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Volatiles of *Solanum* spp.: Analysis, Composition and Ecological Significance

Beata Szafranek* • **Janusz Szafranek**

Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland

Corresponding author: * **chembs@univ.gda.pl**

ABSTRACT

A review of the analysis and composition of volatile organic compounds (VOCs) in *Solanum* plants of worldwide economic importance – potatoes, tomatoes and aubergines – is presented together with some general comments on this field of research. VOC blends consist of green leaf volatiles (C_6 compounds), terpenoids, sesquiterpenoids and aromatics, among other compounds. Two types of sampling are generally applied in VOC trapping: headspace sampling, and direct methods such as extraction and distillation. The structural assignment of VOCs is based mostly on GC and GC-MS procedures: their possibilities and limitations are discussed. In addition to these methods, NMR spectra, which require preparative scale separations, are used for the identification of unknowns. VOCs in *Solanum* include volatiles emitted by potato and tomato foliage, the aroma of vegetables such as tomatoes, volatiles from cooked potatoes and cooked aubergine fruits, and volatiles from diseased potato tubers. Examples of natural VOC blends, as well as, those induced by insect feeding or infections are given. Comparison of the data on *Solanum* volatiles reveals compositional similarities and differences. Green leaf volatiles and β-caryophyllene are present in both potato and tomato foliage blends but in different concentrations; the minor components differ in their compositions in these two species. The ecological significance of potato foliage volatiles is briefly presented. Diseases are one of the major problems affecting potato storage. Monitoring of volatiles produced by diseased potatoes for the detection of infections in stored potatoes is described.

Keywords: aubergine, potato, *Solanum lycopersicum*, *Solanum melongena*, *Solanum tuberosum*, tomato, volatile organic compounds
Abbreviations: CPB, Colorado potato beetle; **EI**, electron ionization; **GC**, gas chromatography; **GC-MS**, gas chromatography-mass spectrometry; **GLVs**, green leaf volatiles; **HS**, headspace; **NMR**, nuclear magnetic resonance; **SPME**, solid phase microextraction; **TOFMS**, time-of-flight mass spectrometry; **VOCs**, volatile organic compounds

CONTENTS

INTRODUCTION 145
ANALYSIS OF PLANT VOLATILES 146
Sampling of volatiles 146
Gas chromatographic analysis 147
NMR spectroscopy of volatiles 147
Chemometric analysis 148
VOLATILE ORGANIC COMPOUNDS FROM *SOLANUM* PLANTS 148
VOCs from potato foliage 148
Ecological significance of potato foliage volatiles 150
VOCs from diseased potato tubers 151
VOCs from cooked potatoes 152
VOCs from tomato fruits 152
VOCs from tomato foliage and their ecological significance 153
VOCs from aubergine fruits 153
CONCLUDING REMARKS 153
ACKNOWLEDGEMENTS 153
REFERENCES 153

INTRODUCTION

Plants produce and release thousands of volatile organic compounds (VOCs) of different chemical structures (Kesselmeier and Staudt 1999). VOCs cover a wide spectrum of compounds, including saturated and unsaturated hydrocarbons, alcohols, aldehydes, short-chain carboxylic acids and esters. Many have no apparent function in the basic processes of growth and development; hitherto, they have been referred to as secondary metabolites (Figueiredo *et al.* 2008).

Analysis of volatiles from different plants and their varieties has revealed quantitative, as well as, qualitative variations. The VOC pattern is characteristic not only of a particular plant species but also of its variety and growing conditions (Figueiredo *et al.* 2008). Plants respond to stress by the biosynthesis of chemical substances able to deter invading insects or pathogens (Dudareva *et al.* 2006). Some of these substances are volatile and are emitted into the surroundings in order to attract or repel insects. Information on the susceptibility of individual plants to infestation, their emissions of volatiles and chemical defence is of interest,

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Invited Review

for example, in the selection of plants for breeding programmes. Moreover, plant volatile identification furthers the understanding of cell molecular processes following insect infestation or microbial infection. Some volatile chemicals are markers of infections in storage (Lui *et al*. 2005a and references cited therein). Last but not least, the VOCs create the aromas of fruits and vegetables (for example tomato fruits), an important point for consumers (Krumbein and Auerswald 1998).

The genus *Solanum* is of worldwide economic importance, and includes major crop species such as the potato (*Solanum tuberosum*), tomato (*Solanum lycopersicum*) and aubergine (eggplant) (*Solanum melongena*). A number of aspects of *Solanum* plant volatiles are of interest; the role of foliage volatiles in host defence against herbivores or pathogens; the detection of pathogens in potato storage; the flavours of eaten tomato and aubergine fruits, and of cooked potatoes. The first part of the paper deals with a brief methodological review of plant volatile analysis. Next, we present the analysis and the composition of *Solanum* volatiles in potatoes, tomatoes and aubergines. We also briefly discuss the role of potato volatiles in the insect-plant relationship.

ANALYSIS OF PLANT VOLATILES

There are many excellent literature reviews of plant volatile analysis. Some focus primarily on the ecological aspects (Tholl and Röse 2006; Tholl *et al.* 2006), others on basic questions of sampling (Luque de Castro *et al*. 1999; Augusto *et al.* 2003) and analytical (Lockwood 2001; Marriott *et al.* 2001; Dewulf and van Langenhove 2002; Merfort 2002) procedures. Before choosing an analytical method in volatile studies, we need to answer one important question: What type of study do we wish to carry out? If it a plant-insect ecological study, a headspace collection of VOCs is needed in order to model the natural conditions of air compositions. Such a collection is also required for the analysis of cooked potatoes or tomatoes, which involves the isolation of the same emitted compounds that are detected by the human nose. In these two cases, the choice of analytical procedures is restricted to sorbent trapping or solid phase microextraction methods, and the size of the headspace sample limits the choice of detection method to gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Moreover, if nothing is known about the flavour composition, all variants of solvent extractions or distillations will have to be used for VOC collections, because more materials are needed for compound separation and identification by nuclear magnetic resonance (NMR) structural studies. In the next chapter we briefly describe the sampling and identification methods used in the analysis of *Solanum* plant volatiles.

Sampling of volatiles

Generally speaking, sampling techniques can be divided into two groups: those collecting plant volatiles already secreted into the air, known as headspace methods (HS), and those collecting the compounds still in plant tissues, such as extraction and distillation. The amounts acquired are significantly different in the two procedures; HS provides quantities of a size sufficient for GC and GC-MS but not for NMR studies. Tholl *et al.* (2006) stated that, compared with solvent extractions, headspace sampling gave a more realistic picture of the volatile profile emitted by plants and detected by insects, so that method was preferred in ecological studies. A recent literature survey (D'Alessandro and Turlings 2006) of the most common collection procedures for herbivory-induced plant volatiles shows that headspace collection on adsorbents followed by desorption with solvents is the most commonly used method. Headspace sampling of the volatile fraction of vegetable matrices is the subject of a recent review by Bicchi *et al.* (2008).

Headspace techniques sample the air matrix above a plant. They are of two types: static headspace or dynamic headspace sampling. For static HS, a plant sample is placed in a chamber and secretes volatiles into a closed volume. The volatile concentrations are proportional to the duration of the secretion process. Volatiles from a static headspace can be transferred directly to GC with a gas-tight syringe or by a solid phase microextraction (SPME) device. A monograph on solid phase microextraction was written by its inventor, J. Pawliszyn (1997). In the HS-SPME method, VOCs are trapped in a small volume of sorbent (liquid or solid) covering the surface of a small fibre attached within the needle of the SPME device. On contact with the probe, analytes are absorbed or adsorbed by the fibre phase (depending on the nature of the coating) until the system reaches equilibrium. The amount of analyte extracted by the coating is governed by the distribution coefficient of the analyte between the coating material and air matrix. After volatile collection, the fibre is retracted into the needle, which is then transferred to a GC injector, where the fibre is exposed to thermal desorption of the compounds. It is a very rapid, effective, solvent-free and simple method for plant volatiles collection. But despite its positive features, there are some shortcomings to SPME sampling. The samples can be injected only once, and the amount of material obtained is generally sufficient only for GC or GC-MS analysis. No NMR data of unknowns can be obtained because the amounts collected are insufficient for spectra acquisition. Quantitative analysis with HP-SPME is possible using external calibration, standard addition or the distribution coefficient (K) of an analyte between the fibre coating and the gaseous phase (Pawliszyn 1997). Martos *et al.* (1997) presented a simple technique for estimating the distribution coefficients (K) between air and the polydimethylsiloxane SPME fibre coating using a linear temperature-programmed retention index system. There is a linear relationship between the log K for a series of n-alkanes and the retention indices that makes it possible to establish K for any volatile compound with its retention index. Zabaras and Wyllie (2001) used this approach to determine the headspace concentration of terpenoid analytes above *Salvia officinalis*. Augusto and Valente (2002) reviewed some applications of SPME for the analysis of live biological samples, including plant VOCs. The authors provided a table with the recommended use of commercially available SPME fibres. The choice of the fibre depends on the polarity of analyte. Nonpolar volatiles are extracted with nonpolar polydimethylsiloxane (PDMS) fibre while polar compounds with polar polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre.

In dynamic headspace sampling, a carrier gas (usually air) flows through the sample chamber. The volatile chemicals released by the sample are carried by the gas to a solid trap, where the analytes are adsorbed and preconcentrated (Tholl and Röse 2006). A variety of different adsorbents can be applied in plant volatile trapping. The most commonly applied sorbents are the polymer-based Porapak Q, Tenax and activated charcoal. Trapped volatiles are usually eluted from the adsorbents with organic solvents such as pentane, hexane, ether, acetone or dichloromethane. It is reasonable to add a compound as an internal standard before extraction, even in semiquantitative studies. An alternative to extraction is thermal desorption, where volatiles are first collected in a trap which is then inserted into a small oven placed on top of a gas chromatograph. When the trap is heated, the volatiles are transferred to the analytical column. But because of interactions between the analytes and the adsorbent surface, higher temperatures may be required for desorption, depending on the compounds. An insufficiently low desorption temperature will result in incomplete release of compounds from the trap, whereas an excessively high desorption temperature can produce artefacts, such as degradation products (Tholl and Röse 2006).

Other sample-preparation techniques include steam distillation, simultaneous steam distillation/solvent extraction (SDE), solvent extraction, supercritical-fluid extraction (SFE) and microwave-assisted extraction (MAE) (Luque de

Castro *et al*. 1999; Augusto *et al.* 2003). SDE isolation (also known as the Likens-Nickerson extraction) is one of the most commonly used methods of preparing volatiles (Chaintreau 2001). In this method, the sample is boiled in stirred water in a flask, which is connected to the left arm of the SDE apparatus, so that the volatiles are steam-distilled. Simultaneously, an organic solvent is boiling in a second flask, connected to the right arm of the SDE apparatus. The vapours of both liquids are condensed on the so-called 'cold finger', where extraction takes place. Then, the condensed water and solvent collect in the separator, from which each returns to its original flask. This one-step method of volatile isolation saves time and solvents, but it also has a number of drawbacks, the most important being the presence of artefacts in the extracts, originating from the solvent or water used or formed by oxidation and thermal reactions.

Direct solvent extraction is the method that localises the site of VOC production in the plant. It can provide volatiles from selected plant tissues. VOCs are usually obtained by dipping different parts of plants in organic solvents (Luque de Castro *et al*. 1999; Augusto *et al.* 2003). Extraction yields volatiles plus some non-volatile lipid components, whereas distillation techniques yield only volatiles. Solvent extraction at room temperature enables the isolation of unstable plant volatiles without artefact generation (Milner *et al*. 1997), but high-purity solvents are required for trace analysis.

Gas chromatographic analysis

Modern gas chromatography (GC) is the most useful technique for the separation, identification and quantification of VOCs. Reviews covering GC in VOC analysis have been published by Lockwood (2001), Marriott *et al.* (2001) and Dewulf and van Langenhove (2002). The gas chromatograph can be coupled to a mass spectrometer (GC-MS), IR spectrophotometer (GC-IR) or different biosensors in order to obtain information on structures and bioactivity. Complete identification can be effected if electron ionization (EI) mass spectra and GC retention data (retention indices) are taken into consideration. The use of retention indices in conjunction with GC-MS studies is routine in volatiles studies.

The combined GC-MS technique is the technique most commonly used for identifying plant volatiles. The most frequent, simple and valid method of identification involves the comparison of the recorded mass spectra with those in standard mass spectral libraries. A good quality mass spectrum with electron impact ionisation can be recorded for a sample with as little as 0.1 ng, i.e. the quantity obtained from different headspace samplings. Mass spectra of plant volatiles are obtained mostly with quadrupole or ion trap detectors because of their rapid scanning performance. However, when there are peaks due to isomers, the identification will be not precise enough and sometimes may even be erroneous from the chemical structure point of view. In view of the great resemblances between the mass spectra of these compounds, peak identification becomes extremely difficult and at times impossible. In order to address the qualitative GC-MS determination of the compositions of complex samples and to improve the reliability of the analytical results, both retention indices and mass spectra appear to be necessary for identification.

Currently, fused-silica capillary columns are used in the analysis of plant volatiles. The most common stationary phases, chemically bound to the inner surface of the column, are DB-5 (95% dimethyl/5% diphenyl polysiloxane; equivalent to RTX-5, HP-5, SE-54, EC-5), DB-1 (100% dimethyl polysiloxane; equivalent to RTX-1, HP-1, SE-30, EC-1) and polar Carbowax 20M (polyethylene glycol). For the different stationary phases used, retention indices such as the Kovats indices and linear temperature-programmed retention indices have been developed to facilitate compound identification. Retention indices and mass spectra have been determined and summarised for several hundred volatile compounds, mostly terpenes (Davies 1990; Adams 1995; Joulain and König 1998). Adams (1995) listed retention indices obtained on a DB-5 column: this, in our opinion, is the best stationary phase for the analysis of complex sesquiterpene mixtures. The most comprehensive data on the retention indices of 35 green leaf volatiles are those of Ruther (2000). This paper gives some practical advice on the use of retention indices in qualitative analysis. No two capillary columns are exactly identical. As a result, the use of columns with different coating thicknesses and different dimensions, supplied by different manufacturers, or used under slightly modified conditions, will lead to errors in retention comparisons. The use of linear temperature-programmed retention indices requires special care to ensure that data from one laboratory to another are reproducible; moreover, constant carrier gas flows are desirable in temperature-programmed runs. To confirm the structural assignments of some VOCs, especially sesquiterpenes, obtained by gas chromatography, two procedures have to be carried out: comparison of measured retention indices with values published in the literature, and co-injection with standards. However, some volatiles are not commercially available as reference standards, and identification is, therefore, sometimes based merely on a comparison of retention indices with library data. It is generally recommended to measure retention times on at least two capillary columns – a polar and a nonpolar one – in combination with the EI mass spectrum. The retention data are an excellent guide to the tentative assignment of volatile components, because the mass spectra of terpenes are not very informative (Adams 1995). For structural identification the retention data should be recorded under the conditions precisely specified in the literature.

When working with a mixture of volatiles that is difficult to separate, two-dimensional gas chromatography (GC×GC) with two columns is needed. This technique allows for orthogonal separation mechanisms on two columns to achieve separation of components that on a single column would remain unresolved. A pair of compounds that elute together as a single GC peak on the first column can be diverted through column-switching techniques to the second column to complete the separation. Shellie *et al.* (2001) demonstrated the three-dimensional GC×GC-TOFMS analysis of a lavender sample. The time-of-flight mass spectrometry (TOFMS) detection of narrow peaks generated under comprehensive GC×GC has been shown to produce a detection sensitivity greater than that achievable by normal GC analysis.

The configuration of the plant volatiles is a crucial factor in the olfactory response of pollinators and herbivores, and it needs to be studied. Direct GC separation of enantiomers relies on utilising chiral stationary phases that form transient diastereoisomers with the targeted chiral molecules. The applications, including the analysis of essential oils, aromas and flavours, of enantiomeric GC have been recently reviewed by He and Beesley (2005). Heptakis (2,3-di-*O*-methyl or ethyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin and octakis (3-*O*-butyryl-2,6-di-*O*-pentyl)-γ-cyclodextrin are popular chiral phases used for this purpose. The chiral columns can be employed in classical GC and GC-MS but also in GC×GC, in GC-isotope ratio mass spectrometry and the LC-GC analysis of volatiles (Bicchi *et al.* 1999).

NMR spectroscopy of volatiles

NMR spectroscopy is undoubtedly a technique of greatest importance in the structural study of organic compounds, providing the most complete information, including the structure and the shape of the molecules, even in the absence of any prior structural knowledge. Little has been done on the NMR of very volatile plant compounds, but in sesquiterpenoid studies, it has often provided conclusive evidence of structural assignments. Two resonances are commonly used in this spectroscopy of simple organic compounds: proton ^{1}H and the ^{13}C isotope nucleus of carbon re-

sonances. Both can be measured as *1-D*, *2-D* or even higher-dimensional spectra, which supply structural information on the basis of chemical shifts, resonance multiplicities and different correlational measurements. Obviously, a greater sample size is needed for ^{13}C NMR recordings than for proton spectra. However, proton decoupled ^{13}C spectra are usually easier to assign by the simple correlation of the data with those published in the literature (Silverstein and Webster 1998).

A good example of NMR structural assignment has recently been presented by Breitmaier (2006) for acanthifolin. The structure was elucidated step by step, starting with MS data for the composition, followed by all the NMR techniques, and finally the relative and absolute configuration assignments. Szafranek *et al*. (2006) recently published an example of the rather standard application of NMR for the identification of two sesquiterpene alcohols (ledol and kunzeaol) in potato leaves. The sesquiterpene alcohols were obtained by steam-distillation and separated first by preparative column chromatography and then by HPLC. All NMR resonances ^{1}H and ^{13}C were assigned correctly. In a recent sesquiterpene study (Faraldos *et al*. 2007), even more sophisticated NMR techniques were used for the structural assignment of (+)-germacrene A, an important intermediate in sesquiterpene biosynthesis in plants. Temperature-variable NMR and nuclear Overhauser effects provided information on the conformations of the flexible cyclodecadiene ring. The sensitivity performance of modern NMR instruments has improved to such an extent that micro-scale measurements are now possible. But the purity of the chemicals used sets a limit to sample size reduction. Recently, an interesting micropreparative GC system based on a megabore capillary column was proposed for the collection of volatiles (Nojima *et al.* 2004). This technique provides a few micrograms of sample of good purity even for *2-D* NMR. All the NMR structural studies of volatiles exemplified here were carried out with the samples that were separated at concentrations optimal for NMR data acquisition.

Chemometric analysis

Chemometrics can be defined as 'the application of mathematical and statistical techniques to chemical data' (Otto 1999) or more generally as 'the use of computational mathematical methods to extract information from analytical data' (Hibbert 1997). Many researchers are now applying these techniques to their data sets in order to obtain informative results. For example in the field of gas chromatographic analysis, chemometrics are a useful technique for the deconvolution of overlapping peaks and makes for a better comparison of the mass spectra with those in the database.

As is the case with any other group of metabolites, the qualitative and quantitative results of VOC analysis can be used for plant taxonomic studies. This can be done with multivariable chemometric methods such as hierarchical cluster analysis (HCA) or principal component analysis (PCA) (Otto 1999). Starting point for HCA and PCA are the analytical data sets arranged as a matrix where objects (e.g. plant varieties) are rows but features (e.g. compound concentrations) are columns. Variances in the columns are information that can be used for classification of the objects. Principal components are the linear combinations of the original variables chosen in the way to describe as much variances as possible. PCA results are visualized by plotting principal components (factors) against each other that aggregate the objects in clusters (**Fig. 1**). Simple chemometric analysis has been applied to identify the chemotypes of commercial potato varieties based on foliage sesquiterpenes (Szafranek *et al*. 2005). Three chemotypes were distinguished in the data set studied. An extremely interesting approach to the analysis of tomato volatiles based on chemometric techniques was published recently by Tikunov *et al*. (2005). This approach consists of three steps: GC-MS metabolic profiling, multivariate comparative analysis of the metabolic phenotype at the individual molecular fragment level, and multivariate mass spectral reconstruction, which permits metabolite discrimination, recognition and identification. Also of great interest is the identification with that procedure of structurally related metabolites derived from the same biochemical precursors. Research procedures of this kind will become standard in similar studies.

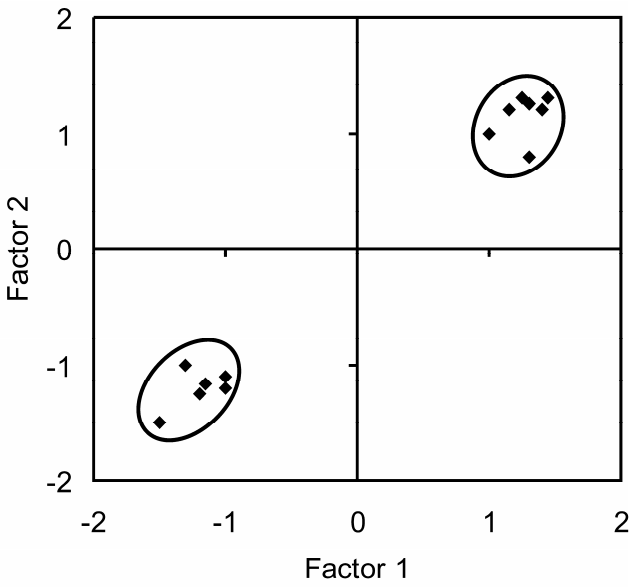

Fig. 1 Example of object classification according to principal component analysis.

VOLATILE ORGANIC COMPOUNDS FROM *SOLANUM* PLANTS

VOCs from potato foliage

The analysis of *S. tuberosum* foliage volatiles began with studies of host selection behaviour in phytophagous insects, such as the Colorado potato beetle (see e.g. Visser and Avé 1978). The main components of potato oil – (*E*)-2-hexen-1-ol, 1-hexanol, (*Z*)-3-hexen-1-ol, (*E*)-2-hexenal, and linalool – were isolated by vacuum steam distillation and identified (Visser *et al.* 1979). The well-known leaf aldehyde 2-hexenal, as well as, leaf alcohols have been identified in other Solanaceous plant species such as *Solanum campylacanthum*, *Solanum lycopersicum*, *Nicotiana alata*, *Capsicum annuum* and *Capsicum frutescens* (Visser *et al.* 1979 and references cited therein). These straight chain, saturated and unsaturated C_6 aldehydes and C_6 alcohols are perceived by humans as a grass-like odour and are known collectively as 'green leaf volatiles' (GLVs). GLVs are formed from linolenic and linoleic acids (Visser *et al.* 1979; Matsui 2006). Green leaf volatiles were identified in the headspace of potato foliage in both intact and damaged plants (**Table 1**). Intact potato leaves emit small quantities of GLVs (Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 1999), but mechanically damaged or beetle-damaged potato plants release large amounts of GLVs and sesquiterpene hydrocarbons. Infestation with CPB larvae resulted in a 7- to 10-fold increase in the amount of volatiles emitted (Bolter *et al.* 1997). Agelopoulos *et al.* (1999) reported that levels of GLV compounds such as (*Z*)-3-hexenal, (*Z*)-3-hexen-1-ol and (*E*)-2-hexenal were 60- to 90-fold higher after mechanical damage.

Terpenes (monoterpenes and sesquiterpenes) represent the largest class of potato volatiles occurring as hydrocarbons or in oxygenated forms (**Table 1**). In the past, several papers have focused on headspace-collected (Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 1999, 2000; Weissbecker *et al.* 2000) or solvent-extracted (Szafranek *et al*. 1998, 2005, 2006) terpenes from *S. tuberosum* foliage. Szafranek *et al*. (2005, 2006) identified 17 sesquiterpene hydrocarbons and 4 sesquiterpene alcohols in the foliage of

Table 1 Volatiles identified in the foliage of *S. tuberosum*.

Compounds	References[3]
Green leaf volatiles	
1-hexanol[1,2]	Visser *et al.* 1979; Agelopoulos *et al.* 1999
hexanal[2]	Agelopoulos *et al.* 1999
(*E*)-2-hexen-1-ol[1,2]	Visser *et al.* 1979; Schütz *et al.* 1997; Agelopoulos *et al.* 1999
(*Z*)-3-hexen-1-ol[1,2]	Visser *et al.* 1979; Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 1999
(*E*)-2-hexenal[1,2]	Visser *et al.* 1979; Schütz *et al.* 1997; Agelopoulos *et al.* 1999
(*Z*)-3-hexenal[2]	Agelopoulos *et al.* 1999
(*Z*)-2-penten-1-ol[2]	Agelopoulos *et al.* 1999
(*Z*)-3-hexen-1-yl acetate[2]	Bolter *et al.* 1997
(*Z*)-3-hexen-1-yl butyrate[2]	Bolter *et al.* 1997
Monoterpenes/Monoterpenoids	
limonene[1,2]	Bolter *et al.* 1997
myrcene[1,2]	Bolter *et al.* 1997; Schütz *et al.* 1997
α-pinene[1,2]	Bolter *et al.* 1997
sabinene[2]	Bolter *et al.* 1997
tricyclene[2]	Bolter *et al.* 1997
linalool[1,2]	Visser *et al.* 1979; Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 2000
1,8-cineole[2]	Bolter *et al.* 1997
Sesquiterpenes	
trans-α-bergamotene[2]	Weissbecker *et al.* 2000; Szafranek *et al*. 2005
trans-β-bergamotene[2]	Weissbecker *et al.* 2000; Szafranek *et al*. 2005
bicyclogermacrene[2]	Szafranek *et al*. 1998; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
β-bisabolene[1,2]	Szafranek *et al*. 1998; Agelopoulos *et al.* 1999, 2000; Szafranek *et al*. 2005
γ-cadinene[1,2]	Bolter *et al.* 1997
δ-cadinene[1,2]	Bolter *et al.* 1997; Szafranek *et al*. 1998; Szafranek *et al*. 2005
β-caryophyllene[1,2]	Bolter *et al.* 1997; Schütz *et al.* 1997; Szafranek *et al*. 1998; Agelopoulos *et al.* 1999, 2000; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
α-copaene[2]	Bolter *et al.* 1997; Szafranek *et al.* 2005
α-cubebene[2]	Bolter *et al.* 1997; Szafranek *et al.* 2005
β-cubebene	Szafranek *et al*. 2005
ar-curcumene[2]	Bolter *et al.* 1997
β-elemene[2]	Bolter *et al.* 1997; Szafranek *et al*. 2005
(*Z,Z*)-α-farnesene[1]	Agelopoulos *et al.* 2000
(*E*)-β-farnesene[1,2]	Bolter *et al.* 1997; Szafranek *et al*. 1998; Agelopoulos *et al.* 1999, 2000; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
(*Z*)-β-farnesene	Szafranek *et al*. 1998; Szafranek *et al*. 2005
germacrene A[2]	Weissbecker *et al.* 2000; Szafranek *et al*. 2005
germacrene D[1,2]	Bolter *et al.* 1997; Szafranek *et al*. 1998; Agelopoulos *et al.* 1999, 2000; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
α-gurjunene	Szafranek *et al*. 2005
α-humulene[2]	Bolter *et al.* 1997; Szafranek *et al*. 1998; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
longifolene[2]	Bolter *et al.* 1997
γ-muurolene[2]	Bolter *et al.* 1997
α-selinene[1,2]	Bolter *et al.* 1997
β-selinene[1,2]	Bolter *et al.* 1997
β-sesquiphellandrene[2]	Bolter *et al.* 1997; Szafranek *et al*. 1998; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
sesquisabinene[2]	Weissbecker *et al.* 2000
α-zingiberene[2]	Weissbecker *et al.* 2000
Sesquiterpenoids	
caryophyllene oxide[2]	Weissbecker *et al.* 2000
α-cadinol	Szafranek *et al*. 2005
germacrene D-4-ol[2]	Szafranek *et al*. 1998; Weissbecker *et al.* 2000; Szafranek *et al*. 2005
kunzeaol	Szafranek *et al*. 2006
ledol[1,2]	Bolter *et al.* 1997; Weissbecker *et al.* 2000; Szafranek *et al*. 2006
Other compounds	
2-benzene-ethanol[1,2]	Schütz *et al.* 1997
decanal[1,2]	Bolter *et al.* 1997; Agelopoulos *et al.* 2000
heptanal[2]	Bolter *et al.* 1997
methyl salicylate[2]	Bolter *et al.* 1997
nonanal[1,2]	Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 2000
(*Z*)-3-nonen-1-ol[2]	Schütz *et al.* 1997
octanal[2]	Bolter *et al.* 1997
3-pentanone[2]	Bolter *et al.* 1997
indole[2]	Bolter *et al.* 1997
furfural[2]	Bolter *et al.* 1997

[1]Present in intact plants
[2]Present in damaged (mechanically or by insects) plants
[3]Methods of volatiles sampling: vacuum steam distillation (Visser *et al.* 1979), headspace (Bolter *et al.* 1997; Schütz *et al.* 1997; Agelopoulos *et al.* 1999, 2000; Weissbecker *et al.* 2000) and solvent extraction (Szafranek *et al.* 1998, 2005, 2006)

10 commercial varieties of potato. The composition of the sesquiterpenes was found to be variety-specific. The eight potato varieties of the main chemotype cluster were dominated by the contents of β-caryophyllene (9-148 ng/cm^2), germacrene D (2-46 ng/cm^2), germacrene D-4-ol (0.4-31 ng/cm^2), β-sesquiphellandrene (1-34 ng/cm^2) and kunzeaol (0.2-37 ng/cm^2). Two further varieties, 'Mila' and 'Vistula', yielded sesquiterpenes with substantially different compositions. **Fig. 2** shows the mean percentage sesquiterpene composition for all ten varieties. The 'typical' composition

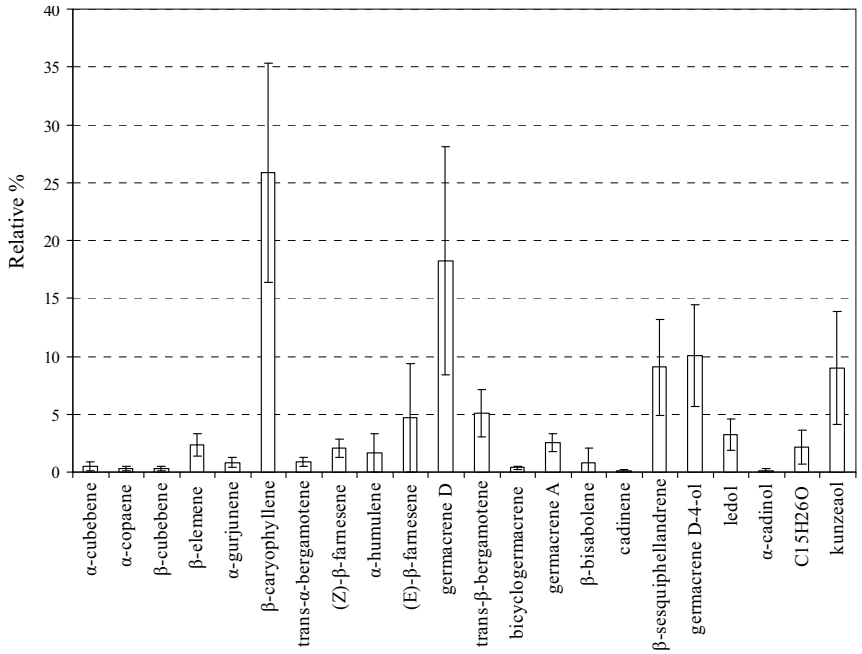

Fig. 2 Composition (mean ± SD, $N = 10$) of *S. tuberosum* sesquiterpenes. The mean and standard deviation were calculated for 10 commercial varieties (Szafranek *et al*. 2005, 2006). All values are percentage contents.

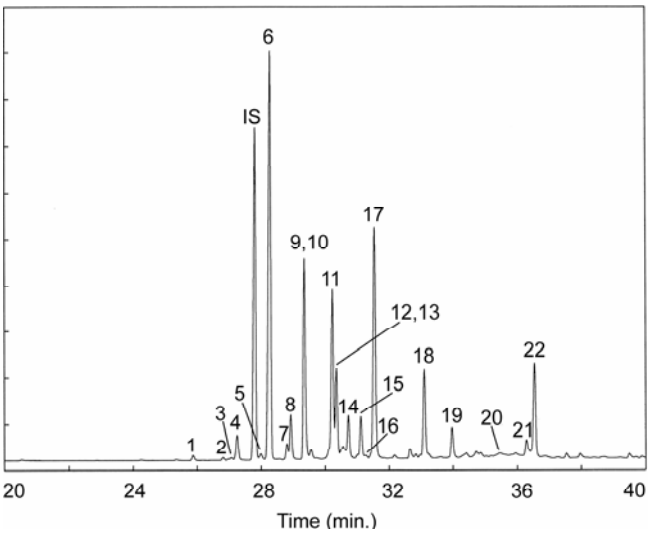

Fig. 3 Gas chromatogram of potato leaf sesquiterpenes of the 'Wolfram' variety obtained on an EC-1 capillary column. Labelling as in **Table 2**. IS – internal standard (*n*–tetradecane). Reprinted from **Szafranek B, Chrapkowska K, Pawińska M, Szafranek J** (2005) Analysis of leaf surface sesquiterpenes in potato varieties. *Journal of Agricultural and Food Chemistry* **53**, 2817-2822, with kind permission from the American Chemical Society, ©2005.

of solvent-extracted potato sesquiterpenes matches the major headspace sesquiterpenes (β-caryophyllene, (*E*)-β-farnesene, germacrene D, β-sesquiphellandrene and germacrene D-4-ol) detected by Weissbecker *et al.* (2000).

The structures of the potato sesquiterpenes were determined on the basis of their EI mass spectra, by comparisons of retention indices on three different capillary columns (polar and non-polar) (Szafranek *et al*. 2005), and by NMR analysis (Szafranek *et al*. 2006). **Fig. 3** shows the typical GC pattern of potato sesquiterpenes. No GC analysis on a single column could separate all the potato leaf sesquiterpenes: for example, α-humulene and (*E*)-β-farnesene overlapped on the EC-1 capillary column, β-sesquiphellandrene and δ-cadinene were not separated on the RTX-5 column, while the best separation of α-humulene and (*E*)-β-farnesene was achieved on a Carbowax column (Szafranek *et al*. 2005). **Table 2** gives the experimental and reference data of the retention indices for potato sesquiterpenes. This data set should be helpful in further chromatographic studies of potato volatiles.

Ecological significance of potato foliage volatiles

The Colorado potato beetle (CPB) (*Leptinotarsa decemlineata*) is a major pest of potatoes. The attractive role of *S. tuberosum* green leaf volatiles in the olfactory orientation of CPBs is well known (Visser and Avé 1978; Visser 1979). The attraction of CPBs to volatiles emitted by mechanically damaged or beetle-damaged potato plants has also been demonstrated (Bolter *et al*. 1997; Schütz *et al*. 1997). Moreover, infestation results in the emission of elevated amounts of potato volatiles. Schütz *et al.* (1997) found that GLVs elicited high response levels in the electroantennographic detector (EAD) employed to identify the volatile compounds that are perceptible by CPB. Dickens (2000, 2002) tested potato volatiles for their behavioural activity in an open Y-track olfactometer and identified volatile blends attractive to both adults and larvae of CPB. The compositions attractive to adults contained either low amounts of the green leaf volatiles (*E*)-2-hexen-1-ol and (*Z*)-3-hexen-1-ol, or (*Z*)-3-hexenyl acetate together with linalool, nonanal, and/or methyl salicylate. CPB larvae were attracted only to a three-component blend consisting of (*Z*)-3-hexenyl acetate, linalool and methyl salicylate. The identification of host volatiles attractive to CPB was the basis for developing a synthetic attractant blend for this pest (Martel *et al.* 2005).

Aphids are another group of phytophagous insects that are important pests of potatoes. The sesquiterpene (*E*)-β-farnesene from the aphid-resistant wild potato *Solanum berthaultii* acts as an alarm pheromone to the green peach aphid *Myzus persicae* (Pickett and Glinwood 2007). However, another sesquiterpene – β-caryophyllene – present along with (*E*)-β-farnesene in *S. tuberosum* volatiles, was found to inhibit its alarm activity. Volatiles from potato plants infected with the potato leaf-roll virus attract and arrest *M. persicae* more strongly than volatiles from non-infected plants (Ngumbi *et al.* 2007). The authors concluded that the arrest of *M. persicae* by virus-infected plants requires the blend of VOCs released by these plants and is not elicited in response to any one compound. The significance of natural green leaf volatiles from potatoes (Vancanneyt *et al*. 2001) in direct defense against an aphid species was demonstrated when a genetically modified line of potatoes with low levels of volatiles was developed and used in the study.

These examples of insect-potato interactions show the importance of potato volatiles. Since host-plant location by insects is controlled largely by plant VOCs, there is a significant potential in commercial pest control for chemicals modifying insect behaviour.

Table 2 Kovats' retention indices on liquid phases.

Peak[a]	Compound	RTX-5		Carbowax		EC-1[b]		EC-1[c]	
		Exp.	Ref.	Exp.	Ref.	Exp.	Ref.	Exp.	Ref.
1	α-Cubebene	1349	1351[d]	1480	1481[e]	1351	-	1361	1362[e]
2	α-Copaene	1375	1376[d]	1519	-	1378	1378[e]	1390	-
3	β-Cubebene	1390	1390[d]	1558	1560[e]	1389	-	1400	1400[e]
4	β-Elemene	1392	1391[d]	1606	1608[e]	1389	-	1400	1400[e]
5	α-Gurjunene	1409	1409[d]	-	-	1410	1413[e]	1423	-
6	β-Caryophyllene	1418	1418[d,f]	1617	1618[e]1617[f]	1417	1417[e]1418[f]	1432	1436[e]
7	*trans*-α-Bergamotene	1435	1436[d]	-	-	1431	-	-	-
8	(*Z*)-β-Farnesene	1442	1443[d]1442[f]	1650	1650[f]	1434	1433[f]	1442	-
9	α-Humulene	-	1454[d]	1680	1680[f]	1446	1447[e]1446[f]	1449	-
10	(*E*)-β-Farnesene	1457	1458[d]1457[f]	1663	1671[e]1664[f]	1446	1446[f]	1449	1426[e]
11	Germacrene D	1479	1480[d]1479[f]	1715	1718[e]1714[f]	1471	1471[f]	1485	1488[e]
12	*trans*-β-Bergamotene	1484	1486[g]	1688	-	1475	-	1485	-
13	Bicyclogermacrene	1493	1494[d]1493[f]	1736	1738[e]1736[f]	1475	-	-	-
14	Germacrene A	1503	1503[d]	-	-	1484	-	-	-
15	β-Bisabolene	1509	1509[d]1507[f]	1726	1726[f]	1500	1496[e]1500[f]	-	-
16	δ-Cadinene	1523	1524[d]1522[f]	1761	1761[f]	1505	1504[e]1508[f]		-
17	β-Sesquiphellandrene	1523	1524[d]1522[f]	1764	1764[f]	1509	1509[f]	1517	-
18	Germacrene D-4-ol	1573	1574[d]1575[f]	-	-	1553	-	1566	-
19	Sesquiterpene I [h]	1600	-	-	-	1576	-	1592	-
20	α-Cadinol	1653	1654[d]	-	-	1627	-	1635	-
21	Sesquiterpene II	1685	-	-	-	1646	-	1661	-
22	Sesquiterpene III [h]	1688	-	-	-	1653	-	1669	-

[a] Peak numbers correspond to those in **Fig. 3**.
[b] Isothermal indices 130°C.
[c] Isothermal indices 150°C.
[d] Reference data (Adams 1995).
[e] Reference data (Davies 1990).
[f] Reference data (Szafranek *et al.* 1998).
[g] Reference data (Weissbecker *et al*. 2000).
[h] Sesquiterpene I was identified as ledol and Sesquiterpene III as kunzeaol (Szafranek *et al*. 2006).
Reprinted from **Szafranek B, Chrapkowska K, Pawińska M, Szafranek J** (2005) Analysis of leaf surface sesquiterpenes in potato varieties. *Journal of Agricultural and Food Chemistry* **53**, 2817-2822, with kind permission from the American Chemical Society, ©2005.

Table 3 Examples of volatiles specific for the infections in potato storage.

Pathogen	Specific volatiles	Reference
Phytophthora infestans	ethoxy-ethene	Lui *et al*. 2005a
	butanal, 3-methylbutanal, undecane, verbenone	de Lacy Costello *et al*. 2001
Pythium ultimum	2-methyl-1-butanol, 2-butanone, 2-methyl-2-butanamine	Lui *et al*. 2005a
Botrytis cinerea	2-2-propenyl-1,3-dioxolane and 3,5-heptadiyn-2-one	Lui *et al*. 2005a
Fusarium coeruleum	2-pentylfuran, copaene	de Lacy Costello *et al*. 2001
Fusarium sambucinum	2,5-norbornadiene, styrene	Lui *et al*. 2005b
Erwinia carotovora spp. *carotovora*	probably furan	Lyew *et al*. 2001
	cyclohexene, diazene, methoxy(l,1-dimethyl-2-dihydroxy-ethyl)-amine	Lui *et al*. 2005b
Erwinia carotovora spp. *atroseptica*	acetic acid ethenyl ester	Lui *et al*. 2005b
Clavibacter michiganensis	3-methyl-2-pentanone	Stinson *et al*. 2006
Ralstonia solanacearum	2-propanone, 2-propanol, 2-butanone, 2-butanol, 2-pentanone, 2-pentanol	Stinson *et al*. 2006

VOCs from diseased potato tubers

Stored *S. tuberosum* tubers are susceptible to infection by different types of microorganisms (Weingartner *et al*. 2001; Lui *et al*. 2005a and references cited therein). A wider range of volatile compounds was detected in infected potatoes than in healthy ones. The quantitative and qualitative changes in the volatiles produced by potato tubers are correlated with the infections (de Lacy Costello *et al*. 1999; Lyew *et al*. 2001; de Lacy Costello *et al*. 2001; Kushalappa *et al*. 2002; Lui *et al*. 2005a and references cited therein). Comparison of the volatiles emitted by healthy and diseased potato tubers showed that there are volatile emissions specific to an infection by pathogens.

The complex mixture of volatiles released consists of a large number of chemical classes, including aldehydes, alcohols, amides, aromatic compounds, carboxylic acids, saturated and unsaturated hydrocarbons (de Lacy Costello *et al*. 2001), alcohols and ketones (Stinson *et al*. 2006). For example, Lui *et al*. (2005a) studied the volatiles from the headspace of potato tubers inoculated with *Phytophthora infestans*, *Pythium ultimum* or *Botrytis cinerea*. GC-MS analysis revealed 39 relatively consistent and abundant metabolites but only a few were specific to one pathogen. Discriminant analysis of metabolic fingerprints showed that potato tubers inoculated with *B. cinerea* produced specific volatiles – 2-2-propenyl-1,3-dioxolane and 3,5-heptadiyn-2-one, whereas those inoculated with *P. ultimum* produced 2-methyl-1-butanol, 2-butanone and 2-methyl-2-butanamine, and *P. infestans* produced ethoxyethene. **Table 3** provides further examples of volatiles specific to fungal or bacterial infections in stored potato tubers.

The monitoring of volatiles produced by diseased tubers can be used in the detection of pathogens by both dynamic and static headspace sampling. The levels of volatiles produced are often low, and concentration of the compounds on adsorbents is required (Lyew *et al*. 2001) or by SPME (Kushalappa *et al*. 2002; Stinson *et al*. 2006). Volatiles detection methods are based on GC-MS or GC-FID fingerprinting. Lyew *et al*. (2001) reported that different volatiles are produced at different times in the course of infection, and that the amounts of some volatiles increased over time, whereas the production of others ceased. The authors reported that the qualitative changes in volatile profiles, indicating the presence of *Erwinia carotovora* in infected potatoes, could be obtained as early as 24 h after inoculation. Quantitative analysis was a less sensitive method; a clear indication of the presence of pathogens was obtained after 60-72

h, by which time the infection was already well established. This means that there is a time lag between the start of infection and the moment of detection possible by instrumental analysis. Studies have been undertaken to build biosensors (Schütz *et al*. 1999) or so called 'electronic noses' (Stinson *et al*. 2006) to facilitate the monitoring of pathogenic infections.

VOCs from cooked potatoes

Raw potatoes contain low levels of flavour volatiles (Whitfield and Last 1991). Potatoes are always cooked (by boiling, baking/roasting or frying) before being eaten, and their volatile composition differs significantly according to the method of cooking. The main flavour precursors are potato sugars, amino acids and lipids. As the potatoes are cooking, volatiles are formed, mostly by Maillard reactions or by potato lipid degradation. Maillard reactions are complex reactions between amino acids and reducing sugars, which usually require heat. It is thought that sulphur-containing compounds are formed by the thermal degradation of sulphur amino acids. Mandin *et al*. (1999) studied the volatile products of a boiled potato-like model system with various combinations of methionine, glucose, linoleic acid and starch. The study demonstrated that the majority of volatile compounds in boiled potatoes were formed as a result of linoleic acid decomposition. The products of Maillard reactions (pyrazines, thiazoles and oxazoles) predominated in the flavour of a baked potato (Whitfield and Last 1991). The Maillard reaction requires a temperature of >100°C for the rate of heterocyclic compound production to be appreciable.

The compounds identified in the volatiles of baked potatoes included hydrocarbons, acids, alcohols, aldehydes, esters, lactones, ethers, furans, halogenated hydrocarbons, ketones, pyrazines, oxazoles, thiazoles and miscellaneous heterocycles (Coleman *et al*. 1981). Recently, potato volatiles have received much attention, and papers on the volatile compounds of boiled (Petersen *et al*. 1998; Mutti and Grosch 1999), oven-baked (Duckham *et al*. 2001; Oruna-Concha *et al*. 2001; Duckham *et al*. 2002) and microwave-baked potatoes (Oruna-Concha *et al*. 2002), and also of potato snacks (Majcher and Jeleń 2005) have been published. According to Duckham *et al*. (2002), the volatile composition of baked potatoes varies according to cultivar, agronomic factors and the conditions of potato storage. The authors suggested that the differences may be explained by variations in the levels of flavour precursors and the activities of enzymes mediating flavour compound formation.

The volatiles were isolated from samples of cooked potatoes by simultaneous steam distillation/solvent extraction (SDE) (Oruna-Concha *et al*. 2001), solvent-assisted flavour evaporation (SAFE) (Majcher and Jeleń 2005) and headspace methods (Ames *et al*. 2001; Duckham *et al*. 2001, 2002; Oruna-Concha *et al*. 2002). The compounds were then identified by GC-MS analysis and retention indices (Duckham *et al*. 2001; Oruna-Concha *et al*. 2001; Duckham *et al*. 2002; Oruna-Concha *et al*. 2002). Petersen *et al*. (1998) used a mild extraction procedure carried out at ambient temperature for the solvent extraction of aqueous suspensions of raw and boiled potatoes. Sanches-Silva *et al*. (2005) studied headspace solid-phase microextraction (HS-SPME) as a solvent-free alternative method for the extraction and characterisation of volatile compounds in stored potato crisps by GC-MS. The preferred fibre for the volatile profile study of the crisps was a divinylbenzene (DVB)–carboxen (CAR)–polydimethylsiloxane fibre.

VOCs from tomato fruits

The tomato (*Solanum lycopersicum*, also known as *Lycopersicon esculentum*) is cultivated worldwide (Labate *et al*. 2007). Special attention has been given to analysing and improving its flavour, as consumers prefer fresh fruits with a full flavour and the characteristic taste. Tomatoes contain over 400 volatile compounds that represent only 0.1% of the total dry material (see the review by Petro-Turza 1987). They include hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, esters, lactones, as well as sulphur- and nitrogen-containing compounds. The main precursors of these compounds are fatty acids, free amino acids, carotenoids and phenolics. No single volatile is responsible for producing the characteristic tomato aroma. Buttery and Ling (1993) suggested that a mixture of compounds, including (*Z*)-3-hexenal, (*E*)-2-hexenal, hexanal, hexanol, (*Z*)-3-hexenol, 2-isobutylthiazole, 6-methyl-5-hepten-2-one, geranylacetone, 2-phenylethanol, β-ionone, 1-penten-3-one, 3-methylbutanol and 3-methylbutanal, is responsible for the fresh tomato aroma. Using gas chromatography-olfactometry and aroma extract dilution analysis Krumbein and Auerswald (1998) determined the six most odour-active aroma volatiles that contribute to the fresh tomato flavour, namely, (*Z*)-3-hexenal, hexanal, 1-octen-3-one, methional, 1-penten-3-one and 3-methylbutanal.

Tandon *et al.* (2000) recommended an increase in the compounds contributing to the floral (6-methyl-5-hepten-2-one and β-ionone), fruity ((*Z*)-3-hexenal and geranylacetone) and fresh (3-methylbutanol and 1-penten-3-one) notes, and a decrease in those contributing to stale (hexanal, (*E*)-2-hexenal and 3-methylbutanal), pungent (2-isobutylthiazole) and alcoholic (2-phenylethanol) notes for improving tomato flavour. The authors also found that there were distinct differences in the aroma descriptors for the compounds in different media and that ethanol and methanol alter the perception of the tomato aroma.

Numerous authors have analysed tomato volatiles using distillation (Buttery *et al.* 1971), headspace collection (Buttery *et al.* 1987a) and solid phase microextraction (Song *et al.* 1998). As Sucan and Russell (2001) stated, however, 'each method gave a different picture of the tomato flavour profile'. Headspace methods may be advantageous in isolating the same emitted compounds that are detected by the human nose; indeed, most studies have used this method. Classical methods such as extraction or distillation may lead to artefact formation and loss of analytes. Quantitative and qualitative analysis of isolated tomato volatiles are usually carried out by GC-MS.

Since there are a lot of drawbacks to classical liquid-liquid extraction, e.g. large amounts of high-purity solvents are required, Aubert *et al.* (2005) developed a rapid method based on liquid-liquid microextraction (LLME) for the analysis of fruit volatiles. LLME is a single-step extraction involving a very high liquid sample/solvent ratio (40 mL of sample juice per 0.25 mL of CH_2Cl_2) and saturation of the aqueous phase with inorganic salts. The important volatiles in tomato flavour were generally better extracted by LLME, and the method was faster, simpler and required only micro-quantities of solvent compared to the classical technique.

The efficiency of headspace sampling of water-soluble volatiles from tomato fruits was poor. Buttery *et al.* (2001) used a simple method of isolating the water-soluble volatile furaneol from fresh tomatoes: the sample was mixed with excess anhydrous sodium sulphate to remove moisture, after which high-flow dynamic headspace sampling was performed. Maneerat *et al.* (2002) used the Porapak Q method to isolate and concentrate tomato fruit volatiles, no matter whether their boiling points were high or low. Briefly, the tomato blend was passed through a column packed with Porapak Q (ethylvinylbenzene-divinylbenzene polymer), and after the column had been flushed with water, the adsorbed volatiles were eluted with diethyl ether. The authors concluded that the method could preserve the natural flavour and yield clearer information on the flavour, because both the low boiling point volatiles and the flavour compounds, that are released as the tomato is eaten (medium-high boiling point compounds), can be isolated with Porapak Q.

VOCs from tomato foliage and their ecological significance

Tomato leaf volatiles have been analysed because of their role in host defence against herbivores (Farag and Paré 2002) or pathogen attack (Thelen *et al.* 2005). Although much more attention has been given to analysing tomato fruit than tomato leaf volatiles, the major volatile components – C_6 aldehydes and alcohols (GLVs), monoterpenes and sesquiterpenes – have been identified (Andersson *et al.* 1980; Buttery *et al.* 1987b). The volatiles identified in intact tomato leaves consist mainly of terpene hydrocarbons (β-phellandrene, 2-carene, limonene, α-phellandrene, terpinolene, α-terpinene, myrcene, α-pinene) and sesquiterpene hydrocarbons (β-caryophyllene, humulene) but also C_6 compounds (hexanal, (*Z*)-3-hexenal, (*E*)-2-hexenal, hexanol, (*Z*)-3-hexenol), several oxygenated monoterpenoids and sesquiterpenoids, and some aromatic compounds. Colby *et al.* (1998) identified additional sesquiterpenes: germacrene C, germacrene A, guaia-6,9-diene (azulane), germacrene B, germacrene D and β-elemene in cherry tomato leaves.

In response to damage or insect feeding, tomato plants release elevated levels of volatiles. The concentrations of C_6 aldehydes were found to be relatively low (< 1 ppm each) in the intact tomato leaves; when the leaves were damaged, however, the concentrations of these compounds increased dramatically (Buttery *et al.* 1987b). The concentration of (*E*)-2-hexenal increased almost 50 times but the concentration of (*Z*)-3-hexenal did not change in blended tomato leaves. The authors concluded that (*Z*)-3-hexenal might be isomerised into (*E*)-2-hexenal as it was formed in damaged leaves.

Tomato leaves damaged by the tobacco hornworm released significantly higher levels of volatiles than did undamaged plants (Farag and Pare 2002); those infected by *Botrytis cinerea* produced elevated amounts of volatiles, α-copaene being the most prominent volatile induced by the tomato leaf-*Botrytis cinerea* interaction (Thelen *et al.* 2005).

The volatiles of tomato leaves were isolated by headspace methods with Tenax adsorbant trapping (Andersson *et al.* 1980; Buttery *et al.* 1987b; Thelen *et al.* 2005), by simultaneous steam distillation/solvent extraction (Colby *et al.* 1998), and recently by headspace solid phase microextraction (Deng *et al.* 2004; Thelen *et al.* 2005). Deng *et al.* (2004) optimised SPME conditions with a 100 μm polydimethylsiloxane fibre, achieving an optimum extraction time of 60 min and temperature of 60°C. The volatile compounds absorbed in the fibre were desorbed at 270°C for 2 min and analysed by GC-MS.

VOCs from aubergine fruits

The aubergine, or eggplant (*Solanum melongena*), is grown for its fruit, which is eaten cooked (Frary *et al.* 2007). To the best of our knowledge, there is only one report on the chemical composition of aubergine fruit volatiles: MacLeod and de Troconis (1983) identified some 37 compounds in the volatiles of the cooked fruit. Over 70% of the aroma was due to hydrocarbons, mostly straight- and branched-chain alkanes from heptane to eicosane, but also three sesquiterpenes (bergamotene, α-humulene and bisabolene) and one monoterpene – car-3-ene. Other compounds of interest were green leaf volatiles (hexanal, hexanol and (*Z*)-3-hexen-1-ol), dimethyl sulphide, heptanal, pentylfuran, benzaldehyde, acetophenone and phenylacetaldehyde.

The chemical composition of aubergine leaf volatiles has not attracted much attention; the leaves of aubergines probably produce fewer volatiles than those of potatoes or tomatoes. The volatile profiles of undamaged and of mechanically damaged aubergine leaves consist mainly of (3*E*)-4,8-dimethyl-1,3,7-nonatriene, (*Z*)-3-hexen-1-ol acetate, 2-methylbutanal-O-methyl oxime, (*Z*)-3-hexen-1-ol and α-bergamotene; leaves attacked by herbivores produce larger amounts of these volatiles (van den Boom *et al.* 2004).

CONCLUDING REMARKS

Modern analytical techniques are able to provide accurate and precise profiles of the volatiles contained in *Solanum* plant tissues, as well as, those released from tissues into the air. For structural studies the most effective procedures are those based on a combination of mass spectra and GC retention index data. After their separation, unknowns need to be identified with NMR. Comparison of the data on *Solanum* volatiles reveals compositional similarities and differences. Green leaf volatiles and β-caryophyllene are present in both potato and tomato blends but in different concentrations; the minor components differ in their compositions in these two species. VOC profiles obtained with multivariable techniques can be used in the chemotaxonomy of species and varieties. The compositions of volatiles change significantly after damage to a plant, herbivory or infection. Herbivory-induced volatiles are also important components in a plant's defence strategy. The bioactivity of plant volatiles suggests that insect infestation and feeding behaviour can be altered, if the volatile compositions are modified through conventional breeding practice. Moreover, tomato fruit volatiles, which are important cues for customers and influence purchasing and consumption decisions, can still be improved. In addition, the flavour of cooked potatoes has also received much attention. The application of modern analytical techniques enables both the qualitative and the quantitative characterisation of *Solanum* plant volatiles in different areas of research such as ecology and agriculture.

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REFERENCES

Adams RP (1995) *Identification of Essential Oils Components Gas Chromatography/Mass Spectrometry*, Allured Publishing Corporation, Carol Stream, USA, 469 pp

Agelopoulos NG, Chamberlain K, Pickett JA (2000) Factors affecting volatile emissions of intact potato plants, *Solanum tuberosum*: variability of quantities and stability of ratios. *Journal of Chemical Ecology* **26**, 497-511

Agelopoulos NG, Hooper AM, Maniar SP, Pickett, JA, Wadhams LJ (1999) A novel approach for isolation of volatile chemicals released by individual leaves of a plant in situ. *Journal of Chemical Ecology* **25**, 1411-1425

Ames JM, Duckham SC, Bakker J (2001) Choice and use of standards for dynamic headspace trapping and application to the analysis of the volatiles of baked potato. In: Rouseff RL, Cadwallader KR (Eds) *Headspace Analysis of Foods and Flavors: Theory and Practice, Advances in Experimental Medicine and Biology* (Vol 488), Kluwer Academic/Plenum Publishers, New York, pp 133-141

Andersson BA, Holman RT, Lundgren L, Stenhagen G (1980) Capillary gas chromatograms of leaf volatiles. A possible aid to breeders for pest and disease resistance. *Journal of Agricultural and Food Chemistry* **28**, 985-989

Aubert C, Baumann S, Arguel H (2005) Optimization of the analysis of flavor volatile compounds by liquid-liquid microextraction (LLME). Application to the aroma analysis of melons, peaches, grapes, strawberries, and tomatoes. *Journal of Agricultural and Food Chemistry* **53**, 8881-8895

Augusto F, Lopes AL, Zini CA (2003) Sampling and sample preparation for analysis of aromas and fragrances. *Trends in Analytical Chemistry* **22**, 160-169

Augusto F, Valente A (2002) Applications of solid-phase microextraction to chemical analysis of live biological samples. *Trends in Analytical Chemistry* **21**, 428-438

Bicchi C, Cordero C, Liberto E, Sgorbini B, Rubiolo P (2008) Headspace sampling of the volatile fraction of vegetable matrices. *Journal of Chromatography A* **1184**, 220-233

Bicchi C, D'Amato A, Rubiolo P (1999) Cyclodextrin derivatives as chiral selectors for direct gas chromatographic separation of enantiomers in the essential oil, aroma and flavour fields. *Journal of Chromatography A* **843**, 99-121

Bolter CJ, Dicke M, van Loon JJA, Visser JH, Posthumus MA (1997) Attraction of Colorado potato beetle to herbivore-damaged plants during herbivory and after its termination. *Journal of Chemical Ecology* **23**, 1003-1023

Breitmaier E (2006) *Terpenes: Flavors, Fragrances, Pharmaca, Pheromones*, Wiley VCH, Weinheim, 223 pp

Buttery RG, Ling LC (1993) Volatile compounds of tomato fruit and plant parts: Relationship and biogenesis. In: Teranishi R, Buttery RG, Sugisawa H

(Eds) *Bioactive Volatile Compounds from Plants. ACS Symposium Series No. 525*, American Chemical Society, Washington, pp 23-34

Buttery RG, Seifert RM, Guadagni DG, Ling LC (1971) Characterization of additional volatile components of tomato. *Journal of Agricultural and Food Chemistry* **19**, 524-529

Buttery RG, Takeoka GR, Naim M, Rabinowitch H, Nam Y (2001) Analysis of furaneol in tomato using dynamic headspace sampling with sodium sulfate. *Journal of Agricultural and Food Chemistry* **49**, 4349-4351

Buttery RG, Teranishi R, Ling LC (1987a) Fresh tomato aroma volatiles: a quantitative study. *Journal of Agricultural and Food Chemistry* **35**, 540-544

Buttery RG, Ling LC, Light DM (1987b) Tomato leaf volatile aroma components. *Journal of Agricultural and Food Chemistry* **35**, 1039-1042

Chaintreau A (2001) Simultaneous distillation–extraction: from birth to maturity – review. *Flavour and Fragrance Journal* **16**, 136-148

Colby SM, Crock J, Dowdle-Rizzo B, Lemaux PG, Croteau R (1998) Germacrene C synthase from *Lycopersicon esculentum* cv. VFNT Cherry tomato: cDNA isolation, characterization, and bacterial expression of the multiple product sesquiterpene cyclase. *Proceedings of the National Academy of Science USA* **95**, 2216-2221

Coleman EC, Ho CT, Chang SS (1981) Isolation and identification of volatile compounds from baked potatoes. *Journal of Agricultural and Food Chemistry* **29**, 42-48

D'Alessandro M, Turlings TCJ (2006) Advances and challenges in the identification of volatiles that mediate interactions among plants and arthropods. *The Analyst* **131**, 24-32

Davies NW (1990) Gas chromatographic retention indices of monoterpenes and sesquiterpenes on methyl silicone and Carbowax 20M phases. *Journal of Chromatography* **503**, 1-24

de Lacy Costello BPJ, Evans P, Ewen RJ, Gunson HE, Jones PRH, Ratcliffe NM, Spencer-Phillips PTN (2001) Gas chromatography–mass spectrometry analyses of volatile organic compounds from potato tubers inoculated with *Phytophthora infestans* or *Fusarium coeruleum*. *Plant Pathology* **50**, 489-496

de Lacy Costello BPJ, Evans P, Ewen RJ, Gunson HE, Ratcliffe NM, Spencer-Phillips PTN (1999) Identification of volatiles generated by potato tubers (*Solanum tuberosum* CV: Maris Piper) infected by *Erwinia carotovora*, *Bacillus polymyxa* and *Arthrobacter* sp. *Plant Pathology* **48**, 345-351

Deng C, Zhang X, Zhu W, Qian J (2004) Gas chromatography-mass spectrometry with solid-phase microextraction method for determination of methyl salicylate and other volatile compounds in leaves of *Lycopersicon esculentum*. *Analytical and Bioanalytical Chemistry* **378**, 518-522

Dewulf J, Van Langenhove H (2002) Analysis of volatile organic compounds using gas chromatography. *Trends in Analytical Chemistry* **21**, 637-646

Dickens JC (2000) Orientation of Colorado potato beetle to natural and synthetic blends of volatiles emitted by potato plants. *Agricultural and Forest Entomology* **2**, 167-172

Dickens JC (2002) Behavioural responses of larvae of Colorado potato beetle, *Leptinotarsa decemlineata* (Coleoptera: Chrysomelidae), to host plant volatile blends attractive to adults. *Agricultural and Forest Entomology* **4**, 309-314

Duckham SC, Dodson AT, Bakker J, Ames JM (2001) Volatile flavour components of baked potato flesh. A comparison of eleven potato cultivars. *Nahrung/Food* **45**, 317-323

Duckham SC, Dodson AT, Bakker J, Ames JM (2002) Effect of cultivar and storage time on the volatile flavor components of baked potato. *Journal of Agricultural and Food Chemistry* **50**, 5640-5648

Dudareva N, Negre F, Nagegowda DA, Orlova I (2006) Plant volatiles: recent advances and future perspectives. *Critical Reviews in Plant Science* **25**, 417-440

Farag MA, Paré PW (2002) C_6-Green leaf volatiles trigger local and systemic VOC emissions in tomato. *Phytochemistry* **61**, 545-554

Faraldos JA, Wu S, Chappel J, Coates RM (2007) Conformational analysis of (+)-germacrene A by variable-temperature NMR and NOE spectroscopy. *Tetrahedron* **63**, 7733-7742

Figueiredo AC, Barroso JG, Pedro LG, Scheffer JJC (2008) Factors affecting secondary metabolite production in plants: volatile components and essential oils. *Flavour and Fragrance Journal* **23**, 213-226

Frary A, Doganlar S, Daunay MC (2007) Eggplant. In: Kole C (Ed) *Genome Mapping and Molecular Breeding in Plants. Vegetables*, Springer-Verlag, Berlin, pp 287-313

He L, Beesley TE (2005) Applications of enantiomeric gas chromatography: a review. *Journal of Liquid Chromatography & Related Technologies* **28**, 1075-1114

Hibbert DB (1997) Chemometric analysis of data from essential oils. In: Linskens HF, Jackson JF (Eds) *Plant Volatile Analysis*, Springer-Verlag, Berlin, pp 119-140

Joulain D, König W (1998) *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*, E.B.-Verlag, Hamburg, 658 pp

Kesselmeier J, Staudt M (1999) Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry* **33**, 23-88

Krumbein A, Auerswald H (1998) Characterization of aroma volatiles in tomatoes by sensory analyses. *Nahrung/Food* **42**, 395-399

Kushalappa AC, Lui LH, Chen LH, Lee B (2002) Volatile fingerprinting (SPME-GC-FID) to detect and discriminate diseases of potato tubers. *Plant Disease* **86**, 131-137

Labate JA, Grandillo S, Fulton T *et al.* (2007) Tomato. In: Kole C (Ed) *Genome Mapping and Molecular Breeding in Plants. Vegetables*, Springer-Verlag, Berlin, pp 1-125

Lockwood GB (2001) Techniques for gas chromatography of volatile terpenoids from a range of matrices. *Journal of Chromatography A* **936**, 23-31

Lui L, Vikram A, Hamzehzarghani H, Kushalappa AC (2005a) Discrimination of three fungal diseases of potato tubers based on volatile metabolic profiles developed using GC/MS. *Potato Research* **48**, 85-96

Lui LH, Vikram A, Abu-Nada Y, Kushalappa AC, Raghavan GSV, Al-Mughrabi K (2005b) Volatile metabolic profiling for discrimination of potato tubers inoculated with dry and soft rot pathogens. *American Journal of Potato Research* **82**, 1-8

Luque de Castro MD, Jiménez-Carmona MM, Fernández-Pérez V (1999) Towards more rational techniques for the isolation of valuable essential oils from plants. *Trends in Analytical Chemistry* **18**, 708-716

Lyew D, Gariepy Y, Raghavana GSV, Kushalappa AC (2001) Changes in volatile production during an infection of potatoes by *Erwinia carotovora*. *Food Research International* **34**, 807-813

MacLeod AJ, de Troconis NG (1983) Aroma volatiles of aubergine (*Solanum melongena*). *Phytochemistry* **22**, 2077-2079

Majcher MA, Jeleń HH (2005) Identification of potent odorants formed during the preparation of extruded potato snacks. *Journal of Agricultural and Food Chemistry* **53**, 6432-6437

Mandin O, Duckham SC, Ames JM (1999) Volatile compounds from potato-like model systems. *Journal of Agricultural and Food Chemistry* **47**, 2355-2359

Maneerat C, Hayata Y, Kozuka H, Sakamoto K, Osajima Y (2002) Application of the Porapak Q column extraction method for tomato flavor volatile analysis. *Journal of Agricultural and Food Chemistry* **50**, 3401-3404

Marriott PJ, Shellie R, Cornwell C (2001) Gas chromatographic technologies for the analysis of essential oils. *Journal of Chromatography A* **936**, 1-22

Martel JW, Alford AR, Dickens JC (2005) Laboratory and greenhouse evaluation of a synthetic host volatile attractant for Colorado potato beetle, *Leptinotarsa decemlineata* (Say). *Agricultural and Forest Entomology* **7**, 71-78

Martos PA, Saraullo A, Pawliszyn J (1997) Estimation of air/coating distribution coefficients for solid phase microextraction using retention indexes from linear temperature-programmed capillary gas chromatography. Application to the sampling and analysis of total petroleum hydrocarbons in air. *Analytical Chemistry* **69**, 402-408

Matsui K (2006) Green leaf volatiles: hydroperoxide lyase pathway of oxylipin metabolism. *Current Opinion in Plant Biology* **9**, 274-280

Merfort I (2002) Review of the analytical techniques for sesquiterpenes and sesquiterpene lactones. *Journal of Chromatography A* **967**, 115-130

Milner CP, Trengove RD, Bignell CM, Dunlop PJ (1997) Supercritical CO_2 extraction of the essential oils of eucalypts: a comparison with other methods. In: Linskens HF, Jackson JF (Eds) *Plant Volatile Analysis*, Springer-Verlag, Berlin, pp 141-158

Mutti B, Grosch W (1999) Potent odorants of boiled potatoes. *Nahrung/Food* **43**, 302-306

Ngumbi E, Eigenbrode SD, Bosque-Pérez NA, Ding H, Rodriguez A (2007) *Myzus persicae* is arrested more by blends than by individual compounds elevated in headspace of PLRV-infected potato. *Journal of Chemical Ecology* **33**, 1733-1747

Nojima S, Kiemle DJ, Webster FX, Roelofs WL (2004) Submicro scale NMR sample preparation for volatile chemicals. *Journal of Chemical Ecology* **30**, 2153-2161

Oruna-Concha MJ, Bakker J, Ames JM (2002) Comparison of the volatile components of eight cultivars of potato after microwave baking. *LWT – Food Science and Technology* **35**, 80-86

Oruna-Concha MJ, Duckham SC, Ames JM (2001) Comparison of the volatile compounds isolated from the skin and flesh of four cultivars of potato after baking. *Journal of Agricultural and Food Chemistry* **49**, 2414-2421

Otto M (1999) *Chemometrics: Statistics and Computer Application in Analytical Chemistry*, Wiley-VCH, Chichester, 314 pp

Pawliszyn J (1997) *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, New York, 247 pp

Petersen MA, Poll L, Larsen LM (1998) Comparison of volatiles in raw and boiled potatoes using a mild extraction technique combined with GC odour profiling and GC-MS. *Food Chemistry* **61**, 461-466

Petro-Turza M (1987) Flavor of tomato and tomato products. *Food Reviews International* **2**, 309-351

Pickett JA, Glinwood RT (2007) Chemical ecology. In: van Emden H, Harrington R (Eds) *Aphids as Crop Pests*, CAB International, Oxfordshire, UK, pp 235-260

Ruther J (2000) Retention index database for identification of general green leaf volatiles in plants by coupled capillary gas chromatography–mass spectrometry. *Journal of Chromatography A* **890**, 313-319

Sanches-Silva A, Lopez-Hernández J, Paseiro-Losada P (2005) Profiling flavor compounds of potato crisps during storage using solid-phase microextraction. *Journal of Chromatography A* **1064**, 239-245

Schütz S, Weissbecker B, Klein A, Hummel HE (1997) Host plant selection of the Colorado potato beetle as influenced by damage induced volatiles of the potato plant. *Naturwissenschaften* **84**, 212-217

Schütz S, Weißbecker B, Koch UT, Hummel HE (1999) Detection of volatiles released by diseased potato tubers using a biosensor on the basis of intact insect antennae. *Biosensors & Bioelectronics* **14**, 221-228

Shellie R, Marriott P, Morrison P (2001) Concepts and preliminary observations on the triple-dimensional analysis of complex volatile samples by using GC×GC-TOFMS. *Analytical Chemistry* **73**, 1336-1344

Silverstein RM, Webster FX (1998) *Spectrometric Identification of Organic Compounds*, Wiley, New York, pp 482

Song J, Fan L, Beaudry RM (1998) Application of solid phase microextraction and gas chromatography/time-of-flight mass spectrometry for rapid analysis of flavor volatiles in tomato and strawberry fruits. *Journal of Agricultural and Food Chemistry* **46**, 3721-3726

Stinson JA, Persaud KC, Bryning G (2006) Generic system for the detection of statutory potato pathogens. *Sensors and Actuators B* **116**, 100-106

Sucan MK, Russell GF (2001) Dynamic headspace analysis of fresh tomato juice. In: Rouseff RL, Cadwallader KR (Eds) *Headspace Analysis of Foods and Flavors: Theory and Practice, Advances in Experimental Medicine and Biology* (Vol 488), Kluwer Academic/Plenum Publishers, New York, pp 165-174

Szafranek B, Chrapkowska K, Pawińska M, Szafranek J (2005) Analysis of leaf surface sesquiterpenes in potato varieties. *Journal of Agricultural and Food Chemistry* **53**, 2817-2822

Szafranek B, Chrapkowska K, Waligóra D, Palavinskas R, Banach A, Szafranek J (2006) Leaf surface sesquiterpene alcohols of the potato (*Solanum tuberosum*) and their influence on Colorado beetle (*Leptinotarsa decemlineata* Say) feeding. *Journal of Agricultural and Food Chemistry* **54**, 7729-7734

Szafranek B, Maliński E, Szafranek J (1998) The sesquiterpene composition of leaf cuticular neutral lipids of ten Polish varieties of *Solanum tuberosum*. *Journal of the Science of Food and Agriculture* **76**, 588-592

Tandon KS, Baldwin EA, Shewfelt RL (2000) Aroma perception of individual volatile compounds in fresh tomatoes (*Lycopersicon esculentum*, Mill.) as affected by the medium of evaluation. *Postharvest Biology and Technology* **20**, 261-268

Thelen J, Harbinson J, Jansen R, Van Straten G, Posthumus MA, Woltering EJ, Bouwmeester HJ (2005) The sesquiterpene α-copaene is induced in tomato leaves infected by *Botrytis cinerea*. *Journal of Plant Interactions* **1**, 163-170

Tholl D, Boland W, Hansel A, Loreto F, Röse USR, Schnitzler JP (2006) Practical approaches to plant volatile analysis. *The Plant Journal* **45**, 540-560

Tholl D, Röse USR (2006) Detection and identification of floral scent compounds. In: Dudareva N, Pichersky E (Eds) *Biology of Floral Scent*, Taylor & Francis, pp 3-24

Tikunov Y, Lommen A, de Vos CHR, Verhoeven HA, Bino RJ, Hall RD, Bovy AG (2005) A novel approach for nontargeted data analysis for metabolomics. Large-scale profiling of tomato fruit volatiles. *Plant Physiology* **139**, 1125-1137

Vancanneyt G, Sanz C, Farmaki T, Paneque M, Ortego F, Castañera P, Sánchez-Serrano JJ (2001) Hydroperoxide lyase depletion in transgenic potato plants leads to an increase in aphid performance. *Proceedings of the National Academy of Sciences USA* **98**, 8139-8144

van den Boom CEM, van Beek TA, Posthumus MA, de Groot A, Dicke M (2004) Qualitative and quantitative variation among volatile profiles induced by *Tetranychus urticae* feeding on plants from various families. *Journal of Chemical Ecology* **30**, 69-89

Visser JH (1979) Electroantennogram responses of the Colorado beetle, *Leptinotarsa decemlineata*, to plant volatiles. *Entomologia Experimentalis et Applicata* **25**, 86-97

Visser JH, Avé DA (1978) General green leaf volatiles in the olfactory orientation of the Colorado beetle, *Leptinotarsa decemlineata*. *Entomologia Experimentalis et Applicata* **24**, 538-549

Visser JH, van Straten S, Maarse H (1979) Isolation and identification of volatiles in the foliage of potato, *Solanum tuberosum*, a host plant of the Colorado beetle, *Leptinotarsa decemlineata*. *Journal of Chemical Ecology* **5**, 13-25

Weingartner DP, Hooker WJ, Stevenson WR (2001) Diseases of potato (*Solanum tuberosum* L.). In: *Common Names of Plant Diseases*, *Plant Pathology Online*, The American Phytopathological Society, USA. Available online: http://www.apsnet.org/online/common/names/potato.asp

Weissbecker B, van Loon JJA, Posthumus MA, Bouwmeester HJ, Dicke M (2000) Identification of volatile potato sesquiterpenoids and their olfactory detection by the two-spotted stinkbug *Perillus bioculatus*. *Journal of Chemical Ecology* **26**, 1433-1445

Whitfield FB, Last JH (1991) Tuber vegetables. In: Maarse H (Ed) *Volatile Compounds in Foods and Beverages*, Dekker, New York, pp 222-231

Zabaras D, Wyllie SG (2001) Quantitative analysis of terpenoids in the gas phase using headspace solid-phase microextraction (HS-SPME). *Flavour and Fragrance Journal* **16**, 411-416