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Thermo-oxidative decomposition of lime, bergamot and cardamom essential oils

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ABSTRACT

The thermal decomposition of three essential oils has been studied at 300 °C, using a 9% oxygen in nitrogen atmosphere, to mimic the thermal environment of flavours under low-temperature tobacco heating conditions. The starting compositions of the lime, bergamot and cardamom oils were determined by gas chromatography/mass spectrometry (GC/MS). The thermo-oxidative decomposition was evaluated by applying on-line pyrolysis-GC/MS. The main constituents of the oils studied were cyclic and linear monoterpenoids; however, the relative intensities of these components were characteristically different between oils. Lime oil was dominated by monoterpene hydrocarbons, while the other citrus oil, bergamot oil contained in addition a significant number of esters and alcohols. Oxygen-containing monoterpenoids were the dominant constituents of cardamom oil. The relative proportion of the constituents of all three essential oil samples significantly altered during oxidative pyrolysis at 300 °C. The strained rings of bicyclic monoterpenes (pinenes, sabinene, and thujene) underwent scission, resulting in the formation of monocyclic monoterpenes (limonene etc.). Both linear and cyclic terpene acetates decomposed via elimination of acetic acid, so linalyl acetate produced myrcene and ocimene, while terpinyl acetate formed mostly limonene and terpinolene. The relative intensities of linalool and eucalyptol were reduced during pyrolysis, which can be explained by dehydration reactions resulting in the formation of myrcene and ocimene, or limonene and terpinolene, respectively. The chemical reactions that occurred were explained by bond splitting and intramolecular rearrangement mechanisms, with oxygen playing a role in the initiation processes.

1. Introduction

Essential oils are natural extracts, comprising complex mixtures of a number of individual aroma compounds, and are used in flavouring and perfumery [1,2]. For commercial applications, quality control is very important, since the proportions of constituents show significant variation, depending on the harvesting time of the extracted plant genotypes, extraction technique, storage, etc. Flavour evaluation is normally carried out by organoleptic analysis, while the chemical analysis of essential oils is almost always performed by chromatographic methods.

Lime essential oil is principally used as a fragrance in cosmetics, and as a flavouring agent in food, soft drinks and medicine. Lime also possesses antioxidant properties [3,4]. The commercial oils are obtained by cold pressing from the peel or by distillation from leaves. The chemical compositions of the essential oils originating from the leaves, peel, flower and fruit of various lemon and lime samples have been widely studied [5–8]. Expressed lime oil, which is obtained from the peel of the fruit, has high amounts of bicyclic hydrocarbons and a relatively high amount of aldehydes, especially citral [9]. Lime oil distilled from crushed lime fruit is rich in terpene alcohols and low in aldehydes and bicyclic hydrocarbons, compared to the expressed lime oil [5]. During the production of distilled lime oil, acid-catalysed reactions of bicyclic hydrocarbons occur, resulting in an increase of terpene alcohols, especially α-terpineol. The terpene aldehydes are almost completely lost during distillation [9].

Bergamot essential oil is another citrus oil. It is extracted from the peel of bergamot fruit, generally by cold-pressing. The bergamot tree is cultivated mainly for its valuable oil, which constitutes an important

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raw material for the cosmetic (e.g., perfume) and food (e.g., Earl Grey tea) industries. Bergamot oil consists of a mixture of monoterpene and sesquiterpene hydrocarbons, oxygenated derivatives and involatile residues [10–13]. The involatile fraction contains coumarins and furocoumarins, which possess photosensitizing activity [11]. The main constituents of bergamot oil are limonene, linalool and linalyl acetate. The quality of bergamot oil is characterised by linalool/linalyl acetate ratio and the summed amount of linalool and linalyl acetate. Genuine bergamot oils contain principally (-)-linalool, with (+)-linalool present only as a trace constituent, and not exceeding 0.5% of the total linalool content [11].

Cardamom seeds are used as spices due to their strong, resinous aroma and sweet flavour. Cardamom essential oil belongs to the so-called fruit oils, which are extracted from the seeds of fruit. Cardamom seed oil possesses antioxidant properties [14–16], and it is used as a flavouring agent in foods, mouth freshener etc. The major components in the oil are terpinyl acetate and eucalyptol [15]; the ratio of these compounds determines the quality of the oil. The composition of the oil is highly dependent on the genotypes, maturity and storage [17]. Loss of aroma compounds occurs during processing of the oil, and microencapsulation is sometimes used for improving the quality of products [18].

The flavour components of essential oils are known to be susceptible to oxidative deterioration during storage. It is known that terpene alcohols (e.g., geraniol) are prone to chemical oxidation upon exposure to air, with the formation of oxidized derivatives, such as hydroperoxides, monoepoxides, diepoxides and aldehydes [19]. A thermo-oxidation study [20] performed in air at 80 °C proved that nerol, a short-chain isoprenoid with a double bond in the *cis* (*Z*) configuration, was oxidatively more stable than its *trans* (*E*) isomer, geraniol. Linalool and limonene can autoxidize to form primarily hydroperoxides, which are potential allergens [21]. Linalyl acetate was seen to be prone to oxidation on exposure to air, with hydroperoxides, an epoxide and an alcohol being formed [22].

A simulated degradation study showed that among the components of lemon oil, β- and α-pinene, and γ-terpinene were the most susceptible to oxidation using Cu catalysts [23]. Hydrolysis of esters to alcohols and acids can occur during steam distillation [12]. An example of this is cardamom oil, which is rich in α-terpinyl acetate. Comparison of the cold pressed and steam distilled bergamot oils revealed [10,12] that the quality of the hydrodistilled bergamot fruit oil is lower due to the decomposition of linalyl acetate and the isomerization of linalool.

Another application of natural and synthetic flavouring compounds is during tobacco processing used for cigarettes [24–26] and more recently for low-temperature heated tobacco products [27]. Here analytical pyrolysis can be performed to assess the theoretical thermal stability of the selected flavour compounds. The information on thermal decomposition reactions and reaction products gives important insight into patterns in thermal stability. Also, it can be used to screen for high risk flavours, and therefore reduce the number of candidates taken forwards for aerosol emission measurements, and the other toxicological assessments performed before a flavour is used in a product [28].

In a number of studies, the oxidation processes reported in the literature were performed under accelerated or simulated conditions on pure or single-sourced raw materials, or concentrated essential oils and may not reflect the situation under real use and storage conditions. Previously, we studied the pyrolysis of single flavour compounds in inert and oxidative atmospheres [27] and established that the majority of the products were the same in both atmospheres; but the presence of oxygen promoted most of the reactions. The goal of this study is to evaluate changes in the composition of essential oils under oxidative pyrolysis at 300 °C with on-line analysis of the products by gas chromatography/mass spectrometry. The pyrolysis conditions were intended to simulate the release, transfer and possible thermo-oxidative conversion of the flavours in tobacco heating products, which constitute a relatively new category of tobacco products where no combustion of the tobacco takes place [29].

2. Experimental

2.1. Materials

Three flavour samples; ANH lime oil (Citrus aurantifolia, cold pressed, 2L8), ANH bergamot oil (*Citrus aurantium* L. *bergamia*, 2B4), and ANH cardamom essential oil (*Elletaria cardamomum*, 2C2) were sourced from Hertz Flavors GmbH & Co. KG (Reinbek, Germany). The samples were undiluted neat essential oils, and were stored in amber essential oil dropper bottles. They were shipped at room temperature and then stored in air-tight container at 4 °C in the refrigerator prior to analysis. The experiments started within two weeks after the arrival of the samples. All experiments were conducted within a 10 day time window after first breaking the seal on the bottles, to minimize oxidation during refrigerated storage.

2.2. Methods

2.2.1. Analysis of the as received samples

The qualitative and semi-quantitative (area-%) composition of the essential oil samples was measured by gas chromatography/mass spectrometry (GC/MS) using Agilent 6890 A GC − 5973 MSD system (Agilent Technologies, Palo Alto, CA, USA). Several solvents were tested and dichloromethane proved to be a good and inert solvent for the oils. The samples were dissolved in dichloromethane to obtain 30 mg/ml concentration. Aliquots of 1 µl solution were injected using helium carrier gas with a split ratio of 100:1. The analysis was performed on a DB-1701 capillary column (30 m × 0.25 mm, 0.25 µm film thickness). The GC oven was programmed to hold at 40 °C for 7 min and heated at 10 °C/min to 280 °C (hold 2 min). Solvent delay of 4 min was applied. The mass range of *m/z* 29–400 was scanned by the mass spectrometer in EI mode at 70 eV. The identification of the compounds was carried out using NIST 2011 and Wiley 2009 mass spectral libraries. The spectra of all identified compounds were available in the spectral libraries; however, for the correct identification of the isomers, the retention data of the oil components published in the literature [2,5–8,11–13,15,17] were taken into account. Five parallel experiments were carried out for each sample. The accurate quantification of the oil components by using internal standards was not the purpose of this study; hence the relative intensity data calculated from the integrated total ion current values were used for evaluating the composition of the essential oils. The chemical structures of the essential oil components and the products studied are sufficiently similar to allow use of relative intensity as a measure of major changes within the mixture. Thus, the area % values of the chromatograms give a good estimation of the compositions.

2.2.2. Low-temperature pyrolysis-GC/MS

Py-GC/MS analyses have been carried out in a Pyroprobe 2000 (CDS Analytical, Oxford, PA, USA) pyrolyser equipped with a platinum coil and a quartz sample tube. A piece of quartz wool was placed in the middle of the quartz tube, and then 0.05 µl essential oil sample was dispensed on it. The pyrolyser was immediately inserted into the pyrolysis chamber, which was preheated to 250 °C. The sample was then heated at a maximal heating rate (set at 999 °C/s) to 300 °C. The pyrolysis was performed for 5 min in 9% oxygen − 91% nitrogen atmosphere using 276 ml/min flow rate. The temperature was chosen as 300 °C in order to mimic the heating conditions for the low-temperature tobacco heating products [27]. The 9% oxygen level was a compromise level, designed to minimize damage to the instrument, while still allowing any major, oxidative pathways to be revealed. The volatile products were purged on-line to the GC/MS, and then the carrier gas was switched to helium. Solvent delay of 7 min was applied to protect