

Clumped methyl isotopes to trace origins of flavors and laboratory standards

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Stable isotope ratios (e.g., $^{13}\text{C}/^{12}\text{C}$, D/H) are commonly used to fingerprint the origins of materials. One such application is to validate natural vs. synthetic products. Here, we present the measurement of two isotopologues derived from methoxyl groups with two rare isotopes ($^{13}\text{CH}_2\text{D}$, $^{12}\text{CHD}_2$), i.e., "clumped" isotopologues, as a fingerprint of the origins of vanillin, methanol, and syringic acid. We focus on vanillin; its "natural" form derived from beans is highly regarded and sought by consumers, but there are a variety of ways to produce "fake" vanillin synthetically (i.e., guaiacol, lignin, rice, corn). Consumers and scientists seek a way to identify synthetic products from natural vanillin. We present clumped isotopologue analyses of vanillin ($n = 11$), vanillic acid ($n = 1$), syringic acid ($n = 2$), and methanol ($n = 8$) to explore the utility of this measurement for source assignment. $^{13}\text{CH}_2\text{D}$ and $^{12}\text{CHD}_2$ values allow us to separate the mechanisms and origins of vanillin. Specifically, synthetic vanillin samples derived from guaiacol have negative $\delta_{^{13}\text{CH}_2\text{D}}$ values (-2.72 to -0.06 ‰; relative to a stochastic reference frame) and negative $\delta_{^{12}\text{CHD}_2}$ values (-22.4 to -6.5‰). Vanillin samples derived from lignin, rice and corn (but not vanilla beans) have $\delta_{^{13}\text{CH}_2\text{D}}$ values that overlap with previously measured wood lignin (ranging from 8.24 to 8.73‰) and $\delta_{^{12}\text{CHD}_2}$ values between -81.0 to -27.9‰. The vanillin sample derived from a vanilla bean has an intermediate $\delta_{^{13}\text{CH}_2\text{D}}$ value of 4.78‰ and an elevated $\delta_{^{12}\text{CHD}_2}$ value of 266.0‰. If such values hold for other natural vanillin samples, it will indicate that this approach can type vanillin sources. Methanol and syringic acid samples from different sources yield $\delta_{^{13}\text{CH}_2\text{D}}$ values from -1.6 to -0.5‰, and $\delta_{^{12}\text{CHD}_2}$ from -13.2 to +37.0‰, consistent with the values seen for synthetic vanillin. Clumped isotope compositions are out of equilibrium for isotopologue-based reconstructed temperatures in all samples but one methanol, indicating kinetic isotope effects control most isotopic compositions in natural and synthetic methoxyl groups. We discuss future uses of these measurements for tracing the sources of methyl groups.