

# They added WHAT to my beer??!

TIBBS Homework 1, Paper 5: Carbon Isotope Ratios in Beer

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**Barley vs Corn.** A recent study<sup>1</sup> of beer finds that the simpler sugars of both corn and cane combined with brewer's yeast are used in American beers to speed fermentation and increase the alcohol content. Because beer producers are not required to list ingredients, determining whether producers are misrepresenting their products with advertised claims of purity is important, both for locations where non-barley sugars are illegal and for the concerned consumer.

The traditional formula for beer is water, malted barley, hops, and yeast. Nonessential additional ingredients may include spices, natural flavors, sugars, or starches. The fermentation process uses yeast to convert the sugar in barley to alcohol. However, when simpler sugars such as those from corn or cane are introduced, the brewing time decreases, increasing the production rate. To determine the prevalence of simpler and less expensive sugars in beer, Dr. J. Renee Brooks with twelve other scientists applied the technique of detecting stable carbon isotopes to 160 beers from many regions of the world purchased in the US and Brazil.

Isotopes of an atomic element have nuclei

with the same number of protons (the same atomic number) but different numbers of neutrons, decreasing or increasing the element's mass. Because different plants discriminate between different isotopes of carbon, it is possible to determine which type of plant the carbon in beer came from, whether barley or another grain, or whether corn, sorghum, or sugar cane.

**The science: Photosynthetic pathways and isotope ratios.** Plants use one of three photosynthetic pathways.  $C_3$  plants such as barley, wheat, and other grains use rubisco to make a three-carbon compound as the first stable product of carbon fixation; more than 95% of earth's plant species can be characterized as  $C_3$  plants.  $C_4$  plants such as corn, sugar cane, and sorghum use PEP carboxylase during initial carbon fixation to make a four-carbon compound that is subsequently transferred to specialized cells where carbon dioxide is internally released and refixed using rubisco; less than 1% of earth's plant species can be characterized as  $C_4$  plants. *CAM* (crassulacean acid metabolism) plants such as cacti can use either the  $C_3$  or  $C_4$  pathway, closing their stomata during the day to reduce water loss and open them at night for carbon uptake; about 3 to 4% of earth's plant species can be char-

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<sup>1</sup>J. Renee Brooks, et al. Heavy and Light Beer: A Carbon Isotope Approach To Detect  $C_4$  Carbon in Beers of Different Origins, Styles, and Prices. *J. Agric. Food Chem.* 2002, 50, 6413–6418.

acterized as *CAM* plants.

These pathways discriminate differently against the heavier carbon isotope,  $^{13}\text{C}$  (6 protons + 7 neutrons = atomic mass 13) as compared to standard  $^{12}\text{C}$  (6 of each), and this leads to different isotopic ratios of carbon in the sugars used to produce the alcohol. The isotopic ratio,  $\delta^{13}\text{C}$ , is the ratio  $R = ^{13}\text{C}/^{12}\text{C}$  in a sample of beer compared to a standard (Pee Dee Belemnite limestone), measured in per thousands or per mille ( $0.001=0.1\%=1\text{‰}$ ). Explicitly,  $\delta^{13}\text{C} = 1000(R_{\text{sample}}/R_{\text{standard}} - 1)$ , so that positive numbers indicates more  $^{13}\text{C}$  in the sample than the standard.  $\delta^{13}\text{C}$  is measured by drying a sample of beer, combusting the residue in an elemental analyzer, and measuring the amounts of carbon isotopes with an isotope ratio mass spectrometer (IRMS).

$C_3$  and  $C_4$  plants have different  $\delta^{13}\text{C}$  ranges, so the  $\delta^{13}\text{C}$  value of a beer is an indicator of the relative amounts of  $C_3$  and  $C_4$  ingredients used to produce it. Others have successfully performed this type of study on wine, brandy, and whiskey. To calculate the percentage of  $C_4$  carbon in beer, they assumed that the carbon in beer residue was either from  $C_3$  plants (barley, rice, wheat), or  $C_4$  plants (corn, sugar cane, sorghum). The amount of carbon coming from other sources, such as hops and yeast, are little enough to be ignored.

**Corn in my beer?** While European beers have little to no  $C_4$  carbon (Germany has outlawed it), most beers from other parts of the world use corn to enhance the fermentation process (Figure 1). Looking at the amounts of  $C_4$  carbon by region, we find only 3 of 20 (15%) European beers use corn, while a large majority of beers from other regions do use corn, 63% in Canada, 71% in USA, 90%

in Brazil, and 100% in Mexico and the Pacific Rim (Figure 2). This is geographically natural because  $C_4$  plants do not generally grow at the high latitudes of Europe, but are grown extensively near the equator, and the USA will tend to produce as much as cheap as possible. Additionally, 93% of US style and Large Brewery beers and use corn, while the smaller Brewery beers do not. More expensive beers tend to avoid the use of corn to improve fermentation (Figure 3), while the less expensive use corn extensively. Pour me a  $C_3$ , please.

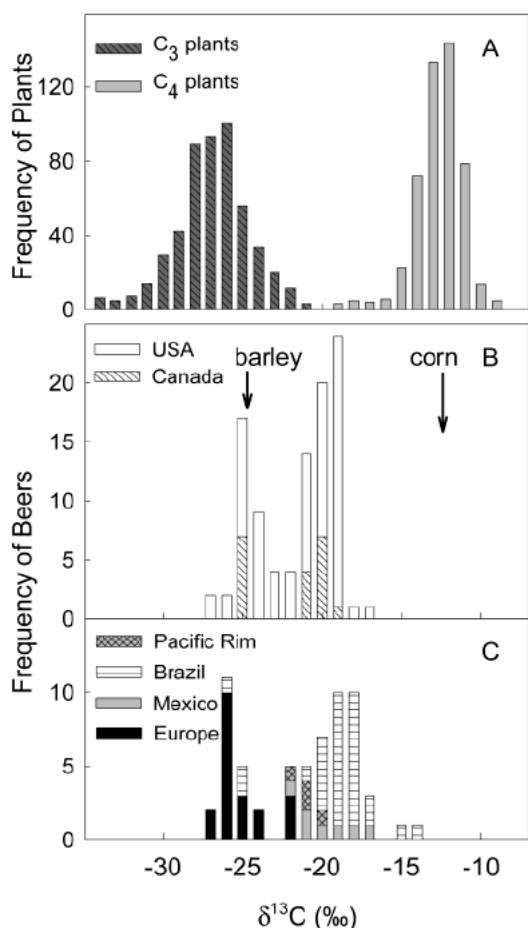


Figure 1: (A) Carbon isotope ratios ( $\delta^{13}C$ ) of  $C_3$  (left group) and  $C_4$  (right group) plants, with arrows noting where barley and corn are located. (B,C) The isotopic ratios of beers from the USA and Canada, and other parts of the world. Note that there are two groups in each plot, indicating beers that use little or no  $C_4$  (corn) plants, and those using significant amounts of  $C_4$  plants for sugar.

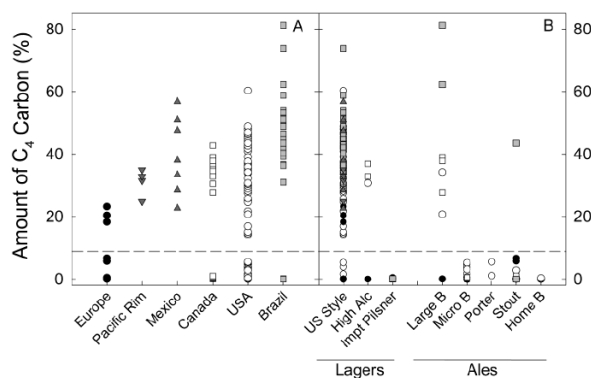


Figure 2: Carbon isotope ratios ( $\delta^{13}C$ ) by country and beer type, show that European beers use little to no corn, while other parts of the world use corn in the fermentation process.

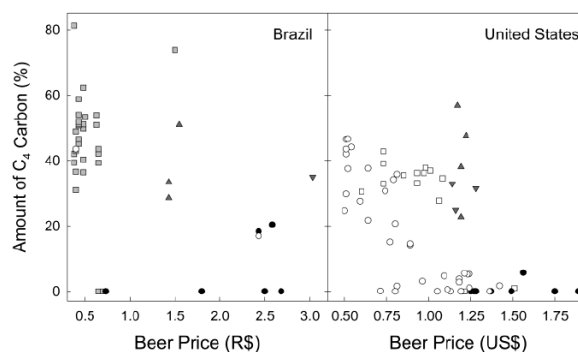


Figure 3: In general, less expensive beers have a higher carbon isotope ratios ( $\delta^{13}C$ ) and so use more corn, than more expensive beers.