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How to guarantee the natural origin of nutraceutical and pharmaceutical products? The potential of the stable isotope ratios analysis

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The analysis of the ratio between the heavy and light isotopes of the elements carbon ($^{13}\text{C}/^{12}\text{C}$), nitrogen ($^{15}\text{N}/^{14}\text{N}$), sulfur ($^{34}\text{S}/^{32}\text{S}$), oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen ($^2\text{H}/^1\text{H}$) is well known for its power to discriminate the geographical origin and guarantee the authenticity of many agri-food products [1]. In recent years, the field of application of this technique has expanded to include nutraceuticals and pharmaceuticals, in particular in order to guarantee their natural origin. Chemically identical molecules are significantly different from an isotopic point of view due to the isotopic fractionation that occurs in different processes and reactions (biological, biochemical, physical, chemical, etc.) which generates unique isotopic signatures in the product synthesized by plants compared to that produced in the laboratory usually starting from fossil sources. Thanks to the coupling of isotopic mass spectrometry to liquid chromatography (LC-IRMS) and gas chromatography (GC-IRMS) it is now possible to discriminate between natural and/or synthetic origin not only of the bulk product but also of its specific components. The "Compound specific analysis" makes it possible to identify much more sophisticated frauds than in the past such as, for example, the addition of a single synthetic component to a natural substrate in order to artificially increase its strength. In this context, the $\delta^{13}\text{C}$ analysis is a suitable tool to discriminate between Monacolin K (contained in red yeast rice-based dietary supplements) and the marketed statin [2] and between natural L-theanine (extracted from *Camellia Sinensis*) and the biosynthetically produced one [3]. The isotope ratios of hydrogen and, in some cases, carbon exhibit significantly different ranges of variability between natural extracts (such as curcuminoids [4] and cannabidiols [5]) and their synthetic adulterant, allowing for the identification of not only the two origins, but also the fraudulent additions of synthetic products to the natural complex (spiked samples). The combination of GC-MS/MS and GC-IRMS is potentially useful for botanical classification between lavender (*Lavandula angustifolia*) and lavandin (*Lavandula hybrida*) essential oils thus representing an additional powerful tool for assessing the authenticity of commercial essential oils [6].

References

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