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Stability of Essential Oils: A Review

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Abstract: In recent years, consumers have developed an ever-increasing interest in natural products as alternatives for artificial additives or pharmacologically relevant agents. Among them, essential oils have gained great popularity in the food, cosmetic, as well as the pharmaceutical industries. Constituting an array of many lipophilic and highly volatile components derived from a great range of different chemical classes, essential oils are known to be susceptible to conversion and degradation reactions. Oxidative and polymerization processes may result in a loss of quality and pharmacological properties. Despite their relevance for consumers, there is a paucity of information available addressing this issue. Therefore, the present review provides a comprehensive summary on possible changes in essential oils and factors affecting their stability. Focusing on individual essential oils, the various paths of degradation upon exposure to extrinsic parameters are outlined. Especially temperature, light, and oxygen availability are recognized to have a crucial impact on essential oil integrity. Finally, analytical methods to assess both genuine as well as altered essential oil profiles are evaluated with respect to their suitability to track chemical alterations. It is believed that only a careful inspection of essential oils by a set of convenient methods allows profound quality assessment that is relevant to producers and consumers alike.

Introduction

Essential oils are composed of lipophilic and highly volatile secondary plant metabolites, reaching a mass below a molecular weight of 300, that can be physically separated from other plant components or membranous tissue (Protzen 1993; Grassmann and Elstner 2003; Schmidt 2010; Sell 2010). As defined by the International Organization for Standardization (ISO), the term "essential oil" is reserved for a "product obtained from vegetable raw material, either by distillation with water or steam, or from the epicarp of citrus fruits by a mechanical process, or by dry distillation" (ISO 9235, 1997), that is, by physical means only. Accordingly, most essential oils available on the market are obtained by hydrodistillation. Physical standards of essential oils are specified by the Association Française de Normalisation (AFNOR) as well as the ISO. Official opinions and guidelines, such as those from the International Fragrance Association (IFRA), the "Bundesinstitut für Risikobewertung" (BfR), the Research Institute for Fragrance Materials (RIFM), and the Scientific Committee on Consumer's Safety (SCCS) regulate maximum quantities and uses of certain oils as well as single compounds therein. Furthermore, essential oils for medical purposes need to comply with national or international Pharmacopoeia. Concerning their dietary intake, essential oils are generally considered as safe (GRAS) for their intended use by the U.S. Food and Drug Administration (FDA) (Smith and others 2005).

In addition to their widespread use as flavoring material (Attokaran 2011), essential oils represent a "green" alternative in the nutritional, pharmaceutical, and agricultural fields due to reported antimicrobial, antiviral, nematicidal, antifungal, insecticidal, and antioxidant properties (Akhtar and Mahmood 1994; Dorman and Deans 2000; Zygadlo and Juliani 2000; Papachristos and others 2004; Cavanagh 2007; Podşedek and others 2009; Adorjan and Buchbauer 2010; Dandlen and others 2010; Ntalli and others 2010; Lang and Buchbauer 2012), or even activities stimulating the nervous system (Buchbauer and Jirovetz 1994; Edris 2007; Heuberger 2010). Taken together, the compiled characteristics result in a broad spectrum of applications: Essential oils have been suggested as antioxidants and preservatives in food (Burt 2004; Lanciotti and others 2004; Fisher and Phillips 2008; Tiwari and others 2009) or even incorporated into foodstuff packaging material (Kuorwel and others 2011). Isman (2000) as well as Adorjan and Buchbauer (2010) pointed out their application as plant and crop protectants. Moreover, promising approaches have been reported using essential oils or components thereof in medicinal products for human or veterinary use (Buchbauer and Jirovetz 1994; Shahi and others 2000; Bakkali and others 2008; Franz 2010; Woronuk and others 2011; Lang and Buchbauer 2012). Therefore, in recent times, essential oils have gained great popularity as consumers have developed a particular ever-growing awareness toward the use of natural ingredients, especially in food, household, and cosmetic products (Yamamoto 2008; Jiang and others 2011). As a matter of fact, trade quantities of a couple of popular oils such as eucalyptus or lemon by far exceed 1000 metric tons *per annum* with an estimated value of several hundred million euros in 2007 (Brud 2010; Franz and Novak 2010). Since a specific knowledge on the chemical composition and properties of essential oil is fundamental for an adequate use, the present review compiles and discusses the

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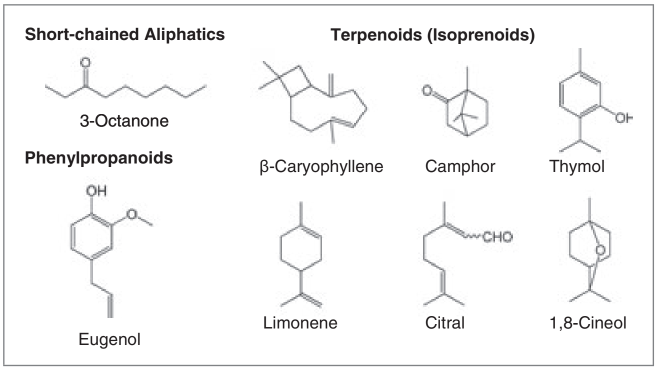

Figure 1–Representative structures typical for essential oils.

hitherto scattered data on factors influencing essential oil stability. It sheds light on the chemistry of decomposition reactions and on analytical approaches to reveal essential oil degradation.

Chemical Composition of Essential Oils

The broad range of possible applications described above results from the large variety in the composition of essential oils. A multitude of different, but often structurally closely related, components have been identified in essential oils. Each oil in turn can be composed of only a few up to a complex mixture of far more than 100 single substances, respectively (Blitzke 2009). Flavor contribution of single compounds though does not strictly depend on their respective concentration but relies on the specific odor threshold that is determined by structure and volatility. Consequently, even minor components deriving from oxidation or degradation reactions may have a strong impact on the flavor if their aroma value is high enough (Grosch 2007).

For the most part, essential oil components can be assigned as lipophilic terpenoids, phenylpropanoids, or short-chain aliphatic hydrocarbon derivatives (Kubeczka 1979) of low molecular weight, with the first being the most frequent and characteristic constituents (Treibs and Merkel 1960). Among these, allylic, mono-, bi-, or tricyclic mono- and sesquiterpenoids of different chemical classes make up the major part in essential oils, such as hydrocarbons, ketones, alcohols, oxides, aldehydes, phenols, or esters. Representative structures are depicted in Figure 1. Due to their low volatility, diterpenes are barely encountered in genuine essential oils obtained by distillation, while tri- and higher terpenoids such as sterols or carotenoids are only present in the nonvolatile fractions such as plant resins or gums and will remain in the residue (Treibs and Merkel 1960; Martinetz and Hartwig 1998; Humphrey and Beale 2006). Comprehensive reviews providing structures, occurrences, and uses of terpenoids or further flavorings have been compiled by Grayson (1990) as well as Surburg and Panten (2006).

Constituents in essential oils generally originate from several major biosynthetic pathways (Franz and Novak 2010). While the aromatic phenylpropanoids are formed via the shikimic acid pathway leading to phenylalanine (Pichersky and others 2006; Colquhoun and others 2010), terpenoids derive from the C_5-building blocks isopentenyl diphosphate (IPP) and its isomer dimethylallyl diphosphate (DMAPP). For structural elucidation in this vast field of compounds, the so-called isoprene rule, established by Otto Wallach in 1887 and subsequently refined by Sir Robert Robinson and Leopold Ružička provided a fundamental milestone, stating that each terpenoid can be basically composed from isoprene units (C_5H_8), mainly in a head-to-tail fashion, either directly or by ways of cyclization, rearrangements, or further conversions from aliphatic isoprenoid precursors (Ružička 1953; Banthorpe and others 1972; Hanson 2003). The knowledge of these biochemical principles may be helpful for tracking structural changes of genuine essential oil constituents.

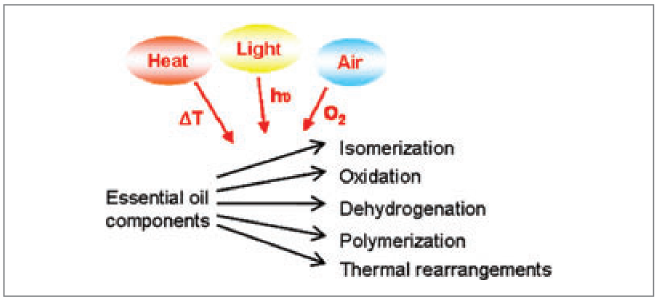

Figure 2–Possible conversion reactions in essential oils.

Alterations of Essential Oils and Possible Consequences

Due to their structural relationship within the same chemical group, essential oil components are known to easily convert into each other by oxidation, isomerization, cyclization, or dehydrogenation reactions, triggered either enzymatically or chemically. Upon stability evaluation of essential oils, it needs to be kept in mind that the chemical composition may already vary in the starting material, being influenced by plant health, growth stage, habitat including climate, edaphic factors, as well as harvest time (Figueiredo and others 2008; Schmidt 2010). An example for the structural pattern as a function of harvest time was given by Masotti and others (2003) who found a decreasing concentration of a hydrocarbon monoterpene in the essential oil throughout the year while the amount of an oxidized immediate metabolic successor rose coevally. Consequently, plant volatiles are subject to natural fluctuations in their composition (Kubeczka 1993) that need to be considered upon quality evaluation.

As terpenoids tend to be both volatile and thermolabile and may be easily oxidized or hydrolyzed depending on their respective structure (Scott 2005), it is well accepted that the chemical composition of essential oils is moreover dependent on the conditions during processing and storage of the plant material, upon distillation as well as in the course of subsequent handling of the oil itself (Schmaus and Kubeczka 1985; Carle and Fleischhauer 1987; Fischer and others 1988; Baritaux and others 1992; Venskutonis and others 1996; Mockutë and others 2005; Schweiggert and others 2007).

Once deprived of the protective compartmentation in the plant matrix (Treibs 1956), essential oil constituents are especially prone to oxidative damage, chemical transformations, or polymerization reactions (Figure 2). These aging processes generally come along with a more or less pronounced quality loss (Fincke and Maurer 1974; Kubeczka 1993). In addition to the frequent development of unpleasant and often pungent flavors, shifting colors such as the formation of a yellow staining in caraway oil (Preuss 1964) or changes in consistency up to resinification have been reported both upon degradation of essential oils as well as of single terpenoids (Bernhard and Marr 1960; Tóth 1967; Dieckmann and Palamand 1974; Pokorný and others 1998; Grassmann and Elstner 2003; Sköld and others 2004; Blitzke 2009). For instance, the aromatic monoterpene *p*-cymene, often identified in aged essential

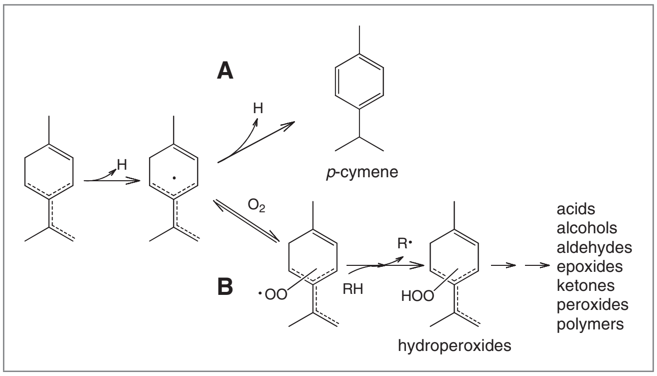

Figure 3–Proposed oxidation scheme of terpenoids. (A) Dehydrogenation and possible hydrogen rearrangements. (B) Autoxidation pathway leading to hydroperoxides and subsequent degradation into secondary oxidation products.

oils (Brophy and others 1989; Hausen and others 1999; Misharina and others 2003; Turek and Stintzing 2011b), has been associated with an off-flavor in lemon oil (Sinki and others 1997), resulting among others from acid-catalyzed depletion of citral or oxidative dehydrogenation of single or double unsaturated monocyclic terpenes (Figure 3A) (McGraw and others 1999; Nguyen and others 2009).

Besides organoleptic alterations and viscosity changes, some aged essential oils as well as oxidized terpenoids have revealed skin-sensitizing capacities (Woeber and Krombach 1969; Hagvall and others 2008; Sköld and others 2008; Bråred-Christensson and others 2010) leading to a hypersensitivity reaction synonymous to allergic contact dermatitis (Divkovic and others 2005). In order to elicit cutaneous inflammation, chemicals first need to be able to penetrate into the epidermis requiring an adequate lipophilicity and, second, must bind to proteins that hence are haptenated. The latter is considered to occur either via nucleophilic–electrophilic reactions if the hapten exhibits an electrophilic functional group or through radical interactions (Karlberg and others 2008; Redeby and others 2010). The allergenic potency in a flavoring could be mainly attributed to terpenoid hydroperoxides intermediately built-up upon autoxidation, while their nonoxidized counterparts as well as most degradation products were proven to be not or only barely irritating (Hellerström and others 1955; Pirilä and Siltanen 1958; Hausen and others 1999; Matura and others 2005; Karlberg and others 2008; Bråred-Christensson and others 2009).

Though autoxidation has been particularly investigated in the field of fatty oils, it also plays a most crucial part for terpenoid deterioration. In the course of this spontaneous, air-induced oxidative process, unsaturated molecules react in a free radical chain mechanism with aerial oxygen into a range of primary and secondary oxidation products (Figure 4). The course of reaction will depend on molecular structure, oxygen concentration, energy input, and the impact of further reaction partners. Promoted by heat, catalytic quantities of redox-reactive metals, and exposure to light, alkyl radicals are initially generated [Figure 4 (1)] and readily react with triplet oxygen to form peroxyl radicals [Figure 4 (3)]. An alternative initiation of radical reaction by means of existing trace levels of hydroperoxides was proposed by Neuenschwander and Hermans (2010) [Figure 4 (2)]. Upon the rate-limiting step of autoxidation, peroxyl radicals selectively abstract weakly bound hydrogen atoms adjacent to a double bond, leading to the formation of hydroperoxides and another alkyl radical, thus propagating the chain reaction [Figure 4 (4)]. As chain-terminating steps, radicals combine to alkyl and peroxyl dimers that may polymerize or decompose further to nonradical products [Figure 4 (9–11)] (Choe and Min 2006; Neuenschwander and others 2010).

Initiation	RH	→	R• + H•	(1)
	ROOH + RH	→	R• + H_2O + RO•	(2)
Propagation and branching	R• + $^3O_2$	→	ROO•	(3)
	ROO• + RH	→	ROOH + R•	(4)
	ROO• + R	→	ROOR•	
	ROOR•	→	R>O + RO•	(5)
	RO• + RH	→	ROH + R•	(6)
	RO• + $^3O_2$	→	R'=O + HO_2•	(7)
	ROOH + ROO•	→	R'=O + HO• + ROOH	(8)
Termination	R• + R•	→	RR	(9)
	ROO• + R•	→	ROOR	(10)
	ROO• + ROO•	→	ROH + R'=O + $^3O_2$	(11)

Figure 4–Main mechanism of autoxidation and some possible branching reactions (Choe and Min 2006; Neuenschwander and Hermans 2010; Neuenschwander and others 2010).

As a rule, primary autoxidation products such as hydroperoxides eventually break down during advanced stages of oxidation depending on their individual stability. Thereby they give rise to a range of stable oxidized secondary products such as mono- to polyvalent alcohols, aldehydes, ketones, epoxides, peroxides, or acids as well as highly viscous, often oxygen-bearing polymers (Figure 3B) (Blumann and Ryder 1949; Pirilä and Siltanen 1958; Bernhard and Marr 1960; Treibs 1960; Schenck and others 1965; Dieckmann and Palamand 1974; Karlberg and others 1994; Shahidi 1997; Sköld and others 2004; Bäcktorp and others 2008). Accordingly, initially formed oxidation products from terpenoids, assigned as hydroperoxides, were reported to decompose in the presence of light, heat, or upon increasing acidity (Hellerström and others 1955; Blakeway and others 1987; Hagvall and others 2007). Borglin and others (1950) observed that peroxidic products resulting from oxidation of the monoterpene terpinolene degraded promptly, even at room temperature.

In addition to their secondary nature, Neuenschwander and others (2010) recently revealed that epoxides [indicated by R > O in Figure 4 (5); note that the addition of the peroxyl radical takes place at a double bond], alcohols [Figure 4 (6)], as well as ketones [denoted by R' = O in Figure 4 (7)] may also be primarily generated in the radical chain mechanism competing with hydroperoxide formation.

Most often the structure of secondary oxidation products still remains unknown. One prominent stable secondary product is caryophyllene oxide (Figure 5A) that ensues from air oxidation of the sesquiterpene caryophyllene (Sköld and others 2006) and can be frequently encountered in stored essential oils (Mockutë and others 2005; Turek and Stintzing 2012). Moreover, carveol and its oxidation product carvone were frequently reported to result from peroxides in the course of limonene autoxidation (Bernhard and Marr 1960; Schenck and others 1965) together with limonene oxide (Figure 5B) (Matura and others 2005). On the other hand, Geier (2006) stated that some oxygen-bearing terpenoids such as menthol, 1,8-cineol, and menthone did not form hydroperoxides upon oxidation but directly converted into ketones, acids, and aldehydes.

Besides oxidation and polymerization reactions, disproportionation as well as cyclization are also considered to be involved in the degradation of monoterpenes, as exemplified with the appearance of cyclic isomers such as limonene, terpinenes, and *p*-cymene in

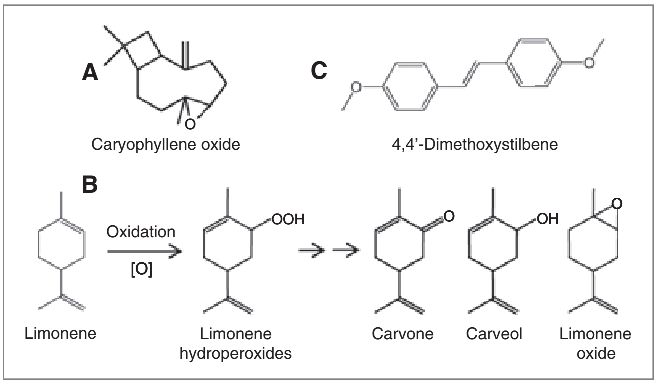

Figure 5–(A) Caryophyllene oxide, stable autoxidation product of β-caryophyllene. (B) Oxidation pathway of limonene into primary and secondary oxidation products following Matura and others (2006). (C) 4,4′-Dimethoxystilbene identified as photo-artifact in stored anise oil.

oxidative experiments with the monoterpene myrcene at elevated temperatures (Dieckmann and Palamand 1974).

Determinants of essential oil stability

To a decisive degree, degradation of essential oils depends on several chemical and edaphic factors that influence both the possibility of the essential oil to oxidize as well as the course of the reaction. Therefore, external factors such as temperature, light, and accessibility to atmospheric oxygen need to be thoroughly considered. Furthermore, essential oil composition, compound structures, and the presence of impurities may also govern stability.

Light. Ultraviolet (UV) light and visible (Vis) light are considered to accelerate autoxidation processes by triggering the hydrogen abstraction that results in the formation of alkyl radicals (Choe and Min 2006). Correspondingly, laurel as well as fennel oil stored in the dark (Misharina and Polshkov 2005) basically underwent the same alterations as upon storage under light, namely a decline in eugenyl acetate, estragol, *trans*-anethole, and several monoterpenes as well as an augmentation of *p*-cymene, eugenol, and anisaldehyde. The same was true for lemon oil in which decreasing amounts of geranial, terpinolene, and γ-terpinene together with a rise in *p*-cymene have been observed (Fincke and Maurer 1974). However, compositional changes proceeded considerably faster when illumination was involved. Especially monoterpenes have been shown to degrade rapidly under the influence of light (Misharina and others 2003). The same study also reported on transformation reactions taken place in marjoram oil during storage under light that led to the formation of several unidentified minor components. Very recently, Turek and Stintzing (2011b; 2012) showed that changes in several essential oils were promoted under the impact of light, however, oils from varying plant species responded differently: While essential oil from thyme did not alter much, rosemary oil turned out to be very susceptible to imitated daylight that readily led to a changing chemical composition. This was mainly revealed by a considerable increase in *p*-cymene, camphor, and caryophyllene oxide concomitant to the degradation of β-caryophyllene and the monoterpenes β-myrcene, α-terpinene, as well as α-phellandrene. Also, one minor compound in lavender oil yet not further identified totally broke down when illuminated, while another unidentified substance was initially built up during the 1st month stored under light but degraded again upon advanced storage (Turek and Stintzing 2012). Such photo-artifacts induced by sunlight or by UV irradiation with a distinct spectral distribution were identified in stored essential oils from anise (photoanethole) and lemon (photocitral) (Miething and others 1990; Nguyen and others 2009). For the former, the light-induced photoanethole, identified as 4,4'-dimethoxystilbene (Figure 5C), was suggested to result from photocycloaddition between anethole and anisaldehyde (Miething and others 1990). Moreover, in sweet fennel oil, *trans*-anethole had completely oxidized to anisaldehyde or isomerized to *cis*-anethole (Figure 6) after 2 mo of storage at room temperature under light (Misharina and Polshkov 2005). *trans*-anethole, the main component in sweet and bitter fennel oil, was reported to be converted into *cis*-anethole when treated with UV rays or high temperatures, the *cis*-isomer being 10 to 12 times more toxic than the *trans*-form (Braun and Franz 1999). In accordance with these data, a range of photochemically catalyzed intramolecular isomerization reactions such as cycloaddition or *trans-cis* conversions of various monoterpenoids had been earlier described by Pfau (1972).

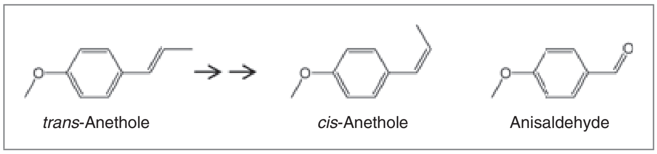

Figure 6–Isomerization and oxidation products of *trans*-anethole detected in fennel oil.

Furthermore, illumination plays a crucial part in a 2nd oxidative pathway named photooxidation in which aerial triplet oxygen is converted into its excited singlet state in the presence of an organic sensitizer. This nonradical electrophilic molecule can directly react with a double bond, thereby abstracting an allylic hydrogen atom leading to hydroperoxide formation (Hamilton and others 1997; Bäcktorp and others 2006). Hydroperoxides derived from this so-called "ene" reaction (Hoffmann 1969) decompose in the same manner as those formed by autoxidation. It is noteworthy that certain oxidation products were only detected subsequent to photooxidation due to a divergent resulting hydroperoxide spectrum (Schenck and others 1964; Nilsson and others 1996; Choe and Min 2006). However, this 2nd way of photo-induced oxidative deterioration is unlikely to occur in essential oils given that singlet oxygen is practically absent in a standard environment due to its high energetic level and the infringement of Hund's rule. Moreover, direct excitation of aerial ground state oxygen into its singlet state by light is almost unattainable, as an actually forbidden change in spin multiplicity is involved in the transition. Instead, activation requires sensitizer molecules such as chlorophylls or porphyrins that are generally absent in distilled essential oils (Pfau 1972; Miskoski and others 1994; Bäcktorp and others 2006).

Temperature. Ambient temperature crucially influences essential oil stability in several respects: Generally, chemical reactions accelerate with increasing heat due to the temperature-dependence of the reaction rate as expressed by the Arrhenius equation (Atkins 2002). Based thereon, the van't Hoff law states that a temperature rise of 10 °C approximately doubles chemical reaction rates, a relation that can be consulted to predict stability at different temperatures (Glasl 1975). Hence, both autoxidation as well as decomposition of hydroperoxides advances with increasing temperature, even more so since heat is likely to contribute to the initial formation of free radicals (Choe and Min 2006). Contrarily, lower temperatures favor the solubility of oxygen in liquids, which in turn may negatively affect essential oil stability (Bernhard and Marr 1960) as further elaborated below in the context of oxygen availability. Concerning hydroperoxide stability, storage experiments of a fatty oil revealed that at low or moderate temperatures, hydroperoxide formation predominated the decomposition rate, while the opposite was true at 50 °C (Aidos and others 2002). However, until recently, no comparable study regarding essential oils could be found in the literature. Only very recently, studies have been performed that pointed out the individual responses of essential oils to varying storage temperatures (Turek and Stintzing 2012; Turek and others 2012). Rosemary oil demonstrated pronounced stability at lower degrees Celsius and oxidation reactions could be prevented during the investigation period of 3 mo when stored at refrigerator temperatures. In essential oil from pine on the other hand, peroxide formation, expressed by the peroxide value (POV), even occurred at 5 °C, however, it was promoted at 23 °C. Contrarily, peroxides were especially built up in lavender stored at 5 °C compared to room temperature, while at 38 °C peroxides had almost completely degraded both in pine oil as well as in lavender oil. Instead, augmentation of storage temperature apparently led to an increase in polar secondary oxidation products not yet identified that were captured by conductivity and pH analyses (Turek and Stintzing 2012; Turek and others 2012). Those data emphasize that essential oils vary in their susceptibility to autoxidation at different storage temperatures.

In general, monitoring of volatile plant extracts and essential oil composition demonstrated that stability forfeits with prolonged storage time as well as a temperature rise from 0 to 28 °C (Gopalakrishnan 1994), 4 to 25 °C (Braun and Franz 1999), and 23 to 38 °C (Turek and Stintzing 2012). Again, upon temperature increase, dominant alterations in essential oils from cardamom, clove bud, lavender, pine, and rosemary were revealed in decreasing amounts of terpenic hydrocarbons such as β-caryophyllene, β-myrcene, β-pinene, sabinene, or γ-terpinene and an overall rise of *p*-cymene (Gopalakrishnan 1994; Turek and Stintzing 2012). Furthermore, Braun and Franz (1999) pointed out that the most striking change occurring during storage of fennel oil at 25 compared to 4 °C was the rapid increase of 4-anisaldehyde (Figure 6) which was proven to be a good quality marker. Moreover, augmentation in degrees Celsius was reported to increase the amount of several unidentified polymerization products formed from myrcene (Dieckmann and Palamand 1974). Terpenoids, especially mere terpenes and aldehydes, are commonly known to be thermolabile and susceptible to rearrangement processes at elevated temperatures. Terpenic conversion reactions upon heating have been reported both for isolated compounds (McGraw and others 1999; Ternes 2008) as well as for essential oils (Tomaino and others 2005). However, temperatures above 100 °C do not necessarily induce the same changes in terpenoids as real-term storage conditions. In doing so, McGraw and others (1999) classified thermal degradation of terpenes into 4 different groups of oxidative reactions: cleavage of double bonds, epoxidation, dehydrogenation into aromatic systems, and allylic oxidation into alcohols, ketones, and aldehydes. As terpenes were heated in a molecular oxygen atmosphere, autoxidation processes were likely to take place. Still, even upon storage under inert gas, Nguyen and others (2009) detected several chemical alterations in lemon oil within 2 wk at 50 °C, mainly a loss of geranial, neral, and terpenic hydrocarbons together with an increase in *p*-cymene. In contrast, other studies carried out at room temperature revealed that lemon oil as well as fennel oil turned out to be quite stable under nitrogen (Tóth 1967; Fincke and Maurer 1974).

Oxygen availability. As oxidation reactions are among the main causes for spoilage of essential oils, if not even the most frequent ones, it is obvious that oxygen access plays a decisive role in essential oil stability. Oxygen consumption upon storage of different monoterpenes has been recorded (Widmark and Blohm 1957) and changes in composition as well as physicochemical properties of essential oils were generally more pronounced in half-filled containers than when only little or no headspace was present (El-Nikeety and others 1998; Turek and others 2012).

Oil oxidation accelerates with the concentration of dissolved oxygen, which in turn depends largely on oxygen partial pressure in the headspace as well as ambient temperature. Without stirring, oxygen diffusion into the sample takes place gradually over time (Choe and Min 2006). According to Henry's law, oxygen solubility is high at low temperature and drastically decreases with an augmentation in degrees Celsius. Therefore, peroxyl radicals as well as hydroperoxides have been reported to be the most numerous compounds upon oxidation of edible oils at lower temperatures. Compounds formed through termination reactions such as polymers were only built up at later oxidation stages and at the end of the induction period, when either the amount of oxygen or oxidizable substrate was exhausted. On the other hand, alkyl or hydroxyl radicals and reactions thereof became more important at elevated temperature as oxygen availability was limited (Velasco and Dobarganes 2002). A recent study revealed the individual character of essential oils regarding their liability toward oxidation: While peroxide formation in essential oils from rosemary and pine was promoted at room temperature, oxygen solubility seemed to play a more decisive role for the peroxide level present in lavender oil and thyme oil stored at 5 °C. In these oils, highest POVs were found upon storage in the refrigerator (Turek and others 2012). These findings make clear that results obtained for one type of essential oil cannot be simply transferred to another one.

Furthermore, both increasing POVs and conductivity values have even been observed in lavender oil and pine oil at 5 and 23 °C as well as in rosemary oil stored at 23 °C in completely filled containers, though to a significant less extent than in half-filled ones (Turek and others 2012). Results obtained for cold-pressed lemon oil stored in almost filled containers were reported to be comparable to samples that were kept under nitrogen as protecting gas: Upon storage at 50 °C, a decrease in α-terpinene, limonene, β-phellandrene, β-caryophyllene, and citral together with an increase in *p*-cymene, limonene oxide, α-terpineol, and geranic acid was been revealed (Nguyen and others 2009). Hence, available atmospheric oxygen dissolved in the oils seemed to be sufficient at least for minor oxidation processes. Moreover, as pointed out previously, essential oils can still undergo other degradation reactions such as rearrangements not further described if oxygen is deficient (Geier 2006). From these results it can be concluded that depending on the particular essential oil and the ambient temperature, oxidation will not necessarily be prevented by avoidance of container headspace. Instead, as shown by Geier (2006), essential oils should be treated with inert gas such as argon, cautiously flushed through to displace remaining air, to prevent the formation of peroxides efficiently.

Metal contaminants. Upon distillation in primitive stills or during storage in metallic containers, impurities of metals can be released into essential oils (Treibs 1960). Equal to light and heat, heavy metals, especially copper and ferrous ions, are considered to promote autoxidation, in particular if hydroperoxides are already present (Guenther 1948; Choe and Min 2006). By catalyzing hydroperoxide decomposition, Fe^{2+} or Cu^{+} as well as Fe^{3+} or Cu^{2+} give rise to alkoxy and peroxyl radicals, respectively, which, in turn, promote radical oxidation reactions (Figure 4). Moreover, the formation of singlet oxygen by ferrous ions and thus the initiation of photooxidation have likewise been reported (Choe and Min 2006).

Water content. Moisture has been considered as a possible reason for essential oil spoilage (Guenther 1948). For instance, water distillation procedures at approximately 100 °C were shown to distort compound spectra. Citral is known to undergo acid-catalyzed reactions in aqueous solutions into *p*-cymene, *p*-cymene-8-ol, α-*p*-dimethylstyrene, methylacetophenone, and cresols (Schieberle and others 1988). Conversely, Rajeswara Rao and others (2011) could not reveal significant changes in different oils stored in the presence of water, even at a water content of 20% (*v*/*v*). This level is above the concentration that might possibly be dispensed in essential oils after hydrodistillation when done properly. Kaul and others (1997a) suggested to dry essential oils subsequent to distillation by addition of water-binding substances, as their study revealed some notable alterations, such as reduced contents of linalool and geraniol content as well as an increase in citronellol and geranyl formate in geranium oil which had been kept at room temperature for 1 y and which contained an undefined amount of water. However, observed chemical shifts might have equally been triggered by the presence of 50% air space in the container.

Compound structure and chemical composition. Susceptibility of essential oils to degradation largely depends on compound spectra (Treibs 1960) as components' molecular structures have a substantial effect on the degree of oxidation. Compounds rich in allylic hydrogen atoms make up most probable targets for autoxidation considering that hydrogen atom abstraction is giving rise to resonance-stabilized radicals highly favored due to lower activation energy (Bäcktorp and others 2006). Polyunsaturated terpenic hydrocarbons that exhibit the structural preconditions to form several radicals stabilized by conjugated double-bonds or isomerization to tertiary radicals are therefore particularly prone to oxidative deterioration (Guenther 1948; Nguyen and others 2009; Neuenschwander and others 2010). Correspondingly, essential oils chiefly containing unsaturated mono- and sesquiterpenes such as those from pine and turpentine readily altered upon storage (Turek and Stintzing 2011b). Moreover, electron-donating groups and increasing alkyl substitution contribute to a stronger carbon-peroxide bond through a hyperconjugative effect, thus leading to more stable and subsequently built-up hydroperoxides (Pratt and Porter 2003), while others are not adequately stabilized and immediately degrade. Caryophyllene hydroperoxides giving instantly rise to the corresponding epoxide state are an example for the latter (Sköld and others 2006).

Furthermore, alterations taking place in each compound may also influence stability of other molecules (Gopalakrishnan 1994): By transferring reactive oxygen, easily oxidized compounds can initiate autoxidation of further substances that are less prone to decomposition. On the other hand, antioxidative components might also prevent others from deterioration. Phenols such as carvacrol, thymol, or the phenolic ether eugenol (Figure 1) are known to disrupt or rather delay autoxidative chain reactions (Treibs 1960). Their antioxidant effectiveness is based on the feasibility to rapidly abstract the phenolic hydrogen atom, thereby forming free, comparably long-living radicals stabilized by isomerization to an alkyl-substituted tertiary position or electron-releasing groups. These so-called primary antioxidants will scavenge free reactive alkyl, alkoxy, or peroxyl radicals, leading to an elevated stability of the product containing them (Deighton and others 1993; Nanditha and Prabhasankar 2009). As a matter of fact, essential oil from thyme, containing up to 80% of phenols, revealed an overall good storage stability (Turek and Stintzing 2011b; Turek and Stintzing 2012; Turek and others 2012). Individual essential oil matrices may thus affect the stability of compounds therein (Guenther 1948), although Hagvall and others (2008) concluded from their study that lavender oil matrix had no protecting effects on the main components linalyl acetate, linalool, and β-caryophyllene when comparing autoxidation rates in the oil with those from isolated substances. However, it needs to be pointed out that oxidation was performed under rather severe conditions in order to obtain detectable hydroperoxides that were in the focus of the study (Hagvall and others 2008).

Altogether, alterations observed in essential oils or isolated substances can not always be attributed to one particular impact but might rather be the result of several interacting factors. This in part may be due to the lack of systematic approaches ruling out conditions that govern essential oil stability. Therefore, contradictory statements concerning the importance of single intrinsic and extrinsic parameters as a cause for deterioration may often be found. The statement of Guenther (1948), considering moisture to have a higher impact on essential oil spoilage than light, was not supported in the published literature and might be based on acid-catalyzed reactions at higher temperatures. Moreover, while Wabner and others (2006) and Našel (2009) suggested not to keep essential oils in the refrigerator based on elevated POVs analyzed in tea tree oil, other studies revealed that degradation reaction in essential oils were altogether promoted at room temperature (see above) (El-Wakeil and others 1986; El-Nikeety and others 1998; Turek and Stintzing 2012; Turek and others 2012). In summary, most degradation events described in the literature were elicited either by light, temperature, or a combination of both and a co-presence of oxygen (Hausen and others 1999; Misharina and others 2003; Hagvall and others 2007). While illumination has been pronounced to trigger more strongly storage-induced changes in flavorings than a temperature rise from 4 to 20 °C (Pfannhauser and others 1987), Carmona and others (1976) as well as El-Wakeil and others (1986) concluded that the influence of temperature at 60 and 25 °C exceeded the one of UV-Vis and daylight, respectively. On the other hand, Karlberg and others (1994) could show that cold and dark storage in a closed vessel effectively prevented autoxidation during 1 y of storage. Hence, temperature, light as well as oxygen availability are considered to exert the most decisive impact on essential oil stability.

Essential oil storage

Essential oils have been proven to undergo alterations upon aging that lead not only to a sensory and technological impairment but might also compromise consumer well-being. Although quality monitoring and a thorough knowledge of essential oil characteristics upon storage is indispensable, only few investigations have hitherto been conducted to survey essential oil stability over time while taking into account the impact of varying storage conditions.

Often, degradation reactions have been investigated using single reference compounds or model systems, whereby oxidation was frequently accelerated with the help of molecular oxygen, metal catalysts, as well as photosensitizers (Blumann and Ryder 1949; Nilsson and others 1996; Nguyen and others 2009). Similar findings have resulted from the field of atmospheric aerosols, simulated by means of smog chamber experiments with ozone, hydroxyl radicals, or nitrous gases (Atkinson and Arey 1998). For that reason, the alterations thereby revealed might not necessarily correspond to those provoked under real or imitated storage conditions mirroring common practice. Moreover, deterioration processes in mixtures, as is the case for essential oils, were described to develop differently as opposed to single substances. This can be explained by the fact that alterations taking place in each compound may also affect the oxidation behavior of others, for example by pro- or antioxidative effects (Guenther 1948; Gracza and Ruff 1981; Gopalakrishnan 1994).

Concerning essential oils, several studies have been performed that focused on the gas chromatographic detection of changes in substance patterns during storage in the presence of air. While Fischer and Still (1967), Tóth (1967), Bhattacharya and others (1998), Brophy and others (1989), as well as Mokutë and others (2005) compared chemical compositions of samples arbitrarily aged under ambient conditions with those from genuine essential oils, Fincke and Maurer (1974), Misharina and others (2003), Misharina and Polshkov (2005), Geier (2006), as well as Nguyen and others (2009) carried out storage experiments both under light and dark conditions. Significant results obtained from these studies are described above. Variation of storage temperature was even less considered in studies on essential oil composition (Gopalakrishnan 1994; Shalaby and others 1995; Braun and Franz 1999; Geier 2006). Storage periods ranged from a couple of days to up to 1 y, respectively. Especially promoted under light and elevated temperatures, remarkable decreases in the amounts of unsaturated terpenes such as γ-terpinene or β-myrcene together with a rise in *p*-cymene were frequently revealed, which was equally confirmed in long-term storage of tea tree oil (Brophy and others 1989). Moreover, depending on the respective essential oil, augmentation of oxidized compounds was reported over time, for instance anisaldehyde in fennel oil or caryophyllene oxide and linalool oxide in marjoram oil (Misharina and others 2003; Misharina and Polshkov 2005). By comparative storage, Misharina and Polshkov (2005), for example, could expose the individual character of essential oils. Sweet fennel oil was extremely unstable even in the dark and had undergone almost complete deterioration within 2 mo under light accompanied by the formation of known oxidation products (see above) as well as several unidentified compounds, whereas under both conditions essential oil from laurel only faintly altered.

More comprehensive studies were conducted by El-Nikeety and others (1998) as well as El-Wakeil and others (1986) complementing GC measurements with the assessment of diverse physicochemical properties. Essential oils from parsley, anise, caraway, and cumin were kept under various storage conditions, however, the results obtained were considered to lack of stringency. Some reported changes in chemical composition are quite ambiguous and might be the result of evaporation or nonaccurate analyses rather than of mere oxidative degradation. For instance, the decline of caryophyllene oxide in stored lemon balm oil (Shalaby and others 1995) or increased amounts of sesquiterpenic hydrocarbons (Kaul and others 1997b) surprisingly differ from results normally expected.

Only recent investigations systematically incorporating different storage conditions have shed light on the particular impact of selected extrinsic parameters on up to 7 essential oils deriving from different plant species. Taking various analytical parameters into account, the authors revealed that the individual character of the essential oils responded both in different ways and to varying extents to light, storage temperature, as well as the availability of oxygen, reliant on the respective chemical composition. In this way, the individual stability of essential oils was comprehensively assessed by monitoring changes of chemical patterns together with well-defined physicochemical properties for up to 18 mo (see above) (Turek and Stintzing 2011b; Turek and Stintzing 2012; Turek and others 2012).

Altogether, reliable and comprehensive studies on essential oil storage are rarely found and concrete specifications on appropriate storage conditions as well as shelf life of essential oil have not been clearly defined to date (Blitzke 2009). Moreover, only a very limited number of volatile oils have been subjected to storage experiments so far.

Analysis of Essential Oils

The many applications of essential oils, which in turn each comprise a wide range of components, require a thorough analysis in order to prove necessary quality and to authenticate identity. Correspondingly, various methods based on physical and chemical properties have been suggested to characterize essential oils, which have moreover been applied to determine essential oil stability upon storage. The determination of several parameters such as relative density, optical rotation, refractive index, freezing point, or compound (class)-specific analyses are, among others, laid down in the European Pharmacopoeia for purity control. As a matter of course, sensory analyses are naturally appropriate, such as verification of a characteristic odor or, though less often, classification of essential oil flavor attributes into so-called odor profiles (Pudil and others 1998).

Chromatographic characterization of genuine essential oils

As a rule, chromatographic methods coupled to various detection modes are applied for the investigation of essential oil composition offering information about identity, possible impurities or falsifications (Scott 2005; d'Acampora Zellner and others 2010) as well as degradation reactions the oil may have gone through. While thin-layer chromatography, easily carried out, previously played a paramount role in essential oil quality control (Fischer and Still 1967; Hefendehl 1993), more recent separation techniques have gained great importance for fragrance analysis.

Gas chromatography. Gas chromatography (GC) usually represents the method of choice nowadays to scrutinize the complex mixture of an essential oil (Cserháti 2010). Naturally suited for the analysis of fragrances due to their volatility, GC measurements are characterized by a high number of theoretical plates, resulting in an outstanding separation capacity. Even more resolving power can be achieved using the latest approaches, such as multidimensional or enantioselective GC, while fast-GC leads to raised productivity. The state of the art related to essential oil investigations has been reviewed several times, notably by Mariott and others (2001), Rubiolo and others (2010), and Tranchida and others (2012). In GC-olfactometry (GC/O), gas chromatographic separation of compounds is combined with sensory detection which is used both for the sensory characterization as well as the perception of off-flavors (Bonnefille 2011; Mahattanatawee and Rouseff 2011). In most cases, however, GC is coupled to flame ionization or mass spectrometry detection modes (FID and MS, respectively), providing suitable tools for terpenoid determinations (Cicchetti and others 2008). The use of electron ionization (EI) GC/MS or GC/FID for compound analysis of essential oils or products containing fragrances has been frequently reported in the literature (Rastogi 1995; Masotti and others 2003; Radulescu and others 2004). Nevertheless, analysis is limited to a relatively low number of compounds with vapor pressures beneath 350 to 400 °C (Cserháti 2010) that are stable upon vaporization and separation temperatures. As a matter of fact, structural alterations of thermally labile or less volatile substances and thus the occurrence of artifacts upon GC analysis of essential oils have been reported (Kallen and Heilbronner 1960; Bruhn 1974; Kubeczka 1974; Miething and others 1990; Mateus and others 2010). In this connection, Kovar and Friess (1980), Wylie and others (1992), Hinshaw (2002), as well as Klee (2010) have pointed out that often neglected decomposition and rearrangement reactions may occur during GC separation due to high injector temperatures or hot and catalytically active liner or column surfaces. Furthermore, for the analysis of nonvolatile or water-based matrices such as toiletries, detergents, foods, or cosmetic products, GC requires mostly time-consuming sample preparation steps (Rastogi 1995; Radulescu and others 2004; Tschiggerl and Bucar 2010).

High-performance liquid chromatography. On the other hand, high-performance liquid chromatography (HPLC) has been demonstrated to be versatile and sensitive for detecting essential oil volatiles (Kovar and Friess 1980; da S Rauber and others 2005; Turek and Stintzing 2011a) as well as thermolabile (Hagvall and others 2007) and less volatile substances (Frérot and Decorzant 2004; Turek and Stintzing 2012). Validated methods as alternatives to GC for the quantification of thymol and carvacrol in thyme oil, as well as of citral in lemongrass oil, were developed by Hajimehdipoor and others (2010) and da S Rauber and others (2005), respectively. Still, only a relatively small number of reports concerning the determination of essential oils in connection with HPLC can be found in the scientific literature. For the most part, it has been applied to separate and identify nonvolatiles in cold-pressed citrus oils (Lockwood 2001; d'Acampora Zellner and others 2010; Tranchida and others 2012). In the field of volatile compounds, the use of HPLC was mostly limited to sample cleanup (Schieberle and others 1987) or prefractionating steps prior to GC analyses (Jones and others 1979; Morin and others 1986; Nilsson and others 1996). Schwanbeck and Kubeczka (1979) reported on the successful separation of several volatile hydrocarbons in compound mixtures, while in rare cases, individual fragrance terpenoids were determined in essential oils by HPLC (Solinas and Gessa 1981; Newbery and others 1983; Mohammed 2009; Wang and Liu 2010; Wu and others 2010). Characterization of essential oils from lemon, bergamot, sage, melissa, mentha, pine needle, eucalyptus, orange, cinnamon, and gum rockrose were performed by Benincasa and others (1990), Hudaib and others (2001), Kovar and Friess (1980), Ogawa and others (2002), Ross (1976) as well as Strack and others (1980), both in reversed and normal phase modes. While work on liquid chromatographic separation of volatile oils published by Komae and Hayashi (1975) as well as Píry and Príbela (1994) lacks compound assignment, McKone (1979) did not show any HPLC chromatograms at all. Lately, Turek and Stintzing (2011a) developed a universal HPLC method that could be applied both for the assessment of single volatiles as well as the characterization of various essential oils. Using an optimized gradient design and an endcapped reversed-phase (RP) column suitable for MS detection at low eluent flow, characteristic fingerprints together with an overall high level of separation could be obtained. As of yet, more systematic approaches to HPLC analyses of essential oils are still quite scattered.

For the detection of essential oil volatiles, UV-Vis or even diode array detectors (DAD), the latter providing spectral information simultaneously for each chromatographic peak, were hitherto almost exclusively utilized due to their variability and selectivity. Fixed wavelengths, ranging from 195 nm (Ogawa and others 2002) to 275 nm (Kovar and Friess 1980), were mostly adapted to the specific spectral absorption behavior of the compounds analyzed. The simultaneous selection of various characteristic wavelengths was reported to ensure the detection of a wide variety of substances derived from several chemical classes, even when components such as α- and γ-terpinene were structurally too similar to be chromatographically distinguishable (Turek and Stintzing 2011a).

Liquid chromatography coupled to mass spectrometry. The combination of liquid chromatography with mass spectrometry (LC/MS) represents a powerful analytical tool for compound identification. However, only recently Turek and Stintzing (2011a) established a hitherto new approach by means of HPLC/DAD coupled in series with tandem MS operating with atmospheric pressure chemical ionization in the positive mode to comprehensively assess compounds in various essential oils complementing GC. The authors concluded that the inferior separation capacity of HPLC compared to GC due to a lower number of theoretical plates could be compensated for, to a certain degree, by the benefit of several detection modes in series such as UV absorption combined with MS and the possibility of simultaneous monitoring at different wavelengths when using a diode array detector (Strack and others 1980; Turek and Stintzing 2011a; Turek and Stintzing 2012).

Chromatographic approaches to monitor essential oil alterations upon storage

Regular quality control of essential oils by producers, traders, or essential oil manufacturers generally covers the quality of essential oil subsequent to production or distribution as a rule under suitable oxidation-preventing conditions. However, storage-induced alterations of essential oils more or less prone to degradation reactions have to date not been fully investigated. Changes in essential oils need to be thoroughly monitored, as they may alter both the sensory as well as the pharmacological properties (see above).

Mostly, essential oil alterations during storage have been assessed only via GC/FID or GC/MS (Tóth 1967; Brophy and others 1989; Misharina and others 2003). Changes in chemical composition were almost solely monitored by comparison of the relative peak area percentages normalized to 100%. However, pronounced evaporation, degradation, or the rise of newly built-up individual components may lead to shifts in relative areas and thus to wrong results using this approach to depict storage-induced changes over time. Moreover, less volatile and up to highly viscous polymerization products formed upon terpenoid oxidation have been reported to escape GC analyses (Bernhard and Marr 1960; Tóth 1967; Karlberg and others 1994).

Conversely, the benefits of HPLC were pronounced to be the suitability for polar and nonvolatile compounds as well as the mild conditions during analysis (Warnke and others 2006). HPLC/UV-Vis was proven appropriate for the detection of selected oxidation products from citral (Liang and others 2004), limonene and linalool (Pokorný and others 1998) at detection wavelengths of 254 and 420 nm, respectively. Moreover, Miething (1990) identified the light-induced artifact photoanethole in stored anise oil using HPLC/DAD; this compound is usually unstable under GC conditions. Apart from that, for individual oxidized products, HPLC has only been addressed by Hagvall and others (2008) for the quantification of linalool and linalyl acetate hydroperoxides in lavender oil evading GC (Sköld and others 2004).

HPLC in combination with MS was successfully applied for the determination of polar terpene oxidation products in atmospheric aerosols by Glasius and others (1999) and Warnke and others (2006), as well as for the detection of thermally labile hydroperoxides formed by linalool and limonene autoxidation by Nilsson and others (2008). However, not until recently, RP-HPLC in combination with DAD and MS detection has been taken into consideration for a comprehensive evaluation of stored essential oils (Turek and Stintzing 2011b; Turek and Stintzing 2012): Aging processes in essential oils from eucalyptus, lavender, may chang, pine, rosemary, thyme, and turpentine, were monitored detecting both polar oxidation products as well as late-eluting compounds with higher molecular masses (Turek and Stintzing 2011b). A distinct impact of varying storage settings on chemical composition and the individual character of each essential oil concerning storage stability was revealed by comparison of the respective HPLC profiles. Depending on the specific essential oil composition, both increasing as well as declining trends and even intermediately built-up components were depicted (Turek and Stintzing 2011b; Turek and Stintzing 2012). Comparative GC/EI-MS measurements matched peak area changes well, thus demonstrating the versatility of HPLC for essential oil analyses. For the detection of storage-induced changes in lavender oil, HPLC-monitoring at 280 nm even appeared to be superior to GC as significantly increasing, most probably polymeric substances, escaped detection in the latter. As a matter of fact, high-boiling oxidation and polymerization products may be missed by GC measurements (Tóth 1967). Interestingly, HPLC determination revealed the presence of another yet unidentified highly photolabile substance in lavender essential oil which was not accessible by GC/EI-MS experiments (Turek and Stintzing 2012).

Further parameters indicating oxidative instability

For isolated terpenes, refractive index, viscosity, relative density, and oxygen consumption have all been shown to increase during the progress of oxidation (Blohm and Widmark 1955; Widmark and Blohm 1957). However, an analytical setup to comprehensively assess essential oil alterations during storage has been rarely addressed in the literature.

Garnero and Roustan (1979), El-Wakeil and others (1986), Kaul and others (1997b), and El-Nikeety and others (1998) monitored several physicochemical properties of stored essential oils, namely specific gravity, refractive index, evaporation residue (El-Wakeil and others, El-Nikeety and others), optical rotation (Garnero and Roustan, Kaul and others), acid and ester value in addition to shifting chemical compositions. However, results often lack unambiguous tendencies, as some values are both increasing and declining within the storage experiment without revealing distinct tendencies. Garnero and Roustan (1979) showed that the amount of aldehydes decreased to less than 10% in sweet orange as well as lemon oil during 105 and 90 d of open storage in the sun accompanied by a rise of the POV. The latter was also true for anise oil stored for 105 d under the same conditions. Moreover, in lemon oil, the acid index rose remarkably (Garnero and Roustan 1979). Turek and Stintzing (2011b) tested several analytical quality parameters to monitor essential oils after storage and evaluated their informative value in order to obtain a more holistic view on oxidation-related alterations than was hitherto known. While refractive index did not correlate with storage time, which might be due to the relatively mild storage conditions chosen, color measurement, POV, pH, as well as conductivity assessment were considered reliable quality parameters. Chapard and others (1972) revealed an increase in hydrosolubility, refractive index, and relative density together with rising chemical indices, however, essential oils were catalytically oxidized, not reflecting real conditions. Moreover, pH determination (Blakeway and others 1987), POV analysis (Garnero and Roustan 1979; Blakeway and others 1987; Hausen and others 1999; Geier 2006; Haddouchi and others 2011), thin-layer chromatography (Preuss 1964; Fischer and Still 1967; Tóth 1967; Chapard and others 1972), odor analysis (Pudil and others 1998), as well as UV- (Fischer and Still 1967) and infrared spectroscopy (Carmona and others 1976) have been applied.

Preuss (1964) observed the formation of a yellow tint in autoxidized essential oil from caraway. Correspondingly, several isolated monoterpenes, originally colorless, became yellow upon oxidation (Widmark and Blohm 1957; Bernhard and Marr 1960). In this context, it must be taken into account that evaporation of water or highly volatile colorless compounds during storage in an open system might also lead to color intensification without any degradation reaction. Essential oils from lavender, may chang, rosemary, and thyme were shown to undergo complete color alterations perceptible with the human eye upon storage at elevated temperature in the presence of imitated daylight and air (Turek and Stintzing 2011b). While Joy and others (2001) stated that essential oils in general became darker in color on long storage coming along with increased viscosity, Turek and Stintzing (2011b) revealed that may chang and thyme oil, naturally yellow, initially faded within 4 wk of storage at 38 °C under imitated daylight accompanied by a declining yellow shade. Thereafter, perceivable color differences between initial values and those taken from stored oils became again less marked during a total storage time of 3 mo. Taken together, color measurements provide useful information about visual alterations in stored essential oils that might be due to aging processes, however, it is less suitable to retrospectively evaluate the previous storage history (Turek and Stintzing 2011b).

Peroxide value. The POV of essential oil has been often determined and was formerly suggested for quality control in order to assess the amount of irritating peroxides (Wabner 2002). However, some limitations concerning its informative value to reflect essential oil quality have been depicted. As hydroperoxides are known to degrade into secondary oxidation products over time, depending on their individual stability (see above), assessed POVs rather reflect mere snapshots of the amount of oxidizing compounds present in the oil at the time of analysis, but overlook preceding reactions. Correspondingly, decreasing POVs have been reported upon storage of essential oils (Pirilä and Siltanen 1958; Geier 2006; Haddouchi and others 2011). Likewise, in essential oils from lavender, augmentation of POV was revealed to be less pronounced when stored at 23 °C compared to refrigerator temperatures (Turek and others 2012) and even less upon storage at 38 °C (Turek and Stintzing 2012). The latter was also true for pine oil, though in all cases, both the assessment of additional quality parameters, as well as chromatographic investigations, pointed to an overall progressed degradation at higher temperatures, respectively (Turek and Stintzing 2012). Thus, the informative value of POV as sole quality parameter to shed light on storage history and degree of aging can be considered deficient. On the contrary, POVs in rosemary oil manifested an opposite trend, indicating that the formation and detection of hydroperoxides varied decisively (Turek and Stintzing 2012; Turek and others 2012). Moreover, stability of peroxides is variable to a great extent and stable peroxides such as ascaridol are suspected to escape detection (Blakeway and others 1987). Adhvaryu and others (2000) stated that formed peroxides were too labile to be captured in most cases. Again, depending on their specific molecular structure, some terpenoids were considered not to form hydroperoxides during aging but to react directly into stable secondary oxidation products (Geier 2006). Furthermore, Barnard and Hargrave (1951) pointed out that in the course

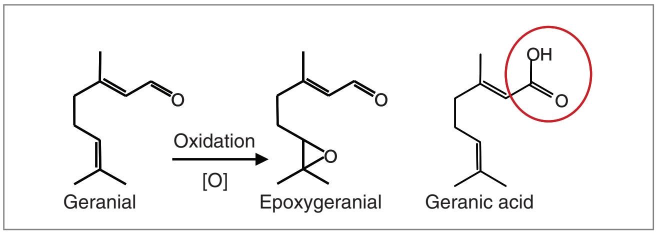

Figure 7–Possible autoxidation pathway after Hagvall and others (2011) leading to increased acidity and conductivity.

of iodometric peroxide titration, iodine adds to olefinic double bonds abundantly present in essential oils, thus leading to false results. As a consequence, monitoring aging processes via peroxide analysis was denoted to be ambiguous and unreliable (Hellerström and others 1957).

Conductivity and pH-value. A new approach combining conductivity and pH assessments has been applied to monitor storage-induced oxidation processes in essential oils complementing POV. For that purpose, stored oils were extracted with water followed by analysis of the aqueous phases (Turek and Stintzing 2011b). While mere terpenic hydrocarbons are not soluble in water, oxygenated derivatives were shown to partly pass into the water phase upon distillation, most likely owed to the capacity to form hydrogen bonds (Rajeswara Rao and others 2002; Edris 2009). Moreover, Borglin and others (1950) as well as Mercier and others (2009) reported that terpenes became water-soluble upon oxidation. Chapard and others (1972) observed the same effect in oxidized essential oils. Less stable hydroperoxides and epoxides, formed as intermediates, were suggested to be hydrolyzed into terpenic polyols in the presence of water (Borglin and others 1950; Lorand and Reese 1950). As a consequence, polar, conductive, and/or acidic secondary products accumulated during terpenoid degradation and subsequently passing into the water phase, might be captured by combined conductivity and pH measurements. Indeed, conductivity has been revealed to rise during storage of essential oils, while the pH value concomitantly declined (Turek and Stintzing 2011b). As a matter of fact, aldehydes, for instance, were described to oxidize into acids (Figure 7) (Treibs 1960; Hagvall and others 2011). Moreover, several storage experiments have indicated a good correlation between storage time, prevailing extrinsic conditions and obtained analytical data, thus emphasizing the suitability of conductivity and pH to more completely reflect the individual storage history of essential oils (Turek and Stintzing 2012; Turek and others 2012). The connection between the degree of oxidative aging and conductivity as well as pH values, respectively, could also be confirmed by oxidation of a set of reference compounds common to essential oils (Turek and others, unpublished data).

Conclusions

Evaluation of existent literature data on essential oil stability revealed that oxidative changes and deterioration reactions, which may lead to both sensory as well as pharmacologically relevant alterations, have scarcely been systematically addressed. The importance of extrinsic storage factors on the physicochemical stability of essential oils revealed that this issue still awaits profound scientific evaluation. For quality control purposes, the utility of HPLC to profiling genuine as well as oxidized essential oils appears promising, which may also be appropriate for the assignment of essential oil components in foods, cosmetics, and pharmaceutical formulas. Besides POV assessment, conductivity and pH measurements should be part of the analytical toolbox to obtain a more complete picture on oxidative events that the respective essential oil may have undergone. Further research is required to underpin recent analytical approaches in order to gain an even deeper understanding of possible oxidation processes and strategies to avoid them. Also, the identification of oxidation products resulting from oxidative events appears to be a valuable future objective.

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