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Influence of the chemical structure on the odor characters of β-citronellol and its oxygenated derivatives

Shaimaa Awadain Elsharif [a], Andrea Buettner [a,b,*]

[a] Department of Chemistry and Pharmacy, Food Chemistry, Emil Fischer Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 9, 91054 Erlangen, Germany
[b] Department of Sensory Analytics, Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Strasse 35, 85354 Freising, Germany

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ABSTRACT

β-Citronellol, **1**, and citronellyl acetate, **2**, are renowned fragrant constituents in perfumes and flavoring agents in foods and beverages. Both substances smell citrussy, fresh and floral. To elucidate the structural features required for these sensory effects, six C-8 oxygenated derivatives of **1** and **2** were synthesized and analytically characterized. All compounds were tested for their odor qualities and odor thresholds in air, revealing that there were no significant differences in odor impressions from the parent monoterpenes and their derivatives in most cases; however, substantial differences in their odor threshold values were observed, with β-citronellol as the most potent (10 ng/L_{air}) and 8-hydroxycitronellyl acetate as the least potent odorant (1261 ng/L_{air}). 8-Oxocitronellyl acetate was the only compound that was described with divergent odor attributes, namely musty, rotten and coconut-like. 8-Carboxycitronellol and 8-carboxycitronellyl acetate were found to be odorless.

1. Introduction

β-Citronellol, **1** (3,7-dimethyloct-6-en-1-ol), an essential oil component of lemon grass or *Cymbopogon citratus* (Abegaz, Yohannes, & Dieter, 1983), citronella grass *or Cymbopogon winterianus* (Quintans-Júnior et al., 2008) and bushy matgrass or *Lippia alba* (Tavares et al., 2005), is used as a flavoring agent in food and beverages (Dziala, Peplonski, Klopotek, Lisicki, & Tecza, 2000; Murakami, Furukawa, Kawasaki, & Ota, 2013). The odor of citronellol has previously been described as being *sweet*, *rose-like* (Hognadottir & Rouseff, 2003; Zhao et al., 2016), while citronellyl acetate, **2**, has been reported to elicit a *fresh*, *fruity* smell associated with a *lemon* scent (Zhao et al., 2016). Due to their pleasant smell properties, **1** and **2** are fragrant compounds that are widely used in perfumes with *citrus*, *floral* notes (Bartsch, Uhde, & Salthammer, 2016; Rios et al., 2013). Owing to the chiral center at carbon 3, β-citronellol has two isomeric forms that both occur in nature. The R-(+)-isomer, a slight *oily light rosy-leafy*, *petal-like* odorous compound (Yamamoto et al., 2004), is the most common isomer found in the Rutaceae family. On the other hand, the S-(−)-isomer with very *fresh light* and *clean*, *rosy*, *leafy*, *petal-like* odor, is less common, and is mainly found in geranium and citronella oils (de Sousa et al., 2006).

Apart from that, **1** came into focus as potential treatment in cardiovascular diseases based on the consideration that the decoction of lemon grass leaves, being rich in **1**, has previously been used as a hypotensive agent in folk medicine (Carbajal, Casaco, Arruzazabala, Gonzalez, & Tolon, 1989). Besides, **1** has been demonstrated to exert some other pharmacological effects such as antibacterial, antifungal, antispasmodic as well as anticonvulsant activity (Brito et al., 2012). Apart from that, this odorant is one of the most effective natural tick repellants against nymphs of *Amblyomma americanum* (L.) or lone star tick (Tabanca et al., 2013), the most common tick reported to bite humans in the southeast and south-central USA which can cause people to develop an allergy to red meat proteins (Wolver, Sun, Commins, & Schwartz, 2013). In addition, **1** has been reported as a fragrance allergen, i.e. in the context of scented consumer products for indoor application (Bartsch et al., 2016). In animal studies it has been shown that oral administration of citronellol to streptozotocin (STZ)-induced diabetic rats enhanced the levels of insulin, hemoglobin and hepatic glycogen, but also ameliorated the production of important carbohydrate-metabolizing enzymes (Srinivasan & Muruganathan, 2016). These findings suggest that **1** may be a beneficial agent in the treatment of diabetes mellitus.

Citronellyl acetate **2** has previously been identified as the main odor compound in fresh rhizomes of ginger where the smell of the

* Corresponding author at: Department of Chemistry and Pharmacy, Food Chemistry, Emil Fischer Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 9, 91054 Erlangen, Germany.

E-mail addresses: Shaimaa.elsharif@fau.de (S.A. Elsharif), andrea.buettner@fau.de, andrea.buettner@ivv.fraunhofer.de (A. Buettner).

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substance has been described as *rose-like* (Nishimura, 1995). In addition, **2** has been described as one of the most important aroma compounds in kumquat peel oil; in that study its odor was described as *citrus*, *kumquat-like* (Choi, 2005). Interestingly, in a study regarding the smell characteristics of both enantiomers of **2**, the odor of the S-isomer was described as *fresh*, *lime*- and *citrus-like* with a *camphoraceous* note, whereas the additional note of the R-isomer, apart from *fresh, lime*- and *citrus-like*, was reported as being *dirty aldehydic*, without any further specification of this annotation. However, these smell character assignments were provided in the course of an odor threshold (OT) determination of the two enantiomers of **2** in an aqueous ethanol solution applying a triangular test (Yamamoto et al., 2004). Accordingly, the additional sensory influence of ethanol cannot be excluded.

Apart from that, citronellyl acetate has been shown to act as an antinociceptive agent, like citronellol. **2** is also present as major constituent in *Corymbia citriodora* (Rios et al., 2013). This plant, also known as *Eucalyptus citriodora* resin, has been demonstrated to be a potent antihepatoma agent with pro-apoptotic activity in HepG2 cells (human hepatoma cells); moreover, it also exerts antifungal, antibacterial and insect-repellent activity (Shen, Chen, & Duh, 2012).

Recent studies of our group showed that oxygenated derivatives of potent odorous terpenoid compounds can exert interesting and pleasant odor effects. Apart from that, our comprehensive revision of reports of such substances on their occurrence in nature, and of other potential effects of these derivatives in plant and animal kingdom, revealed that such derivatives may be underrated, and that some of these compounds might still await their future discovery. For that reason, we previously established a comprehensive database on oxygenated derivatives of linalool, geraniol, nerol and their acetates (Elsharif, Banerjee, & Buettner, 2015; Elsharif & Buettner, 2016). The aim of the present study was to further expand this database, now focusing on derivatives of citronellol and its acetate.

Among all oxygenated derivatives of **1** and **2** (Fig. 1), only two compounds have previously been identified in nature, namely 8-hydroxycitronellol, **5**, as one of the diol constituents of the polar extract of the rose flowers (*Rosa damascena* Mill.) (Knapp et al., 1998), and the R-isomer of 8-carboxycitronellol, **7** (Table 1). The latter substance has been isolated from a Chinese herb called *Cistanche salsa*, and has further been reported to be an antiosteoporotic compound (Yamaguchi, Shinohara, Kojima, Sodeoka, & Tsuji, 1999). It is important to note that compounds 8-oxocitronellol, **3**, 8-oxocitronellyl acetate, **4**, and 8-hydroxycitronellyl acetate, **6,** have not been previously identified in nature as constituents in plants or animals, yet they were synthesized in some studies for different purposes. To mention but some examples, compound **3** was synthesized in a study on the selective oxidation of primary allylic alcohols to their corresponding aldehydes (Kalsi, Chhabra, Singh, & Vig, 1992), whereas compound **4** was synthesized as an intermediate in the synthesis of the minor sex pheromone component of two Brazilian soybean stink bugs (Het.: Pentatomidae) (Zarbin et al., 2000). Similarly, compound **6** was synthesized in a study showing the exclusive 1,2 reduction of functionalized conjugated aldehydes containing other reducible and acid-sensitive functionalities with sodium triacetoxyborohydride to obtain allylic alcohols (Singh, Sharma, Kaur, & Kad, 2000). As for 8-carboxycitronellyl acetate, **8**, this substance has neither been identified in nature nor synthesized before, thus, is a newly reported odorant of this study.

Apart from that, no systematic data are to date available on the odor characteristics of these oxygenated derivatives of citronellol and citronellyl acetate, let alone their potential further effects on humans or other animals. To close this gap, the aim of our study was to systematically evaluate the odor qualities and OTs of these substances as we previously did in a comparative approach for the related derivatives of linalool (Elsharif et al., 2015) and geraniol (Elsharif & Buettner, 2016). To achieve this aim we synthesized, starting from **1** and **2**, derivatives with oxygenated functional groups at C-8, and determined their respective odor qualities and OTs in air. This substance library should provide us with the opportunity of evaluating if β-citronellol and its ester are the only odorous compounds in this substance class, or if related compounds

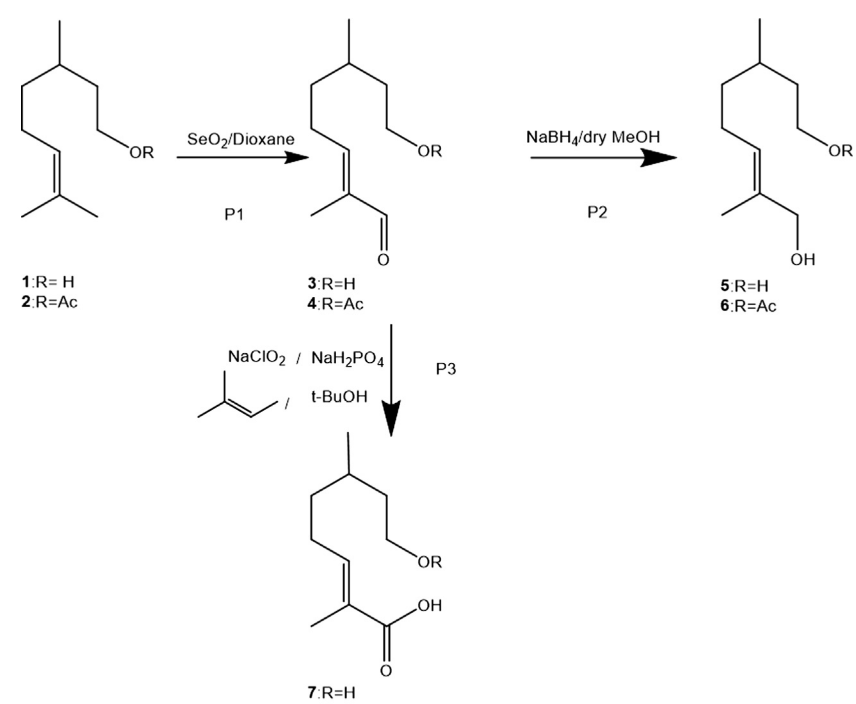

Fig. 1. Synthetic pathways leading to the target oxygenated derivatives of β-citronellol and citronellyl acetate.