

## Quince as a source of interesting aromas in fruit wine

Petersen, Mikael Agerlin; Mathiesen, Ida Løkken; Toldam-Andersen, Torben Bo

Published in: Chrom+food FORUM

Publication date: 2017

Document version
Publisher's PDF, also known as Version of record

Citation for published version (APA): Petersen, M. A., Mathiesen, I. L., & Toldam-Andersen, T. B. (2017). Quince as a source of interesting aromas in fruit wine. Chrom+food FORUM, 9, 36-37.

Download date: 08. Apr. 2020



Prof. Dr. Mikael Agerlin Petersen | Ida Løkken Mathiesen | Torben Bo Toldam-Andersen

Analysis of volatiles by the use of headspace GC-MS is a well-established technique for identification and quantification of components being potentially important for the aroma of a food product. Headspace sampling is used to extract volatiles from the food matrix, gas chromatography (GC) is used to separate the complex mixtures of volatiles that are sampled, and mass spectrometry (MS) is used to identify and quantify the individual compounds.

Volatiles have very different odour intensities, and measurement of concentration alone is therefore not enough to determine if a compound is important. GC-olfactometry (GC-O) is a technique that is often used to overcome this problem. In a setup for GC-O analysis, the outlet from the gas chromatographic column is typically split between a detector (for example an MS, GC-MS/O) and a 'sniffing port', where a judge can sniff at the effluent and evaluate the odour of the compounds as they elute from the column. This means that odour intensity and odour quality of the individual compounds can be determined. In this study a GC-MS/O setup with a triple split (2 judges and an MS) was used to identify important aroma compounds in cryoconcentrated juice from quince (Cydonia oblanga cv Piwa) and apple (Malus domestica cv Rubinstep).

The background for the choice of these products is the decreasing fruit production in Denmark. Due to falling prices, and high cost of labour the business possibilities are limited. To stay in business added value is needed and some producers have therefore decided to process the fresh produce, for example into fruit wine. Traditionally, wine has been produced from a variety of fruits, among others apples. Apple wine is, however, not as rich in flavour as grape wine, both due to lower alcohol content and to the aroma profile in general. One way to obtain a richer wine is to cryoconcentrate the juice before fermentation. Cryoconcentration is a gentle, simple technique that increases concentration of both sugars, acids and volatiles. The juice is frozen and then left to thaw slowly, and the first liquid melting off is very concentrated compared to the original must. The longer

time melting is continued, the less concentrated the collected liquid will be. The degree of concentration can therefore be controlled, and fruit wines with alcohol content similar to that of grape wines can be made. Even sweet dessert ice-wine styles are possible from the first high concentrates. Another way to make a richer wine is to use juice from other, and in some cases less known, fruits which can contribute with new interesting aromas. The present study was carried out on cryoconcentrated juice from apple and quince, since both of these at present are being tested in fruit wine production in Denmark, including mixes with different berries. Quince is known to be a very aromatic fruit, but is not suited for raw consumption because of its hard texture and harsh or astringent flavour. Some kind of processing is needed to overcome this, for example milling and pressing into juice. Few studies have been done on the aroma of quince, and to our knowledge none of them included GC-O.

In this study, cryoconcentrated juice from apple and quince was supplied by Cold Hand Winery (www.coldhandwinery.dk). Extraction of aroma from the samples was carried out by dynamic headspace sampling as described earlier. [1] The volatiles were purged off the sample using a flow of nitrogen and collected on a Tenax-trap. From the trap, the volatiles were transferred to the GC-MS/O by the use of thermal desorption. The GC-MS/O system (Fig. 1) included a 3-way splitter directing 40% of the column flow to each of two judges and 20% of the flow to an MS. The judges (four in total) were instructed to press the button of an Olfactory Intensity Device when an odour appeared and not release it until the odour disappeared. The judges

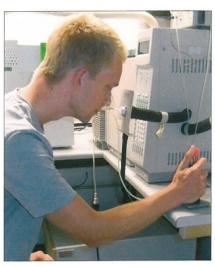


Fig. 1: GC-MS/O setup used in the study

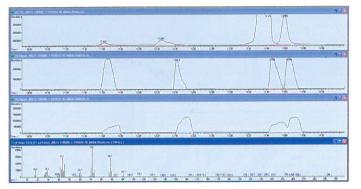


Fig.2: Example of data from GC-MS/O. Top pane shows a section of the GC-MS Total lon Chromatogram.

The next two panes are the profiles generated by the two judges through the Olfactory Intensity

Devices. The bottom pane shows the mass spectrum of the peak at 11.61 min (ethyl butanoate).

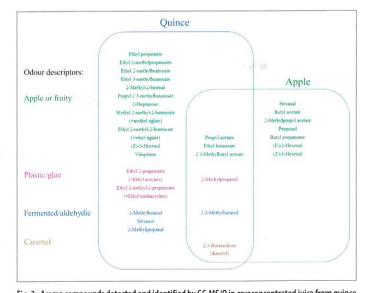


Fig. 3: Aroma compounds detected and identified by GC-MS/O in cryoconcentrated juice from quinco and apple.

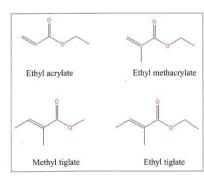


Fig. 4: Structure of four esters detected only in quince

were also asked to describe the odours, and their voices were recorded digitally. Signals from the Olfactory Intensity Devices and the MS were sampled simultaneously, and formed the basis for the identification of the dominant odours (see Fig. 2).

Fig. 3 gives an overview of the compounds detected by GC-O. It includes 29 compounds which were detected by at least three judges and therefore can be considered the most aroma active compounds. Five odour signals which could not be identified were excluded. Since no instructions were given to the judges, they used different words to describe the odours, but the descriptors could roughly be grouped into four groups: 'Apple or Fruity' (mainly esters and aldehydes), 'Plastic/glue' (two esters and an alcohol), 'Fermented/aldehydic' (two alcohols and two esters), and 'Caramel' (diacetyl).

Six compounds, representing all four groups, were detected in both guince and apple. It is evident, that guince had a higher number of aroma active compounds than apple, and that fits well with the general impression of guince being very aromatic. There were, however, also some qualitative differences since quince had a number of rather unusual esters: ethyl acrylate, ethyl methacrylate, methyl tiglate and ethyl tiglate. These esters have a certain structure in common, namely the double bond in the 2-position on the acid moiety of the ester, see Fig. 4, creating a conjugated system (also known as α,β-unsaturated carbonyl compounds). α,β-Unsaturated carbonyl compounds have been reported to be degradation products of carotenoids in tomato [4]. The presence of these compounds could cause some concern since some α,β-unsaturated carbonyl compounds are under suspicion of being toxic or carcinogenic. Ethyl acrylate and ethyl tiglate have, however, been examined thoroughly by FDA and FAO/WHO [2, 3] and are evaluated to be safe in the very small amounts that are found in food. Ethyl acrylate and ethyl methacrylate have odours that are plastic-like or acrid, while the tiglates were described as fruity. These types of compounds have already been reported in quince [4-7], but it has not been documented before that they are aroma active. It seems very likely, that these compounds in combination with the high number of other aroma active esters with fruity odours and the norisoprenoid vitispirane (exotic fruit odour) are responsible for the strong and characteristic odour of quince, and explain the richness of quince wine.

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## Authors | Contact

## Torben Bo Toldam-Andersen | Ida Løkken Mathiesen Prof. Dr. Mikael Agerlin Petersen

University of Copenhagen | Department of Food Science Rolighedsvej 26 | DK-1958 Frederiksberg C | Denmark | www.food.ku.dk