CHARACTERISATION OF STRAWBERRY TREE DISTILLATE (*ARBUTUS UNEDO L.*) PRODUCED IN SARDINIA

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Abstract

This study investigated the macro- and micro-constituents present in strawberry tree (*Arbutus unedo L.*) distillates produced in Sardinia.

The results were compared with the data present in the literature for the distillates obtained from the same berries in Portugal and Greece, where they are traditional products.

Aroma analyses were performed by HRGC-FID and HRGC_MS techniques with direct GC injection of full proof distillates.

In the distillates produced in Sardinia it was clear that acetaldehyde and ethyl acetate were rather low, thus contributing notable merit to the distillate; low values were observed for the acetates, whereas C_6 to C_{10} ethyl ester values were higher, all compounds with a pleasant fruity tone. C_{12} to C_{18} fatty esters were also limited, compounds reduced in the reduction phase to the distillate degree by refrigeration and filtering.

C_6 or 'leaf' alcohols were highlighted with an unusual confirmation of the rather high cis-3-hexen-1-ol content.

Finally, the aromatic contribution of anethole, with aniseed tones, appeared at much lower levels than in the product of Greek origin, since aniseed seeds are added to the latter distillates.

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Introduction

Upgrading of some of the spirits of the Sardinian Region (Italy) was begun some time ago with characterisation of the myrtle liqueur (*Myrtus communis L.*) (1), currently protected by EC Reg. N°. 110/2008, which set up Geographical Indication (GI) branding. Recently various fruit distillates made from typical varieties of Sardinian apples (2) and pears were studied, including a particular wild pear (*P. amygidaliformis,Vill.*), as well as single-variety grappas from characteristic cultivars of the region (Vermentino, Malvasia of Bosa and Cannonau).

Among the products coming from the Mediterranean macchia of Sardinia strawberry tree (*Arbutus unedo L.*) distillate has also been studied, with its unique, pleasant aroma.

This distillate is included in the Community spirits envisaged both by Reg. N°. 1576/89 and the recent update N°. 110/2008, to be precise with two denomination of origin distillates from Portugal (*Medronho do Algarve e do Buçaco*), where it is a traditional product.

In Portugal the *aguardente de Medronho* culture is so well-rooted that the Council of Ministers has considered the production areas in the Algarve mountains a precious patrimony to be protected and defended with Resolution N° 58/2003.

Strawberry tree berries are gathered in various periods and undergo an air fermentation process in cement vats lasting on average between thirty and sixty days.

The purée is then distilled, mainly in traditional alembics without a rectification column, obtaining a distillate with an alcohol by volume ranging from 40 - 50% vol. The distillate is often aged in oak barrels for some years.

As part of a leading Community project, in-depth research was carried out at the beginning of the nineties on the aromatic composition and production problems of the Portuguese strawberry tree distillate of the Algarve zone (3).

The study highlighted rather high values of ethyl acetate (acescent tones) and acetic acid (a pungent tone) together with impure hints attributed to compounds deriving from funguses like 1-octen-3-olo, borneol, etc. The aromatic ensemble presented a notable variety of compounds that contributed to giving a complex fruity-balsamic tone thanks, above all, to the contribution of norisoprenoid compounds including some typical of the Riesling wine from the Rhine area.

The problems concerning the above-mentioned negative tones have diminished or been solved both by changes in distillation plant, introducing a rectification column which increased the alcohol by volume, thus enabling a reduction in head products (ethyl acetate and other low-boiling products) and tail ones (acetic acid), and in the collection and fermentation phases of the fruit.

There were changes, moreover, both in harvesting timescales, which initially lasted longer than a month as it was conditioned by free time and limited to the weekend, and in the fermentation phase, no longer carried out on the pressed fruit with no protection from the air, but in recipients to be filled at each harvest.

Furthermore, both the use of selected yeasts has been introduced, even simply that for bread-making, and the acidification of the purée to a pH of around 3 - 3.5. These innovative approaches in technology have led to courses being started up at the University of Faro (4) and improved results reported at various Symposiums (5), obtaining products with decidedly lower ethyl acetate values.

Strawberry tree distillate also constitutes a traditional product of Greece with the name of 'Koumaro'; its composition and production technologies were recently the subject of investigation (6). In this case the strawberry tree berries are collected on ripening and subsequently transferred into wooden barrels of 30-500 L and sometimes up to 50 hL capacity.

The barrels are filled with the product up to 30-45 cm below the surface, covered up with leaves and distaff corn or wool blankets, and left to ferment. Before distillation aniseed seeds are added to the purée.

Then small quantities of water are added progressively in order to assist the fermentation procedure. According to local producers, the fermentation period lasts from 5 to 6 months because of the gradual collection of the raw material, the low winter temperatures (usually below 20 °C) and the fact that, unlike grapes, the fruit is not crushed before fermentation.

Distillation takes place in discontinuous copper alembics following traditional technology which, by re-distillation and cutting processes, results in a product that is transferred, before dilution with water, into oak barrels and left to age 1 year before consumption.

The final product has an alcohol by volume of approximately 40° of ethanol % vol.

In Sardinia (Italy) the strawberry tree is found in many zones as it is an important component of the characteristic Mediterranean scrub of the

island and was used up to recent times, in its flowering period, in the production of a characteristic 'bitter' honey with a particularly original scent, due above all to norisoprenoid compounds (7).

As part of a research project aimed at promoting the minor fruits of Sardinia, an experiment was carried out in collaboration with a company on the territory with the purpose of optimising strawberry tree distillate production.

In this work the aroma fraction of arbutus brandies obtained in Sardinia in two different years (2003-2005) was characterised.

The results were compared with the data present in the literature on traditional distillates from Greece and Portugal.

Materials and methods

Having been harvested before completely ripening, in order to avoid breakage processes and the appearance therefore of abnormal fermentation, the fruit was stored until ripe and subsequently reduced to purée with a pH slightly corrected to 3.2 by adding diluted strong acids.

The lightly sulphated purée inoculated with selected yeasts of the *Saccharomyces cerevisiae* species for enological use was left to ferment in steel recipients of approx. 15 hl with a mechanical agitator to favour fermentation process at a controlled room temperature of approx. 25 °C. At the end of fermentation lasting at the most 10 days, starting with purées with 12.1 °Brix in 2003 and 15.50 °Brix in 2005, distillation was performed within a week at a Metalinox (Trento) company discontinuous plant with a water bath and an 8-tray rectification column.

Aroma analyses of rough distillates obtained from berries harvested during the winters of 2003 and 2005 were performed by HRGC-FID and HRGC_MS techniques with direct GC injection following the procedure reported by Versini et al. (2009).

Results and discussion

The distillates were sensorially characterised by descriptors such as sage-rosemary type floral tones, balsamic tones and cinnamon and coriander spiciness, fruity green banana with leaf/cocoa hints and light vegetable tones.

The data on the aromatic fraction of the Sardinian strawberry tree distillates are shown in Tables 1 and 2. For a comparison with spirits obtained from other regions, in the same tables are present the data reported in the literature for Greek and Portuguese brandies.

As regards the macroconstituents (Table 1), we observe that the content of methanol in the Sardinian brandies is near the legal limit of 1.2 g% ml a.a. established by EC Reg. N° 1014/90 and subsequent amendments (EC Reg. N°. 110/2008). The higher level of alcohol in the two distillates examined is similar to that of a grappa (typical Italian denomination of marc distillates), and is higher than that of the Portuguese product, probably due to the different fermenting and distilling conditions.

Acetaldehyde and ethyl acetate are quite low and therefore accord notable worth to the distillate, whereas the Portuguese and Greek distillates have higher values; the ethyl acetate values of these latter in particular are decidedly high. As far as the Portuguese products are concerned, following the technological improvements made (4-5), products were obtained with clearly lower ethyl acetate values.

TABLE 1

CONTENT OF MACROCOSTITUENTS IN THE AROMATIC FRACTION OF DISTILLATES PRODUCT IN SARDINIA FROM STRAWBERRY TREE AND COMPARISON WITH THE GREEK AND PORTUGUESE SPIRITS

(mg % ml a.a)

Area of production	**Sardinia**		**Greece[1]**	**Portugal[2]**
Year	**2003**	**2005**		
alcoholic proof	71.54	76.62	n.d.	n.d.
methanol	808	1,016	744.0	898.3
1-propanol	20.0	21.5	n.d.	14.12
2-butanol	<0.5	<0.5	n.d.	1.23
2-methyl-1- propanol	64.0	42.0	43.0	45.48
1-butanol	0.5	<0.5	7.0	0.31
2- methyl -1- butanol	80.5	44.0	47.0	32.77
3- methyl -1- butanol	273.5	195.5	155.0	99.78
total higher alcohols	438.5	303.0	260.0	193.1
acetaldehyde	14.0	24.0	100.0	57.32
diacetal	7.0	10.0	n.d.	45.74
ethyl acetate	29.5	31.5	340.0	494

n.d. = not determined

[1] data published in reference (6) - [2] data published in reference (3)

Among the minor compounds of fermentative origin we note a reduced level of acetates while the C_6 to C_{10} ethyl esters are higher, all compounds with a pleasant fruity tone. Moreover, C_{12} to C_{18} fatty esters were also limited, compounds that are reduced in the reduction phase to the degree of distillate by refrigeration and filtering. There are limited levels also for 2-phenylethanol with rose/carnation tones, as well as for the four primary alcohols, C_5 to C_9, characteristic for their floral hints. The ethyl lactate content is also very low, an indication of proper fermentation.

The C_6 or 'leaf' alcohols confirm the unusual qualities of this distillate compared with both the Portuguese and Greek distillates, in that cis-3-hexen-1-ol and 1-hexanol content is rather high. Both these alcohols derive from enzymatic degradation of the fatty acids to C18. This alcohol certainly contributes to the specific tone of the Sardinian distillate, with a hint of green leaf/banana skin; its olfactory threshold in the distillates may be considered one sixth of that of 1-hexanol (8).

The presence of monoterpenes is also confirmed, with linalool, α-terpineol and citronellol of sensorial importance, as well as noriso-prenoids like TDN (1,1,6-trimethyl-1,2-dihydronaphthalene) with its kerosene tone and the Riesling acetal with balsamic-resinous vitispirane tones.

Of interest for the aromatic specificity there are also methyl and ethyl salicylates with hints of honey, ethyl benzoate and benzaldehyde with balsamic hints. Finally, there is the aromatic contribution of anethole, with aniseed tones, as found by Soufleros et al. (6)

In the product of Greek origin this compound is present in much greater quantities as aniseed seeds are added. Other interesting compounds are the farnesenes and hexyl 2-methylbutanoate.

The particular complex of compounds in Table 2 may explain many of the olfactory and taste-olfactory sensations of the Sardinian distillate, with its pleasant features different from the Portuguese and Greek ones.

TABLE 2

CONTENT OF MICROCOSTITUENTS IN THE AROMATIC FRACTION OF DISTILLATES PRODUCT IN SARDINIA FROM STRAWBERRY TREE AND COMPARISON WITH THE GREEK AND PORTUGUESE SPIRITS

(mg % ml a.a)

Area of production	**Sardinia[1]**		**Greece[2]**	**Portugal[3]**
Year	**2003**	**2005**		
1-hexanol	3.80	4.60	0.50	1.65
trans 3-hexen-1-ol	0.10	0.14	0.14	0.25
cis 3-hexen-1-ol	3.60	4.70	n.d.	n.d.
trans 2-hexen-1-ol	<0.05	<0.05	0.14	0.08
Σ alcohols C_6	7.55	9.49	078	1.98
trans furan linalool oxide	0.05	0.11	n.d.	0.13
cis furan linalool oxide	0.05	0.05	n.d.	0.08
linalool	0.08	0.12	n.d.	0.92
α-terpineol	0.09	0.14	n.d.	0.44
citronellol*	0.06	0.04	n.d.	n.d.
nerolidol*	0.02	0.02	n.d.	n.d.
farnesol*	0.08	0.04	n.d.	n.d.
borneolo	<0.01	<0.01	n.d.	0.02
carveol	<0.01	<0.01	n.d.	0.02
Σ terpens	0.43	0.52		0.90
benzylic alcohol*	0.02	0.01	n.d.	0.11
ethyl benzoate*	0.01	0.01	n.d.	n.d.
benzaldehyde*	0.07	0.25	n.d.	n.d.
methyl salycilate*	0.10	0.04	n.d.	n.d.
ethyl salycilate*	<0.01	<0.01	n.d.	n.d.
anethole*	0.03	<0.01	144	n.d.
Σ benzoic compounds	0.24	0.33		
vitispiranes*	0.15	0.09	n.d.	0.188
riesling acetale*	0.03	0.03	n.d.	n.d.
TDN*	0.01	0.01	n.d.	n.d.
Σ norisoprenoids	**0.19**	**0.13**		
isoamyl acetate	0.29	0.63	0.50	1.65
n-hexyl acetate	<0.05	<0.05	0.14	0.25
cis-3--hexyl acetate*	<0.01	0.01	n.d.	n.d.
phenilethyl acetate*	0.03	0.03	0.14	0.08
Σ minor acetate	**0.38**	**0.72**	**0.78**	**1.98**
ethyl hexanoate	0.36	1.10	0.51	0.59
ethyl octanoate	1.80	4.50	0.47	1.47

...continued

Area of production	Sardinia[1]		Greece[2]	Portugal[3]
Year	**2003**	**2005**		
ethyl decanoate	3.80	6.90	0.40	1.46
Σ esters C_6-C_{10}	**5.96**	**12.5**	**1.38**	**3.52**
ethyl dodecanoate	0.88	2.50	0.02	0.73
ethyl tetradecanoate	0.63	0.84	0.02	0.35
ethyl hexadecanoate	2.70	3.40	n.d.	1.24
ethyl octadecanoate	0.23	0.22	n.d.	n.d.
ethyl 9-octadecenoate	0.15	0.51	n.d.	n.d.
ethyl 9,12-octadecadienoate	1.60	2.50	n.d.	0.71
ethyl 9,12,15-octadecatrienoate	0.18	1.01	n.d.	0.15
Σ esters C_{12}-C_{18}	**6.37**	**10.98**		**3.18**
1-pentanol*	0.19	0.24	n.d.	n.d.
1-heptanol*	0.03	0.02	n.d.	0.05
octanol*	0.09	0.18	n.d.	0.16
nonanol*	0.06	0.03	n.d.	0.08
Σ alcohols C_5 - C_9	**0.37**	**0.47**		**0.29**
2-phenylethanol	1.50	2.30	2.60	1.94
ethyl lactate	0.13	0.19	6.20	3.45
furfural	2.60	6.10	n.d.	3.48
α– farnesene isomer*	0.02	0.02	n.d.	n.d.
α–farnesene*	0.6	0.55	n.d.	n.d.
hexyl 2-methylbutanoate*	0.02	0.13	n.d.	n.d.

n.d. = not determined

*compounds analysed by GC-MS and quantified as 2-octanol response factor 1

[1] data were presented in part on "Giornale dei distillatori" anno XXII N° 257, 2009.

[2] data published in reference (6)

[3] data published in reference (3)

Conclusions

The study drew attention to the aromatic characteristics of strawberry tree distillate (*Arbutus unedo L.*) obtained in Sardinia, the specificity of which was highlighted in comparison with the data for the Greek and Portuguese distillates. The particular complex of micro- and macro-compounds explains the olfactory and taste-olfactory sensations of the distillate of Sardinian origin. These differences can partly be attributed to the introduction of innovations in the preparation of the purée but also to the use of the improved distillation technologies adopted.

Sardinian strawberry tree distillate is characterised, compared with that of other geographical regions, by a lower content of C_7 to C_9 primary alcohols and in general by a higher content of C_6 to C_{10} ethyl esters and C_{12} to C_{18} fatty esters.

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