Quality Control of Commercially Available Essential Oils by Means of Raman Spectroscopy

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The essential oils of different spices and aroma plants were investigated fast and nondestructively by means of Raman spectroscopy. The main ingredients of these oils, mostly monoterpenes and phenylpropane derivatives, were identified. A hierarchical cluster analysis shows that the oils of the investigated plants cluster chemotaxonomically, which means according to their chemical composition and not according to their botanical degree of relationship. In addition, cross-sections of anise seeds were analyzed applying the Raman mapping technique to localize and investigate the distribution of the oil in situ.

INTRODUCTION

Essential oils have found wide fields of application today. In industry, they are used as ingredients in cosmetics, pharmaceutics (*1*), and food products due to their intense flavor. In addition, essential oils are commercially available; they are used, for example, to improve compartment air by fragrance lamps or airsprays. Because they are regarded as having a relaxing and inspiring effect on the body, they have also found applications as massage oils or bath additives in aroma therapies.

The extraction and production of essential oils is time-consuming; therefore, the isolated oils are often very expensive. The quality and the price of the essential oils depend on their qualitative and quantitative composition. Growing conditions (*2*) and harvesting time as well as the method of extraction (steam distillation, cold-pressing, or alcoholic extraction) can also affect the quality of the respective oils (*3−6*).

As the demand of essential oils has increased in the last years, the supply has escalated as well. So, essential oils can be purchased nearly everywhere, for example, at pharmacies, drugstores, or even local market places.

With an increasing number of providers, the need for product control has also increased. Therefore, fast methods for the quality control of essential oils are necessary. Up to now, the standard method used for this purpose has been gas chromatography analysis combined with mass spectroscopy (GC/MS).

However, Raman spectroscopy has been shown to be a powerful tool for the analysis of the chemical composition of various biological materials (*7−9*), including medicinal and spice plants (*10−20*). Rösch et al. established micro-Raman spectroscopy for the characterization and comparison of extracted essential oils also applying the SERS technique (*21*).

The chemical composition of *Laminaceae* species was characterized by Daferera et al. applying Fourier transform Raman spectroscopy (*22*). With deconvolution analysis, they developed a method to simultaneously quantify the major components of the essential oils of oregano and thyme (*23*). Direct in situ measurements of the essential oils in fennel seeds were performed by Strehle et al. (*20, 24*).

In the present article, we investigate the essential oil of anise in situ in the anise seed. With Raman mapping experiments on anise cross-sections, we show the local distribution of the essential oil in the respective section of the seed.

In addition micro-Raman spectra of a number of commercially available essential oils were measured and compared with spectra of the pure terpenes and aromatic standards in order to analyze their chemical composition. We succeeded in the characterization of the main components of the investigated oils. Applying chemometrical methods, the spectra of the essential oils of different botanical families were clustered according to their spectral similarities. Combining Raman spectroscopy with hierarchical cluster analysis, we demonstrate a very fast method of quality control in comparison to standard GC/MS techniques where a time-consuming sample preparation is necessary. Regarding the need for such fast analysis to investigate the chemical composition and the purity of different essential oils, this seems to be a promising method.

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MATERIALS AND METHODS

Samples. The essential oils investigated were purchased at a local pharmacy. They were labeled as 100% natural products. Pure standard substances were purchased (Sigma-Aldrich, München, Germany, and Roth, Karlsruhe, Germany) and used without further purification. The anise seeds were obtained from the Federal Center for Breeding Research on Cultivated Plants (BAZ) in Quedlinburg, Germany. For Raman mapping experiments, cross-sections of anise fruits (*Pimpinella anisum*) were prepared on a microscope slide, embedded in water, and covered with a cover slip.

Raman Spectroscopy. The Raman spectra were recorded with a micro-Raman setup (LabRam invers, Jobin-Yvon Horiba). The spectrometer had a focal length of 800 mm and was equipped with a 300 lines/mm grating. For the standard substances and the isolated oils, the 830 nm line of a diode laser (Sacher Lasertechnik Group, TEC100) with a laser power of 4 mW incident on the sample was selected. The scattered light was detected by a CCD camera operating at 220 K.

For the Raman mapping experiments, the 532 nm line of a frequency-doubled Nd:YAG (Coherent Compass) with a laser power of 10 mW was focused onto the samples applying an Olympus MPL 50× objective. For the spatially resolved measurements, an *x*/*y* motorized stage (Merzhäuser) with a minimal step size of 0.1 μm was used. The spot size of the laser was approximately 1 μm, and the applied scanning step size was 0.5 μm with an integration time of 3 s at each position.

GC/MS. The measurements were done with a GC/MS combination SATURN II from Varian Inc. The separation was performed under the following conditions: column DBWAX (30 m × 0.32 mm ID, 25 μm (J&W)), carrier helium (48 cm/s, measured at 70 °C), injector (220 °C), oven (5 min at 70 °C and 70−210 °C at 10 °C/min), transfer line (180 °C).

Density Functional Theory (DFT) Calculations. DFT calculations were performed with the exchange functional of Becke in combination with the correlation functional of Lee, Yang, and Parr (B3LYP) and the 6-31G(d) split valence basis set using Gaussian98 (*25*) in order to simulate the Raman spectrum of carotol. Vibrational frequencies were scaled with a factor of 0.9614 (*26*).

Hierarchical Cluster Analysis. The hierarchical cluster analysis was performed with the program OPUS IDENT from Bruker. The spectra were all baseline corrected and interpolated before further treatment.

RESULTS AND DISCUSSION

In Situ Raman Mapping Experiments on Cross-Sections of Anise Seeds. With Raman spectroscopy, direct in situ measurements on plant cross-sections are possible (*24, 27, 28*). So, the essential oils can be investigated directly in the plants without further extraction or isolation procedures. A Raman mapping experiment was performed on a cross-section of an anise seed. **Figure 1A** shows a microscopic image of the cross-section in the endosperm region (50×). The square indicates the scanned region.

In the endosperm tissue, the fatty oils are accumulated. In intact seeds, the essential oils are localized in so-called schizogenic excretory canals in the pericarp region, which is the outermost tissue layer of the seed. When the fruit is cut with the microtome in order to prepare a cross-section, the excretory canals are broached and the essential oil leaks out. As the essential oil is highly soluble in the fatty oils of the endosperm, it can also be found in the endosperm region, where it accumulates after a few hours when a two-dimensional Raman mapping experiment is performed.

Single point spectra of the cross-sections from the points marked in the microscopic image (**Figure 1A**) are shown in **Figure 2**. Spectrum A was taken directly in an oil droplet. Here, one can see bands that are due to anethole, the main component of the essential oil of anise (see **Figures 3A** and **4A**). The peak at 1436 cm^{-1} results from the fatty oil components. This band can be assigned to the CH$_2$ deformation modes of the lipids (*29*).
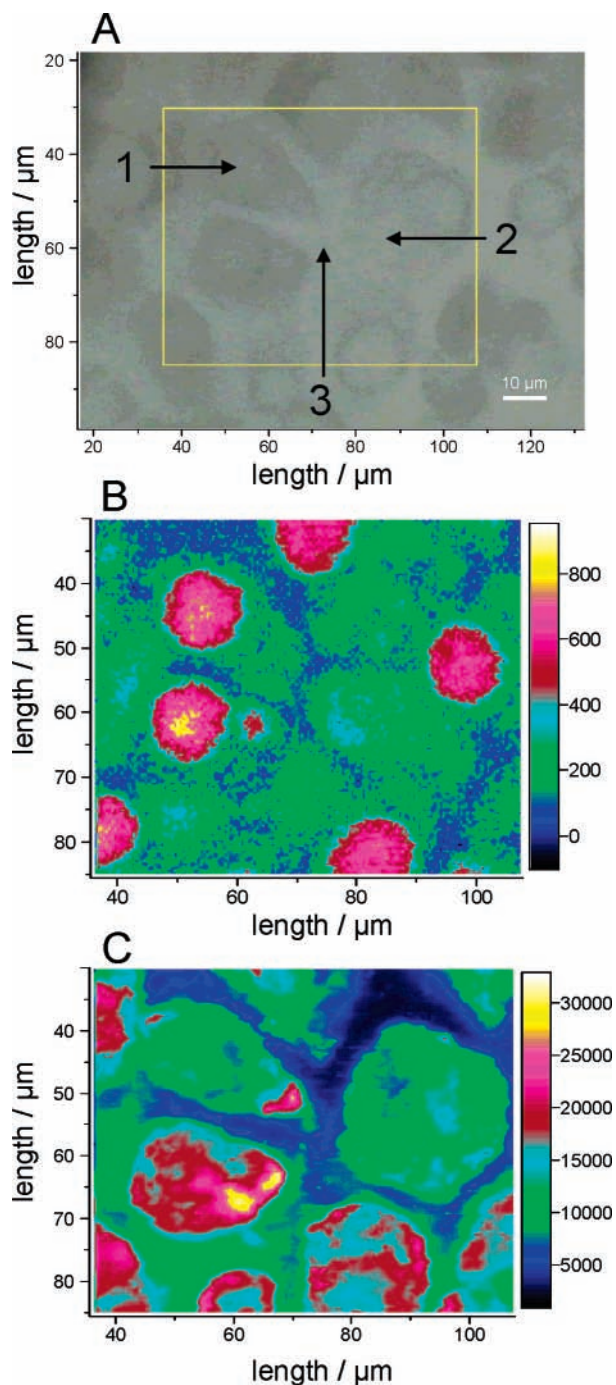

Figure 1. Raman mapping in the endosperm region of an anise seed. (**A**) Microscopic image of the scanned region. (**B**) False color plot representing the spatial distribution of the intensity of the wavenumber area between 1573 and 1618 cm^{-1} with baseline subtraction. (**C**) False color plot representing the intensity of the same wavenumber region without baseline correction.

Spectrum B was taken in the cell of the endosperm region, and spectrum C was taken in the cell walls. They differ due to the increased fluorescence of the cells as compared to the cell walls.

The false color plot, which is depicted in **Figure 1B**, indicates the spatial distribution of the peak intensity in the wavenumber region between 1574 and 1618 cm^{-1}. This peak can be regarded as a marker band for the anethole concentration (*6*), which is the main component of the essential oil of anise (see **Figure 1A**). The more intense band at a wavenumber position around
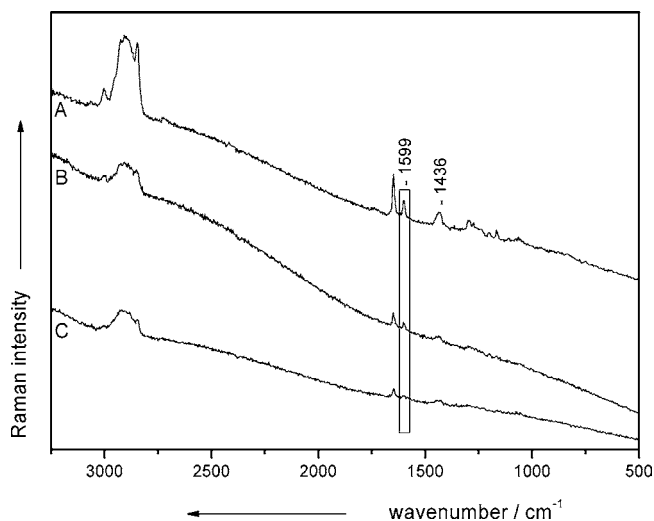
Figure 2. Single point spectra of the scanned region. (**A**) Spectrum taken at point 1 in an oil droplet. (**B**) Spectrum taken in the cell at point 2. (**C**) Spectrum of the cell wall taken at point 3. The marked box depicts the wavenumber region, which was used to calculate the false color plots in **Figure 1**.

1653 cm^{-1} was not used as lipids and fatty acids give signals in this area as well. Before the false color plot was calculated, a baseline correction was performed at each point of measurement.

In **Figure 1C**, the intensity of the same peak area is plotted without a previously performed baseline correction. One can clearly see the single cells of the plant tissue due to the decreased fluorescence of the cell walls (blue region).

Essential Oils and Their Chemotaxonomic Characterization. Besides these mapping experiments, the chemical compositions of commercially available, isolated essential oils were investigated with Raman spectroscopy. This is a very fast method, which provides the possibility to evaluate unknown oils according to their main ingredients. Therefore, a fast quality and purity control of such commercially available oils is feasible. In **Figure 3**, Raman spectra of common essential oils purchased at the local pharmacy mainly from plants belonging to the *Apiaceae* familiy like anise (*Pimpinella anisum*, **A**), fennel (*Foenicum vulgare*, **B**), cumin (*Cuminum cyminum*, **C**), dill (*Anethum graveolens*, **D**), caraway (*Carum carvi*, **E**), coriander (*Coriandrum sativum*, **F**) and carrot seed (*Daucus carota*, **I**) in comparison to lavender (*Lavandula angustifolia*, **G**) and spike lavender (*Lavandula spica*, **H**), which belong to the botanical family of *Laminaceae*, are shown.

They differ strongly due to their various chemical compositions. The spectrum of each oil is a superposition of the spectra of the main components of the respective oils, which where also recorded and are shown in **Figure 4**. Molecular structures of the representative terpenes are depicted in **Figure 5**.

The spectra of the essential oils of anise and fennel (see **Figure 3A,B**) are very similar and mainly dominated by bands that are characteristic for anethole (**Figure 4A**), which is the main component of both oils. Bands at 631, 837, 1168, 1203, and 1604 cm^{-1} result from vibrations of the para-substituted benzene ring of anethole (*30*). Via GC/MS analysis (see **Table 1**), it could be proven that the anethole is the main component (89.3%) of the essential oil of anise. Other components of the essential oil of anise are 3.1% estragole and 2.6% limonene beyond the detection limit of Raman spectroscopy but can be detected with the more sensitive GC/MS technique.

The composition of the essential oil of fennel is dominated by 37.8% anethole and 24.1% fenchone (see **Table 1**). Besides the characteristic bands originating from anethole, the additional appearance of bands at 589, 653, and 880 cm^{-1} in the spectra of fennel oil can be assigned to the terpene fenchone (**Figure 4B**). A peak at 661 cm^{-1} is predominant in the spectra of α-pinene (**Figure 4C**) and can be regarded as a marker band, which results from a kind of ring briefing vibration of the
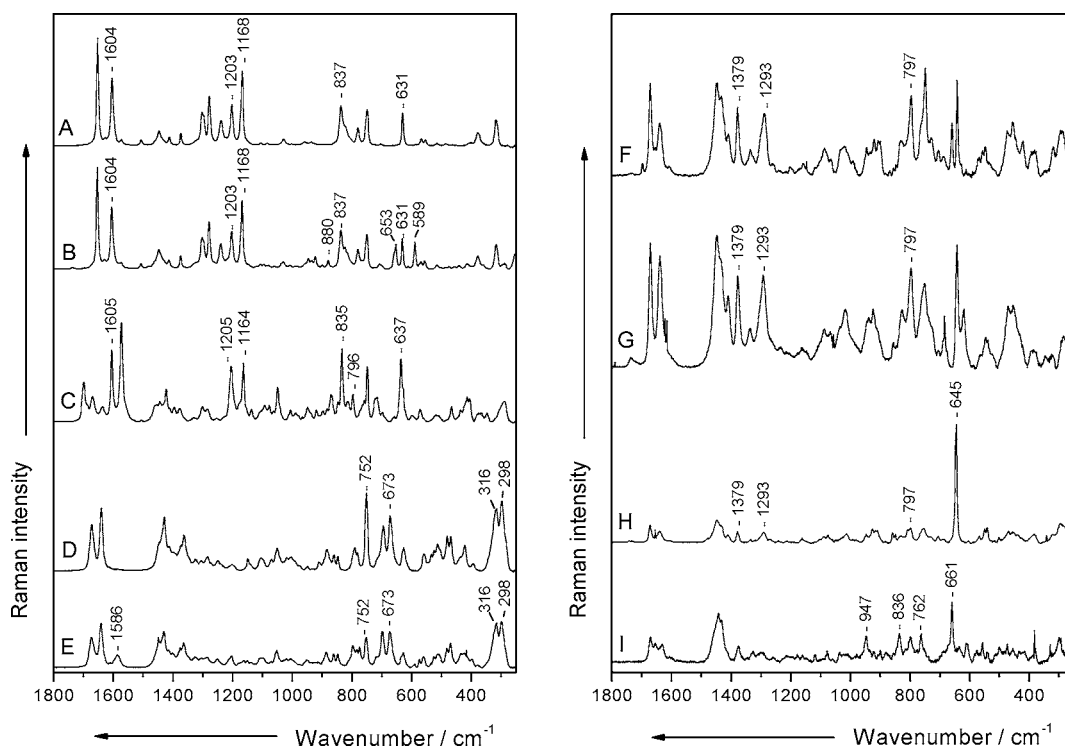

Figure 3. Micro-Raman spectra of the essential oils of anise (**A**), fennel (**B**), cumin (**C**), dillweed (**D**), caraway (**E**), coriander (**F**), lavender (**G**), spike lavender (**H**), and carrot seed (**I**).
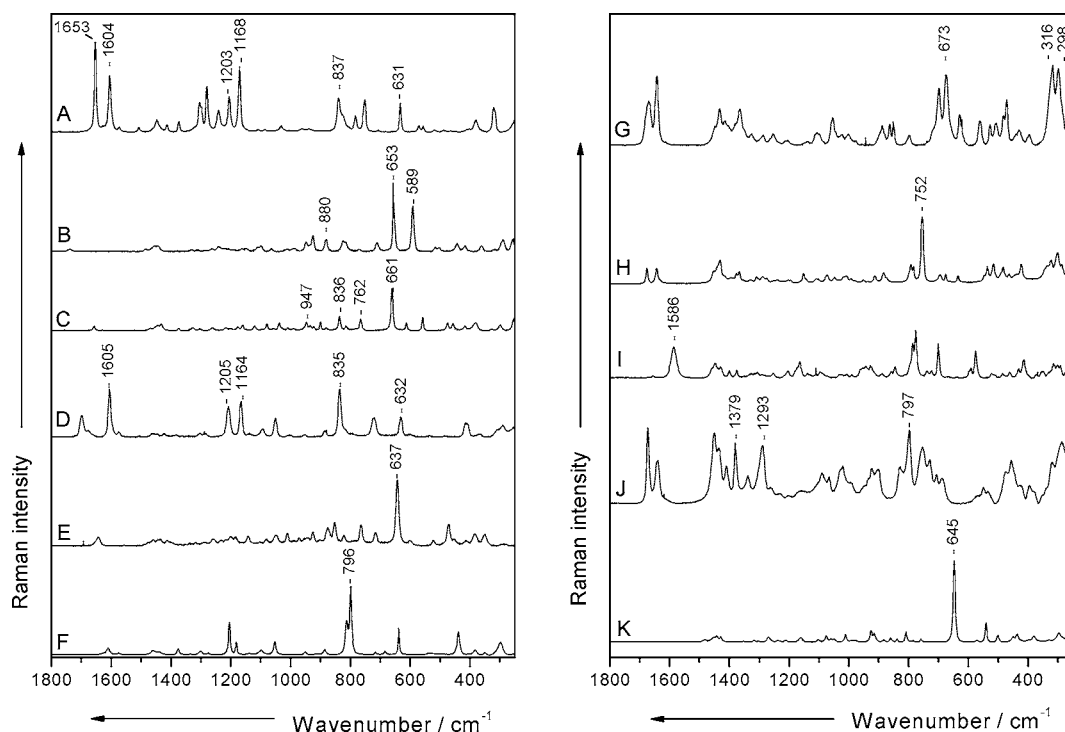
Figure 4. Micro-Raman spectra of selected, pure terpenes and aromatic compounds of the discussed essential oils anethole (**A**), fenchone (**B**), α-pinene (**C**), cuminaldehyde (**D**), β-pinene (**E**), *p*-cymene (**F**), carvone (**G**), limonene (**H**), α-pellandrene (**I**), linalool (**J**), and eucalyptol (**K**).
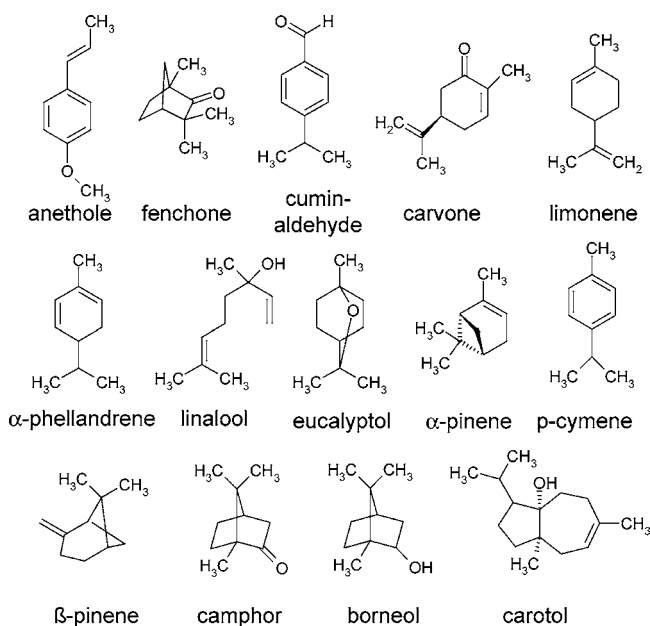
Figure 5. Molecular structures of selected terpenes.

Table 1. Main Components of the Essential Oils Measured by GC (Only Components >2% GC Are Listed as They Could Be Identified)

essential oil	composition (%)
anise	85.0 anethole, 3.1 estragole, and 2.6 limonene
fennel	37.8 anethole, 24.1 fenchone, 9.7 α-pinene, 6.5 anisketone, 6.1 anisaldehyde, 4.2 *p*-cymene, 2.7 estragole, and 2.3 limonene
cumin	27.3 cuminaldehyde, 18.6 *p*-cymene, 15.5 β-pinene, 15.1 γ-terpinene, 6.2 safranal, 4.2 myrtenal, and 3.2 alloaromadendrene
dillweed	42.6 carvone, 20.0 limonene, 15.4 α-phellandrene, 8.4 dill ether, 4.5 *p*-cymene, and 2.8 β-phellandrene
caraway	56.0 limonene, 38.2 carvone, and 2.8 α-phellandrene
coriander	71.0 linalool, 5.7 camphor, 4.5 γ-terpinene, 4.0 geraniol acetate, 3.0 α-pinene, 2.3 limonene, and 2.1 geraniol
lavender	38.1 linalool, 32.8 linalyl acetat, 4.5 eucalyptol, 3.2 camphor, 2.4 borneol, and 2.2 *cis*-ocimene
spike lavender	47.6 linalool, 19.4 eucalyptol, 14.8 camphor, 4.4 linalyl acetate, and 2.1 borneol
carrot seed	21.0 carotol, 16.5 α-pinene, 6.7 sabinene, 3.8 β-pinene, 3.5 geraniol acetate, 3.1 myrcene, 2.8 geraniol, and 2.2 limonene

bicyclus (see molecular structures in **Figure 5**) (*31*). GC/MS analysis revealed that in the available essential oil of fennel this terpene is present at 9.7%. Looking at the band shape of the peak at a wavenumber position of 653 cm⁻¹ in the spectra of the essential oil of fennel, one can assume that this peak is a superposition of the fenchone band and the α-pinene marker band.

The Raman spectrum of the essential oil of cumin (**Figure 3C**) exhibit few bands, which are characteristic for para-substituted benzene derivatives at 632 (overlapped), 835, 1164, 1205, and 1605 cm⁻¹ (*30*). In comparison to the one of anethole in the spectra of anise and fennel oil, they are slightly shifted as in the oil of cumin; these bands are due to the presence of a different para-substituted aromatic compound, namely, cumi-

naldehyde (**Figure 4D**). Besides cuminaldehyde (27.3%), which is the main component, GC/MS analysis showed that *p*-cymene (18.6%), β-pinene (15.5%), and γ-terpinene (15.1%) are also present in the oil mixture. The characteristic marker band in the spectrum of β-pinene (**Figure 4E**) is at 637 cm⁻¹ and can be identified in the spectrum of the essential oil of cumin (**Figure 3C**) where this band is overlapped with the very weak peak at 632 cm⁻¹ of the cuminaldehyde. This band again originates from a kind of ring breathing mode of the bicyclic system of the terpene (*31*). The small peak at 796 cm⁻¹ in the oil spectrum might be due to the ring breathing mode of the aromatic compound *p*-cymene (see **Figure 4F**) (*29*). In the wavenumber region of the aliphatic C=C stretching modes
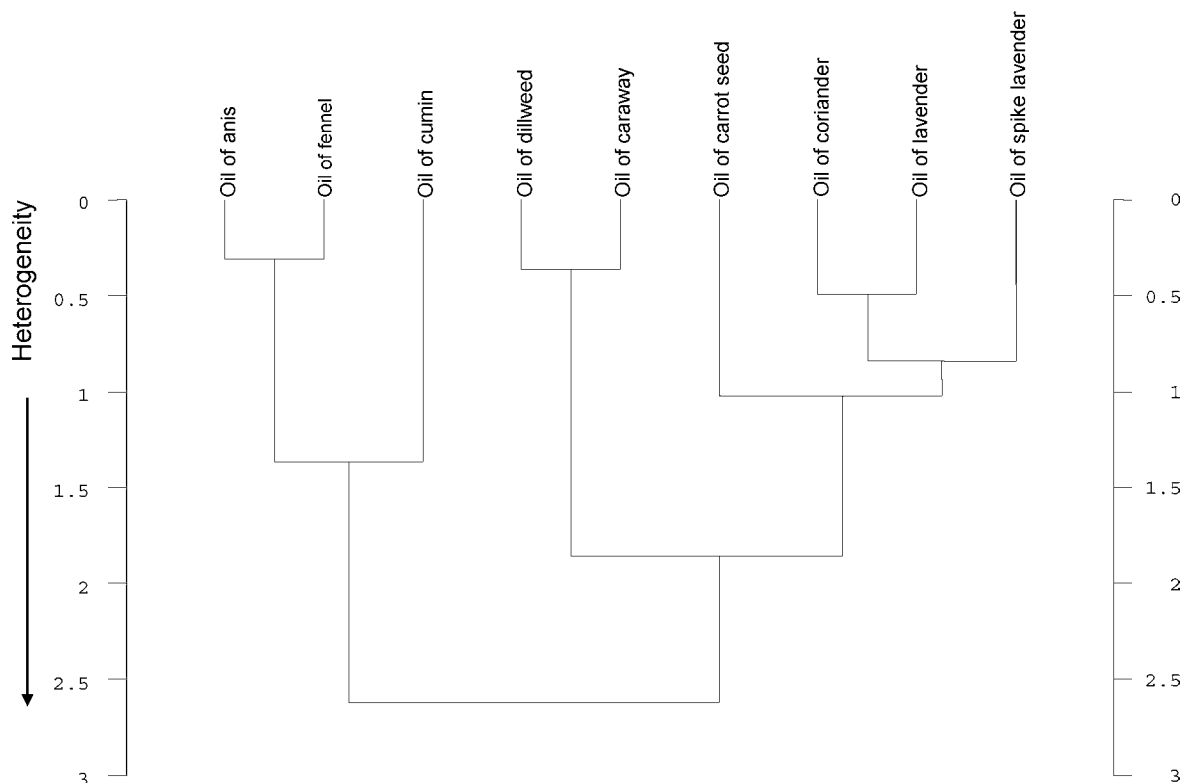
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Figure 6. Cluster analysis (Ward's algorithm) based on the micro-Raman spectra (spectral range, 300–2000 cm^{-1}) of the essential oils shown in **Figure 3**.

(1620–1700 cm^{-1}), one can see a superposition of different compounds, as besides cuminaldehyde the other trepenes have no aromatic system.

The chemical compositions of dillweed and caraway oil are very similar (see **Figure 3D,E**). As compared to the essential oils mentioned above, the spectra of these oils as well as the following ones exhibit no peaks, which could be assigned to an aromatic benzene ring as the two main components of both oils are the nonaromatic terpenes limonene and carvone. In the oil of caraway, these two components comprise nearly 95% of all ingredients (see **Table 1**). The peaks at a wavenumber position of 298, 316, and 673 cm^{-1} are very significant for the terpene carvone (**Figure 4G**), whereas the band at 752 cm^{-1} can be assigned to the terpene limonene (**Figure 4H**). When comparing the relative intensities of the bands at 752 and 673 cm^{-1} in the spectra of those two essential oils, one can see that in the oil of caraway the content of limonene is increased as compared to the carvone content. GC/MS analysis supported this observation as the ratio limonene/carvone for caraway is 1.46 as compared to 0.47 for the oil of dillweed. In the Raman spectrum of dillweed oil, there is an additional band at a wavenumber position of 1586 cm^{-1} resulting from an increased content of α-phellandrene (see **Figure 4I**).

When looking at the spectra of coriander, lavender, and spike lavender (see **Figure 3F–H**), they resemble each other. Especially the spectra of the oil of coriander and lavender are very similar. All of these three spectra show bands at wavenumber positions around 1379, 1293, and 797 cm^{-1}, which are characteristic for the terpene linalool (**Figure 4H**). The spike lavender oil spectrum (**Figure 3H**) is dominated by one significant peak at 645 cm^{-1}. This peak is a superposition of bands originating from the different terpenes eucalyptol, camphor, and borneol, which GC/MS analysis revealed to be present in the essential oil of spike lavender. Raman spectra of the

above-mentioned terpenes show all one characteristic band at this wavenumber position. In **Figure 4J**, the Raman spectrum of eucalyptol is exemplarily depicted showing the characteristic feature band at 645 cm (1) resulting from a kind of ring breathing mode of the bicyclic ring system (19). When looking at the molecular structures of these terpenes, they show structural similarities as they all consist of a bicyclic ring system (see **Figure 5**). In the aliphatic C=C stretching region, one can see again a superposition showing that different components of the respective essential oil contribute to these bands.

The Raman spectrum of the essential oil of carrot seed is dominated by bands originating from the monoterpene α-pinene. Peaks at wavenumber positions at 661, 765, 836, and 947 cm^{-1} result from this terpene (see **Figure 4D**). GC/MS analysis revealed that besides α-pinene (16.5%), carotol (21.0%) is the main component of the essential oil. As carotol was not commercially available, DFT calculations [B3LYP/6-31G(d)] were performed in order to simulate the Raman spectrum of carotol (for the molecular structure, see **Figure 5**). With the help of these calculations, the bands at 1671, 1443, 1374, and 610 cm^{-1} could be clearly assigned to this bicyclic compound. So, nearly all characteristic features in the Raman spectrum of the essential oil of carrot could be attributed. GC/MS analysis showed that besides these two main components there are a lot of minor components resulting in small contributions to the Raman spectrum of the respective essential oil. An assignment of bands originating from contributions with less than 8% is difficult and cannot be performed unambiguously. For trace analysis, the GC/MS method is the more appropriate technique, but with the purpose of fast quality control, Raman spectroscopy can be applied successfully.

A deeper insight and a more objective one into the degree of relationship between the spectra of diverse oils is possible when applying chemometrical methods. Up to now, few groups have

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analyzed Raman data with chemometrical methods on the level of different species of one genus (*31*−*33*).

In the following, a hierarchical cluster analysis is performed on representative Raman spectra of the different isolated essential oils belonging to two different botanical families. All of the spectra are baseline-corrected, smoothed, and interpolated before further processing.

In **Figure 6**, a dendrogram of the cluster analysis performed with the standard method and applying the Ward's algorithm is depicted. The presented chemometrical results correlate very well with the chemical compositions of the different oils, which were measured with standard GC/MS methods (see **Table 1**) for reference. There are two main clusters containing the oils of anise, fennel, and cumin on the one hand and the oils of dillweed, caraway, carrot seed, coriander, lavender, and spike lavender on the other hand. The main ingredients of the oils of the first cluster are aromatic compounds (anethole and cuminaldehyde) whereas for the second cluster the essential oils consist mainly of monoterpenes (limonene, carvone, α-phellandrene, linalool, eucalyptol, and α-phellandrene). As the spectrum of each oil is a superposition of the main compounds and as the similarity between the different oil spectra is taken as the basis for the cluster analysis, this fact is not striking. When looking at the relationship between the oils of coriander, lavender, and spike lavender, one can see that the chemical composition of lavender has more similarities with the one of coriander than with spike lavender although the latter are botanically more related to each other. The spectrum of spike lavender is mainly dominated by eucalyptol (19.4%), which has a large Raman cross-section. In the essential oil of lavender, eucalyptol is only present at a level of 4.5%; therefore, the eucalyptol marker band does not dominate the Raman spectrum.

To summarize, one can say that Raman spectroscopy in combination with chemometrical methods is a unique tool for the chemical classification of unknown essential oil samples and therefore provides a very fast tool for the quality control of commercially available oils. In comparison to the standard reference GC/MS method, the above presented method is nondestructive and very fast as nearly no sample preparation and pretreatment are required. So, one has to deliberate if a very fast but rough characterization via Raman spectroscopy is sufficient or if a more detailed but time-consuming GC/MS analysis is necessary.

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