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Formic acid, acetic acid and methanol: their relevance to the verification of the authenticity of vinegar*

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Abstract

The presence of formic acid is an indirect indicator of the addition to vinegar of chemical acetic acid, derived from the pyrolysis of wood. The quantity of formic acid in cider vinegar can vary between 65-305 mg/L.

Modern technology for the analysis of acetic acid added to vinegar is based on SNIF-NMR + ^{13}C - IRMS (site specific natural isotope fractionation-nuclear magnetic resonance spectroscopy + ^{13}C - isotope ratio mass spectrometry). The analysis of methanol is by gas chromatography, and of formic acid by HPLC (high pressure liquid chromatography), or by enzymatic analysis. The authenticity of vinegar is still important, because fraud with chemical acetic acid is unfortunately on the increase in certain countries.

Methanol comes from pectin, which is hydrolysed partially to pectic acid and to methanol, due to pectinesterase. The quantity of methanol in wine vinegar varies between 20-90 mg/L, in cider vinegar between 40-380 mg/L.

Keywords: *Fermentation vinegar, diluted acetic acid, essence vinegar, pyrolysis of wood, formic acid, methanol*

Résumé

Importance de l'acide formique, de l'acide acétique et du méthanol dans la vérification de l'authenticité des vinaigres.- *Le méthanol provient de la pectine, qui est hydrolysée partiellement en acide pectique et en méthanol, grâce à la pectinestérase. La quantité de méthanol dans le vinaigre de vin varie entre 20-90 mg/L, dans le vinaigre de cidre entre 40-380 mg/L. Les esters de l'acide formique se trouvent dans le vinaigre de vin. La présence d'acide formique est un indicateur indirect de l'addition, au vinaigre, d'acide acétique chimique provenant de la pyrolyse du bois. La quantité d'acide formique dans le vinaigre de cidre peut varier entre 65-305 mg/L. La technologie moderne pour l'analyse de l'acide acétique ajouté au vinaigre se base sur la méthode SNIF-NMR + ^{13}C - IRMS (site specific natural isotope fractionation-nuclear magnetic resonance spectroscopy + ^{13}C - isotope ratio mass spectrometry). L'analyse du méthanol se fait par chromatographie en phase gazeuse, et celle de l'acide formique par HPLC (chromatographie en phase liquide à haute pression), ou par analyse enzymatique. L'authenticité du vinaigre est encore importante, car la fraude avec l'acide acétique chimique augmente malheureusement dans certains pays.*

Mots-clés: *Vinaigre de fermentation, acide acétique dilué, essence de vinaigre, pyrolyse du bois, acide formique, méthanol*

* *This paper is dedicated in memoriam of Prof. G. Turian*

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Introduction

Vinegar certainly appeared at the same time as the first alcoholic beverages, produced from dates, in the times of the Babylonians (probably 2000 B.C.). Ethanol is oxidized into acetic acid by acetic acid bacteria. Geber, an alchemist in Seville, was the first to discover acetic acid by the distillation of vinegar, in the 8th century.

Many people do not know that vinegar essence, produced from chemical acetic acid, can contain arsenic and heavy metals, such as lead, mercury, copper, zinc, and whereas fermentation vinegar can contain small quantities of methanol.

The addition of chemical acetic acid to vinegar was already an indication of fraud more than 80 years ago. Fritsch wrote in 1923: «*The sure differentiation between fermentation vinegar and wood vinegar (or vinegar essence) is by analysis of formic acid. Fermentation vinegar does not normally contain formic acid, whereas wood vinegar does contain this acid. The analytical process is based on the reduction of $HgCl_2$ in HgCl with formic acid*».

In 1863, 60 years before Fritsch, Sestini mentioned for the first time the presence of formic acid and its esters, in balsamic vinegar.

In 1930 Wüstenfeld wrote: «*Formic acid does not exist in spirit vinegar. On the contrary, vinegar essence, produced by the dry distillation or pyrolysis of wood, always contains small quantities of this acid (less than 0.5 g in 100 g of acetic acid)*». In 1942 Reif described a method to detect the presence of formic acid by distillation, and thus to find out whether chemical acetic acid had been added to fermentation vinegar.

In 1955 Haeseler wrote: «*It is considered to be a fraud when vinegar contains more than 0.5% in weight of formic acid in anhydrous acetic acid*».

50 years ago, Bourgeois (1957b) wrote: «*It is difficult to differentiate between these 2 types of vinegars (by fermentation and by synthesis). Fraud continues to exist. [It still does so in the present with chemical acetic acid]. Unlawful mixtures can be detected by the analysis of amino acids. Whereas fermentation vinegar contains amino acids, this is not the case with vinegar essence*».

Aurand et al. (1966) and Kahn et al. (1972) found ethyl formate in spirit vinegar by means of gas chromatography and of mass spectrometry. This difference of results - with the presence or not of formic acid - in balsamic vinegar (Sestini 1863) and in spirit vinegar (Wüstenfeld 1930) is probably due to differences in the above mentioned analytical methods used over the last 60 or 70 years.

Methanol in vinegars comes from pectin, which is hydrolysed partially to pectic acid and to methanol, due to pectinesterase.

Furthermore, in Switzerland there was another type of fraud. It consisted in adding cider vinegar (cheaper in those days) to wine vinegar. Werder (1929) used a method to analyse sorbitol, a sugar present in fruit juices and cider, with only traces in wine. Werder managed to eliminate this fraud in wine vinegar. At present, the analysis of sorbitol is again used to detect the fraudulent addition of crystallized fruit to wine for its acetification.

This work deals with the importance of analysing formic acid and methanol in different vinegars. The presence of formic acid is an indirect indicator of the addition to vinegar of chemical acetic acid, derived from the pyrolysis of wood. Modern methods of analysis like the association SNIF-NMR + ^{13}C-IRMS (site specific natural isotope fractionation-nuclear magnetic resonance spectroscopy + ^{13}C – isotope ratio mass spectrometry) allow the detection of added chemical acetic acid, coming from petroliferous raw materials.

Materials and methods

Formic acid and its esters. They were analysed by the enzymatic method, as described by Boehringer (R-Biopharm 1997), or by high-pressure liquid chromatography (HPLC).

Acetic acid. The analysis of acetic acid uses the technique of ^{14}C. Acetic acid coming from petroliferous raw materials does not give an activity in ^{14}C, contrary to what happens when it has a recent organic origin like wood. This technique of ^{14}C can be used to differentiate both sorts of acetic acid.

SNIF-NMR + ^{13}C–IRMS. Using this technique it is not only possible to know whether the acid originates from petroliferous raw materials or from more recent organic matter, but also, in this latter case, it is possible to know the actual origin (Hermann 2001). Whether the acid is derived from the pyrolysis of wood can be ascertained, as well as from other origins, for example from wine, alcohol from sugar beets and cane, etc. This method, which is an AFNOR[1]

[1] Association Française de Normalisation, Tour Europe 92049 Paris La Défense Cedex.

norm, is also recommended by the "Manuel suisse des denrées alimentaires" (2001), in order to detect possible fraud.

Methanol. It was analysed by gas chromatography.

Results and Discussion

The results of the analysis of formic acid and its esters, of methanol, in various vinegars and in wine, are shown in Table 1.

Formic acid. In cider vinegar, its content varies between 65-305 mg/L according to Chabert et al. (1987).

Formic acid esters. Carnacini and Gerbi (1992) have observed the presence in Italian wine vinegars of: ethyl, methyl, isobutyl, isoamyl formate.

Methanol. In wine, its concentration varies between 50 and 325 mg/L, according to Lee et al. (1975). In wine vinegar, Gerbi et al. (1995) mention 40 mg/L, Amati et al. (1990) 50-90 mg/L, and Quiros (1990) 70-80 mg/L in sherry vinegar. In cider vinegar, Gerbi et al. (1995) mention 370-380 mg/L. According to these authors: «*The presence of methanol within the limits allowed, can be considered to be a parameter of authenticity in fruit vinegars*».

The results of the methanol analysis of Spanish spirit and wine vinegars, by gas chromatography, are shown in Fig. 1.
We only know that *Acidimonas metanolica* can grow in the presence of methanol, a precursor of formic acid. Asai (1968) wrote: «*The oxidizability of methyl alcohol is extremely weak*».

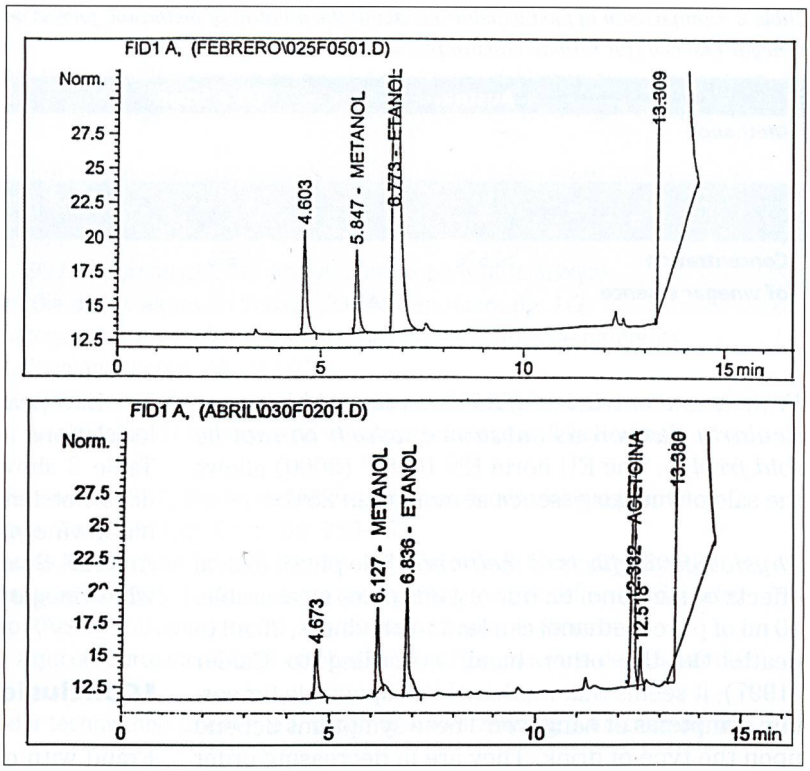

Fig. 1. Methanol analysis by gas chromatography of Spanish vinegar: spirit (A), wine (B).

Physiological effects of acetic acid and methanol

Vinegar is produced for human consumption. Therefore it is necessary to control the amount of methanol and formic acid, because of their potential physiological effects on the human organism.

Physiological effects of acetic acid. Acetic acid can lead to death at a certain concentration. In 2004 the «Swiss information center of toxicology» informed that: «*a young lady died 3 days after absorbing acetic acid at 80%*». According to a communication of the «Office fédéral de la santé publique» in Berne, dated 16.11.2005: «*Acetic acid concentrate is corrosive for mucous membranes and skin; it can cause serious injuries to the eyes and lungs...*

Table 1. Analysis of formic acid and its esters, of methanol in various vinegars and in wine.

	organic cider vinegar	cider vinegar	sherry vinegar	It. wine vinegar	Sp. wine vinegar	bals. vinegar	wine	spirit vinegar
formic acid (mg/L)	—	65-305	—	—	—	+	20-90	+
formic acid esters (mg/L)	—	—	—	+	—	+	+	+
methanol (mg/L)	40-60	370-380	70-80	40-90	20	—	50-325	10-25

Table 2. Comparison of food legislations about the amount of methanol, formic acid, and acetic acid in vinegars, alcohol, and vinegar essence (for human consumption).

	Austria	EU + Spain	Spain	Switzerland
Methanol	—		<1000 mg/L in wine vinegar	<500 mg/L in pure ethanol
Formic acid	<1000 mg/Kg of acetic at 100%	<500 mg/L of acetic acid at 99.8%	—	—
Concentration of vinegar essence	>25%	>25%	>25%	<14%

From a concentration of 25%, acetic acid is a particularly dangerous substance, which cannot be sold freely». The EU norm EN 13189[2] (2000) allows the sale of vinegar essence at more than 25%.

Physiological effects of methanol. The physiological effects of methanol on our organism are measurable. 10 ml of pure methanol can lead to blindness, 30 ml to death. On the other hand, according to Calder (1997), it seems that methanol is responsible for certain symptoms of hangover. These symptoms depend upon the type of drink. They are in decreasing order in the following examples: brandy, red wine, whisky, white wine, gin and vodka.

Methanol is metabolised by the enzymatic systems of alcohol-dehydrogenase and catalase, into formaldehyde and formic acid, producing metabolic acidosis.

Legislation

As mentioned before, vinegar is produced for human consumption, and therefore submitted to food legislation.

The «Ordonnance du Département fédéral de l'intérieur sur les potages, les épices et le vinaigre» art. 18, dated 27.12.2005 confirms the limit of the acetic acid percentage of vinegar essence at 14%, in Switzerland.

At the International Vinegar Congress at the Hague, Bourgeois (1957a) made a communication about the concentration of vinegar essence in Switzerland, saying: «*Vinegar essence can only be sold at a maximum acid concentration of 14%. Previously, vinegar essence was sold up to 80%. The new legislation avoids fatal accidents which happened before in Alpine valleys*».

The European countries have tried to unify their food legislations for vinegar, with only partial results, as Table 2 shows it. The EU norm EN 13188[2] (2000) does not limit formic acid in fermentation vinegar, but in vinegar essence, in that case half as much as in Austria[3]. Spain is the last country to limit methanol in wine vinegar[4].

Conclusion

Fraud with chemical acetic acid is increasing in certain countries. Depending on its origin, apart from the compounds mentioned previously, there are most certainly traces of arsenic and of heavy metals such as lead, mercury, copper, zinc, which come from the catalysers used for the production of acetic acid. The EU norm 13189[2] (2000) allows a maximum of 5 mg of heavy metals per kg of pure acetic acid.

In view of its supposed risk for the consumer, the relevant authorities should be required to legislate stricter regulations, which would limit and control these practices.

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[2] European Committee for Standardization (Brussels)

[3] see "Austrian food Manual" B 8 & 23, Hollinek Brüder Verlag, Vienna

[4] according to the "Boletín oficial del Estado", BOE 293 (1993)

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