RAMAN SPECTROSCOPIC INVESTIGATION OF FENNEL SEED USING RAMAN MAPPING

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Abstract: This contribution reports on a Raman spectroscopic study on the essential oil occurring in fennel. Cross sections of fennel seed were investigated by use of Raman spectroscopy and Raman mapping to localize the essential oil and to analyse its chemical composition directly in the plant.

Essential oils are one of the most valuable natural products. The price of special essential oils that can be purchased on the marked strongly depends on the quality of the product. The quality which depends on the quantitative and qualitative variation of different monoterpenes varies with respect of the origin and the harvesting period. [1, 2]

Raman spectroscopy can be applied as a fast and easy method to analyze the essential oils. [3] Since some essential oils are very sensitive towards chemical modification during extraction an analytical method with little or even no sample preparation would be preferable. Therefore an analysis method which can be performed directly inside or at the surface of plants provides more reliable information about the quality of essential oil plants. Micro-Raman spectroscopy reveals information about the chemical composition of the oils and allows a spatial resolution down to 1 µm. This method is extremely suited to measure directly e. g. inside glandular trichomes of mint plants. [4] With such measurements not only information about the oil quality can be achieved but also chemotaxonomic classification of the plants can be performed. Combining a controllable xy-mount with the micro-Raman setup so-called Raman mappings can be performed. Here a two- or three-dimensional distribution of substances can be achieved. [5]

The fennel seeds (*Foeniculum vulgare* var. dulce MILL.) usually contain 2 – 6 % essential oil. The essential oils of fennel seeds consist mainly of anethole (85 – 90 %) and an almost negligible amount of pinene, limonene, dipentene and phellandrene, whereas the fatty oils contain unsaturated fatty acid esters as fat storage. Fennel oil is used for medical purposes; it has for example therapeutic and expectorant application. We show that it is possible to localize both the essential and fatty oils directly in fennel seeds by means of Raman mapping.

Figure 1 shows a Raman spectrum of sweet fennel oil (directly measured in fennel seed) as well as Raman spectra of the pure standard substances anethole and fenchone. Comparing the spectra of fennel (a) and anethole (b) shows that all prominent Raman bands of anethole can be found in the essential oil of fennel. No characteristic Raman bands of fenchone (c) are observed.

Raman mapping was performed to obtain the distribution of the oil in a cross section of the fennel seed. The scans were done in two different regions of the seed; the endosperm that is located around the embryo and the pericarp that is located around the endosperm encasing the seed. The endosperm is rich in unsaturated lipids and protein bodies. As carbohydrate storage material mannan is accumulated at the cell walls of the endosperm. All these components can be located by means of Raman mapping. The pericarp contains excretory channels were the essential oil is

located. However, also in the cells of the pericarp oil droplets that contain essential oil rich in anethole can be found.

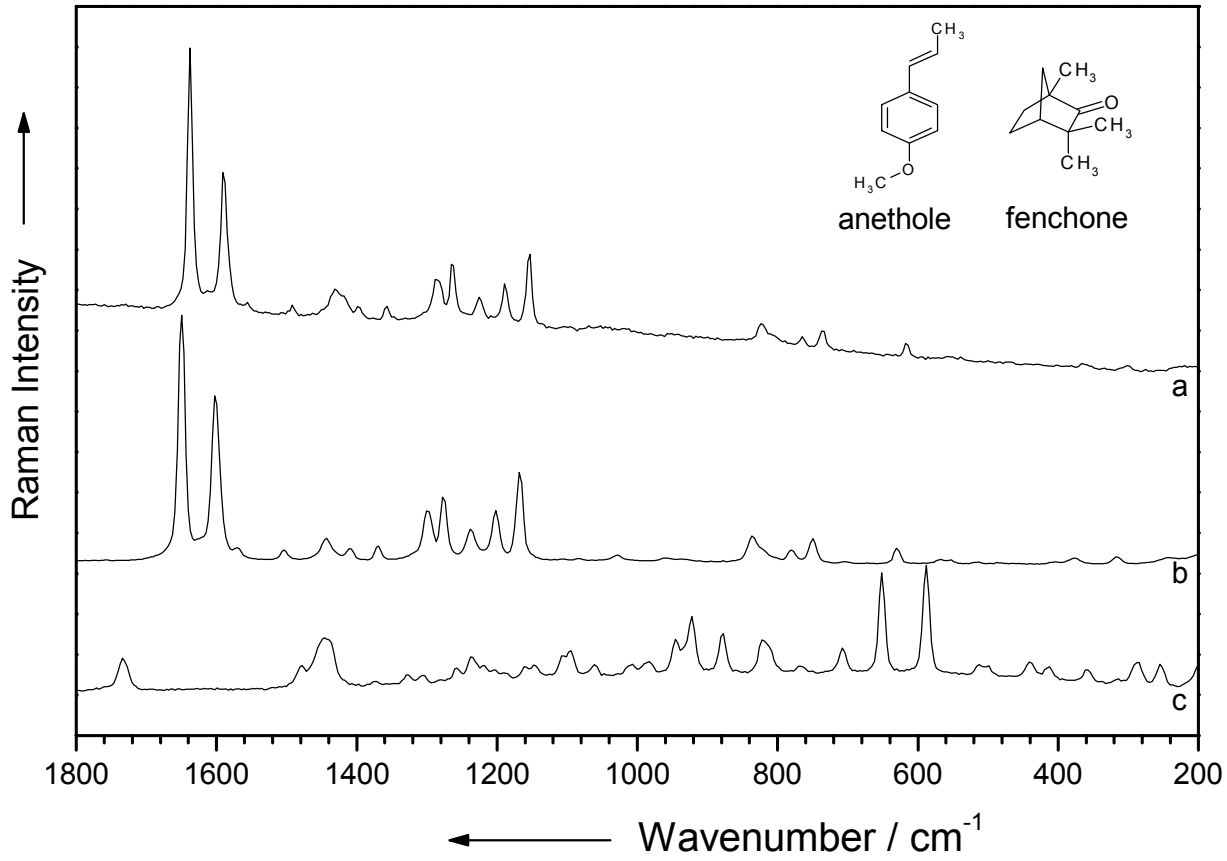

Fig. 1. Raman spectra of fennel oil (a) directly measured in fennel seed, the main component of the essential oil anethole (b) and fenchone (c).

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