction catalyzed by 2-ketoisovalerate reductase (KIVR) enzyme [50,52,67–70]. KIVR has a significant role in the biosynthesis of BEAs as was clearly understood when BEA production was inhibited in a KIVR knock-out B. bassiana mutant [67]. Kiv is formed from pyruvate during the biosynthesis of valine and it is the key intermediate in several metabolic pathways, including pantothene biosynthesis in fungi, bacteria, and plants. It is also involved in producing phosphopantetheinyl prosthetic groups of acyl or peptidyl carrier proteins and co-enzyme A (Figure 5) [50,52,67,69,70].
Zhang and coworkers [51] cloned and characterized the 9413 bp beauvericin synthase gene (fpBeas) from *Fusarium proliferatum*. The C1, A1, and T1 domains within the first module of FpBEAS and ESYN (EA module) synthases have the same role in cyclodepsipeptide formation [51]. Nevertheless, the two depsipeptide synthases differ in the A2 domain substrate specificity within module 2 (ESYN EB module), i.e., apart from that of enniatin synthase, beauvericin synthase preferably accepts N-methyl-L-phenylalanine and some other aliphatic hydrophobic amino acids (e.g., leucine or isoleucine) [50]. Furthermore, their incorporation efficiency reduces with the length of side chains, where ortho-, meta-, and para-fluoro-substituted phenylalanine derivatives and N-methyl-L-leucine, N-methyl-L-norleucine, and N-methyl-L-isoleucine residues could replace N-methyl-L-phenylalanine.

Domains C2, T2a;b, M2, and C3 within module 2 of BEAS and ESYN play the same role in both synthases (Figure 4B [50,66]).

**Figure 4.** Biosynthesis of fungal cyclodepsipeptides (A) and model of beauvericins (BEAS) synthase structure with domain roles (domains not to scale) (B) according to Xu et al. [50,52].
Figure 5. Synthesis of 2-ketoisovalerate (Kiv), a substrate used in the formation of D-2-hydroxyisovaleric acid (D-Hiv) moiety by 2-ketoisovalerate reductase (KIVR) according to Xu et al. [67]. BCAAT: branched-chain amino acid aminotransferase.

Significant sequence homologies were identified for certain *Fusarium* enzymes, which shows a common genetic background for the synthesis of both depsipeptide compounds. Zhang et al. [51] revealed in their analysis that FpBEAS (GenBank acc. no. JF826561.1) has 64% identity to ESYN (GenBank acc. no. CAA79245) as it was proven that some *Fusarium* species, like *F. poae*, *F. proliferatum*, or *F. oxysporum* were found to produce ENNs and BEA simultaneously. This is justified by the fact that both toxins share a metabolic pathway [1,44,71,72]. Reports suggest that there is a high probability that the single PCR based *esyn1*- and/or *BEAS*- specific marker can detect potential BEAs and ENNs-producing fungi from contaminated soil and plant material [39,55,73].

4. *Fusarium* Species and Cyclodepsipeptide Mycotoxins in Food and Feed

Plant crops are critical mainly in terms of yield and diverse use for foods and feeds. They suffer from a range of fungal diseases and *Fusarium* species are among the most damaging pathogens, producing toxic secondary metabolites, such as cyclodepsipeptides. Cyclodepsipeptides biosynthesis has been observed for 44 *Fusarium* species (Table 2) and *F. acuminatum*, *F. concentricum*, *F. proliferatum*, *F. verticillioides*, *F. oxysporum*, and *F. tricinctum* produce a broad spectrum of ENN, BEA, and BEAE analogues. The remaining *Fusarium* species formed only individual mycotoxin groups, such as BEA, ENNs, or a mixture of these. However, in a few research papers, it was not specified which *Fusarium* species produced ENNs and the presence of mycotoxins was described as a “mix of ENNs” (Table 2).

*Fusarium* species can cause many plant diseases and one of them is *Fusarium* head blight (FHB), which is devastating for cereal species, particularly as it is a major problem regarding wheat production in many countries. Usually, one or more *Fusarium* species (*F. graminearum*, *F. culmorum*, *F.avenaceum*, *F. poae*, and *F. sporotrichioides*) are involved as causal agents [74]. The occurrence of many *Fusarium* species may increase the accumulation of mycotoxins in grains or plants and introduce them into the food chain [71,75,76]. Humidity and temperature determine the disease severity, but geographical conditions, plant genotype, and local pathogen populations also play essential roles [54,77].
| **Fusarium Species** | **Compound** | **References** |
|----------------------|--------------|----------------|
| *F. acuminatum*      | BEA, ENN A, ENN A₁, ENN B, ENN B₁, ENN B₂, ENN B₃, ENN B₄, ENN P₁, ENN P₂, BEA C, BEA D, BEA G₁, ALLOBEA C | [2,3,5,21,39,47,78] |
| *F. acutatum*        | BEA, mix of ENNs | [79] |
| *F. ananatum*        | BEA, ENN A, ENN B, ENN B₁ | [39] |
| *F. anthophilum*     | BEA, ENN A, ENN B, ENN B₁ | [39,78] |
| *F. arthrosperoides* | mix of ENNs | [15] |
| *F. avenaceum*       | BEA, ENN A, ENN A₁, ENN B, ENN B₁, ENN B₂, ENN B₃, ENN B₄ | [25,39,78,80,81] |
| *F. beomiforme*      | BEA | [78] |
| *F. bulbicola*       | BEA | [79] |
| *F. circinatum*      | BEA | [79,82] |
| *F. concentricum*    | BEA, ENN A, ENN A₁, ENN B, ENN B₁, BEA A/F, BEA B, BEA C, BEA D, BEA E, BEA G₁, BEA G₂, BEA J, BEA K, BEA L, BEAE A, BEAE B, BEAE G₁/G₂/G₃, BEAE L, ALLOBEA A, ALLOBEA B, ALLOBEA C | [2,3,39,79,82] |
| *F. compactum*       | ENN A, ENN A₁, ENN B, ENN B₁, ENN B₂ | [47] |
| *F. culmorum*        | mix of ENNs, ENN B | [83] |
| *F. denticulatum*    | BEA | [79] |
| *F. dlamini*         | BEA, ENN A, ENN A₁, ENN B₁ | [39,78,79] |
| *F. equiseti*        | BEA, ENN A, ENN A₁, ENN B, ENN B₁ | [39,78] |
| *F. fujikuoii*       | BEA | [79] |
| *F. globosum*        | BEA | [84] |
| *F. guttiforme*      | BEA | [79,82] |
| *F. graminearum*     | ENN A, ENN A₁, ENN B, ENN B₁ | [85] |
| *F. konzum*          | BEA | [86] |
| *F. kyushuense*      | ENN B, ENN B₁ | [87] |
| *F. lactis*          | BEA, ENN A, ENN A₁, ENN B, ENN B₁ | [39,79] |
| *F. langsethiae*     | BEA, ENN A₁, ENN B, ENN B₁ | [87] |
| *F. lateritium*      | mix of ENNs | [15] |
| *F. longipes*        | BEA | [78] |
| *F. merismoides*     | mix of ENNs | [15] |
| *F. nygamai*         | BEA, ENN A, ENN A₁, ENN B | [39,78,79] |
| *F. oxysporum*       | BEA, BEA A/F, BEA B, BEA C, BEA D, BEA E, BEA G₁, BEA G₂, BEA J, BEA K, BEAE A, BEAE B, BEAE L, ALLOBEA A, ALLOBEA B, ALLOBEA C, ALLOBEA H, ENN I, ENN MK₁688 | [2,3,39,44,78] |
| *F. poae*            | BEA, ENN A, ENN A₁, ENN B, ENN B₁ | [39,71,78,87] |
| *F. phyllophilum*    | BEA | [79] |
| *F. proliferatum*    | BEA, ENN A₁, ENN B, ENN B₁, BEA A/F, BEA B, BEA C, BEA D, BEA E, BEA G₁, BEA G₂, BEA J, BEA K, BEAE A, BEAE B, BEAE L, ALLOBEA A, ALLOBEA B, ALLOBEA C | [2,3,39,84] |
| *F. pseudoanthophilum* | BEA | [82] |
| *F. pseudocircinatum* | BEA | [79] |
Table 2. Cont.

| Fusarium Species | Compound | References |
|------------------|----------|------------|
| *F. redolens*    | BEA      | [37]       |
| *F. sacchari*    | BEA      | [79]       |
| *F. sambucinum*  | BEA, mix of ENNs | [15,78] |
| *F. scirpi*      | mix of ENNs | [15] |
| *F. semitectum*  | BEA      | [88]       |
| *F. sporotrichioides* | BEA, ENN A, ENN B, ENN B₁, ENN A₁ | [39,71,87] |
| *F. subglutinans*| BEA, ENN A, ENN B, ENN B₁ | [39,88–90] |
| *F. succisae*    | BEA      | [79]       |
| *F. temperatum*  | BEA, ENN A, ENN A₁, ENN B, ENN B₁ | [39,90] |
| *F. torulosum*   | ENN B    | [91,92]    |
| *F. tricinctum*  | BEA, ENN A, ENN A₁, ENN B, ENN B₁, ENN B₄, ENN J₁ | [5,36,39,93] |
| *F. verticillioides* | BEA, ENN B, ENN B₁, BEA C, BEA D, BEA G₁, BEA K, BEAE A, ALLOBEA C | [2,3,39,94] |

“ENN”—enniatin; “BEA”—beauvericin; “ALLOBEA”—allobeauvericin; “BEAE”—beauvenniatin.

Available literature data relate both to identifying *Fusarium* fungi isolated from various hosts and analyzing their mycotoxin biosynthesis capacity (Table 3). Efforts are also being made to assess contamination levels with these toxins in raw plant materials and food and feed products (Table 4). Mainly, the content of BEA and four ENNs (ENN A, ENN A₁, ENN B, ENN B₁) has been investigated [8,25]. BEA and ENNs are common contaminants and were detected in plant crops and grains throughout the world. The occurrence of BEA, ENN A, ENN A₁, ENN B, and ENN B₁ in naturally contaminated crops has been studied much more extensively than the occurrence of other cyclodepsipeptides [1,39]. Table 3 summarizes the most effective producers of depsipeptides among *Fusarium* fungi isolated from different crops and geographical areas. *F. avenaceum*, *F. equiseti*, *F. proliferatum*, and *F. sporotrichioides* were the most common species isolated from plants. The best producer of BEA was *F. proliferatum* (FPG61_CM), isolated from garlic in Spain, with the concentration reaching 671.80 μg/g [6]. The highest yielding producers of ENNs were *F. avenaceum* (KF1330), isolated from wheat in Poland, and *F. tricinctum* (3405), isolated from wheat in Finland [5,39]. Both strains produced in the highest amounts ENN B (895.46 μg/g, 690 μg/g) and ENN B₁ (452.46 μg/g, 1200 μg/g) [5,39].

Table 4 presents the maximum amounts of BEA and ENNs in naturally contaminated plant crops described in the literature. The highest contamination level of BEA was found to be 1731.55 μg/g in Polish maize [95]. When compared to other cyclodepsipeptides, it was also the highest concentration of mycotoxin in crops. In Tunisian sorghum, maximum concentrations of ENN A (95.6 μg/g) and ENN B₁ (120.1 μg/g) were detected [96]. The highest amount of ENN A₁ was 813.01 μg/g and 814.42 μg/g in Spanish maize and rice, respectively [97]. ENN B was found with a maximum level of 180.6 μg/g in Tunisian wheat [96]. The data show very high variability of investigated cyclodepsipeptides and it can be concluded that each strain of *Fusarium* species possesses a unique ability to biosynthesize these compounds. In addition to crops, cyclodepsipeptides are also found in food and feed [98–103]. Cyclodepsipeptides were identified mainly in cereal food, with very high levels of ENN A₁ and B₁ in breakfast cereals from Morocco (668 and 795 μg/g, respectively) [99]. In feed samples, ENNs and BEA levels were very low and did not exceed 0.48 μg/g for BEA (poultry feed) and 2.19 μg/g for ENNs (poultry feed) [101].
Table 3. The strains of *Fusarium* species from different origin and hosts, producing the highest amounts of cyclodepsipeptides [µg/g].

| Species          | ID Strain | Host      | Origin    | ENN A | ENN A1 | ENN B | ENN B1 | ENN B2 | ENN B3 | BEA     | Analytical Method | Reference |
|------------------|-----------|-----------|-----------|-------|--------|-------|--------|--------|--------|---------|------------------|-----------|
| *F. acuminatum*  | KF 3713   | Pea       | Poland    | 19.62 | 26.92  | 90.89 | 31.49  | NA     | NA     | 5.31    | HPLC             | [39]      |
|                  | KF 3803   | Asparagus | Poland    | ND    | <0.01  | 0.03  | ND     | NA     | NA     | ND      | HPLC             | [39]      |
|                  | KF 3717   | Pea       | Poland    | 6.09  | 5.65   | 6.71  | 11.46  | NA     | NA     | ND      | HPLC             | [39]      |
|                  | Fa40      | Wheat     | Italy     | 165.8 | 109.2  | 35.5  | 60.2   | NA     | NA     | 27.68   | HPLC             | [39]      |
|                  | Fa34      | Wheat     | Italy     | 332.8 | 181.7  | 64.9  | 101.9  | NA     | NA     | ND      | HPLC             | [39]      |
|                  | KF 3390   | Maize     | Poland    | 29.12 | 32.40  | 255.08| 138.15 | NA     | NA     | ND      | HPLC             | [39]      |
| *F. concentricum*| KF 3755   | Pineapple | Costa Rica| 11.40 | 8.69   | 17.33 | 18.17  | NA     | NA     | 312.2   | HPLC             | [39]      |
| *F. culmorum*    | KF 3798   | Asparagus | Poland    | ND    | ND     | 0.06  | ND     | NA     | NA     | ND      | HPLC             | [39]      |
|                  | KF 3563   | Asparagus | Poland    | 43.47 | 36.81  | 29.18 | 30.39  | NA     | NA     | ND      | HPLC             | [39]      |
| *F. equiseti*    | KF 3749   | Tomato    | Poland    | 39.27 | 38.18  | ND    | 29.22  | NA     | NA     | ND      | HPLC             | [39]      |
|                  | KF 3430   | Banana    | Ecuador   | 31.17 | 32.15  | 32.98 | 41.22  | NA     | NA     | ND      | HPLC             | [39]      |
|                  | Feq16     | Wheat     | Italy     | ND    | ≤0.01  | ≤0.01 | ≤0.01  | NA     | NA     | ≤0.01   | LC-MS/MS         | [105]     |
|                  | Feq136    | Wheat     | Italy     | ≤0.01 | 0.02   | ≤0.01 | 0.02   | NA     | NA     | ND      | LC-DAD           | [71]      |
| *F. fujikuroi*   | KF 3631   | Rice      | Thailand  | ND    | ND     | ND    | ND     | NA     | NA     | 428.09  | HPLC             | [39]      |
| *F. globosum*    | 6646      | Maize     | South Africa| NA   | NA     | NA    | NA     | NA     | NA     | 110     | LC-MS            | [84]      |
| *F. lactis*      | KF 3641   | Pepper    | Poland    | 30.97 | 26.94  | ND    | ND     | NA     | NA     | ND      | HPLC             | [39]      |
| *F. nygamai*     | KF 337    | Pigeon Pea| India     | 10.45 | 9.50   | ND    | NA     | NA     | NA     | 22.86   | HPLC             | [39]      |
| *F. oxysporum*   | KF 3567   | Garlic    | Poland    | ND    | 6.42   | 8.23  | 7.28   | NA     | NA     | 80.03   | HPLC             | [39]      |
|                  | KF 3805   | Asparagus | Poland    | ND    | ND     | ND    | ND     | NA     | NA     | 0.53    | HPLC             | [39]      |
### Table 3. Cont.

| Species             | ID Strain  | Host      | Origin     | ENN A | ENN A₁ | ENN B | ENN B₁ | ENN B₂ | ENN B₃ | BEA  | Analytical Method | Reference |
|---------------------|------------|-----------|------------|-------|--------|-------|--------|--------|--------|------|-------------------|-----------|
| **F. poae**         | Fp26       | Wheat     | Italy      | ≤0.01 | 0.07   | 0.03  | 0.05   | NA     | NA     | 3.5  | LC-DAD            | [71]      |
|                     | 156        | Wheat     | Italy      | ≤0.01 | 0.03   | 0.03  | ND     | ND     | ND     | 10.5 | LC-MS/MS          | [105]     |
|                     | Fp49       | Wheat     | Italy      | ≤0.01 | 0.1    | 0.05  | 0.04   | NA     | NA     | 9.4  | LC-DAD            | [71]      |
|                     | KF 2576    | Maize     | Poland     | 34.31 | 26.89  | 28.71 | ND     | NA     | NA     | 37.53| HPLC              | [39]      |
| **F. proliferatum** | KF 3382    | Pineapple | Hawaii     | ND    | ND     | ND    | ND     | NA     | NA     | 3.39 | HPLC              | [39]      |
|                     | FPG61_CM   | Garlic    | Spain      | NA    | NA     | NA    | NA     | NA     | NA     | 45.13| HPLC              | [39]      |
|                     | KF 3363    | Garlic    | Poland     | ND    | ND     | ND    | ND     | NA     | NA     | 45.13| HPLC              | [39]      |
|                     | KF 3792    | Asparagus | Poland     | ND    | 0.39   | 0.13  | 0.06   | NA     | NA     | 0.41 | HPLC              | [39]      |
|                     | KF 3584    | Rice      | Thailand   | ND    | 6.39   | 12.92 | 19.64  | NA     | NA     | 291.87| HPLC              | [39]      |
|                     | KF 3560    | Rhubarb   | Poland     | ND    | ND     | ND    | ND     | NA     | NA     | 149.67| HPLC              | [39]      |
|                     | KF 496     | Maize     | Italy      | ND    | 5.48   | 9.61  | 12.89  | NA     | NA     | ND    | HPLC              | [39]      |
| **F. sambucinum**   | 179        | Wheat     | Italy      | ND    | ND     | ND    | ND     | ND     | ND     | 10.1 | LC-MS/MS          | [105]     |
| **F. subglutinans** | 1084       | Maize     | South Africa | NA  | NA     | NA    | NA     | NA     | NA     | 700  | LC-MS             | [84]      |
| **F. sporotrichioides** | KF 3815   | Asparagus | Poland     | ND    | 0.09   | ND    | ND     | NA     | NA     | 0.21 | HPLC              | [39]      |
|                     | KF 3728    | Pea       | Poland     | 12.67 | ND     | 5.99  | 18.15  | NA     | NA     | 5.13 | HPLC              | [39]      |
|                     | Fsp50      | Wheat     | Italy      | ND    | ≤0.01  | ≤0.01 | 0.02   | NA     | NA     | 13.7 | LC-DAD            | [71]      |
|                     | 194        | Wheat     | Italy      | ND    | ND     | ND    | ND     | ND     | ND     | 6.89 | LC-MS/MS          | [105]     |
| **F. temperatum**   | KF 3321    | Pineapple | Costa Rica | 27.79| 34.39  | 39.20 | 29.21  | NA     | NA     | 290.97| HPLC              | [39]      |
|                     | RCFT 934   | Maize     | Argentina  | NA    | NA     | NA    | NA     | NA     | NA     | 1151 | HPLC              | [106]     |
|                     | KF 506     | Maize     | Poland     | ND    | ND     | 15.17 | 9.88   | NA     | NA     | 17.47 | HPLC              | [39]      |
|                     | KF 3795    | Asparagus | Poland     | 0.1   | 0.17   | 0.28  | 0.38   | NA     | NA     | 0.55 | HPLC              | [39]      |
| **F. tricinctum**   | 27B14      | Malting barley | Italy    | 8.45 | 118    | 39    | 124    | 27     | 0.13  | NA   | LC-MS/MS          | [104]     |
|                     | 3405       | Wheat     | Finland    | NA    | 94     | 690   | 1200   | NA     | NA     | 33   | HPLC              | [5]        |
| **F. verticillioides** | KF 393   | Maize     | USA        | ND    | ND     | 8.75  | 12.43  | NA     | NA     | 2.34 | HPLC              | [39]      |

“ND”—not detected; “NA”—not analyzed.
Table 4. Maximum levels [µg/g] of naturally occurring depsipeptides in foods and feeds from different countries.

| Sample   | Origin      | ENN A  | ENN A1 | ENN B  | ENN B1 | BEA | Reference |
|----------|-------------|--------|--------|--------|--------|-----|-----------|
| Asparagus| Poland      | ND     | 0.05   | 0.06   | ND     | NA  | 0.1       | [8]       |
|          | Italy       | ND     | ND     | ≤0.01  | NA     | 0.02| ≤0.01     | [100]     |
|          | Italy       | 0.02   | 0.06   | 0.07   | NA     | ≤0.01|          | [104]     |
|          | Finland     | 0.95   | 2      | 9.76   | 5.72   | NA  | 0.02      | [1]       |
|          | Morocco     | ND     | 220    | 49     | 32     | NA  | 5         | [107]     |
|          | Norway      | ≤0.01  | 0.04   | 0.49   | 0.17   | NA  | ≤0.01     | [108]     |
|          | Spain       | ND     | 361.57 | 21.37  | 45.94  | NA  | 6.94      | [97]       |
|          | Tunisia     | 33.6   | 149    | 29.2   | 31     | NA  | NA        | [96]       |
| Barley   | Brazil      | ≤0.01  | 0.31   | ≤0.01  | ≤0.01  | NA  | 0.16      | [109]     |
|          | Croatia     | NA     | NA     | NA     | NA     | NA  | 1.84      | [110]     |
|          | Denmark     | ≤0.01  | ≤0.01  | 0.58   | 0.09   | NA  | 0.09      | [111]     |
|          | Japan       | NA     | NA     | NA     | NA     | NA  | 0.03      | [112]     |
|          | Morocco     | ND     | 445    | 100    | 8      | NA  | 59        | [107]     |
|          | Poland      | NA     | NA     | NA     | NA     | NA  | 1.73      | [95]       |
|          | Serbia      | 0.02   | 0.03   | ≤0.01  | 0.02   | NA  | 0.14      | [7]        |
|          | Slovakia    | NA     | NA     | NA     | NA     | NA  | 3         | [113]     |
|          | Spain       | ND     | 813.01 | 6.31   | 4.34   | NA  | 9.31      | [97]       |
|          | Tunisia     | ND     | 29.6   | ND     | 17     | NA  | NA        | [96]       |
| Maize    | USA         | NA     | NA     | NA     | NA     | NA  | 0.5       | [114]     |
| Oats     | Finland     | ≤0.01  | ≤0.01  | ≤0.01  | ≤0.01  | ND  | 0.05      | ≤0.01     | [100]     |
|          | Italy       | ND     | ≤0.01  | ≤0.01  | ND     | 0.05| ≤0.01     | [100]     |
|          | Norway      | ≤0.01  | ≤0.01  | 0.05   | 0.02   | NA  | 0.02      | [108]     |
| Rice     | Iran        | ≤0.01  | ND     | ≤0.01  | ND     | ND  | ≤0.01     | [115]     |
|          | Spain       | ND     | 814.42 | 7.95   | ND     | NA  | 11.78     | [97]       |
| Rye      | Finland     | ≤0.01  | 0.05   | ≤0.01  | NA     | ND  |           | [1]        |
|          | Italy       | ≤0.01  | ND     | ≤0.01  | ND     | ≤0.01| ≤0.01     | [100]     |
| Sorghum  | Tunisia     | 95.6   | 480    | ND     | 120.1  | NA  | NA        | [96]       |
| Spelt wheat| Italy    | ≤0.01  | ND     | ND     | ND     | ND  | ND        | [100]     |
| Wheat    | Finland     | 0.49   | 0.94   | 18.3   | 5.1    | NA  | ≤0.01     | [1]        |
|          | Italy       | ≤0.01  | ≤0.01  | 0.02   | ≤0.01  | 0.04| ≤0.01     | [100]     |
|          | Morocco     | 0.08   | 0.13   | 2.57   | 0.35   | NA  | 0.02      | [116]     |
|          | Morocco     | 34     | 209    | 11     | 19     | NA  | 4         | [107]     |
|          | Norway      | ≤0.01  | 0.02   | 0.79   | 0.18   | NA  | ≤0.01     | [108]     |
|          | Poland      | 0.27   | 3.6    | 28.52  | 11.8   | NA  | 0.02      | [57]       |
|          | Romania     | 0.14   | 0.36   | 0.41   | 0.51   | NA  | NA        | [117]     |
|          | Spain       | ND     | 634.85 | ND     | ND     | NA  | 3.5       | [97]       |
|          | Tunisia     | 75.1   | 177.7  | 180.6  | 58.5   | NA  | NA        | [96]       |
|          | UK          | 0.04   | 0.17   | 0.13   | 0.30   | NA  | NA        | [85]       |
Table 4. Cont.

| Sample          | Origin          | ENN A | ENN A₁ | ENN B | ENN B₁ | ENN B₄ | BEA | Reference   |
|-----------------|-----------------|-------|--------|-------|--------|--------|-----|-------------|
| Breakfast cereals | Morocco         | 29.7  | 688    | 81.1  | 795    | NA     | 5.3 | [99]        |
|                 | Spain           | ND    | 268.54 | ND    | ND     | NA     | 3.12| [97]        |
|                 | Tunisia         | 121.3 | 480    | 295   | 120.1  | NA     | NA | [96]        |
| Infant cereals  | Morocco         | ND    | 52     | 5.7   | 14.5   | NA     | 10.6| [99]        |
| Pasta           | Italy           | ≤0.01 | ≤0.01  | 0.11  | ≤0.01  | ≤0.01  | ND  | [100]       |
| Oat flour       | Spain           | ND    | 388.38 | ND    | NA     | NA     | 4.18| [97]        |
| Wheat flour     | Japan           | ≤0.01 | 0.03   | 0.63  | 0.09   | NA     | ≤0.01| [112]       |
| Corn grits      | Japan           | ND    | ND     | ND    | ND     | NA     | 0.03| [112]       |
| Bovine feed     | Spain           | ND    | ≤0.01  | 0.04  | 0.02   | NA     | 0.05| [98]        |
| Ovine feed      | Spain           | ND    | ≤0.01  | 0.09  | 0.03   | NA     | 0.13| [98]        |
| Caprine feed    | Spain           | ND    | ≤0.01  | 0.02  | ≤0.01  | NA     | 0.02| [98]        |
| Horses feed     | Spain           | ND    | ≤0.01  | 0.04  | ≤0.01  | NA     | 0.03| [98]        |
| Porcine feed    | Finland         | 0.31  | 0.55   | 1.51  | 1.85   | NA     | 0.41| [102]       |
|                 | Spain           | ND    | ≤0.01  | 0.06  | 0.02   | NA     | ≤0.01| [98]        |
| Poultry feed    | Brazil          | ND    | ≤0.01  | ≤0.01 | ≤0.01  | NA     | 0.02| [109]       |
|                 | Spain           | ND    | ≤0.01  | 0.05  | 0.02   | NA     | 0.02| [98]        |
|                 | UK              | 0.04  | 0.03   | 2.19  | 0.40   | NA     | 0.48| [101]       |
| Rabbits feed    | Spain           | ND    | ≤0.01  | 0.05  | 0.02   | NA     | ≤0.01| [98]        |
| Dogs feed       | Spain           | ND    | ≤0.01  | 0.02  | ≤0.01  | NA     | 0.04| [98]        |
| Cats feed       | Spain           | ND    | ND     | ≤0.01 | ≤0.01  | NA     | ND  | [98]        |
| Fish feed       | Scotland/Norway/| ≤0.01 | ≤0.01  | 0.03  | ≤0.01  | NA     | 0.08| [103]       |

“ND”—not detected; “NA”—not analyzed.

5. Conclusions

Fungi from the *Fusarium* genus produce a unique set of cyclodepsipeptide analogues of different amounts. The described mycotoxins are involved in plant-pathogen interaction, thus they were detected in a range of foodstuffs or feeds originating from many countries. They may be very dangerous for human health because of their biological activities. On the other hand, cyclodepsipeptides possess antimicrobial, insecticidal, antifungal, and antibiotic activities, which may help develop new drugs. In addition, because of their cytotoxicity, cyclodepsipeptides may have applications in anti-cancer therapy. Moreover, new BEAs, ENNs, or BEAEs with different amino/hydroxy acid compositions are detected each year inside in vitro fungal cultures. It was proven that not only fungi from *Fusarium* genus naturally produce cyclodepsipeptides, but also other fungi belonging to *Beauveria*, *Acremonium*, and *Paecilomyces* genera. Therefore, it is essential to continually improve the knowledge regarding these compounds, their structure, diversity, and toxicity to screen products of fungal secondary metabolism and monitor the dispersion of phytopathogenic fungi, which are potent producers of threatening mycotoxins. Moreover, it would be beneficial to bettering the understanding of cyclodepsipeptide biosynthesis to investigate the diversity and evolution history of the BEAS/ESYN synthase gene cluster from various fungi.
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