

Progress in Food Fermentation

**Proceedings of the seventh European
Conference on Food Chemistry**

Valencia, Spain, September 20-22, 1993

F ECS Event No. 189

Volume 2

**Quality Assurance and Control
Processed Foods and Beverages**

ZEPPA GIUSEPPE

PUBB.

**Instituto de Agroquímica y Tecnología de Alimentos
Consejo Superior de Investigaciones Científicas
Jaime Roig 11, 46010 Valencia, Spain**

IMPORTANCE OF THE QUALITY CONTROL OF VINEGAR FOR VALORIZATION OF TYPICAL PRODUCTS

A. Antonelli⁽¹⁾, G. Zeppa⁽²⁾, G. Gerbi,⁽²⁾ A. Carnacini⁽¹⁾ and N. Natali⁽¹⁾

⁽¹⁾Istituto di Industrie Agrarie, Via S. Giacomo 7, I 40126 Bologna, Italy.

⁽²⁾DI.VA.P.R.A., via P. Giuria 15, I 10126 Torino, Italy.

Abstract

Study of the fixed fraction of 101 vinegars has been performed. Cluster analysis is able to separate the different vinegar from the different vegetal sources. The main important parameters seem to be glycerol, tartaric acid and proline for wine products; sorbitol for apple vinegar and a general lack of all the fixed compounds in alcohol vinegars always well distinguished from the others.

Introduction

By law vinegar is the yield of the acetic fermentation of agricultural alcoholics like wine, cider, beer and so on. These products belong to fermented vinegar, to be distinguished from that deriving from the fermentation of diluted distilled ethanol (distilled vinegar). All these products may be commercialised in EEC under the denomination of vinegar (1) and at least in four countries also diluted acetic acid solutions are present on the market, not always clearly distinguished from the others.

Each country uses the typical alcoholic product to elaborate its own vinegar: Italy and Spain wine, France wine and cider, etc. Nevertheless vinegar was for long considered a spoilage product without particular interest. Only recently has this tendency weakened showing a new trend to differentiate the product, particularly regarding origin and alcoholic matrix.

From this there arises the necessity to specify objective parameters of quality able to discriminate the different products, particularly for wine vinegar, a typically Mediterranean product. It must be emphasized that not only the genuineness of the product is our main purpose, for which specific analyses have already been developed (2), but determination of vinegar quality and the related parameter for its identification. This task is even more difficult for vinegar compared to other fermented products, because it undergoes double fermentation.

This paper is a preliminary attempt to face this problem particularly with analysis of the fixed compounds. It will be completed with volatile compounds and sensory evaluation.

Materials and methods

The vinegars analysed, were purchased on the market. They are divided into different classes according to the different alcoholic source. Another classification was made taking into account the different total acidity content (<7% and >7 %) according to Italian law (3) that distinguishes between normal (6%) and quality vinegar (7%).

The analyses performed are reported in tables 1 and 2 where the means and their standard errors of wine and other source vinegars are shown. The statistical elaboration of the outcomes was performed with SPSS/PC package.

Some of the samples were not statistically elaborated for two reasons. In some cases the small amount of the sample did not allow us to perform the whole set of analyses, in others the presence of only one sample made any statistical elaboration impossible. In this last case some considerations were made with all the limitations for the outlined situation

Results and Discussion

Table 3 shows the results of the Duncan test. Letter "a" indicates the lowest mean and the others the greater ones organised in alphabetical order of size.

Alcohol vinegars are the most easily recognizable due to their extremely poor composition. All the substances are at the lowest levels except for acidity whose value is only due to the volatile fraction. Other substances worthy of mention are the polyols, such as arabitol and mannitol, and acetoin produced by bacterial metabolism since distilled alcohol is an extremely pure product.

DETERMINATIONS		ALCOHOL	APPLE	HONEY	MALT
Density		1.0010 ± 0.0002	1.0080 ± 0.0010	1.0200	1.0100
Alcohol	% vol.	0.46 ± 0.31	0.22 ± 0.04	0.96	0.06
Total acidity	g/100 mL	7.46 ± 0.64	5.36 ± 0.13	6.48	6.12
Volatile acidity	g/100 mL	7.59 ± 0.64	4.65 ± 0.13	5.82	5.49
Fixed acidity	g/100 mL	0.07 ± 0.00	0.97 ± 0.14	0.82	1.05
Reduced extract	g/L	1.73 ± 0.93	15.80 ± 1.34	25.00	9.50
Ash	g/L	0.23 ± 0.03	2.23 ± 0.14	0.96	1.20
Alkalinity of ash	meq/L	1.47 ± 0.13	24.11 ± 1.72	9.60	8.40
Glycerol	g/L	0.23 ± 0.12	1.60 ± 0.27	3.42	1.60
Proline	mg/L	3 ± 2	13 ± 3	2	179
pH		2.34 ± 0.02	3.02 ± 0.03	2.72	2.78
Tartaric acid	g/L	0.09 ± 0.05	0.02 ± 0.01	0	0
Malic acid	g/L	0.06 ± 0.04	0.68 ± 0.26	0.18	0.57
Lactic acid	g/L	0.02 ± 0.02	0.72 ± 0.09	0.68	0.43
Citric acid	g/L	0.02 ± 0.01	0.15 ± 0.05	0.41	0
Succinic acid	g/L	0.03 ± 0.02	0.53 ± 0.06	0.20	0.35
Total polyphenols	mg/L	7 ± 7	601 ± 205	133	239
Tannic polyphenols	mg/L	7 ± 7	138 ± 27	49	32
Non-tannic polyphenols	mg/L	0 ± 0	463 ± 196	84	207
Catechins	mg/L	2 ± 1	50 ± 18	13	7
Proanthocyanidins	mg/L	7 ± 4	220 ± 58	134	21
O.D. 420 nm		0.190 ± 0.190	0.330 ± 0.040	0.170	0.390
Luminosity	%	0.70 ± 0.06	0.77 ± 0.02	0.80	0.70
Saturation	%	22.0 ± 6.0	28.3 ± 2.1	15.5	34.4
Dominance	nm	579 ± 0.54	576 ± 0	575	575
Iron	mg/L	0.60 ± 0.08	3.34 ± 0.45	3.54	0.37
Copper	mg/L	0.02 ± 0.02	0.07 ± 0.02	0.1	0.3
Zinc	mg/L	0.03 ± 0.03	0.16 ± 0.02	0.10	0.10
Manganese	mg/L	0.01 ± 0.01	0.42 ± 0.07	1.15	0.10
Lead	mg/L	0.01 ± 0.01	0.02 ± 0.01	0.05	0.23
Sodium	mg/L	14 ± 4	27 ± 5	26	15
Calcium	mg/L	73 ± 4	113 ± 16	49	26
Potassium	mg/L	38 ± 27	894 ± 81	483	365
Magnesium	mg/L	22 ± 7	46 ± 5	27	52
Acetoin	mg/L	7 ± 3.5	693 ± 118.6	1874	308
Erythritol	mg/L	1 ± 1.1	24 ± 2.8	10	11
Xylitol	mg/L	0 ± 0.1	45 ± 9.5	2	11
Arabitol	mg/L	18 ± 6.9	117 ± 21.5	39	5
Mannitol	mg/L	34 ± 9.5	110 ± 27.5	607	43
Sorbitol	mg/L	12 ± 9.8	3172 ± 475.0	393	185
scyllo-Inositol	mg/L	1 ± 0.7	4 ± 1.2	10	1
myo-Inositol	mg/L	11 ± 6.2	78 ± 9.8	76	86

Tab. 1: Analytical determinations of non-wine vinegars. Means and standard errors for each class of products.

DETERMINATIONS	ITALIAN VINEGARS				NON-ITALIAN VINEGARS					
	Decolored		White		Red		White		Red	
	\bar{x}	s^2	\bar{x}	s^2	\bar{x}	s^2	\bar{x}	s^2	\bar{x}	s^2
Density	1.012 ± 0.000	1.012 ± 0.000	1.012 ± 0.001	1.013 ± 0.000	1.014 ± 0.001	1.001 ± 0.000	1.000 ± 0.001	1.015 ± 0.000	1.021 ± 0.001	
Alcohol	0.10 ± 0.08	0.10 ± 0.01	0.50 ± 0.15	0.15 ± 0.04	0.54 ± 0.10	0.25 ± 0.07	0.87 ± 0.82	0.35 ± 0.12	0.19 ± 0.03	
Total acidity	6.18 ± 0.07	6.23 ± 0.05	7.42 ± 0.07	6.28 ± 0.05	7.27 ± 0.19	5.54 ± 0.36	6.84 ± 0.36	6.12 ± 0.43	5.83 ± 0.13	
Volatile acidity	5.90 ± 0.13	6.13 ± 0.10	7.07 ± 0.17	6.07 ± 0.09	6.97 ± 0.23	4.56 ± 0.37	5.12 ± 0.36	5.57 ± 0.49	5.83 ± 0.14	
Fixed acidity	0.24 ± 0.03	0.21 ± 0.02	0.40 ± 0.11	0.27 ± 0.04	0.36 ± 0.08	0.87 ± 0.20	1.72 ± 0.17	0.81 ± 0.20	1.44 ± 0.27	
Reduced extract	10.18 ± 1.76	11.58 ± 0.42	15.08 ± 0.92	12.31 ± 0.71	16.05 ± 0.85	12.10 ± 2.29	17.00 ± 7.20	14.48 ± 2.25	15.29 ± 1.87	
Ash	1.52 ± 0.09	2.02 ± 0.13	2.03 ± 0.14	1.78 ± 0.07	2.11 ± 0.09	2.21 ± 0.46	2.25 ± 0.84	2.73 ± 0.50	2.18 ± 0.25	
Alkalinity of ash	12.80 ± 0.37	17.01 ± 1.14	16.68 ± 1.44	15.96 ± 0.94	19.49 ± 1.35	17.75 ± 5.42	19.33 ± 7.36	20.93 ± 3.59	15.17 ± 3.25	
Glycerol	1.67 ± 1.15	2.49 ± 0.27	4.27 ± 0.21	3.06 ± 0.16	3.75 ± 0.25	1.90 ± 0.10	1.84 ± 0.11	2.43 ± 0.38	2.38 ± 0.31	
Proline	2.87 ± 9	2.79 ± 41	3.82 ± 9.8	3.06 ± 1	3.69 ± 45	2.32 ± 46	2.13 ± 32	3.47 ± 32	2.51 ± 33	
pH	2.65 ± 0.09	2.79 ± 0.05	2.69 ± 0.05	2.73 ± 0.04	2.73 ± 0.04	1.90 ± 0.10	2.85 ± 0.12	2.88 ± 0.04	2.81 ± 0.05	
Tartaric acid	0.90 ± 0.25	1.06 ± 0.13	1.77 ± 0.08	1.44 ± 0.15	1.81 ± 0.07	0.84 ± 0.16	1.33 ± 0.06	0.87 ± 0.09	1.31 ± 0.20	
Malic acid	0.13 ± 0.02	0.27 ± 0.04	0.37 ± 0.09	0.17 ± 0.03	0.27 ± 0.04	0.22 ± 0.07	0.69 ± 0.29	0.19 ± 0.05	0.34 ± 0.14	
Lactic acid	0.63 ± 0.22	0.53 ± 0.10	0.65 ± 0.17	0.48 ± 0.09	0.57 ± 0.13	0.44 ± 0.10	0.51 ± 0.32	0.20 ± 0.07	0.55 ± 0.26	
Citric acid	0.10 ± 0.02	0.16 ± 0.04	0.26 ± 0.04	0.08 ± 0.02	0.18 ± 0.03	0.12 ± 0.02	0.18 ± 0.03	0.09 ± 0.02	0.18 ± 0.07	
Sucinic acid	0.57 ± 0.08	0.58 ± 0.05	0.61 ± 0.05	0.55 ± 0.04	0.63 ± 0.05	0.33 ± 0.02	0.37 ± 0.07	0.52 ± 0.07	0.57 ± 0.05	
Total polyphenols	9.4 ± 13	163 ± 13	238 ± 22	548 ± 45	792 ± 58	204 ± 68	295 ± 148	604 ± 76	448 ± 120	
Tannic polyphenols	49 ± 20	70 ± 15	115 ± 18	233 ± 40	493 ± 59	58 ± 27	205 ± 192	249 ± 64	173 ± 48	
Non-tannic polyphenols	45 ± 28	98 ± 19	141 ± 29	280 ± 33	321 ± 38	146 ± 41	134 ± 18	337 ± 42	276 ± 84	
Anthocyanidins	##	##	##	10 ± 2	9 ± 1	##	##	9 ± 3	10 ± 7	
Catechins	8 ± 2	10 ± 1	19 ± 7	50 ± 7	53 ± 8	16 ± 2	10 ± 3	34 ± 13	74 ± 54	
Procyanocoupling	14 ± 7	45 ± 9	81 ± 13	452 ± 43	539 ± 71	55 ± 24	50 ± 29	365 ± 126	283 ± 190	
O.D. 420 nm	0.01 ± 0.10	0.08 ± 0.02	0.40 ± 0.13	0.83 ± 0.06	1.19 ± 0.12	0.88 ± 0.76	1.01 ± 0.77	1.50 ± 0.27	1.22 ± 0.39	
O.D. 520 nm	##	##	##	0.80 ± 0.06	1.20 ± 0.12	##	##	0.81 ± 0.12	1.24 ± 0.35	
Intensity	##	##	##	1.65 ± 0.12	2.41 ± 0.24	##	##	2.25 ± 0.29	2.91 ± 0.57	
Turbidity	##	##	##	1.02 ± 0.04	1.08 ± 0.11	##	##	1.57 ± 0.43	1.66 ± 0.52	
Luminosity	0.87 ± 0.01	0.84 ± 0.01	0.77 ± 0.04	0.93 ± 0.02	0.25 ± 0.03	0.93 ± 0.02	0.78 ± 0.04	0.27 ± 0.03	0.32 ± 0.05	
Saunton	2.46 ± 0.10	6.49 ± 0.57	19.73 ± 5.10	45.94 ± 2.93	65.52 ± 3.08	10.43 ± 2.47	16.66 ± 1.45	54.70 ± 5.30	73.96 ± 5.53	
Dominance	##	##	##	5.98 ± 1	5.98 ± 2	5.76 ± 1	5.76 ± 1	5.95 ± 3	5.90 ± 5	
Iron	7.01 ± 5.04	3.91 ± 0.88	4.72 ± 1.17	4.01 ± 0.80	7.50 ± 1.39	4.28 ± 1.17	7.00 ± 1.00	9.93 ± 2.67	26.00 ± 19.00	
Copper	0.64 ± 0.01	0.10 ± 0.02	0.13 ± 0.03	0.13 ± 0.02	1.11 ± 0.91	0.11 ± 0.03	0.09 ± 0.01	0.39 ± 0.17	0.15 ± 0.04	
Zinc	0.8 ± 0.4	0.3 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	1.0 ± 0.4	0.4 ± 0.2	1.3 ± 0.4	1.6 ± 0.7	1.1 ± 0.3	
Manganese	0.4 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.7 ± 0.2	0.9 ± 0.1	0.6 ± 0.1	0.3 ± 0.1	0.6 ± 0.1	0.8 ± 0.1	
Lead	0.90 ± 0.00	0.05 ± 0.01	0.06 ± 0.02	0.10 ± 0.02	0.16 ± 0.09	0.00 ± 0.00	0.07 ± 0.03	0.05 ± 0.03	0.04 ± 0.02	
Sodium	60 ± 33	65 ± 11	74 ± 15	52 ± 12	78 ± 15	27 ± 5	46 ± 5	54 ± 19	38 ± 9	
Calcium	60 ± 17	108 ± 21	97 ± 15	96 ± 15	100 ± 12	212 ± 35	229 ± 29	227 ± 53	233 ± 38	
Potassium	510 ± 17	670 ± 50	708 ± 51	619 ± 43	761 ± 39	582 ± 138	719 ± 358	837 ± 145	647 ± 169	
Magnesium	43 ± 8	58 ± 5	54 ± 7	55 ± 5	57 ± 5	38 ± 9	46 ± 10	47 ± 6	45 ± 6	
Acetone	628 ± 109	787 ± 121	1028 ± 165	794 ± 123	627 ± 109	849 ± 211	1278 ± 192	727 ± 160	1185 ± 243	
Erythritol	32 ± 4	39 ± 3	62 ± 13	39 ± 4	50 ± 2	30 ± 8	25 ± 4	45 ± 10	58 ± 18	
Xylitol	4 ± 1	3 ± 1	2 ± 1	2 ± 1	4 ± 1	1 ± 1	3 ± 1	6 ± 2	5 ± 1	
Arabinol	181 ± 37	136 ± 43	98 ± 40	94 ± 31	109 ± 29	154 ± 42	184 ± 99	194 ± 44	252 ± 79	
Mannitol	48 ± 39	90 ± 25	94 ± 10	128 ± 46	110 ± 11	40 ± 4	73 ± 19	159 ± 97	280 ± 100	
Sorbitol	15 ± 12	22 ± 4	25 ± 3	30 ± 6	42 ± 4	13 ± 3	15 ± 6	22 ± 5	39 ± 6	
xylo-hexosol	18 ± 13	18 ± 2	27 ± 3	22 ± 2	32 ± 3	14 ± 1	18 ± 3	24 ± 4	35 ± 4	
myo-D-xitol	71 ± 53	93 ± 17	143 ± 14	106 ± 12	152 ± 16	108 ± 12	135 ± 29	164 ± 34	195 ± 25	

Tab. 2: Analytical determinations of wine vinegars. Means and standard errors for each class of products.

	ITALIAN WINE VINEGAR					NON-ITALIAN WINE VINEGAR				NON-WINE VINEGAR				
	Decolorized 6°	White < 7°	White > 7°	Red < 7°	Red > 7°	Honey- made	White < 7°	White > 7°	Red < 7°	Red > 7°	Alcohol > 7°	Apple < 6°	Malt 6°	Honey 6°
Density	abc	abdefg	edegh	abdefg	ceh	a	abcd	cdefgh	bcdefgh	cdefgh	ab	abdefgh	abede	cdefgh
Alcohol	a	a	a	a	a	b	a	a	a	a	a	a	a	a
Total acidity	abcd	bde	df	bcde	df	abc	ab	cdef	bcde	cdef	df	a	abcd	abdefg
Volatile acidity	edef	defg	dgh	defg	fh	a	ab	abc	bcde	bcde	fh	a	abcd	abdefg
Fixed acidity	a	a	a	a	a	f	bcd	ef	b	ce	a	bcd	bcde	abc
Reduced extract	ab	bcd	bcdf	bcde	bcdf	fg	bcde	bdefg	bcdef	bcdef	a	cef	abc	g
Glycerol	abc	cde	fh	cdefg	fgh	cdef	bcd	bc	bcde	bcde	a	b	abc	cdefg
Proline	abd	ad	d	ad	d	abd	ad	abd	d	ad	a	abc	abcd	a
pH	bed	bd	b	bd	bed	bedef	bcd	bed	bed	bed	a	cef	bc	b
Tartaric acid	ac	c	d	c	d	e	ac	ed	c	e	a	ab	a	ab
Malic acid	abc	abdefg	abdefg	abde	abdefg	cg	abdefg	abdefg	ab	abdefg	a	bcdfg	abdefg	abcd
Lactic acid	abc	b	b	b	b	ab	bcd	bde	b	bde	a	ce	abc	cde
Succinic acid	bc	bc	bc	bc	bc	bc	b	bc	bc	bc	a	c	bc	bc
Total polyphenols	ab	abcd	abdefg	befgh	efg	abdefgh	abde	abdefgh	befgh	abdefgh	a	befgh	abdefg	abc
Proanthocyanidins	a	abc	abdefg	befgh	efg	abdefgh	abde	abdefg	abdefgh	abdefgh	a	bcdefg	ab	abdefg
Potassium	ab	b	b	b	b	b	b	b	b	b	a	b	ab	ab
Erythritol	bcdef	bcdefg	fgh	bcdefg	bcfgh	h	bde	abcd	bdefgh	fgh	a	abc	ab	abc
Xylitol	a	a	a	a	a	a	a	a	a	a	a	a	a	a
Ambitol	abcd	acd	abc	abc	abc	abc	acd	acd	acd	ad	ab	bc	a	abc
Mannitol	ab	abc	abc	abdefg	abede	abcd	a	ab	abdefg	bdf	a	abede	ab	g
Sorbitol	a	a	a	a	a	a	a	a	a	a	a	b	a	a
scyllo-Inositol	abcd	acd	acef	acdef	df	g	abc	abdefg	acdef	df	ab	ah	a	abc
myo-Inositol	ab	bde	bdfgh	bcdef	dh	i	bcdefg	bdefgh	dgh	dh	a	bc	abcd	b

Tab.3: Duncan test ($p = 0.05$) for all the samples.

Apple vinegars are lower in total acidity and have higher pH, probably due to the low alcoholic strength of cider, the presence of malic acid easily metabolised by lactic bacteria and the lack of tartaric acid. Also proline is present in low quantities. On the other hand, polyphenolic fractions are more represented in apple products, particularly leucoanthocyanidins probably due to easily oxidizable composition of apple and sometimes to wine-making technology. According to Santa Maria and coll. (4) the polyalcohols, with the exclusion of glycerol, could be considered a fingerprint of the raw material particularly in the case of the apple. In these samples sorbitol is the main compound of this class and as a matter of fact its content, over 80% of the whole class, is indicative of its apple origin. In a less sharp way mannitol characterizes our honey vinegar.

All these vinegars are characterized by very low quantities of tartaric acid, this being a fingerprint of wine origin. Also proline and glycerine are typical of wine products. The former is in any case, found in comparable amounts in malt vinegar while the latter is well represented in honey vinegars (fig. 1).

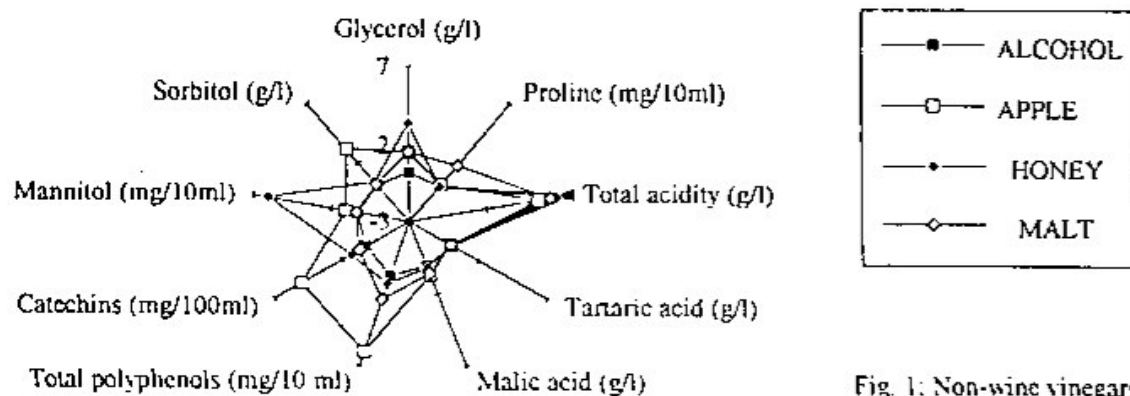


Fig. 1: Non-wine vinegars.

Among the non-Italian wine vinegars there are slight or no differences, with the exception of fixed acidity. This surprising fact is due to the wide variability of the samples because of their geographical origin, the technology adopted for their production and their composition which enhance the variance within each class. The Swiss samples are characterised by poorer compositions of all the fixed parameters compared to the Italian ones. French and German vinegars are in an intermediate situation as shown in figure 2.

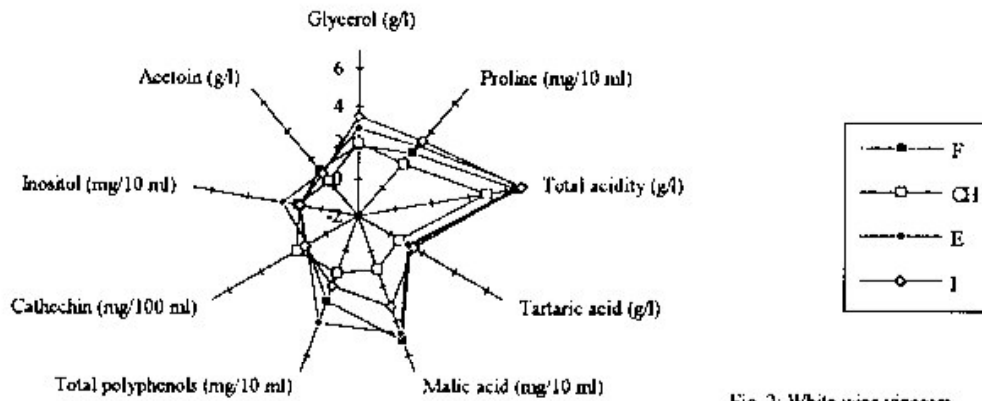


Fig. 2: White wine vinegars

The use of cluster analysis applied to all white vinegars, employing all the determinations, gave the dendrogram of figure 3 where three main groups are defined: wine, alcohol and apple vinegars.

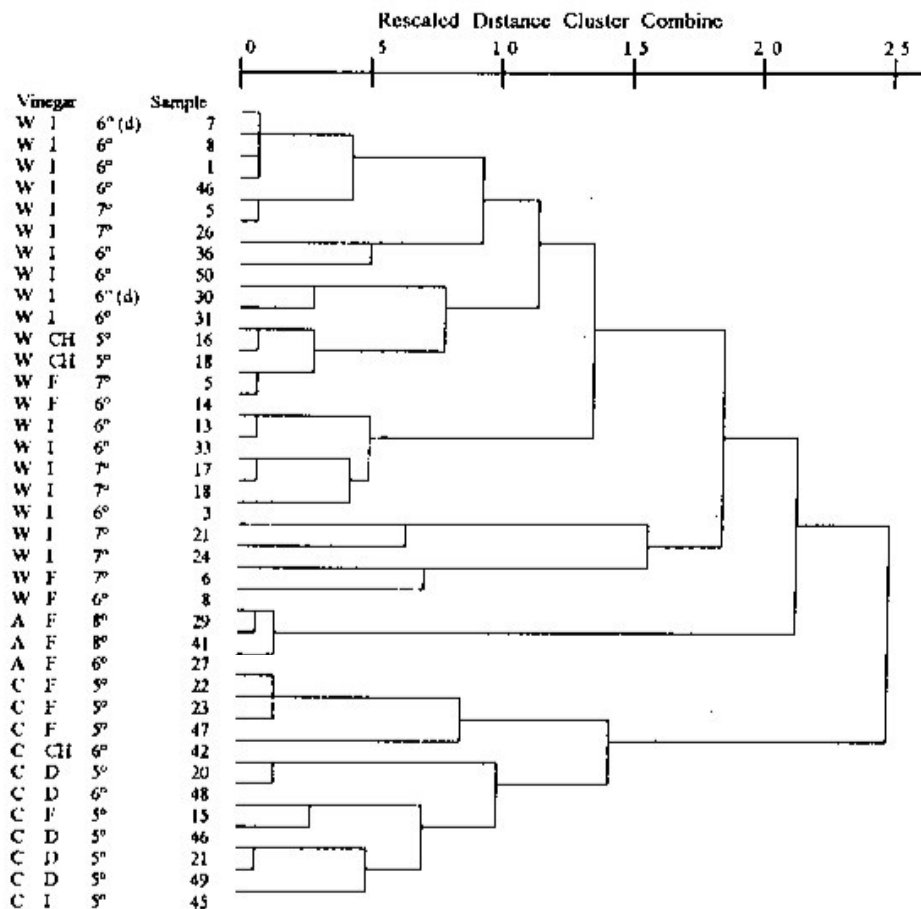


Fig. 3: Clusters of the white vinegars.

Legend: W = wine; A = alcohol; C = apple; I = Italy; CH = Swiss; F = France; D = Germany; d = decolorized

Among the wine samples there are situations of great similarity: the first four samples (7, 8, 1, 46) are produced by the same firm but commercialised with different labels. Similar events are shown for samples 5 and 26, and for samples 30 and 31.

Concerning total acidity, in conformity with Italian law, no cluster is recognizable. It must be said that sometimes the experimental acidity was not in accordance with that declared particularly for non-Italian vinegar. In a further cluster analysis considering only the Italian samples this classification is perfectly defined as a direct consequence of Italian legislation.

Different-country vinegars are not gathered in different clusters either, the similarity of composition on geographic origin being prevalent as for samples 16 and 18 (Switzerland) grouped with samples 5 and 14 (France), all of them characterised by a weak composition of the fixed compounds.

Apple vinegars are well resolved from other products and the classification of the different country is better defined than for wine: samples 22, 23 and 47 are French, sample 42, well separated from the others, is Swiss, but the situation is more complex for German samples. In this last case the cluster includes a French and an Italian sample. A cluster elaboration performed on this class alone gave a different distribution of the samples regardless of origin. In this analysis quality seems to be more important as a grouping factor as confirmed by organoleptic assays still in progress. In any case this last consideration is still under investigation at the moment, and in future works we shall probably be able to be more precise.

The best results of cluster analysis are achieved for alcohol vinegar. In fact, these samples are strictly clustered together (samples 27, 41 and 29). This behaviour is due to the simple composition of these products very diversified compared to other vinegars.

Conclusions

The use of cluster analysis seems to give some help for this first approach to the complex problem of vinegar quality and to identification of its descriptors. Using of the analytical parameters we are able to distinguish products of different botanical and geographical origin.

Exploiting all the analyses in our possession and the whole potential of statistics (principal component analysis, discriminant analysis) this goal will probably be reached. In further papers we are going to study these problems considering also aroma compounds.

References

1. EEC interpretative communication, (C270/91).
2. Kanno Koichi, Kavamura Yoshiya and Kato Kikuo. *Nippon Nogeikagaku Kaishi*, **63** (1989) 153.
3. Italian regulation for vinegar (258/86).
4. Santa-Maria G., Olano A. and Tejedor M., **20** (1985) 197.
5. Carnacini A., Gerbi V., Antonelli A., Zeppa G. and Natali N. Presented at R.A.I.S.A. Symposium, Volterra (Italy) 1-4.XII.1992.

Acknowledgements

We thank CNR of Italy, Project RAISA, subproject n° 4, for funding this research.