Chemical Fingerprinting of Olive Oil Aroma

Abigail Koss, Luigi Ciotti
TOFWERK, USA & Switzerland

Our enjoyment of the flavor and aroma of olive oil stems from its rich and complex content of volatile organic compounds (VOCs), including a wide range of aliphatic, carbonyl, alcohol, terpene, and heteroatom compounds. For example, ethyl propionate and hexyl acetate contribute to sweet, fruity flavors, while undesirable oxidative rancidity may be associated with compounds such as heptanoic acid, 2-methyl-1-butanol, or saturated aldehydes [1,2].

VOCs also create a unique chemical signature, or fingerprint, that contains information about the geographical origin of the olive oil, the olive cultivar, fruit ripeness, and how the oil has been processed, packaged, and stored. The VOC fingerprint can be used as a quality assurance check, in order to determine flavor and aroma consistency from a single producer. It can also be used to detect forgeries or improperly labeled products.

In this experiment, VOCs from fifteen olive oil samples were measured using a Vocus 2R PTR-TOF. The goal of this study was to characterize the VOC fingerprint of each sample based on geographical origin and quality.

Nine samples were high-quality extra virgin oil with certified regionally-specific Italian origin. One sample was extra-virgin olive oil with known Italian origin (but not certified), one sample was a mixture of extra virgin oil from several regions in Italy, and two samples were mixtures of non-Italian European extra virgin oil. Finally, two “composed” oils were measured, one of which was a mixture of refined pomace oil and virgin oil, and the other a mixture of refined and virgin oil.

Approximately 500 µL of each olive oil were added to a temperature controlled (32C) headspace sampler, and measured in sequence, in triplicate. Ambient background was subtracted based on measurement of an empty vial (blank). 290 VOCs were quantified and their chemical formulas identified (Figure 1).

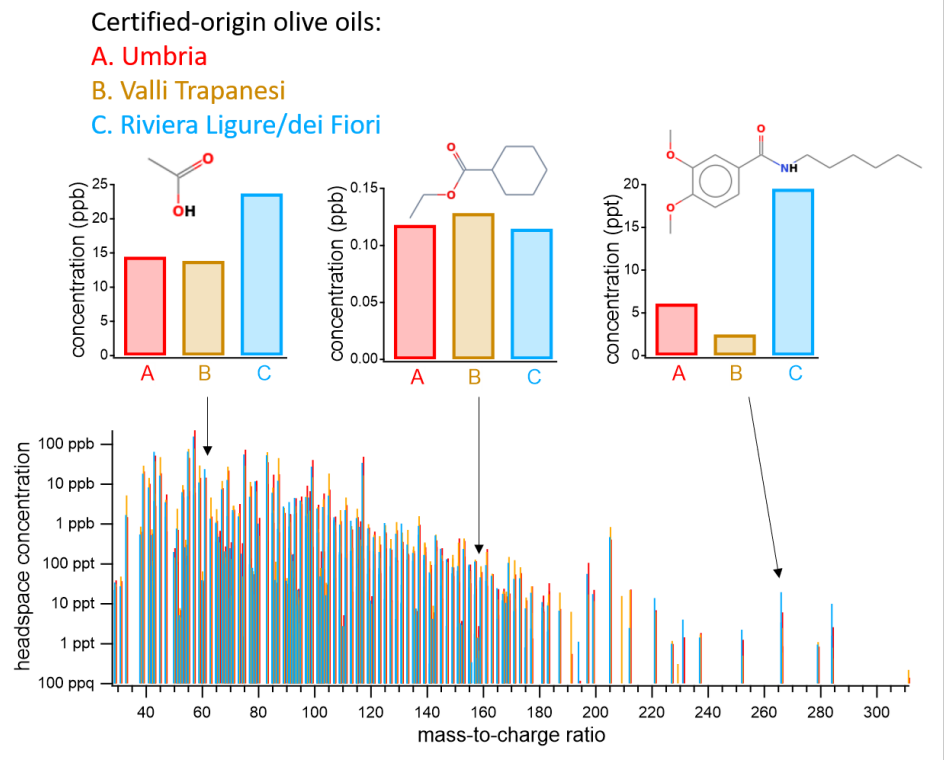

***Figure 1**. Top: The headspace concentrations of three detected VOCs are compared between olive oil from Umbria, Valli Trapanesi, and Riviera Ligure/dei Fiori. An example molecular structure is suggested for each VOC. Bottom: Mass spectra including 290 identified VOCs, with headspace concentration ranging between 100 ppq and more than 100 ppb.*

Among many others, detected compounds include decadienals, decanal, and nonanal (fatty or fried flavor), ethyl cyclohexylcarboxylate (aromatic, fruity), t-2-decenal (fishy), hexenals (green, leaf-like), hexenyl acetate (green, fruity), octadienone (geranium-like), and C2-C8 acids (sour and rancid flavors).

Principal component analysis (PCA) was used to find the VOC features that distinguish the chemical fingerprint of each olive oil. PCA is a mathematical tool that can be used to simplify complex datasets and visualize patterns. Figure 2 visualizes the complex VOC profiles of the olive oil samples using just two principal components. The two axes of the figure each represent a covarying group of compounds responsible for differences in the VOC profile of different oils.

Oil produced from olives grown in Italy, and oils from other sources, are easily separable using these two groups of compounds. PTR can be used not only to identify forgeries simply mislabeled as Italian oil, but also sniff out cleverer forgeries that dilute high-quality Italian oil with cheaper oil from elsewhere or, in

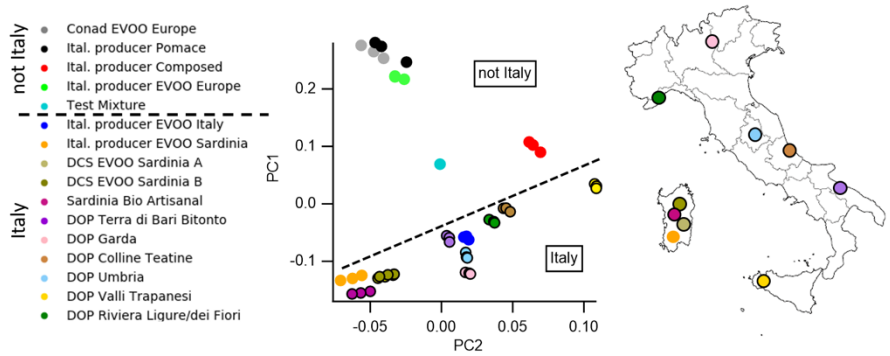

***Figure 2**. PCA separates olive oils produced inside and outside Italy. Markers with a black outline denote samples with certified origin.*

addition to sensory analysis, as a quality control to differentiate between extra-, virgin- and lampante olive oils. The point labeled “test mixture” was an approximately 50:50% mixture of the Italian producer_EVOO Italy sample and the Italian producer EVOO Europe sample, and appears on the plot halfway between the two original samples.

Adding a third principal component (Figure 3) shows that the geographical origin can be pinpointed very precisely: even oils from the same region of Italy occupy a distinct space, defined by their VOC profile and recognizable by PTR. The high reproducibility and chemical detail in the profile can be used to assure absolute consistency in the flavor profile of oils from a certain region and manufacturer.

Contact

ptr@tofwerk.com

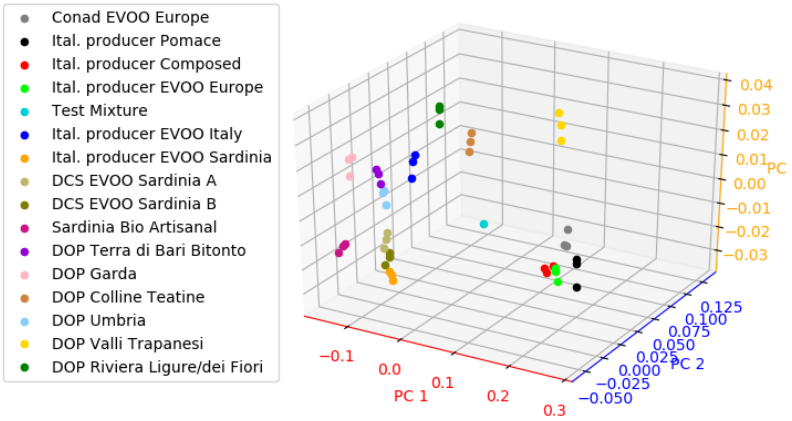

***Figure 3**. Three-dimensional PCA visualization, showing clear distinction between samples from different regions in Italy. Click on the figure to rotate and explore the visualization. Mouse over each data point to identify the sample.*

References

[1] Kalua, C. M., Allen., M.S., Bedgood, D.R. Jr., Bishop, A.G., Prenzler, P.D., Robards, K.: Olive oil volatile compounds, flavour development and quality: A critical review, Food Chemistry 100, 273-286, 2007.

[2] Cecchi, L., Migliorini, M., Giambanelli, E., Rosetti, A., Cane, A., Mulinacci, N.: New volatile molecular markers of rancidity in virgin olive oils under nonaccelerated oxidative storage conditions, Agricultural and Food Chemistry 67, 13150-13163, 2019.