METEORITIC VERSUS BIOTIC AMINO ACIDS: AN UPDATE ON AIB AND IVA

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Introduction: In CM2 and CM3 carbonaceous chondrites (CC), α-aminoisobutyric acid (Aib; 2-amino-2-methylpropanoic acid) and isovaline (Iva; 2-amino-2-methylbutanoic acid) are among the most abundant non-proteinogenic amino acids. Their extraterrestrial origin is attributed to well-known synthetic pathways such as the Bucherer-Bergs and Strecker cyanohydrin synthesis. It is expected that these abiotic processes should result in racemic mixtures. However, in many CC of various classes, slight to significant enantiomeric excesses of L-Iva have been measured [1]. These L-enantiomeric excesses may have been produced by circularly polarized UV radiation in interstellar clouds, followed by an unknown amplification mechanism, for example during aqueous alteration in the meteoritic parent bodies, the asteroids [2]. Once an enantiomeric excess of Iva is present, it will usually be preserved because of the resistance of Iva against racemization [3]. Recently, however, it has been observed that at 200 °C L-Iva was slowly transformed into the D-enantiomer when the amino acid was intercalated in the clay mineral montmorillonite [4]. Because Aib and Iva are biosynthesized by microfungi [5], terrestrial contaminations are possible, which have been outlined by Elsila et al. [6]. The former findings are updated in the following.

Results and Discussion: A continuously increasing number of ubiquitous terrestrial and marine filamentous fungi, comprising approximately 20 genera, have been recognized to produce Aib-containing polypeptides. Aib frequently occurs together with either D- or L-Iva or even both enantiomers in the same peptide. This group of polypeptides is known under the acronym peptaibols/peptaibiotics. As of May 2016, 1,351 peptide sequences have been compiled in the "Peptaibiotics Database" [7], which is freely accessible (https://peptaibiotics-database.boku.ac.at). Consequently, the possibility of contamination of meteorites (or geological samples in general) by microfungi or their peptaibiotic metabolites has to be taken into account. However, for critical assessment, the entire structural diversity of non-proteinogenic amino acids occurring altogether in a specimen of CC and the lower variety in microbial metabolites of interest has to be considered:

(i) In CM and CR type meteorites, Aib and Iva are accompanied by other non-proteinogenic α-dialkylated amino acids, which occur in lower concentrations. For the detection and enantioseparation of chiral α-dialkylated amino acids, LC/TOF-MS [2] or capillary gas chromatography on modified cyclodextrin phases are highly suitable [8].

(ii) Filamentous fungi produce free [5] and peptide-bound Aib, often together with Iva. The latter is present as D-Iva (trichotoxins A-40 from *Trichoderma asperellum*; antiamoebins from species *of Emericellopsis*, *Stilbella*, *Clonostachys*), L-Iva (efrapeptin G from *Tolypocladium inflatum* and *T. geodes*; peptaivirin from *Trichoderma* sp.) or even as D- and L-Iva in the same peptide (integramide A from *Dendrodochium* sp.; acretocins from *Acremonium crotocinigenum*). The production of peptaibiotics by a phylogenetically characterized marine sediment bacterium (microbactericins from *Microbacterium sediminis*, exclusively containing L-Iva) and by a yeast (neoefrapeptins from *Geotrichum candidum* containing both L- and D-Iva) is indicative of the potential of microorganisms to produce a myriad of peptaibiotics [9, 10].

(iii) The $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios of Aib and Iva in peptaibiotics are consistent with a biotic origin, whereas in meteoritic amino acids the heavy isotopes are relatively enriched [6].

Conclusions: *Abiotically* synthesized Aib and Iva have been detected in CM-type CC, together with other α-dialkylated and further non-proteinogenic amino acids in exponentially decreasing concentrations in homologous series (altogether approaching about 80 compounds). *Biotically* synthesized Aib – frequently occurring together with Iva – has been found in >1,350 structurally characterized microbial peptides, which are assembled non-ribosomally by multi-enzyme complexes. However, the structural diversity of the non-proteinogenic amino acids in CM-type meteorites is not displayed in individual fungal peptides.

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