Adulteration of Fruit Juices and Syrups

Introduction

The purpose of this study is to evaluate our ability to identify adulterated fruit juices and expensive sweeteners and starches using carbon isotope analysis ($\delta^{13}C$). The method is based on differences in $\delta^{13}C$ values between plants that utilize different metabolic pathways: C3, C4, and CAM. These metabolic pathways fractionate carbon isotopes differently, leading to distinct isotopic signatures, which can be used to discriminate between different carbon sources. For example, orange juice comes from a C3 plant leading to a different $\delta^{13}C$ value than corn syrup, which is derived from a C4 plant.

Methodology

We purchased commercially available orange juice, apple juice, pineapple juice and maple syrup from multiple suppliers and countries of origin. We also purchased corn syrup, cane sugar and beet sugar. Samples were analyzed using a MAT252 IRMS coupled with an EA and ConFlo III system.

Results

The results are summarized in Table 1. They are consistent with the expected values for the materials analyzed. Orange juice, apple juice, maple syrup, tapioca and beet sugar are C3 plant derived and therefore have low $\delta^{13}C$ values. Cane sugar and corn starch are C4 plant derived and therefore have higher $\delta^{13}C$ values. Pineapple is a CAM plant and has intermediate values.

Material	**Number of Samples**	**Number of Analyses**	**Minimum $\delta^{13}C$ VPDB (‰)**	**Maximum $\delta^{13}C$ VPDB (‰)**	**Mean $\delta^{13}C$ VPDB (‰)**
orange juice	9	18	-27.4	-24.6	-25.6
apple juice	2	4	-23.6	-25.1	-24.3
pineapple juice	2	4	-12.5	-12.2	-12.3
maple syrup	6	17	-25.6	-24.8	-25.2
tapioca starch	1	2	-27.9	-27.0	-27.4
cane sugar	1	5	-	-	-12.5
corn syrup	2	4	-10.8	-10.3	-10.6
beet sugar	1	2	-	-	-26.7

Table 1. Summary of results.

Using the measured ranges of each material, we can evaluate the impact of adulteration by different sugars on the $\delta^{13}C$ value of the product. This is done using a simple, two component linear mixing model as follows:

$$\delta^{13}C_{final} = X * \delta^{13}C_{adulterant} + (1 - X) * \delta^{13}C_{pure}$$

Where X is the fraction of carbon derived from the adulterant material. Figure 1 demonstrates the effect of adding each type of sugar to each product.

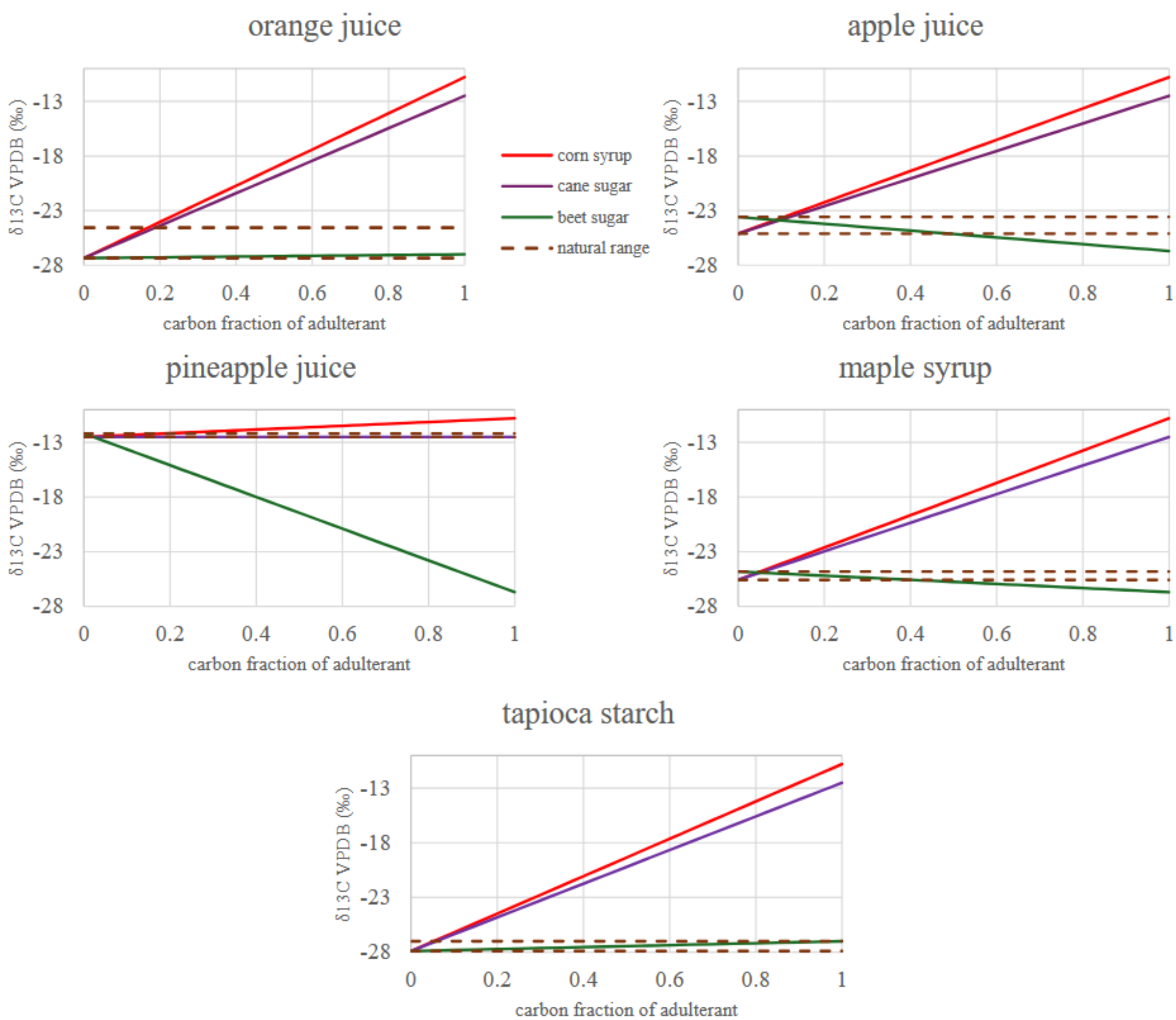

Figure 1. Mixing models for adulteration using corn syrup, cane sugar and beet sugar. Dashed brown lines indicate the measured range of each pure product. Adulteration would be detectable when the mixture falls outside the natural range of the product (when the different colored lines are outside of the range indicated by the dashed brown lines).

As expected, adulteration of C3 derived products with C4 derived sugars (and vice versa) is readily detectable, while adulteration by a C3 sugar is difficult to detect. Table 2 summarizes the approximate detection limits defined as the point at which the $\delta^{13}C$ value of the adulterated product is outside of the natural range for the product. It is important to note that we likely did not fully characterize the natural range of each product, which could lead to an overestimation of the detection ability. If the true natural range is larger, adulteration may be more difficult to detect.

	adulterant			
product		*corn sugar %*	*cane sugar %*	*beet sugar %*
	orange juice	20	20	NA
	apple juice	15	15	55
	pineapple juice	25	NA	5
	maple syrup	10	10	45
	tapioca	10	10	NA

Table 2. Approximate detection limit of adulteration of different products. NA indicates combinations where the adulteration cannot be detected at any percentage because its $\delta^{13}C$ value is within the natural range of the product.

Testing the method with a real-world product

We purchased a single "orange juice" product that has a declared addition of high-fructose corn syrup and other ingredients besides juice concentrates. The nutritional label states that 12 of the 14 grams of sugar (~86%) are added. Assuming that sugars are the main carbon source in the product and assuming a corn syrup $\delta^{13}C$ value of -10.6‰ and an orange juice $\delta^{13}C$ value of -24.5‰, the linear mixing model predicts a $\delta^{13}C$ value of -12.6‰. The measured value for the product was -12.2‰, in good agreement with the expected value considering the assumptions made in the calculation.

Empirical test of adulteration

To verify our ability to measure adulteration in juices, we created a suite of adulterated juices by adding variable amounts of cane and beet sugar to apple and pineapple juice samples. Figure 2 demonstrates the results, with empirical data plotted with the theoretical mixing model calculations. The fraction of added carbon is calculated based on the measured carbon percentage of the adulterated samples compared to the pure juice. The results indicate good agreement between the theoretical mixing model and measured values.

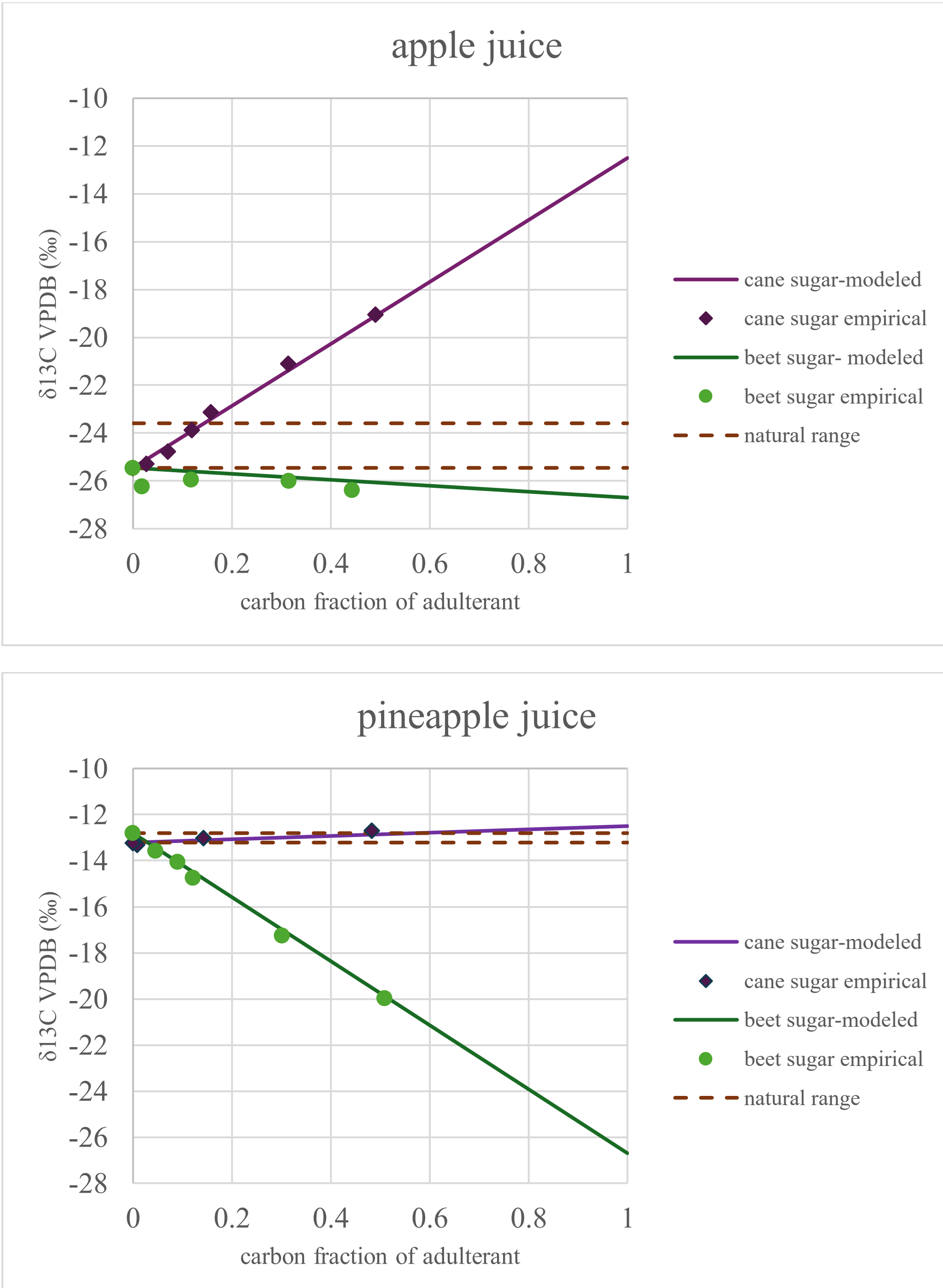

Figure 2. Empirical test of adulteration mixing model.