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Polyalcohols in vinegar as an origin discriminator

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Polyalcohol content in vinegars of different botanical and geographical origin was studied by means of capillary gas chromatography. The data were statistically evaluated in order to discriminate the different vinegar types. Wine vinegars did not show a characteristic polyalcohol pattern, while apple vinegars and alcohol vinegars were well recognizable. The former had high sorbitol content and the latter showed the lowest amount of polyalcohols.

Statistical analysis showed that polyalcohol determination is a possible tool to discriminate vinegar raw material at least for white products. © 1997 Elsevier Science Ltd

INTRODUCTION

The EU production of vinegar has reached 450 000 000 litres/year. The greatest quantity is produced from alcohol (320 000 000 litres), 90,000,000 litres being derived from wine and the rest from different sources (mainly malt and apple). Italy produces about 54 000 000 litres of vinegar/year, nearly exclusively from wine, and, because of this, both Italy and Spain, (also a wine vinegar producer) are interested in emphasising the quality of this product, obtained from a raw material of high commercial value.

However, the value of the product can only be underlined if suitable chemical-physical and/or sensorial parameters are found, to express differences in composition on the basis of the origin of the vinegar, manufacturing techniques and commercial type.

The level and nature of polyalcohols in fermented foods could provide useful information about the genuineness, botanical origin and microbiological conditions of the raw material and of the final product.

Researchers have long known about the presence of polyalcohols in wine-based products (Dubernet *et al.*, 1974; Bertrand & Pissard, 1976; Drawert *et al.*, 1976; De Smedt *et al.*, 1979; Versini *et al.*, 1984; Sponholz & Dittrich, 1985). Polyalcohols are constituents of the grape and are synthesised by microorganisms during fermentation. Molds, such as *Botritys cinerea*, a common grape desease, could also contribute to their accumulation (Sponholz *et al.*, 1987; Ravji *et al.*, 1988). Consequently it would be interesting to carry out polyalcohol quantification on vinegars since this product undergoes at least two different fermentations and its botanical origin may be extremely diversified. In fact, polyalcohols have been studied by several authors using different techniques (Santa-Maria *et al.*, 1985; Tejedor & Santa-Maria, 1984).

The aim of this work was to evaluate the polyalcohol content in a series of vinegars of different botanical and geographic origins and to determine if this parameter could be used as an origin indicator.

MATERIALS AND METHODS

One hundred vinegar samples acquired in Italian, French, Spanish and Swiss markets were analysed. The samples were divided into 15 categories according to raw material, declared total acidity and country of production (Table 1).

Each sample represents a different commercial brand. While this ensured that the samples were representative, the number of vinegars per category was not uniform because certain vinegar types (alcohol, apple, malt) were commercialised by few or even just one brand.

Polyalcohol quantification was carried out through an analytical procedure especially set up for the purpose (Antonelli *et al.*, 1994).

The data were processed using a Statistical Package for Social Science for Windows, Version 5.02 (SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Table 2 shows the mean values and standard deviations calculated for each polyalcohol concentration of all vinegar categories of Table 1. These data underline the differences in polyalcohol content that were more attributable to the raw material used than to the commercial category of the vinegar. AL were easily distinguished by very low or no polyalcohol content, as high levels of sorbitol characterise AP. HO showed high levels of mannitol. Our hypothesis that raw material affected the polyalcohol content of vinegars was confirmed by the results of Multivariate Variance Analysis (MANOVA) (Table 3) carried out on all categories of vinegar with at least five samples, regardless of the colour.

Table 1. Vinegar categories analysed and their identification code

Vinegar categories	Identification code	Number of sample
Italian white wine (acidity 6%)[a]	IWW6	20
Italian white wine (acidity 7%)	IWW7	13
Italian wine (decolorized)	IDEW	2
Italian red wine (acidity 6%)	IRW6	9
Italian red wine (acidity 7%)	IRW7	10
French red wine	FRW	5
French white wine	FWW	5
Spanish white wine (Jerez)	EWW	4
Swiss red wine	CHRW	1
Swiss white wine	CHWW	2
Alcohol	AL	8
Apple	AP	14
Malt	MA	1
Honey	HO	3
Alcohol-wine	AW	3

[a] as total acidity expressed in % acetic acid.

Among wine vinegar categories there were some differences, not always related to total acidity content. In fact, IRW7 was significantly different from IWW6, IRW6, FRW and FWW. Moreover, IWW7 was significantly different from IRW6 and FRW. We examined three FWW samples with 6% total acidity, and two with 7% total acidity. FRW vinegars included three samples with 6% total acidity and two with 7%. We did not consider these differences since in France and all over Europe there is no commercial distinction on total acidity, as in Italy.

Besides MANOVA, Cluster Analysis (CA) can also be used to show similarities in samples, whatever their commercial classification.

Figures 1 and 2 show white and red vinegar dendogrammes obtained by Ward's method (Norusis, 1985). Samples without all polyalcohol concentrations available (i.e. alcohol) were excluded from this analysis.

Table 2. Means ($\bar{x}$) and standard deviation (s) of polyalcohol contents of the different vinegar categories

Vinegar categories	Erythritol		Xylitol		Arabitol		Mannitol		Sorbitol		s-Inositol		m-Inositol	
	$\bar{x}$[a]	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
IWW6	56	27	5	7	133	144	124	91	48	37	23	10	124	61
IWW7	63	25	4	4	134	123	114	41	49	37	27	7	168	46
IDEW	32	6	4	1	181	52	48	54	15	16	18	18	71	74
IRW6	39	11	2	2	94	93	128	138	30	16	22	5	106	35
IRW7	50	7	4	3	109	92	110	35	42	12	32	10	182	49
FRW	28	18	4	2	233	182	113	128	21	10	22	6	134	40
FWW	24	7	3	1	196	129	62	28	14	7	16	4	119	42
EWW	84	12	9	5	244	85	398	217	45	10	41	2	228	62
CHRW	44	nd[b]	2	nd	95	nd	38	nd	21	nd	25	nd	212	nd
CHWW	39	19	1	0	114	62	36	10	12	8	15	4	121	33
AL	0	0	0	0	7	10	31	34	1	4	0	0	2	4
AP	26	10	44	34	160	129	117	94	3296	1552	4	4	96	61
MA	11	nd	11	nd	5	nd	43	nd	185	nd	1	nd	86	nd
HO	16	10	2	1	39	50	958	305	42	22	10	14	76	35
AW	4	6	1	1	45	14	38	6	36	55	4	3	36	20

[a]means are expressed in mg/litre.
[b]not determined.

Table 3. MANOVA results on some vinegar categories

	IWW6	IWW7	IRW6	IRW7	FRW	FWW	AL	AP
IWW6		ns	ns	*	ns	ns	**	**
IWW7			*	ns	*	ns	**	**
IRW6				**	ns	ns	**	**
IRW7					**	**	**	**
FRW						ns	**	**
FWW							**	**
AL								**
AP								

ns: not significant.
*significant at $p \leq 0.05$.
**significant at $p \leq 0.01$.

Clusters were formed on the basis of raw material, country of origin or the vinegar production firm, but the acidity of the sample seems unimportant for both white and red vinegars. The presence of numerous clusters formed by vinegars, produced by the same company but distributed under various commercial brand names, could have interesting applications, and indicates that production techniques, especially acetic bacteria, had an effect on the polyalcohol content of vinegars. Other clusters were formed by AL, AP and EWW. AL were grouped with AW both characterised by the lowest polyalcohol content. It is noteworthy that MA were also grouped together with AL, probably because they were scarcely differentiated. HO samples were very inconsistent, since they were grouped in three very different clusters in the dendogramme, sometimes with AL, at other times with AP and also in a group of their own. Craftsmen-like techniques used to produce these vinegars could be the reason for this lack of uniformity. The placement of sample 69 (IWW6) amongst EWW, is also difficult to interpret.

Both the MANOVA and CA results tend to show that the subdivision of the samples on the basis of commercial categories does not always reflect differences in polyalcohol content.

Since the greatest divergences in polyalcohol content arise between vinegars produced from different raw materials, it is possible to use this parameter to identify the raw material employed to produce a given vinegar. After limiting the study to those vinegars with a sufficient number of samples (i.e. white wine vinegars, AL, AP) Linear Discriminant Analysis (LDA) was used for this purpose.

On the basis of MANOVA results, the wine vinegar group included Italian vinegars at 6 and 7% as well as French vinegars. Decolorised Swiss and Spanish vinegars were excluded since their low number of available samples did not permit preliminary variance analysis to evaluate their uniformity in other product categories. AW and AL were grouped together.

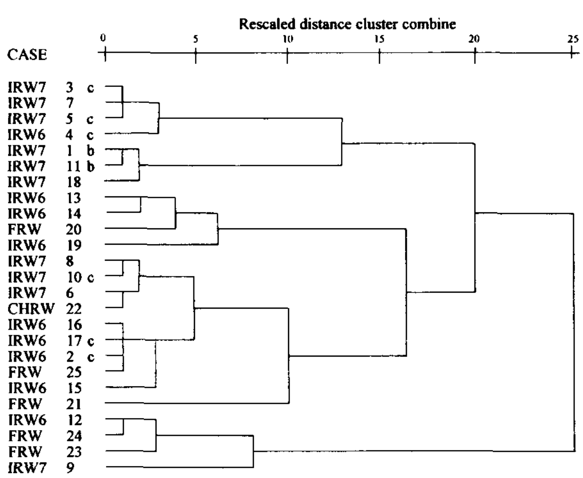

Fig. 1. Dendrogram of cluster analysis on white vinegars. Same letters indicate vinegars of the same producer.

The whole data set was subdivided at random into two equal parts, the training set used for building the discriminant model and the test set used for checking the discriminant potential of the model. All AW and wine vinegars were included in the test set.

The discriminant model that resulted (Table 4) had a reclassification potential of 97% for the training set (Table 5) and 83% for the test set (Table 6).

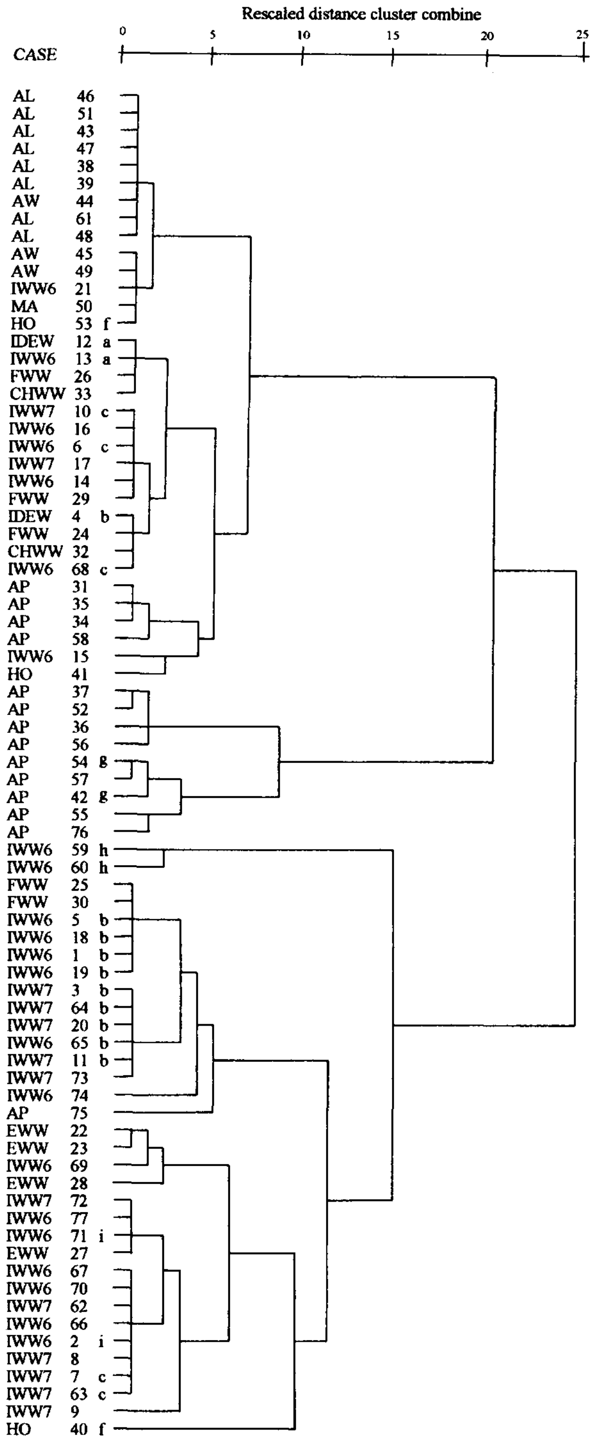

Fig. 2. Dendrogram of cluster analysis on red vinegars. Same letters indicate vinegars of the same producer.

Table 4. Coefficients of the two discriminant functions for white vinegars

	Function 1	Function 2
Erythritol	−0.188	0.693
Xylitol	0.294	0.088
Arabitol	0.207	−0.035
Sorbitol	1.017	0.201
Mannitol	0.544	−0.323
s-Inositol	−0.109	0.234
m-Inositol	−0.197	0.476

Table 5. Reclassification of white wine vinegars among the discriminated categories

Actual category	No. of samples	Forecast category		
		Wine	Alcohol	Apple
Wine	20	19	1	0
Alcohol	6	0	6	0
Apple	8	0	0	8

Table 6. Reclassification of white vinegars by the determined discriminant model

Actual category	No. of samples	Forecast category		
		Wine	Alcohol	Apple
Wine	18	15	3	0
Alcohol	5	0	5	0
Apple	6	1	1	4

The distribution of the samples on the plane obtained from the first two discriminant functions (Fig. 3) confirmed the role of sorbitol and mannitol in the characterisation of AP. AL were also well distinguished by their low or very low concentrations of all the polyalcohols.

In the test set, AW and wine vinegars were reclassified correctly and grouped together with AL. There were some problems for the reclassification of wine vinegars and AP since one sample of wine vinegar was reclassified as an AL, and two samples of AP were not correctly classified, one as a wine vinegar and the other as an AL.

Therefore, while the category of AL is well characterised, wine vinegars and AP are less correctly characterised because of the great lack of uniformity in these categories.

CONCLUSIONS

Multivariate statistical analysis of 100 samples of vinegar has shown that polyalcohol content was mainly affected by raw material and production techniques while total acidity is not always a significant factor for characterisation.

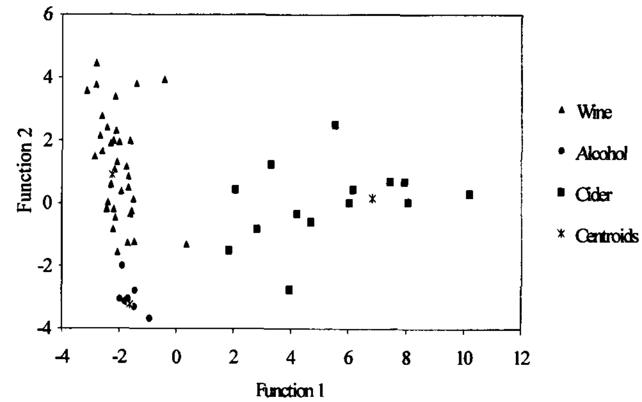

Fig. 3. Distribution on the plane obtained from the first two discriminant functions for white wine vinegars, apple vinegars, and alcohol vinegars.

In particular, AP were the richest in polyalcohols while AL were the poorest.

Polyalcohol content can therefore be used to discriminate the origin of vinegars, especially in cases where there is suspected adulteration of wine vinegars with less expensive AL. For wine vinegars, polyalcohols were not sufficient to discriminate between various products and the use of other analytical parameters is probably required.

Only EWW can be discriminated on the sole basis of polyalcohol content, but it is noteworthy that the Spanish vinegars examined were all produced from sherry, that is a particular raw material.

The discriminant functions obtained allow a good characterisation of wine-based, AL and AP and constitute an easily applicable tool for sector operators.

The determination of polyalcohol content in a sufficiently large number of samples will extend the use of the procedure to other categories of vinegar that were not included in this study (malt vinegars, honey vinegars, etc.).

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