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Original Research Article

Stable carbon isotopic composition of Brazilian beers—A comparison between large- and small-scale breweries

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ABSTRACT

The carbon stable isotope ratio ($\delta^{13}C$) has become an important tool to determine the composition and quality of various beverages, indicating the amount of C_3- and C_4-sources used in brewing. Accordingly, we assessed the isotopic composition of beers produced in Brazil and abroad, in order to quantify the use of C_4-sources as adjuncts. We also related the presence of such adjuncts to beer price, and compared the current results to similar studies, in order to assess any differences regarding beer composition over time. The mean $\delta^{13}C$ value for Brazilian beers was around −22.0‰, indicating a high addition of C_4-adjuncts during the brewing process. A dichotomy of beer isotopic signatures was observed: beers from large breweries had higher $\delta^{13}C$ values (around −20.0‰) than beer from artisanal breweries (−25.0‰). Beer price per L was directly related to $\delta^{13}C$ values in Brazil and abroad. This significant relationship, in addition to the ^{13}C-enrichment observed in this study, may reflect a change in the Brazilian beer market, in which a greater variety of beverages are produced and marketed following traditional recipes regarding their purity.

1. Introduction

Beer history is intrinsically related to mankind's development. With the expansion of cereal crop cultivation, a strong link between cereal and brewed beverage production began, particularly in ancient Egypt, Mesopotamia and the Near East around 6,000 BCE (Hornsey, 2003). Probably the best-known alcoholic beverage of this group is beer, which is the result of a complex fermentation series of starch products, mainly malted barley, wheat, rice and maize (Linko et al., 1998; Zuppardo, 2010). Nowadays it is the third most commonly consumed beverage in the world (Bamforth, 2003; Hornsey, 2003). With the advent of crop cultivation, beer production has evolved, and many brewers have begun using adjuncts substituting the original ingredients, notably maize.

Currently, Brazilian *per capita* consumption of beer rose from 41.8, in 1994, to 57 L per year, in 2008, with the country being the third largest beer producer in the world, with a production of 12.6 million L, behind only China (40 million L) and the United States (35 million L) (SINDICERV, 2011). The recent rise of Brazilian consumption is linked to a change in the beer market. Formerly, the availability of foreign beers was limited and Brazilian production was limited to large-scale industries. These industries produced beers with a high addition of maize, as observed in a global comparison of beer composition done by Brooks et al. (2002). More recently, the beer industry experienced the rise of a myriad of brands in the Brazilian market, most of them linked to micro-(small-scale) breweries that today are responsible for 4.5% of 10.3 billion L of beer produced in 2007 (SINDICERV, 2011). Generally these micro-breweries typically seek the production of a differentiated beverage, using mainly malted sources during brewing.

Brazilian legislation, decree no. 2314 (Brazil, 1997), establishes that part of malted barley can be replaced by supplements (maize, barley, rice, wheat, rye, oats and sorghum – using whole-grain, flakes or its starch parts) and carbohydrates (sugar) of plant origin.

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The replacement of malt extract or its adjuncts must not exceed 50% (Sleiman et al., 2008). The most common adjuncts used are the high maltose maize syrup, maize grits, broken rice, and the possible introduction of sugar cane (Sleiman and Venturini Filho, 2008). Maize sugar is more rapidly fermented by brewer's yeasts than are more complex barley sugars (Brooks et al., 2002), which accelerates the brewing process and increases the alcohol content with minimal amount of ingredients and at lower cost for breweries. Unfortunately, breweries are not required to describe all the ingredients in beer composition, hampering beer validation (Brooks et al., 2002). With the flourishing of beer businesses and the rise of novel brands in the Brazilian market, an accurate and inexpensive method that is also faster for accurately detecting some adjuncts in beer would be useful.

Isotopic analysis is an important tool in the determination of composition, source origin and quality of food and beverages (Kellya et al., 2005; Jahren et al., 2006; Papesch and Horacek, 2009). As the isotopic values of the raw materials are very similar to the respective values of the processed product, this method is helpful in detecting fraudulent adulteration, assuring the authenticity of a variety of products. Carbon isotope ratios ($\delta^{13}C$) of alcohol have been successfully used to detect adjunct ingredients in alcoholic beverages such as wine, brandy and whiskey (Koziet et al., 1978; Arvanitoyannis et al., 1999; Giménez-Miralles et al., 1999; Pissinatto et al., 1999; Suhaj and Kovac, 1999; Ogrinc et al., 2001; Oliveira et al., 2002; Calderone et al., 2007; Martinelli et al., 2009).

This detection is possible since the $\delta^{13}C$ value of organic carbon in the sugars used to produce alcohol reflects the photosynthetic pathway of the plant producing the substrate. As each photosynthetic pathway reacts differently to the heavier carbon isotope (^{13}C) present in atmospheric CO_2, we observe that C_3- and C_4-pathways create distinct plant $\delta^{13}C$ values (Farquhar et al., 1982; Martinelli et al., 2011). This means that the $\delta^{13}C$ of an alcoholic beverage is an indicator of the amount of C_3- and C_4-ingredients used to produce this beverage. For example, many grains, including barley, are C_3-plants, which have $\delta^{13}C$ values around −28‰ (Farquhar et al., 1982). On the other hand, C_4-plants (which have $\delta^{13}C$ values around −12‰) such as maize, sorghum, and sugar cane produce the most common inexpensive sugars available on the world market, being commonly used as additives to certain alcoholic beverages (Simpkins and Rigby, 1982; Pissinatto et al., 1999). These differences can be used to track the relative contribution of C_4- and C_3-carbon sources in organic carbon mixtures (Boutton, 1996; Buchmann and Ehleringer, 1998).

In this paper we used the isotopic tool in order to determine the presence of C_4-derived adjuncts in Brazilian beers produced by large industries and micro-breweries. We also compare these Brazilian beers with several beer brands produced in other countries and imported to Brazil.

2. Materials and methods

2.1. Beer sampling

We analyzed 77 brands of beer, including 49 brands produced in Brazil and 28 produced in Europe, South and North Americas and China (Table 1) at the Laboratório de Ecologia Isotópica – CENA/USP, Piracicaba, SP, during December, 2010.

Most of the beer brands were acquired at Brazilian supermarkets, mainly in the municipality of Piracicaba, SP. Some beers were also acquired overseas. We recorded beer price, as well as information regarding beer style, volume, alcoholic strength, and manufacturing location, obtained from the labels of cans and bottles.

Table 1
Description of some characteristics of the beers analyzed.

Type	Style	Brand	Beer origin	Alcoholic gradation (%)	$\delta^{13}C$ (‰)
Ale	American Pale Ale	Schmitt Ale	Brazil	4.5	−25.4
		Yanjing Beer	China	3.6	−22.8
	Barley Wine	Baden Baden Red Ale	Brazil	9.2	−26.5
	Belgian Pale Ale	Eisenbahn Pale Ale	Brazil	4.8	−26.7
		Palm	Belgium	5.4	−27.3
		Tilburg's Dutch	Netherlands	5.0	−26.1
	Cream Ale	Baden Baden Golden Ale	Brazil	4.5	−26.0
	Dry Stout	Guinness Draught	Ireland	4.1	−27.2
		La Brunette	Brazil	4.5	−26.6
		Murphy's	Ireland	4.0	−27.2
	German Dunkelweizen	Erdinger Dunkel	Germany	5.6	−26.9
	German Weizen	Erdinger	Germany	5.3	−26.7
		Oettinger Hefeweizen	Germany	4.9	−26.2
	India Pale Ale	Brooklyn East India Pale Ale	USA	6.8	−25.3
		Colorado Indica	Brazil	7.5	−24.2
	Porter	Colorado Demoiselle	Brazil	6.0	−25.4
	Sweet Stout	Caracu	Brazil	5.4	−18.3
	Weissbier	Bohemia Weiss	Brazil	5.6	−19.6
		Colorado Appia	Brazil	5.5	−26.4
		Harbin Wheat King 10°	China	3.6	−22.6
Lager	Dark Lager	Bohemia Escura	Brazil	5.0	−19.1
		Crystal Malzbier	Brazil	4.2	−15.5
		Petra Escura Premium	Brazil	4.4	−19.1
	Lite American Lager	Tecate Light	Mexico	3.9	−20.1
	Malzbier	Antarctica Malzbier	Brazil	4.0	−15.1
		Brahma Malzbier	Brazil	4.0	−15.6
		Itaipava Malzbier	Brazil	4.2	−15.8
		Nova Schin Malzbier	Brazil	4.3	−17.8
	Munich Dunkel	Nova Schin Munich	Brazil	4.7	−16.7
	Pilsner	1795	Czech Republic	4.7	−22.6
		1906 Reserva Especial	Spain	6.5	−21.1
		Czechvar	Czech Republic	5.0	−26.8
		Harbin Beer	China	4.8	−18.0
		Hofbrau Original	Germany	5.1	−26.3
		Warsteiner Premium Verum	Germany	4.8	−25.5

Table 1 (*Continued*)

Type	Style	Brand	Beer origin	Alcoholic gradation (%)	$\delta^{13}C$ (‰)
	Premium American Lager	Bavaria Premium	Brazil	5.5	−25.0
		Birra Moretti	Italy	4.6	−22.5
		Brahma Extra	Brazil	5.5	−17.9
		Colorado Cauim	Brazil	4.5	−26.4
		Dado Bier Larger	Brazil	5.0	−19.1
		Dama Bier	Brazil	4.8	−26.6
		Eisenbahn	Brazil	4.8	−26.6
		Estrella Galicia	Spain	5.5	−20.8
		Heineken	Brazil	5.0	−27.4
		Paulistânia	Brazil	4.8	−25.8
		Therezópolis Gold	Brazil	5.0	−26.2
	Rauchbier	Eisenbahn Rauchbier	Brazil	6.5	−26.7
	Standard American Lager	Antartica	Brazil	4.9	−18.3
		Antartica Original	Brazil	5.0	−18.7
		Antartica Subzero	Brazil	4.6	−18.8
		Bavaria Classica	Brazil	4.3	−18.9
		Bohemia	Brazil	5.0	−18.4
		Brahma	Brazil	5.0	−19.3
		Cevada Pura	Brazil	4.8	−25.8
		Colônia	Brazil	4.0	−19.2
		Crystal	Brazil	4.5	−18.9
		Devassa Bem Loura	Brazil	4.8	−19.9
		Devassa Loura Tropical Lager	Brazil	4.8	−22.1
		Dos Equis	Mexico	4.5	−17.9
		Glacial	Brazil	4.4	−17.7
		Itaipava	Brazil	4.5	−19.6
		Itaipava Fest	Brazil	5.0	−19.2
		Kaiser	Brazil	4.5	−19.9
		Kaiser Summer Draft	Brazil	4.7	−18.6
		Modelo Especial	Mexico	6.0	−21.1
		Norteña	Uruguay	5.0	−18.6
		Nova Schin	Brazil	4.7	−18.4
		Patricia	Uruguay	5.0	−19.1
		Schneider Cerveza Rubia	Argentina	4.7	−20.5
		Skol	Brazil	4.7	−18.4
		Skol Beats	Brazil	5.2	−17.4
		Snow Beer	China	4.0	−19.2
		Sol	Brazil	4.5	−19.2
		Sol	Mexico	4.5	−18.2
		Tecate	Mexico	4.5	−17.5
		Zanni	Brazil	4.0	−21.4
	Malt liquor	Oettinger Super Forte	Germany	1.0	−27.1

2.2. Data analysis

A sample of 1.1 μL of each beer was placed into a tin capsule containing Chromosorb® porous polymers using a volumetric pipette. As we wished to assess the isotopic composition of beer and addition of extra C_4-compounds after the brewing process (*i.e.*, use of sugar syrup and caramel), no distillation procedures were made to obtain samples with a high alcoholic grade and a low concentration of volatile compounds other than ethanol (Spitzke and Fauhl-Hassek, 2010). The capsules were combusted in a Carlo Erba Elemental Analyzer (Milan, Italy). The CO_2 generated from the combustion was purified in a gas chromatographic column and passed directly to the inlet of a gas isotope ratio mass spectrometer (IRMS Delta Plus; Finnigan Mat, San Jose, CA, USA).

Internal standards (sugarcane leaves, $\delta^{13}C = -12.7‰$; %C = 43.82%) were included in every run. The isotope ratio ($\delta^{13}C$) is reported, according to Farquhar et al. (1982):

$$\delta^{13}\mathrm{C}(\text{sample}, \text{standard}) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right] \times 1000,$$

where R_{sample} and R_{standard} are the $^{13}C/^{12}C$ ratios of the sample and standard (Pee Dee Belemnite limestone). The analytical error is 0.3‰ for $\delta^{13}C$.

We then determined the content of C_4-plants (maize, for example) used as adjuncts during the brewing process by means of a mixing model (Martinelli et al., 2009):

$$C_4(\%) = \frac{\delta^{13}C_{\text{beer}} - \delta^{13}C_{\text{barley}}}{\delta^{13}C_{\text{maize}} - \delta^{13}C_{\text{barley}}} \times 100,$$

where $\delta^{13}C_{\text{beer}}$ is the isotopic composition of the beer analyzed; $\delta^{13}C$ barley is the mean isotopic signature of barley (−25.2‰); and $\delta^{13}C_{\text{maize}}$ is the mean isotopic signature of maize (−12.5‰) (Martinelli et al., 2009). This model is widely used to determine the relative amount of C_3- and C_4-plants in many studies involving a mixture of sources at many levels (Brooks et al., 2002; Martinelli et al., 2003; Nardoto et al., 2006).

We also used the calibration equation proposed by Sleiman et al. (2008), in order to determine the percentage of malt in beer according to the isotopic signature of the sample, within a confidence interval of 90%. We used the following equation to determine $\delta^{13}C$ values of beers containing 50 and 100% of malt in their composition:

$$h_{\text{adjunct}} = c + d \times W,$$

where h_{adjunct} is the malt content (%) in the sample; c is the linear coefficient of the line; d is the angle coefficient of the line; and W is the sample's $\delta^{13}C$ value.

Finally, a confidence interval of 90% (based on Hoffman and Vieira, 1998) was determined by means of the equation:

$$IC(Y) = h_{\text{adjunct}} \pm t_{(n-2)} \times s_e \times \sqrt{\left[1 + (1/n) + \frac{(W - W_m)^2}{\sum (W - W_m)^2}\right]},$$

where $IC(Y)$ is the confidence interval for Y axis; $h_{adjunct}$ is the malt content (%) in the sample; $t_{(n-2)}$ = critical values of the Student's-t distribution; s_e is the root mean square residual; W is the $\delta^{13}C$ value observed; and W_m is the $\delta^{13}C$ mean value of n observations.

2.3. Statistical analysis

We first grouped imported beers according to the continent on which they were produced to facilitate comparing Brazilian and foreign beers. Afterwards, we grouped beer by the locality and country it was produced.

Data distribution was tested using the Shapiro–Wilk W test. As distribution was not normal, we used the Box–Cox transformation to transform data properly. We used a one-way ANOVA followed by a *post hoc* Tukey HSD test to determine differences among beers from Brazil and other countries. In order to quantify the influence of the content of C_4-plants used as adjuncts on beer price, we used a simple general linear model.

All statistical analyses were performed using the software STATISTICA, version 10 for Windows (StatSoft, 2011). A probability level of 0.05 was used as a critical level of significance in all tests.

3. Results

Brazilian beers had a mean $\delta^{13}C$ value of -21.1 ± 0.6‰. Similar means were found for other South American beers, as well as for those from North America and Asia. Only European beers had a distinctive isotopic signature ($P < 0.001$), with a mean isotopic signature of -25.3 ± 0.9‰ (Fig. 1 and Table 2). We then grouped the Brazilian beers according to the commercial scale in which they were brewed, and we observed a dichotomy of isotopic signatures. Beers from large-scale breweries had higher $\delta^{13}C$ values than those artisanally brewed in small and micro-breweries: -19.6 ± 0.5‰, compared to -24.8 ± 0.6‰ ($P < 0.001$), respectively.

When we used the $\delta^{13}C$ values in a mixing model, once again, Brazilian artisanal beers differed from large-scale ones. Beers from small and micro-breweries had a lower mean percentage of C_4-source addition (9.3 ± 4.2%) compared to beers from large breweries (45.0 ± 3.2%) ($P < 0.001$). Notwithstanding European beers, whose mean C_4-source content was 7.3 ± 4.9%, the other imported beers also had a high contribution of such adjuncts: 45.7 ± 2.9%, in South American beers; 39.9 ± 9.1%, in North American beers; and 35.8 ± 7.2% in Asian beers ($P < 0.05$).

Using the calibration and confidence interval equation proposed by Sleiman et al. (2008) (Fig. 2), we observed that beers with a mean $\delta^{13}C$ value of -26.2‰ (and a confidence interval between -25.9 and -26.5‰) contain 100% malt. On the other hand, beers with an isotopic signature of around -18.8‰ (and a confidence interval between -18.7 and -18.9‰) are composed of only 50% malt, which is permitted by Brazilian regulations.

Based on these values, we noticed that 21 beers (11 brewed in Brazil, and 10 from abroad) exclusively used malt, a C_3-source, during brewing. On the other hand, the isotopic values of 16 Brazilian beers indicate high presence of C_4-sources in their composition. From these, the highest values observed belonged to five *malzbiers*, a *Munich dunkel* and a sweet stout, beers where the addition of sugar syrup and caramel colorant during the production process is known. Only five imported beers had $\delta^{13}C$ values higher than -18.8‰: one from Asia, one from South American and three from North America. No European beers were within this value interval.

Finally, we found a strong relationship between beer $\delta^{13}C$ values and their final cost per liter, either including all samples analyzed ($r^2 = 0.56$; $P < 0.05$) or only beers produced in Brazil ($r^2 = 0.53$; $P < 0.05$) (Fig. 3).

Table 2
Comparisons between beer $\delta^{13}C$ values from the present study and similar studies, including Brazilian beers in the analysis.

Study	Year	Beer $\delta^{13}C$ (‰)		
		Brazilian	Imported	European
Present study	2011	-21.1 ± 0.6[a] ($n=49$) -21.9 ± 0.6[b] ($n=42$)	-22.9 ± 0.4 ($n=28$)	-25.3 ± 0.9 ($n=15$)
Brooks et al. (2002)[c]	1994	-19.7 ± 2.4 ($n=31$)	-22.6 ± 2.7 ($n=99$)	-25.6 ± 1.5 ($n=20$)
Oliveira et al. (2002)	2000	-20.1 ± 0.7 ($n=13$)	-23.4 ± 1.1 ($n=9$)	-24.9 ± 0.8 ($n=6$)
Sleiman et al. (2010)	2004–2006	-21.8 ± 0.7 ($n=161$)	*N.A.*	*N.A.*

[a] Mean calculated including all Brazilian beers analyzed.
[b] Mean calculated excluding beers with recognized addition of adjuncts from C_4-sources (*i.e.*, sugar syrup and caramel colorant) ($n=7$).
[c] Personal communication.
N.A. Data not available.

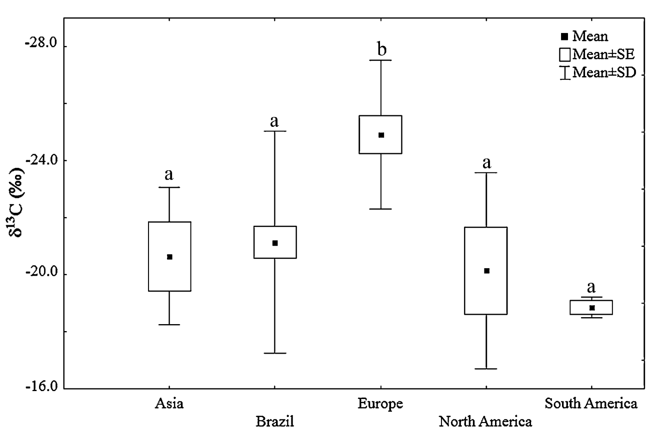

Fig. 1. Variation in $\delta^{13}C$ values (mean ± standard error; mean ± standard deviation) of beers analyzed.

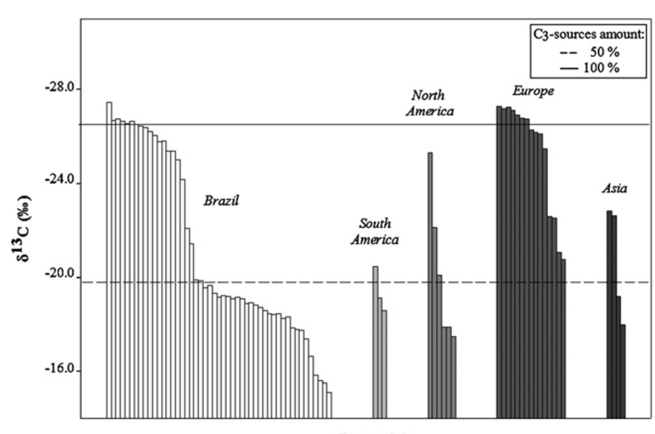

Fig. 2. Variation in $\delta^{13}C$ values of national and imported analyzed beers: Brazilian, South American, North American, European and Asian beers. The full line (—) indicates the $\delta^{13}C$ value of pure malt beers (100% of C_3-plants), which is -26.2‰, and the short-dashed line (- - -) indicates the $\delta^{13}C$ value of beers with 50% of C_4-plants (maize), -18.8‰. Based on the model proposed by Sleiman et al. (2008).

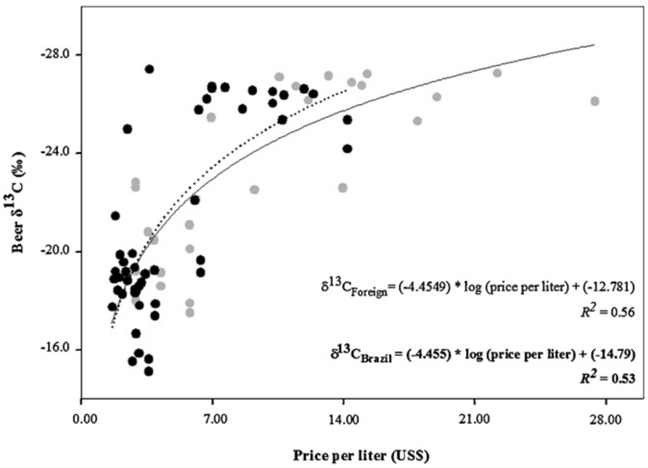

Fig. 3. Relationship between Brazilian (●) and foreign (●) beer $\delta^{13}C$ values and their price per L (US$). The full line indicates the fitted curve for the GLM including all beers analyzed, which is written normally. The dotted line indicates the fitted curve for the GLM including only the Brazilian beers analyzed, which is written in bold. An American Dollar (US$1.00) is equivalent to 1.57 Brazilian Reais (R$1.57). *Source*: http://coinmill.com (retrieved April 24, 2011).

4. Discussion

We found in this study that beers from large-scale breweries use more C_4-sources than beers from small and micro-breweries. The beers from industries with large-scale production represent 94% of the Brazilian market (Saorin, 2011), and such industries follow a general formula and add maize products (mainly maize syrup) to cut beer manufacture costs (Venturini Filho, 2000; Sleiman et al., 2010).

An opposite trend is observed for beers from Brazilian artisanal breweries, as well as European ones. The majority of such beers had a characteristic $\delta^{13}C$ value for no addition of maize products, suggesting they are pure malt beers. However, we cannot exclude the possibility that they were using an adjunct of C_3-origin, like rice.

As most of the barley used in the Brazilian beer industry is imported (Amabile et al., 2004; FAO, 2008; EMBRAPA, 2011), the substitution of some part of malted barley not only reduces costs of importation, but also beer production. Therefore, the use of imported barley is linked to a rise in beer production cost, resulting in an increase in final beer cost to consumers. Additionally, the use of these regional C_4-sources also decreases brewing time, due to the acceleration of the brewing process and increase in beer alcohol content. As a consequence, the production rate has increased, diminishing the cost of beer production (Brooks et al., 2002).

Despite the fact that ingredient expenses are only a small fraction of the cost of beer (Brooks et al., 2002), we found a strong inverse relationship between price and C_4-content (Fig. 3). Therefore, it is curious to note that more than half of the variability of the beer cost to consumers can be explained by the amount of C_4-derived adjuncts used in beer production.

5. Conclusion

In conclusion, our objective was to determine whether the change in the Brazilian beer market, with the inclusion of foreign and artisanal beverages would reflect a variation of the isotopic signatures. Based on our results, we observed that the majority of most conventional beer brands produced on a large scale are still composed of a noted mixture of C_3- and C_4-sources. On the other hand, artisanal beers, which occupy a growing niche in the beer market, seem to be composed only of C_3-cereals. Thus, we can conclude that the isotopic tool indicates a new pattern in beer production in Brazil with the use of fewer C_4-sources during the brewing process.

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