KEY ODORANTS OF THE TYPICAL AROMA OF SHERRY VINEGAR

R.M. CALLEJÓN [1], M.L. Morales[1], A.M. Troncoso[1], and A.C. Silva Ferreira[2]

[1] *Área de Nutrición y Bromatología, Facultad de Farmacia, Universidad de Sevilla. c/ P. García González nº 2, E- 41012, Sevilla, Spain*
[2] *Escola Superior de Biotecnología, Universidade Católica Portuguesa. R. Dr. Antonio Bernardino de Almeida, 4200-072 Porto, Portugal*

Abstract

A representative Sherry vinegar was analysed by gas chromatography-olfactometry (GC-O). Two GC-O techniques were used targeting compounds with impact on the perceived quality of Sherry vinegar, i.e. detection frequency and aroma extract dilution analysis. A total of 108 aromatic notes were detected and 64 of them were identified. Diacetyl, isoamyl acetate, acetic acid, and sotolon reached the highest frequency and flavour dilution (FD) factors. Ethyl acetate accounted for the maximum frequency but had only a FD factor of 4. Similarity tests were performed between the Sherry vinegar and model solutions of all possible combinations of these compounds. The highest value from the similarity test was observed when diacetyl, ethyl acetate and sotolon were added simultaneously. The profile of this model solution and the representative Sherry vinegar showed a good similarity in the general aroma description, which emphasises the important contribution of these 3 compounds to the global aroma of this vinegar.

Introduction

There is a need for the characterization of the typical sensory properties of traditional products not only for the industrialization of food production, but also for laws on food safety and even for the development of innovative products. Sherry vinegar is one of the most renowned products of this type in the world. A minimum period of six months of aging in wood barrels is mandatory for these products. Its main characteristics are a high acetic degree (legally, a minimum of 7º) and a special flavour which resembles that of Sherry wine. The aroma composition of these vinegars has been studied by several authors (1, 2). However, systematic studies to indicate the odorants responsible for the characteristic bouquet of Sherry vinegar have not been reported up to now.

Targeting substances with large impact on the perceived quality of a food product represents one of the most challenging tasks in flavour research. The main difficulty is correlation between sensory and chemical data. Despite of controversial reports concerning the best suited technique for a given matrix, several methods using gas chromatography with olfactometry have been applied to the purpose of ranking substances by their respective impact on the overall aroma of a foodstuff (3, 4).

This work deals with the evaluation of "sensory quality" of Sherry wine vinegar and with the presentation of substances, which plays an important role on the perceived character of Sherry vinegars. We have used two gas chromatography-olfactometry (GC-O) techniques: aroma extract dilution analysis (AEDA) and frequency counting (FC) using simultaneously two exits on a customised "multipost" sniffer ODO-II. They have been compared to define their respective discrimination ability.

Experimental

Vinegar sample. A representative 2 year-old vinegar (“Vinagre Reserva”, VR1) was selected by the sensory panel as being a Sherry vinegar “type”.

Chemical analysis. Major volatile compounds were determined by direct injection GC-Flame Ionization Detector (GC-FID) (5). A total of 52 minor compounds were determined by Headspace Sorptive Extraction-Gas Chromatography-Mass Spectrometry (HSSE-GC-MS) (6) and sotolon by Liquid-Liquid Extraction GC-MS (7).

Gas Chromatography-Olfactometry. Dichloromethane extracts of the VR1 sample were analysed by GC-O customised by Dr. Silva Ferreira´s group with two olfactory outlets in order to obtain simultaneous odour evaluations from multiple panellists (8).

Sensory analysis. Descriptive analysis (8) and similarity tests between VR1 and each aroma model solution were carried out (7). Aroma model solutions were prepared in a 7% (w/v) acetic acid solution by diluting the compounds, which reached the highest scores in GC-O, in the same concentrations found for the sample VR1.

Results

The GC-O study revealed the presence of 108 aromatic notes among which 64 could be described by the panellists. Table 1 shows compounds reaching high detection frequency in GC-O. Among them, a variety of odour-active regions, identified as ethyl acetate, diacetyl, isoamyl acetate, acetic acid, butyric acid, isovaleric acid and sotolon, reached the highest detection frequencies (100%). Good correlations were observed among the simultaneous AEDA ($r > 0.90$) carried out by two panellists. Only 19 odour compounds showed differences of more than one dilution factor. By sniffing serial dilutions, 26 odour-active compounds accounted for FD factors ≥ 256. Nine of them could not be identified.

By comparing results obtained with the two techniques used in this study, detection frequency and AEDA, we can see that they agree in many cases. Hence, diacetyl, isoamyl acetate, acetic acid and sotolon, reached the maximum frequency and the highest FD factors, therefore, being potent odorants of Sherry vinegar. However, results were not in agreement for certain odorants ($r< 0.45$). For example, ethyl acetate displayed the highest frequency (9/9) but only a FD factor of 4. Various authors have critically compared the different GC-O methodologies, using either mixtures of references standards or real food systems (9) and discrepancies in results existed since they are based on different principles. Each of the GC-O methodologies has advantages and limitations. Hence, the use of both techniques allows more information to be obtained and reduces the errors when using just one of them.

Similarity tests between solutions and Sherry vinegar were performed to check the sensory impact of those compounds with a FD factor ≥ 512 and detected in all sniffing trials, i.e. diacetyl, isoamyl acetate and sotolon. In addition, ethyl acetate was also selected in spite of its low FD factor because it was detected in all sniffing trials. Moreover, it is one of the typical sensory attributes of Sherry vinegar used as descriptor in the descriptive sensory analysis chart for Sherry vinegars (10). The highest value from the similarity test was observed when diacetyl, ethyl acetate and sotolon were added simultaneously (Table 2).

Table 1. *Detection frequency and AEDA of the odours of VR1 Sherry wine vinegar.*

RI	Odour Quality	Odorant (tentative identification)*	Detection Frequency	FD1	FD2
1063	Glue	Ethyl acetate	9	2	4
1080	Strawberry	Ethyl isobutyrate	7	512	1024
1084	Butter	Diacetyl	9	4096	4096
1118	Cherry, strawberry	Butyl acetate	6	128	1024
1123	Banana, mulberry, strawberry	Isoamyl acetate	9	4096	4096
1422	Pungent	Acetic acid	9	1024	1024
1468	Mulberry, fruit, banana, strawberry	Unknown	8	1	2
1484	Boiled potato	Methional	7	4	4
1496	Strawberry, sweet	Unknown	8	8	16
1532	River water, vapour	Unknown	9	1	2
1557	Mulberry, fruit	Benzaldehyde	7	2	4
1563	Aspirin, mulberry	Ethyl nonanoate	8	128	256
1595	Cheese, feet	Isobutyric acid	8	64	128
1655	Burned, burned hair	Unknown	7	8	16
1661	Cheese, vomit	Butyric acid	9	256	256
1705	Cheese	Isovaleric acid	9	128	128
2054	Clove	Eugenol	8	2	2
2151	Flower, fruit, banana	Unknown	7	128	512
2201	Curry, liquorice, “oloroso sherry wine”	Sotolon	9	512	512
2255	Sweet-rancid, wood, liquor	Unknown	7	512	512
2360	Liquor, liquorice, sweet	Unknown	7	512	512

* Identification of odorants: Comparison of mass spectra, chromatographic retention index (RI) and odour description with experimental and literature data.

Table 2. *Results obtained from sensorial analysis by comparison test.*

Aroma Model Solutions	Similarity Value (SV)	Standard Deviation (SD)
a.s. + [1] + [2] + [4]	5.38	0.55
a.s. + [1] [2] + [3] + [4]	4.59	0.58
a.s. + [1] + [3] + [4]	4.57	0.58
a.s. + [2] + [3] + [4]	4.35	0.62
a.s. + [2] + [4]	4.11	0.58
a.s. + [3] + [4]	4.08	0.61
a.s. + [2] +[3]	3.57	0.55
a.s. + [1] + [4]	3.55	0.55
a.s. + [1] + [2]	3.25	0.62
a.s. + [1] + [2] +[3]	3.15	0.58
a.s. + [4]	2.76	0.58
a.s. + [2]	1.83	0.62
a.s. + [1] +[3]	1.79	0.62
a.s. + [1]	1.70	0.55
a.s. +[3]	1.54	0.58

a.s.: acetic acid solution (7 % v/v); [1] diacetyl, [2] ethyl acetate; [3] isoamyl acetate; [4] sotolon

The profile of this model solution and the representative Sherry vinegar showed similar intensities in the “sweet aroma”, “pungent sensation” and “alcohol/liquor” descriptors, in addition to a good similarity in the “general impression” (Figure 1).This result emphasises the important contribution of these 3 molecules (diacetyl, ethyl acetate and sotolon) to the global aroma of this Sherry vinegar. Hence, they can be considered as key odorants of Sherry vinegar.

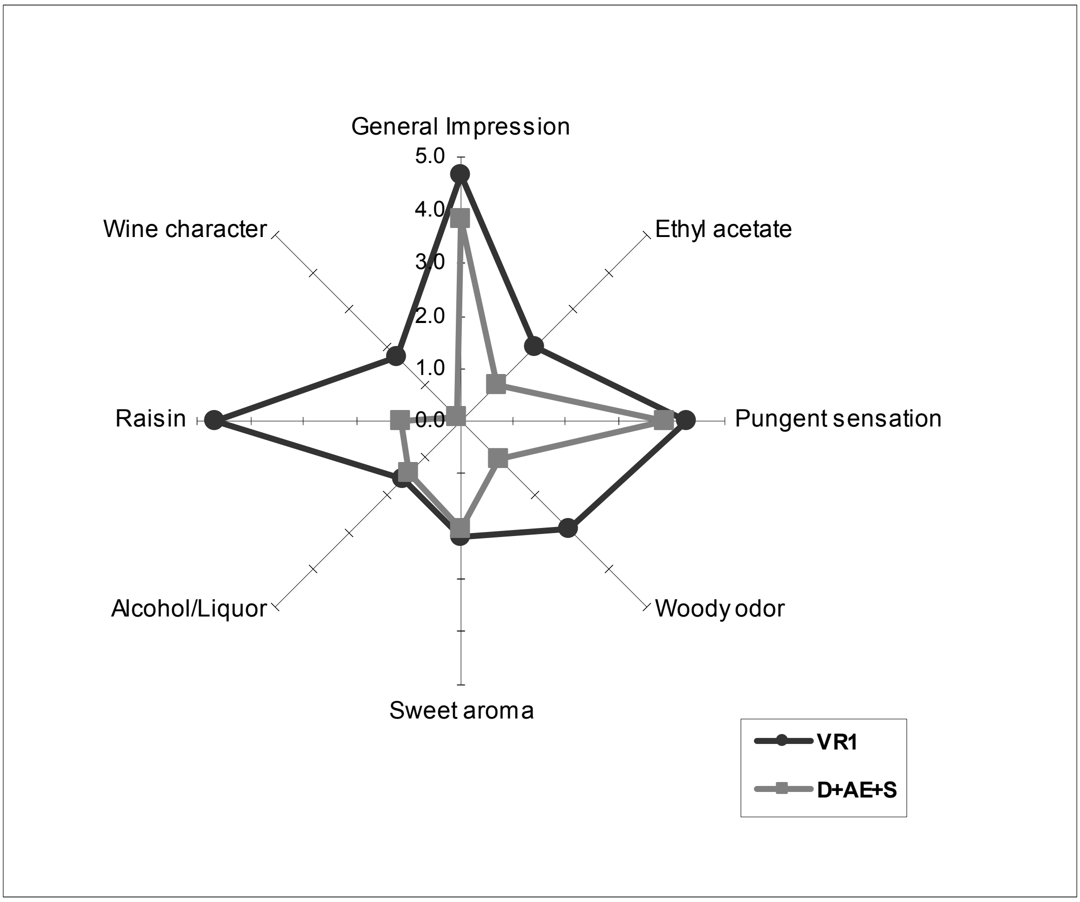

Figure 1. *Flavour profiles of VR1 sample (black line) and aroma model (grey line).*

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