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Essential oils can contain allergenic hydroperoxides at eliciting levels, regardless of handling and storage

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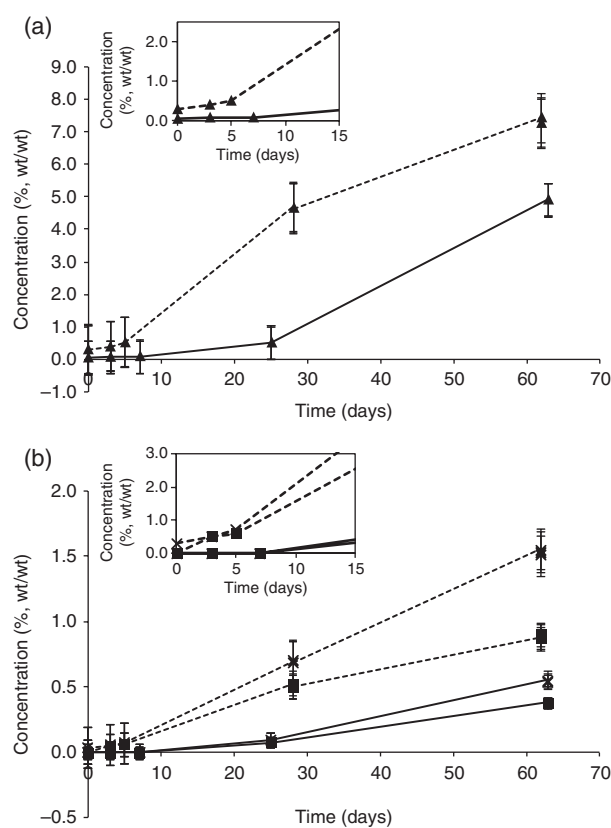
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Essential oils in perfumed products are important skin sensitizers (1). Upon air exposure, lavender oil, with the major components linalool and linalyl acetate, has been shown to produce strongly allergenic hydroperoxides (2). Furthermore, linalool of natural origin was found to contain a higher concentration of hydroperoxides than synthesized linalool (3). We have previously studied autoxidation of sweet orange oil (main compound R-limonene) and petitgrain oil (major compounds linalool and linalyl acetate) with liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) (4). The investigation was performed at room temperature, under a daylight lamp (12 hrs a day), and the oils were stirred 1 hr four times a day, according to previous experience (5, 6). In the present study, the importance of handling conditions for hydroperoxide formation was investigated. The hydroperoxide concentrations of R-limonene, linalool and linalyl acetate were analysed over time.

Results

Sweet orange oil and petitgrain oil (Kurt Kitzing GmbH, Wallerstein, Germany) showed contents of R-limonene,



Data are expressed as the means $\pm$ standard deviation of triplicate experiments.

Fig. 1. Comparison of hydroperoxide concentrations under different handling conditions: without stirring or a daylight lamp (---), and with use of stirring and a daylight lamp (—) (4). (a) Limonene-2-hydroperoxide ($\blacktriangle$) in sweet orange oil. (b) Linalool hydroperoxides ($\blacksquare$) and linalyl acetate hydroperoxides ($\times$) in petitgrain oil. The results from the first 2 weeks of the autoxidation period studied are enlarged.

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and of linalool and linalyl acetate, in accordance with ISO standards (7, 8). LC/MS/MS analyses detected limonene-2-hydroperoxide (0.05% wt/wt) in sweet orange oil, and linalyl acetate hydroperoxides (lower than the limit of quantification) in petitgrain oil, at the time of purchase (4). After 1 year of storage in darkness at 4°C (refrigerator), the content of limonene-2-hydroperoxide was 0.29% wt/wt in sweet orange oil. In petitgrain oil, the concentration of linalyl acetate hydroperoxides had increased to 0.03% wt/wt, and linalool hydroperoxides were now also detected in the oil. However, the quality of the oils still agreed with the chromatographic profile of parent components according to ISO standards. Autoxidation experiments at room temperature without stirring or use of a daylight lamp were performed. The results showed hydroperoxide formation at rates independent of stirring and daylight when compared with the results from our previous investigations which contained stirring and daylight (4) of the same oils (Fig. 1).

Discussion

Eliciting levels of terpene hydroperoxides can be formed in the essential oils, regardless of handling and storage, as long as, from a kinetic point of view, saturation with respect to oxygen has been reached. In such a case, the rate-determining step is hydroperoxide formation from peroxy radicals, and additional oxygen supplied by stirring is not important.

Sensitive ISO methods for hydroperoxide detection in products are important. The existing ISO standards for essential oil profiling are not sufficient for the detection of low but hazardous concentrations of hydroperoxides. The level of limonene-2-hydroperoxide (0.29% wt/wt) in sweet orange oil after 1 year of storage in a refrigerator is similar to the concentrations used in patch tests (9). Even low concentrations, such as 0.05% wt/wt of linalool hydroperoxides found in petitgrain oil after a few days of air exposure, can cause elicitation in individuals with known contact allergy to air-oxidized linalool (10).

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