

SPATIAL AND TEMPORAL DEPENDENCE OF THE ^{13}C AND ^{14}C ISOTOPES OF WINE ETHANOLS

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ABSTRACT. More than 1000 authentic samples of ethanols were extracted by quantitative distillation from vintage wines and brandies prepared from grapes harvested in well-defined regions and years. The ^{13}C contents of these ethanols were determined by isotope ratio mass spectrometry (IRMS) and the ^{14}C activity of most of these samples was determined by liquid scintillation counting (LSC). We show that the ^{13}C content of a C_3 plant such as grape vine, which strongly depends on water availability, spans nearly a 10‰ range worldwide. The efficiency of the ^{14}C content of grape ethanols as a tracer of the CO_2 turnover after the peak of the nuclear test in the 1960s is also discussed in terms of geographical effects. Finally, the necessity of a multi-isotopic approach, including ^{13}C and ^{14}C isotopes, for detecting sophisticated adulterations is illustrated in the case of wines and brandies.

INTRODUCTION

The ^{13}C content of an agricultural product is an excellent criterion for characterizing the C_3 (Calvin) or C_4 (Hatch-Slack) photosynthetic metabolism of the plant from which it is produced (O'Leary 1988) and it is frequently assumed that C_3 or C_4 molecules should have $\delta^{13}\text{C}$ values on the order of -25‰ or -11‰ , respectively, with respect to PDB. However, it should be emphasized that in C_3 metabolism, isotopic fractionation is controlled not only by the enzymic step of carboxylation of ribulose biphosphate but also by the diffusion rate of carbonic anhydride through the leaves. As a consequence, environmental factors that influence the physiology of the plant also contribute to modify its overall ^{13}C content. This behavior may be relatively important for plants such as grape vine, which have very large foliar surfaces and evaporate a great quantity of water by transpiration. It has indeed been shown that a large range of $\delta^{13}\text{C}$ values may be observed for ethanol from grapes harvested in typical soil and climatic conditions (Day *et al.* 1995). This point must be carefully considered for regulatory purposes where upper limits of $\delta^{13}\text{C}$ are stated as proofs of the genuineness of wine origin. On the other hand, the ^{14}C content of ethanol that is largely used for determining its status as agricultural or synthetic may be an indicator of the short-term dating of wines or spirits (Guerain and Tourlière 1975). Indeed, the natural ^{14}C content of atmospheric carbonic anhydride and of the corresponding living pool significantly increased in the 1960s after the aerial nuclear tests, regularly decreasing following its peak in 1964. Hence, comparing the ^{14}C content of a wine or a spirit with the values of a calibration curve gives an indication of the harvest year of the plant from which the product has been produced. However, as Craig (1957) showed, ^{13}C and ^{14}C fractionations are intricate phenomena; more recently, the international recommendations for reporting ^{14}C data (Stuiver and Polach 1977) required that ^{14}C values be corrected on the basis of $^{13}\text{C}/^{12}\text{C}$ fractionation. Our purpose here is to present and discuss the dependence of the ^{13}C and ^{14}C contents of wine ethanols on the region and year of production.

MATERIALS AND METHODS

Nature and Origin of the Samples Studied

More than 1000 authentic wine ethanols contained in the Eurodat[®] databank (Eurofins–Nantes) were analyzed by IRMS and LSC. The grapes corresponding to the wines were collected during several years in the most important wine production areas. About 265 different region and vintage sit-

uations were investigated. In France, for example, authentic wines and grapes collected or obtained from specialized research centers (INRA) include 1970 to 1994 vintages from most of the French production areas. To investigate the post-World War II period, we obtained brandies from private firms or professional organizations. Wines and spirits from European countries and the Southern Hemisphere were obtained with the help of the Office International de la Vigne et du Vin (OIV) and from commercial sources.

Preparation of the Samples for Isotopic Determinations

Wines and spirits were distilled according to the procedure recommended by the OIV and European Union regulation 2676/90. To avoid any isotopic fractionation, the yield of ethanol extraction was >97% and 99% for wines and spirits, respectively; the alcoholic grade, determined according to the Karl-Fischer procedure, was >91%w/w. This parameter is of crucial importance for the computation of the ^{14}C content expressed per gram of carbon; the precision of the Karl-Fischer determination is better than 0.05%w/w in absolute value.

These conditions keep the thermodynamic isotopic fractionation under 0.1‰ (Moussa *et al.* 1990).

^{13}C Determinations

The determinations of the ($^{13}\text{C}/^{12}\text{C}$) isotope ratios were carried out in duplicate using a Carlo Erba microanalyzer on line with a Finnigan Delta E spectrometer. The results are reported on the δ scale with respect to the carbonate standard PDB (Craig 1957). The repeatability of the whole experiment is equal to 0.1‰.

To avoid any isotopic fractionation that would be induced by improper encapsulation of ethanol in the microanalyzer, a third combustion is carried out when the results of the duplicate measurements differ by $\geq 0.2\text{‰}$.

^{14}C Determinations

The ^{14}C activity was determined by LSC using a Packard Tricarb[®] 2250 CL instrument, according to the procedure described elsewhere (Thibault, Naulet and Martin 1994). Routinely, the ^{14}C contents were obtained directly on ethanol itself using the quenching curve procedure: 50/50% precisely weighted mixtures of ethanol and Instagel[®] from Packard were carefully introduced into clean 20-ml low-potassium borosilicate vials. The samples used for the determination of the quenching curve are pure ethanol of fossil origin (background determination) and ethanol from beet root (working standard). Their stable isotopic contents ($\delta^2\text{H}$, $\delta^{13}\text{C}$) were determined beforehand in order to check their origin. In order to detect the possible occurrence of systematic deviations, the influence of various experimental factors was studied: water content, contribution of tritium and impurities of the distillate (esters and higher alcohols) (Hanekom, de Villiers and Houtmann 1978).

To check that the correction procedures carried out with the quenching curve technique do not introduce systematic errors or long-term deviations, an aliquot of the working standard was periodically transformed into benzene: ethanol was burned in a high-pressure combustion bomb to form CO_2 that was used for preparation of benzene *via* a transformation into acetylene (Tamers 1965). The resulting benzene was calibrated relative to an internationally accepted secondary standard: Australian National University (ANU) sucrose (Polach 1989a). No significant difference at the 98% confidence level was found between the values determined by the two procedures. The repeatability of the determinations is better than 0.2 dpm gC^{-1} and the reproducibility is on the order of 0.3 dpm gC^{-1} .

Expression of the Results

The ¹³C/¹²C isotope ratios R are reported in *per mil* deviations with respect to PDB

$$\delta_i\text{‰} = ((R/R_{\text{PDB}}) - 1) 1000 , \tag{1}$$

where R_{PDB} = 0.0112372.

The ¹⁴C activity, A_s, is measured in counts per minute and converted to 1 g of carbon (dpm g C⁻¹).

A_s should be normalized for any differential carbon isotopic fractionation estimated by the δ¹³C deviation of the sample with respect to the accepted value of -25‰ (Stuiver and Polach 1977).

$$A_{\text{SN}} = A_s [(1000 - 25) / (1000 + \delta^{13}\text{C})]^2 \tag{2}$$

In addition, the result must be corrected for the ¹⁴C decay that would have occurred between the time of the collection of the plant (t_k) and that of the measurement (t_m):

$$A_{\text{SN}}^{\text{COR}} = A_{\text{SN}} \exp\left(\frac{t_m - t_k}{8267}\right) \tag{3}$$

For a 50-yr range such a correction does not exceed 0.1 dpm gC⁻¹ and is negligible.

The results may conveniently be represented on the Δ *per mil* scale (Stuiver and Polach 1977)

$$\Delta = \left(\frac{A_{\text{SN}}}{A_{\text{abs}}} - 1 \right) 1000 \tag{4}$$

where A_{abs} is the value of the NBSOX (Olsson 1970) indirectly determined from the experimental value of ANU Sucrose (Polach 1989a) by the benzene procedure (Thibault, Naulet and Martin 1994).

RESULTS AND DISCUSSION

Spatial and Temporal Variations of ¹³C Isotope in Wine Ethanol

Since knowledge of δ¹³C is required to normalize ¹⁴C measurements, it worth discussing beforehand the influence of natural factors on δ¹³C. The primary source of variation of δ¹³C in ethanol is related to the photosynthetic metabolism of the plant from which the glucides were obtained; typical values are reprinted in Table 1. The mean values of δ¹³C measured on ethanol prepared from C₄, CAM, C₃ and fossil materials spread over a 20‰ range, with the C₃ ethanol apparently occupying a very narrow 1‰ domain (Remaud *et al.* 1992). However, this small range is misleading, since the mean computed on a very large number of data levels the regional influence on the different plants. Examination of the next Table 1 entries, concerning the δ¹³C values of ethanol prepared from grapes harvested in countries having very different climates, shows that in fact the δ¹³C data expand over a 3‰ range. The regional averages were computed on a few dozen wines, except for Morocco–South Africa (14), New Zealand (7), and France, for which 1200 wines were considered. The general mean of -26.5‰ given in Table 1 masks the great diversity of situations encountered when regional and temporal factors are considered. First of all, examination of Figure 1A demonstrates that the distribution of ¹³C isotopic normals in France extends over a 3‰ range, the same width as that observed for the different countries studied in the world (Table 1). An *isotopic normal* (ISONO) may be

defined in the same way as the *climatic normals* (CLINO) of the World Meteorological Organization: it is the weighted average of the $\delta^{13}\text{C}$ values observed in a given region for a number of years (30 yr for CLINO). For the present study, the isotopic normals for 44 French regions of production were computed over 10–25 yr, depending on the importance of the region as far as viticulture is concerned.

TABLE 1. Variation of the Average ^{13}C Content in Ethanols Prepared from Plants Having Different Photosynthetic Metabolism and Physiology and in Ethanols from Grapes Harvested in Different Environments

Ethanols from plants having different photosynthetic metabolisms								
Photosynthetic metabolism	C_4		CAM	C_3				Fossil
Plant	Maize Sorghum	Cane	Pineapple	Wheat Barley	Grape	Orange Apple	Potato Beet	Synthesis
$^{13}\text{C}\text{‰}$	-10.2	-12.2	-14.7	-25.6	-26.2	-26.7	-26.8	-31.0
Ethanols from grapes harvested in different countries								
Country	Morocco	Spain	Australia	USA West Coast	Italy	France	Germany Switzerland	New Zealand
$^{13}\text{C}\text{‰}$	-24.5	-24.8	-25.8	-26.2	-26.4	-26.5	-26.8	-27.3

Now, consider the influence of vintage on a given region of production: the Bordeaux area has a $\delta^{13}\text{C}$ ISONO value equal to -26.5‰ , but when 15 vintages (1980 to 1994) corresponding to the main production areas (Medoc, Graves, Sauternes, St. Emilion, Entre-deux-Mers) are included in the graph (Fig. 1B), a 2‰ range is observed. Generally speaking, the ranges observed for a given region vs. different vintages and for a given vintage vs. different regions are not superimposed, and the 206 different spatiotemporal situations studied in France lead to 6.5‰ range of $\delta^{13}\text{C}$ values (Fig. 1C)!

These results illustrate that the ($^{13}\text{C}/^{12}\text{C}$) isotope ratios of plants that have a given C_3 photosynthetic metabolism, like grape vines, but that are also significantly water-dependent, are influenced not only by the enzymic carboxylation of ribulose but in addition by the stomatal conductance of the leaves in relation to the water stress of the plant (Dingkuhn *et al.* 1991). From this point of view, a significant relationship at the 98% confidence level was computed between $\delta^{13}\text{C}$ and the amount of precipitation P in a very precisely defined vineyard studied for several years (Day *et al.* 1995)

$$\Delta(^{13}\text{C})\text{‰} = -0.08 \Delta(\text{P}) \text{ mm} , \quad (5)$$

where Δ represents the differences in ^{13}C or in rain between two given years of production.

As far as the normalization of ^{14}C measurements is concerned (Eq. 2), the range of $\delta^{13}\text{C}$ values observed for wine ethanols induces a small but significant effect ($<0.5 \text{ dpm gC}^{-1}$), which will be discussed later. Moreover, this natural variation of $\delta^{13}\text{C}$ in wines may have important consequences for origin assessment and adulteration control. For example, in the European Union the enrichment of wines by sucrose before fermentation is strictly regulated and can be isotopically controlled. Thus, when a $\delta^{13}\text{C}$ value higher than -25‰ is observed it is necessary either to consider carefully the meteorological conditions of the year to which the suspected wine belongs, or to look at a detailed data bank such as that prepared for the E.U. by the Joint Research Centre at Ispra, before diagnosing an addition of C_4 sugar. In the same way, different countries of North and South America tend to suspect brandies of adulteration by C_4 ethanols or spirits such as distilled maize or tequila when their $\delta^{13}\text{C}$ values are higher than -25‰ or -26‰ , whereas genuine Spanish brandies, for example, may have $\delta^{13}\text{C}$ values as high as -23.5‰ .

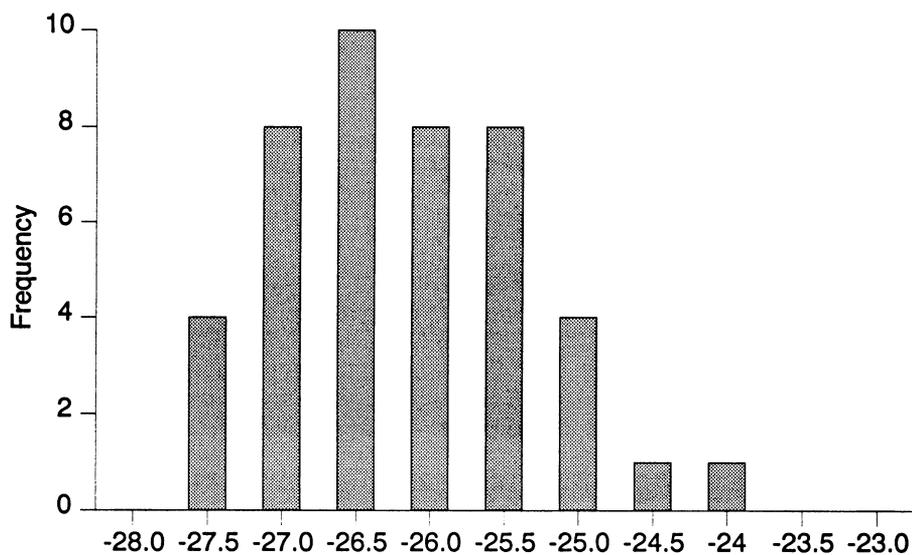


Fig. 1A. Normal isotopic distribution of $\delta^{13}\text{C}$ in French wines from different regions

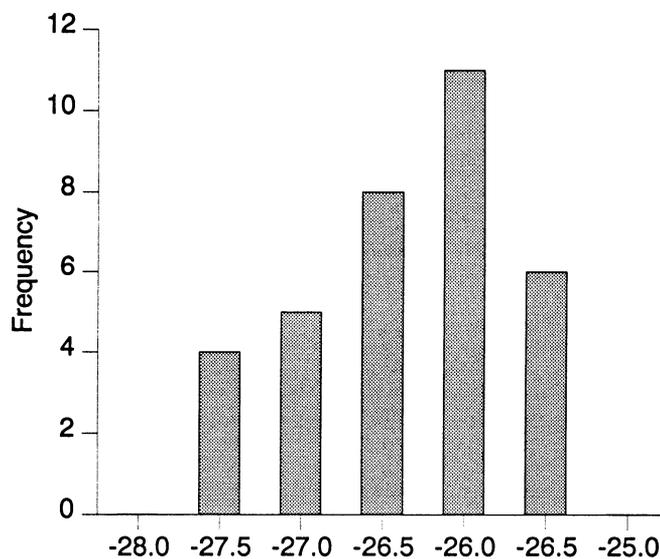


Fig. 1B. $\delta^{13}\text{C}$ distribution in Bordeaux wines from different vintages (ISONO = -26.5‰)

Temporal and Spatial Variation of ¹⁴C Isotope in Wine Ethanols

Radiocarbon is a very efficient tracer for environmental investigations and a number of studies relate ¹⁴C variations to natural and anthropogenic contributions to the atmospheric CO₂. From this point of view, the ¹⁴C content of ethanol seems to be a good indicator and some curves representing variations of alcohol activities with time have been published for Scotch whiskies (Baxter and Walton 1971)

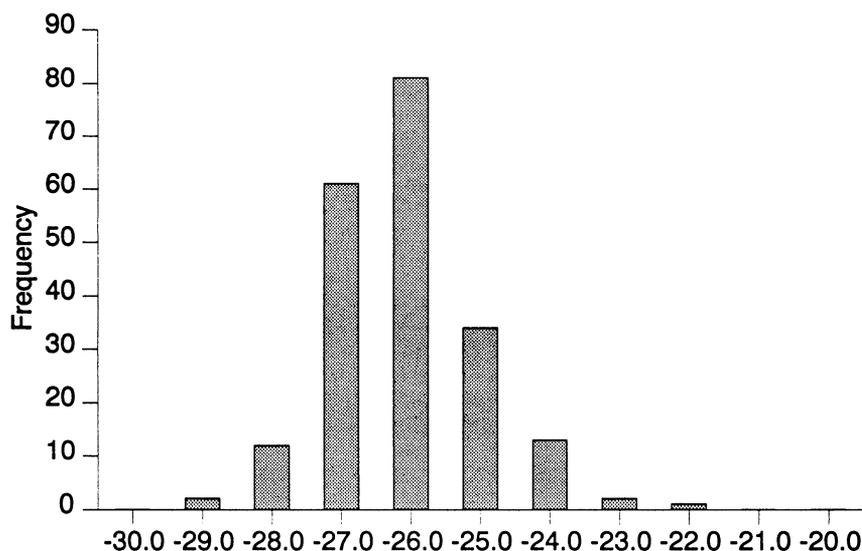


Fig. 1C. $\delta^{13}\text{C}$ distribution in French wines from different regions and vintages

and for wines from the Northern Hemisphere (Simon, Rauschenbach and Frey 1968; Stefani 1974; Lopes Sousa, Pinto and Almendra 1975; Fischer *et al.* 1980; McWeeny and Bates 1980; Marques Gomes, Perrera and De Almeida Saavedra 1981; Burchuladze *et al.* 1989; Schönhofer 1992).

Figure 2 shows the mean values of the ^{14}C variation of grape ethanol as a function of the vintage between 1950 and 1993. The corresponding full error estimates have also been represented.

If we except the measurement errors associated with the random nature of ^{14}C decay and with the LSC methodology that are well documented (Polach 1989b), several other natural factors contribute to the overall uncertainty.

In practice, the ^{13}C correction that is required to normalize the ^{14}C data induces a very small variation in the case of grape ethanol. Considering that the mean and standard deviation, σ , of the ^{13}C values of the worldwide population of grape ethanols are equal to -26.2‰ and 1.4‰ respectively, the $(\pm 1\sigma)$ range of $\delta^{13}\text{C}$ will correspond to a ± 0.05 variation of A_{SN} . Likewise, the age correction does not exceed ± 0.05 for A_{S} .

Interestingly, most of the uncertainty of the mean of the ^{14}C data determined for the different years investigated is probably due to environmental factors. First of all, if we compare the mean standard deviation (MSD) of the ^{14}C activity determined for each year in France with that of the literature concerning European wines we obtain values respectively equal to 0.30 and 0.52. The larger dispersion observed for the ^{14}C activities of grape ethanol from Germany, Georgia, Italy, France, Spain, Portugal, *etc.*, compared to the data concerning only one country, reflects the influence of regional effects. These spatial effects may be split into significant temporal contributions. When examining the curve of Figure 2, it appears that the two specific periods, 1957 to 1963 and 1970 to 1973, are characterized by a relatively high dispersion of ^{14}C activities (MSD = 0.76), whereas the years investigated before 1957 and after 1974, including the period 1964 to 1969, have much less scattered ^{14}C values (MSD = 0.39).

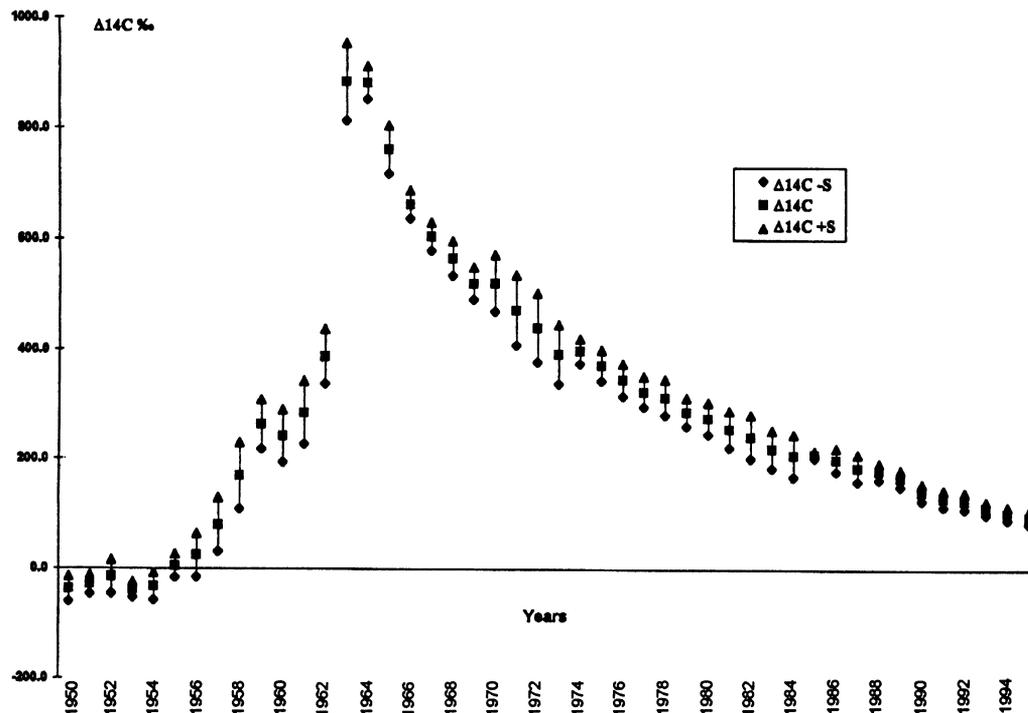


Fig. 2. ¹⁴C contents of European wines. The values for 1994 and 1995 correspond to a small number of samples

The present results are a source of further information on the influence of the regional variations of radioactive fallout after the peak periods of the nuclear tests in 1955 and 1961–1962. This phenomenon was previously discussed by Levin, Munnik and Weiss (1980) and Nydal and Lövsseth (1983). Since the ¹⁴C contents of wine ethanols are related to the turnover of the atmospheric CO₂, an exponential decrease of A_{SN} as a function of time may be expected in the absence of a pseudo-stationary state, *i.e.* after the 1964 maximum. The decrease in A_{SN} was computed between 1964 and 1994 for several series of geographically consistent data extracted from the whole set of European grape ethanols. Thus, the series considered were respectively constituted by the European (1), Georgian Republic (2) and French (3) grape ethanols. In the last case, we considered wines from different regions of production and from more specific areas such as Cognac (4) and Armagnac (5).

A simple exponential model

$$A_{SN} = a + b \exp(-kt) \tag{6}$$

fits the experimental data reasonably well between 1964 and 1994 (mean standard deviation ≤ 0.2 dpm, except for Georgia (0.53)); however, the intercept, a, which should be identified with the natural activity in 1945, varies significantly between the different series of data considered. Then the intercept was forced to be equal to 13.6 dpm gC⁻¹:

$$A_{SN} - 13.6 = b \exp(-kt) \tag{7}$$

The results given in Table 2 indicate a good consistency of the rate constants, k, calculated for the five series of data. The value of k computed from the most consistent series, *i.e.*, French grape ethanols,

is equal to 0.065 yr^{-1} with a standard deviation on the order of 0.003 yr^{-1} . From this rate constant, the explicit mean life of CO_2 in atmosphere is estimated at 15.4 yr (0.7). The activities, A_{SN} , computed from Equation (7) for 10, 20 and 30 yr after the peak of 1964 fit the experimental values very nicely. The different series of activities corresponding to the Northern Hemisphere were merged in order to obtain a calibration curve for the short-term datation of wines and spirits (Fig. 2).

TABLE 2. Modelization of the ^{14}C decrease in wines as a function of time (yr) during the period 1964–1994. Model $y-A = b \times \exp(-kt)$; MSD=mean standard deviation; *data not available.

Region	Model parameters				Predicted (existing) values of A_{SN}			
	A	b	k	MSD	t=0	t=10	t=20	t=30
1. Europe	13.60	10.89	0.067	0.194	24.49 (24.8)	19.17 (19.1)	16.45 (16.5)	15.06 *
2. Georgia	13.60	10.74	0.067	0.528	24.34 (25.6)	19.10 (18.95)	16.41 (16.5)	15.04 *
3. France	13.60	11.25	0.065	0.228	24.85 (25.6)	19.47 (19.5)	16.67 (16.75)	15.20 (15.05)
4. Cognac	13.60	10.65	0.062	0.054	24.25 (24.2)	19.33 (19.35)	16.68 (16.6)	15.26 *
5. Armagnac	13.60	10.41	0.061	0.134	24.01 *	19.26 (19.35)	16.67 (16.7)	15.27 *

Regional Variations of ^{14}C in Grape Ethanol

Very few studies exist of ^{14}C content of food products from the Southern Hemisphere. Two analyses of radiocarbon activities of South African wines (Hanekom *et al.* 1978; Fischer 1980) concluded that, for the period 1960–1970, there were noticeable differences between wines from the two hemispheres. In particular, a shift is observed in the maximum of ^{14}C content, which appears later in the Southern than in the Northern Hemisphere and with a smaller intensity. Therefore, a separate study was conducted on wines from Southern Hemisphere. The measured ^{14}C activities of ethanol from Australia, New Zealand, Brazil, Argentina and South Africa are summarized in Figure 3. A rate constant of 0.062 yr^{-1} is calculated.

Although the rate constant is similar in both series, the overall activities are slightly lower in the Southern Hemisphere. This trend may be considered significant even if the differences between the individual ^{14}C activities for a given year are on the same order of magnitude as the experimental uncertainty.

If we now consider French wines from several regions of production for 1984 and 1990 in the $^{13}\text{C}/^{14}\text{C}$ plane, interesting behaviors appear (Fig. 4). The wines from the 1990 vintage are clearly enriched in the ^{13}C isotope (+2‰) as compared to those of 1984. This observation may be rationalized in terms of water stress of the vine during the very dry 1990 vintage in several regions of production. For example, the mean precipitations (mm/month) and temperature ($^{\circ}\text{C}$) during the growing period of grape vines were equal to 64.8 (56.2) and 16.5 (18.3) for the years 1984 and 1990, respectively. On the other hand, the ^{14}C activity of wine ethanol between the two considered vintages decreases by *ca.* 1 dpm gC^{-1} , but in both years, wines from the lower Rhône Valley (Gard) are clearly enriched in ^{14}C (1 to 2 dpm gC^{-1}) with respect to the mean of the years. This increase in ^{14}C , which leads to ages several years too young for the wines of this region, is probably related to the existence of nuclear power stations in the area.

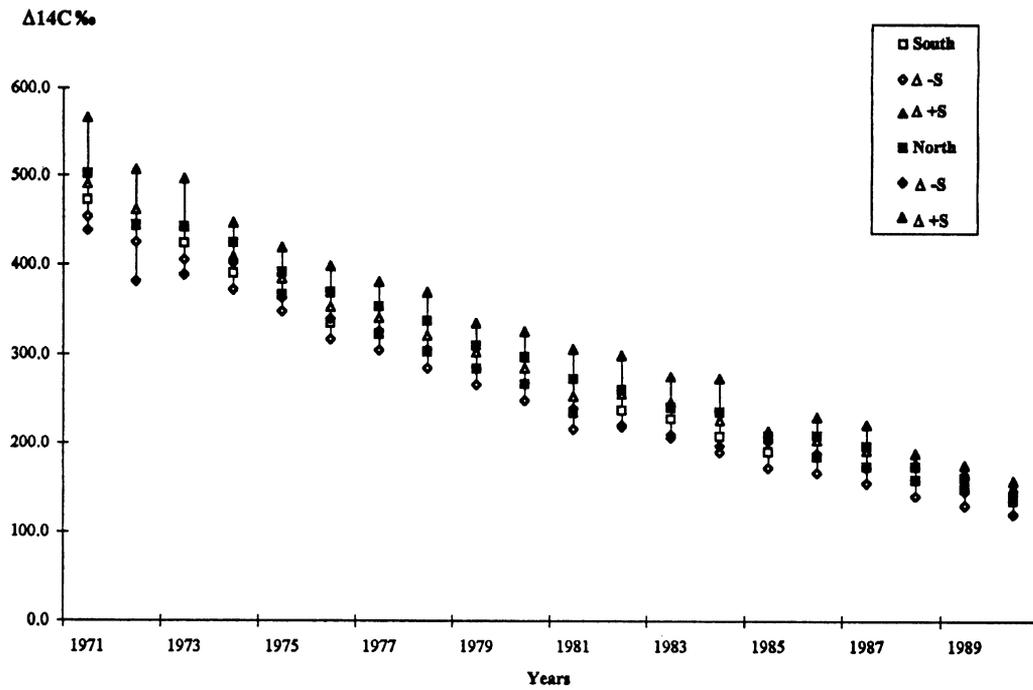


Fig. 3. Comparison of the ^{14}C contents of wines from the Southern and Northern hemispheres

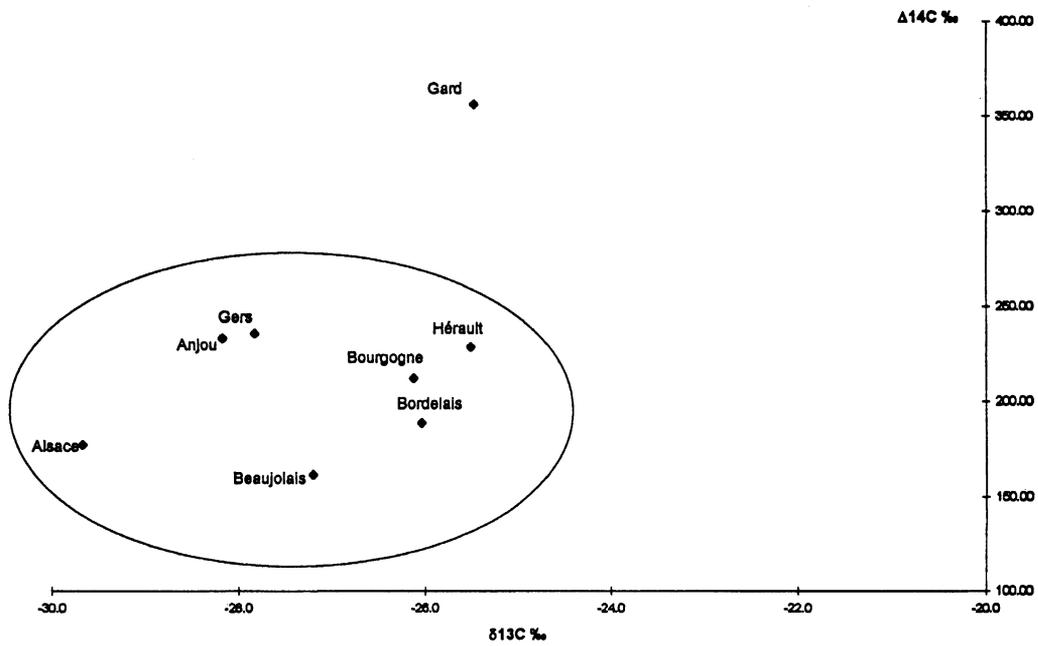


Fig. 4A. Representation in the plane ^{13}C - ^{14}C of ethanols obtained from grapes harvested in 1984 in several French regions of production

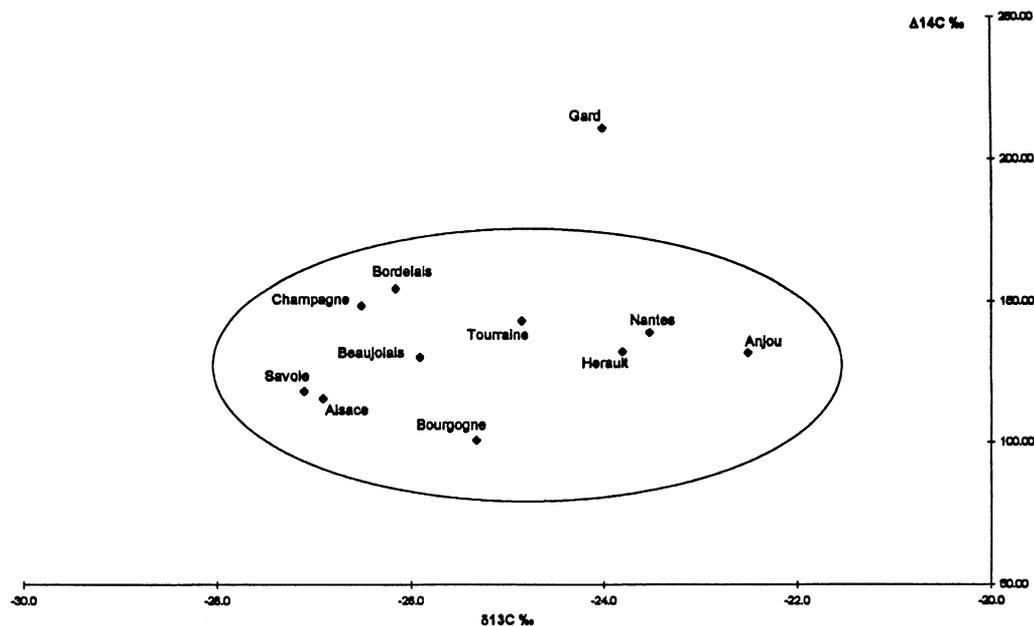


Fig. 4B. Representation in the plane ^{13}C - ^{14}C of ethanols obtained from grapes harvested in 1990 in several French regions of production

Multi-Isotopic Strategies in the Detection of Adulterations

To conclude, a multi-isotopic strategy for authenticating the botanical origin of ethanol will be considered. Generally speaking, wine ethanol has the highest commercial value and is frequently adulterated by other agricultural (beet, cane, maize) or even synthetic ethanols. In this respect, the hydrogen isotope ratio, $(\text{D}/\text{H})_1$ (isotopomer $\text{CH}_2\text{DCH}_2\text{OH}$), determined by NMR spectroscopy and the $(^{13}\text{C}/^{12}\text{C})$ ratio determined by IRMS are two powerful probes for determining the addition of beet and cane ethanol into wine ethanol (Martin and Martin 1988). The addition of synthetic ethanol in any of the agricultural ethanols can be checked by measuring the ^{14}C content of the suspected alcohol (Martin *et al.* 1981), at least if the year of production of the agricultural ethanol is known. In practice, however, complex mixtures of exogenous ethanols may be found in commercial products. For example, in high-priced fortified wines or brandies, it may happen that the alcoholic component contains ethanols from C_3 (grape and beet), C_4 (cane) and fossil origins. Beet and cane ethanols arise from the chaptalization process and fossil ethanol is used as a very cheap substitute for wine ethanol or even to artificially mature a brandy produced in the 1980s. In such complicated quaternary mixtures at least three independent isotopic probes should be considered to resolve the ethanol composition. As an example, we shall consider a brandy or a spirit that is claimed nowadays to be 50 yr old and is therefore very high priced. If this sample is characterized by a ^{14}C content on the order of 14.6 dpm gC^{-1} , it cannot be suspected as adulterated on this basis. However, a full isotopic analysis of this brandy gives the following values:

$$\delta(\text{D}_1) = -330.0\text{‰} \quad \delta^{13}\text{C} = -25.2\text{‰}$$

where $\delta(\text{D}_1)$ is the deuterium isotope value at the methyl site ($\text{CH}_2\text{DCH}_2\text{OH}$) in per mil. These parameters are directly related to the botanical origin of the sugar precursor of ethanol (Martin and Martin 1988, 1995). From an appropriate data bank, it is possible to find the $\delta(\text{D}_1)$ and $\delta^{13}\text{C}$ values

of authentic grape ethanols corresponding to the region of production of the brandy; thus, the means and standard deviations of the populations of reference ethanols are the following:

	Grape	Beet	Cane	Synthesis
δ(D _i) (‰)	-346 (8)	-405 (6)	-281 (6)	-196 (10)
δ ¹³ C (‰)	-26.3 (0.8)	-27.2 (0.6)	-12.2 (1.0)	-31 (1.5)

Roughly speaking, the isotopic characteristics of the unknown brandy are not drastically inconsistent with those of a pure wine ethanol, but an enrichment of the must before fermentation by a mixture of beet and cane sucrose can be suspected. According to the additive properties of isotope ratios and to the mixture rules, quite inconsistent compositions are computed for the brandy (mf = molar fraction):

$$(mf) \quad \text{Grape: 1.13} \quad \text{Cane: 0.07} \quad \text{and} \quad \text{Beet: -0.20}$$

Considering now that we could be faced with a brandy manufactured from chaptalized wines from a rather recent vintage, containing a small quantity of fossil ethanol for artificially maturing the product, we in fact compute for a 1985 vintage (16.5 dpm gC⁻¹) the following composition:

	Grape	Cane	Beet	Fossil
(mf)	0.60	0.13	0.10	0.12

which can prove the severe adulteration of the brandy.

CONCLUSION

The combined use of the radioactive and stable carbon isotopes is a very powerful tool for investigating environmental effects on the elaboration of plant products. The dependence of the ¹³C and ¹⁴C contents of grape ethanol on the region and year of production derived from the study of many authentic samples enables specific behaviors to be recognized. Thus, whereas the ¹³C isotopic normals of grape ethanol are restricted to a 3‰ range, the distribution of the δ¹³C values for the 200 different spatial and temporal situations studied span a 6–7‰ domain. This carbon fractionation, which reflects the response of grape vine to climatic effects, must be taken into account when analyzing ¹⁴C radioactivity. The mean ¹⁴C activity of grape ethanols computed from the data collected in this work for the large set of authentic samples and from literature values, exhibits a typical evolution as a function of the year of production. As a result of the increase in atmospheric radioactivity due to nuclear tests in the 1960s, ¹⁴C incorporated into grape sugars and consequently into ethanol exhibits a significant peak in 1964 followed by a continuous decrease that can be satisfactorily modeled. The rate constant of the exponential decay of ¹⁴C gives a realistic value of the mean lifetime of CO₂ in the atmosphere. Similar decreases in ¹⁴C activity are observed for both hemispheres; however, the Southern Hemisphere is characterized by slightly lower values. The present study also confirms the potential of a multi-element isotopic analysis of ethanol to prove sophisticated adulterations of brandies.

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