JKSP
http://e-journal.sari-mutiara.ac.id/index.php/KIMIA
Jurnal Kimia Saintek dan Pendidikan
Vol. 8, (1) 2024
eISSN 2615-3378
DOI: https://doi.org/10.51544/kimia.v8i1.5101
ORIGINAL RESEARCH

ANALYSIS OF HAZARDOUS COMPOUNDS IN REFILLABLE ROLL-ON PERFUMES CIRCULATING IN GORONTALO CITY USING GC-MS

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Abstract. This study aims to analyze the potentially hazardous compounds in refillable roll-on perfumes. The analytical method employed was GC-MS. The results from GC-MS analysis revealed hazardous compounds including Alpha-Pinene with concentrations in samples A-E = 0.0048 ppm, 0.0035 ppm, 0.0105 ppm, 0.0038 ppm, 0.0034 ppm; Dipropylene glycol with concentrations in samples A-E = 0.0322 ppm, 0.0162 ppm, 0.0692 ppm, 0.0493 ppm, 0.0465 ppm; Limonene with concentrations in samples A-E = 0.0705 ppm, 0.0373 ppm, 0.0222 ppm, 0.1462 ppm; Linalool with concentrations in samples A-E = 0.0092 ppm, 0.0568 ppm, 0.0146 ppm, 0.1298 ppm, 0.1233 ppm; Linalyl Acetate with concentrations in samples A-E = 0.1207 ppm, 0.0719 ppm, 0.0413 ppm, 0.1418 ppm, 0.1285 ppm. The levels of these compounds in the samples are below exposure thresholds, suggesting their current use is considered safe. However, stringent government oversight is necessary for refillable perfume products available in Gorontalo City.
Keywords: Refillable roll-on perfumes, Hazardous compounds, GC-MS analysis, Gorontalo City

INTRODUCTION

Perfume is a product that plays an important role in enhancing appearance and boosting the confidence of its users [1]. With the variety of perfume scents available on the market, consumers can choose fragrances that match their personality and preferences[2]. However, the limited availability of natural ingredients for perfume production has driven manufacturers to use synthetic chemicals to create a wide range of scents. The production process involves blending various chemical substances, both natural and synthetic, in specific formulas. Many perfumes on the market contain only a small amount of natural essence and primarily consist of synthetic chemicals, which may pose health risks [3].

According to the Environmental Working Group (EWG), the average fragrance product tested contains 14 secret chemicals not listed on the label. Some of these chemicals are known to cause hormonal disruptions and allergic reactions, and many have not been deemed safe for use in personal care products. Most of the basic ingredients in perfumes are synthetic chemicals derived from petrochemicals, which have been proven to contain neurotoxins (toxins that can damage the nervous system) and carcinogenic substances (cancer-causing agents)[4].

Previous research identified several hazardous compounds in refillable perfumes, such as dipropylene glycol, linalool, linalyl acetate, lily aldehyde, benzenepentanol, dimethyl benzyl carbinyl acetate, dihydro methyl jasmonate, and alpha-hexyl cinnamic

aldehyde [5]. Given the potential dangers of these compounds, further analysis of hazardous substances in refillable perfumes circulating in Gorontalo City is necessary.

The analysis and determination of the levels of compounds in perfumes can be conducted using qualitative and quantitative methods with Gas Chromatography-Mass Spectrometry (GC-MS) instruments [6], [7]. The GC-MS method is a combined analytical technique that utilizes the advantages of gas chromatography (GC) in separating chemical components and mass spectrometry (MS) in detecting and identifying these components based on their mass spectrum [8]. This process involves injecting the sample into a carrier gas stream, where the molecules of the substances are distributed between the gas and liquid phases within the chromatography column, and then detected and analyzed by the mass spectrometer.

Therefore, this study aims to analyze the hazardous compounds in refillable perfumes circulating in Gorontalo City using the GC-MS method. The results of this analysis are expected to provide deeper insights into the safety of using refillable perfumes and to help raise awareness among consumers and manufacturers about the importance of using safe ingredients in fragrance products.

RESEARCH METHOD

Equipment and Materials

The equipment used in this study includes a QP2010 Plus gas chromatography-mass spectrometry (GC-MS) system (Shimadzu), beakers, measuring cylinders, pipettes, and vial bottles. The materials used in the study were five types of almond-scented perfume samples available in Gorontalo City, anhydrous alcohol p.a (Mallinckrodt), and ethanol (Sceelze Hannover).

Preparation of Rice Straw Compost

The samples were collected from perfume retailers and labeled as samples A, B, C, D, and E. Each of the five refillable perfume samples was taken in a volume of 1 mL and then diluted with 2 mL of ethanol in a stoppered volumetric flask. These samples were then analyzed using the Shimadzu QP2010 Plus GC-MS system [9]. Sample analysis was performed using the GC-MS QP2010 SE ISO 17025:2017 with the following analytical conditions: the column type was Rtx-5MS, 30 mm in length, with an internal diameter of 0.25 mm. The carrier gas used was helium with an injector temperature of 200ºC, a pressure of 36.2 kPa, a total flow of 101.3 mL/min, a column flow of 0.75 mL/min, a linear velocity of 31.6 cm/s, and an oven temperature program of 60-320ºC.

RESULTS AND DISCUSSION

For the analysis process, 1 mL of each sample was injected into a preheated injection port. The heated sample was carried by the carrier gas, helium, through the column for separation. The stationary phase in the column selectively retains components based on their distribution coefficients. The Rtx-5MS column is semi-polar, consisting of 5% diphenyl and 95% dimethyl polysiloxane cross-linked bonds. Helium was chosen as the carrier gas due to its compatibility with the MS detector, as well as its inert nature, which prevents reactions with the sample during the elution process. The sample was then directed to the detector, which provided signals that could be observed on the reading system.

The detector analyzed the compounds in the form of spectra, showing the retention times of the

compounds. The recorded retention times were compared with the library data to identify the separated compounds. The library contains references for compounds and their retention times, allowing for comparison with the retention times of the sample. The Similarity Index can be used as a benchmark for identifying the analyzed compounds; the higher the Similarity Index, the more closely the compound in the library matches the analyzed compound, confirming that the sample compound is the same as the library reference.

The chromatograms of each sample showed more than 20 peaks, indicating the number of compounds in each sample. Each sample exhibited relatively consistent retention times for a specific compound, as shown in Table 1. To enhance the analysis results, the MS instrument was used to observe the fragmentation patterns of the compounds by comparing the sample spectra with the library spectra.

Table 1. The Compounds Found in Perfume Samples Circulating in the City of Gorontalo

Compounds	Rt (minutes)	Sample area (%)				
		A	B	C	D	E
Alpha Pinene	4.135-4.278	0.48	0.35	1.05	0.38	0.34
Beta Pinene	4.840-4.845	0.46	0.25	0.13	1.55	2.07
Dipropylene Glycol	5.355-5.409	3.22	1.62	6.92	4.93	4.65
Benzene, methyl(1-methylethyl)-(CAS)	5.445-5.455	0.59	0.26	0.27	0.38	0.99
Limonene	5.514-5.527	7.05	3.73	2.22	14.62	12.91
Tripropylene Glycol	5.610-5.620	1.73	1.37	3.89	3.18	3.02
Linalool	6.128-6.509	0.92	5.68	1.46	12.96	12.33
Linalyl Acetate	8.760-8.778	12.07	7.19	4.13	14.18	12.85
alpha.-iso-methyl ionone	12.055-12.604	8.24	4.73	4.71	0.64	0.68
Lily Aldehyde	12.66-12.67	30.43	21.50	0.95	2.19	1.27

Based on the GC spectrum obtained, potentially hazardous compounds were identified in all analyzed samples. Some of the compounds identified with potential hazards in all samples include alpha pinene, dipropylene glycol, limonene, linalool, and linalyl acetate. Each compound was identified at relatively similar retention times. Differences in peak heights for each compound in the samples occur due to the varying amounts of each component present in the samples. The peaks in the GC chromatogram are directly proportional to the quantity of each component in the samples.

Alpha Pinene

Alpha Pinene is a bicyclic monoterpene compound available as a colorless oily liquid with a density of 0.859 g/ml at 20°C, a boiling point of 156°C, and a refractive index of 1.466 [10]. Alpha Pinene is one of the constituents of perfumes that produce a fresh, herbal aroma similar to rosemary and pine. Alpha Pinene can cause respiratory irritation and has tumorigenic potential based on oral and dermal testing in rats and rabbits. Tests on rats indicated that Alpha Pinene causes sensory irritation, with concentrations reducing the respiratory rate by 50% (RD50) ranging from 1.053 to 1.107

ppm [11]. The compound Alpha Pinene was detected in all five analyzed samples at different retention times, with MS analysis results showing a molecular ion peak at m/z = 136 (M+), followed by fragments at m/z 121, 93, 77, and 53. The fragmentation pattern of the compound is depicted in (Figure 1).

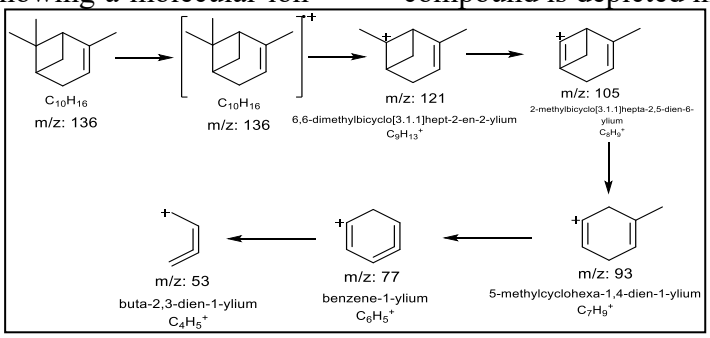

Figure 1. Alpha Pinene Fragmentation Pattern

Mass spectra revealed a molecular ion peak M+ at m/z = 136, corresponding to the molecular weight of the compound $C_{10}H_{16}$. Fragmentation of the $C_{10}H_{16}^{+}$ molecular ion involved the release of a CH_3• radical, resulting in the $C_9H_{13}^{+}$ fragment with m/z = 121. Subsequent elimination of CH_4 generated the $C_7H_9^{+}$ fragment at m/z = 93. Further fragmentation of $C_7H_9^{+}$ involved the release of CH_4, yielding the C6H5+ fragment with m/z = 77, followed by the elimination of C2 to produce the $C_4H_5^{+}$ fragment with m/z = 53.

Dipropylene Glycol

Dipropylene glycol is a colorless and nearly odorless glycol alcohol with a boiling point of 230.5ºC, soluble in ethanol with a solubility of 1.0206 g/cm³ [12]. It is widely used in the cosmetic and skincare industry to enhance texture and formulation stability, as a solvent, viscosity-decreasing agent, masking agent, and fragrance ingredient. Acute skin toxicity studies in rabbits showed that a dose of 5.01 g/kg body weight did not result in mortality but caused erythema and eye irritation in rabbits. The exposure limit according to the US Department (ACGIH) is 200 ppm [13]. Although the molecular ion m/z values of the sample and standard differ, the standard SI value is sufficiently high at 97%, making it suitable for comparison. The MS results showed a spectrum where the molecular ion peak m/z = 89 (M+) was followed by fragments at m/z 71, 59, and 45, with a fragmentation pattern of the compound as seen in (Figure 2).

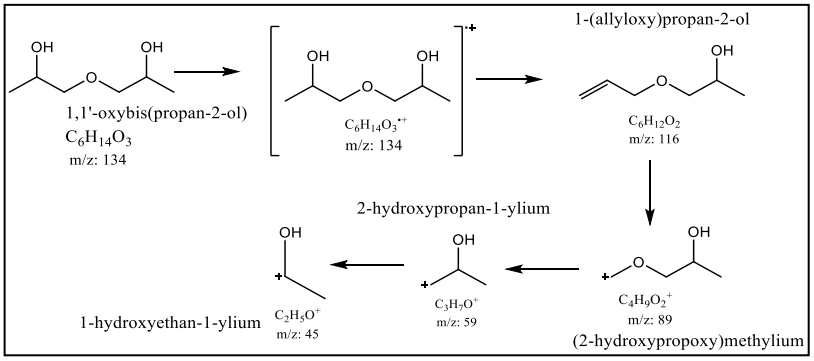

Figure 2. Dipropylene Glycol Fragmentation Pattern

Limonene

Limonene is a monoterpenoid compound consisting of two isoprene units. It is a colorless liquid with a boiling point of 176ºC, soluble in acetone, dimethyl sulfoxide, and ethanol. Limonene is used

as a flavor and fragrance additive in cleaning and cosmetic products [14]. It imparts a characteristic citrus fruit aroma, such as lemon and orange. Limonene is also widely used as a solvent and as an additive in resin production, as a wetting and dispersing agent, and as a blending ingredient in insect control products. Limonene can be synthesized from geranyl pyrophosphate through nerol carbocation cyclization [15]. Material Safety Data Sheets (MSDS) indicate that limonene has potential hazards such as eye and skin irritation. Eye inflammation is characterized by red, watery eyes and itching. Skin inflammation presents as itching and redness. Limonene in its unoxidized form causes allergies in 0.2% of dermatitis patients when tested with 2-3% usage. Limonene irritates at concentrations of 70-8%, is a weak irritant at 50%, and is non-irritating at concentrations of 20-30%. The exposure limit for limonene based on experiments is LD50 rabbit (skin) 500ppm, LD50 rat (oral) 500 ppm. The limonene exposure limit is 450 ppm in humans, causing irritation and a decrease in vital capacity [16]. The MS results showed a spectrum where the molecular ion peak m/z = 136 (M+) was followed by fragments at m/z 121, 93, 68, 67, 41, with a fragmentation pattern of the compound as seen in (Figure 3).

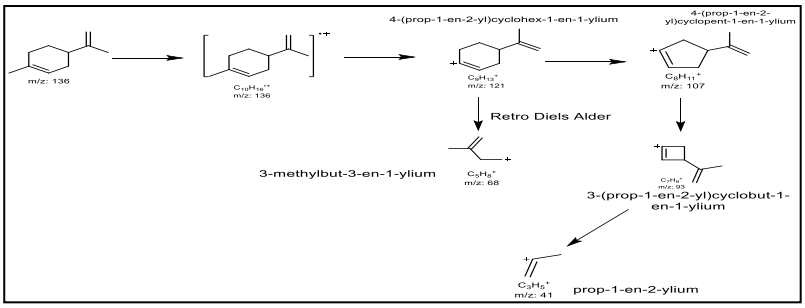

Figure 3. Limonene Fragmentation Pattern

Linalool

Linalool is an acyclic monoterpene compound that is a colorless liquid with a boiling point of 198-199ºC and a water solubility of 1.58 g/cm³. Linalool is the compound responsible for the lavender aroma [17]. At higher concentrations, it causes respiratory irritation in humans and can lead to loss of consciousness. Linalool is a contact allergen because even though it acts as an impurity, this compound has the potential to experience auto-oxidation and/or metabolic activity that contributes to the formation of allergies [18]. The exposure limit for linalool based on experimental animals is LD50 rat (oral) 2,790 ppm, LD50 rat (skin) 5,610 ppm [19]. Although the molecular ion m/z values of the sample and standard differ, the standard SI value is sufficiently high at 97%, making it suitable for comparison. The MS results showed a spectrum where the molecular ion peak m/z = 154 (M+) was followed by fragments at m/z 136, 121, 93, 71, 55, and 43, with a fragmentation pattern of the compound as seen in (Figure 4).

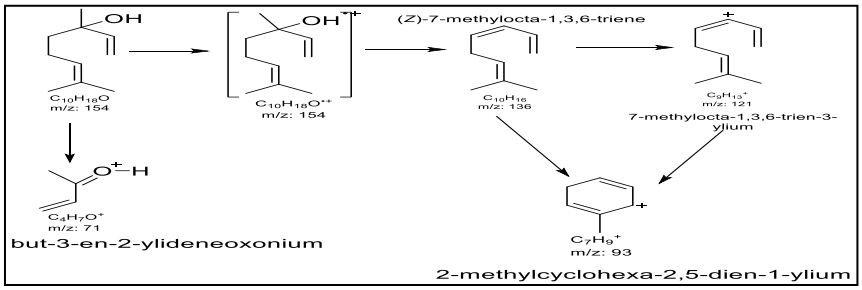

Figure 4. Linalool Fragmentation Pattern

Linalyl Acetate

Linalyl acetate is an acetate ester compound of linalool, formed during the linalool synthesis process. Linalyl acetate also contributes to the lavender aroma as it is an acetate ester compound of linalool [20]. It is a colorless liquid with a boiling point of 220ºC, soluble in ethanol and diethyl ether. Linalyl acetate is synthetically obtained through esterification reaction between linalool and acetic acid or anhydrous acetate in an acidic medium. Contact with skin can cause discoloration and eczema. It can cause respiratory tract irritation, and if inhaled in high concentrations, it can cause shortness of breath. The exposure limit for linalyl acetate based on experimental animals is LD50 rat (oral) 12 ppm, rabbit (skin) 13,934 ppm [21]. Although the molecular ion m/z values of the sample and standard differ, the standard SI value is sufficiently high at 98%, making it suitable for comparison. The MS results showed a spectrum where the molecular ion peak m/z = 196 was followed by fragments at m/z 136, 121, 93, 80, 71, 55, and 43, with a fragmentation pattern as seen in (Figure 5).

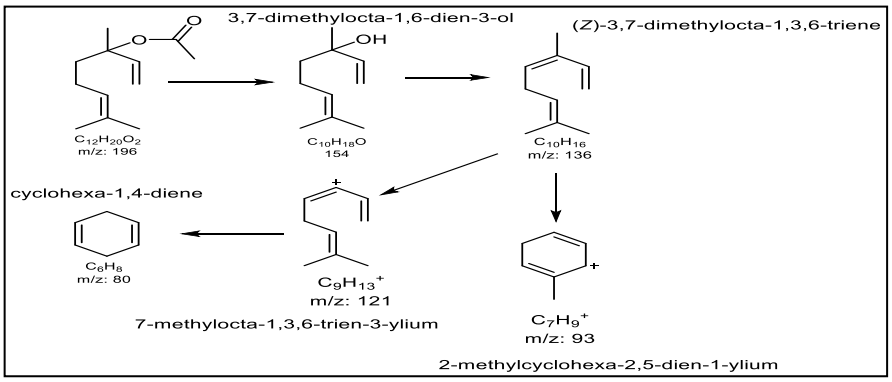

Figure 5. Linalyl Acetate Fragmentation Pattern

The mass spectrum reveals an ion peak M+ at m/z = 196, which corresponds to the molecular weight of the compound $C_{12}H_{12}O_2$. The compound $C_{12}H_{12}O_2$ undergoes the loss of a C_2H_3O molecule, resulting in a fragment $C_{10}H_8O$ with m/z = 154. Subsequently, the compound $C_{10}H_8O$ loses a water molecule to form $C_{10}H_{16}$ with m/z = 136, which further loses a CH_3 group to produce the fragment $C_9H_{13}^+$ with m/z = 121. The molecule $C_9H_{13}^+$ can undergo the loss of C_2H_4 to form the fragment $C_7H_9^+$ with m/z = 93. Additionally, the molecule $C_{10}H_{16}$ can directly lose a C_3H_7 molecule to yield the fragment $C_7H_9^+$ with m/z = 93. Furthermore, the molecule $C_9H_{13}^+$ undergoes the loss of C_3H_5 to produce the fragment $C_6H_8^+$ with m/z = 80.

The compounds analyzed in this study, including alpha pinene, beta pinene, dipropylene glycol, benzene, methyl(1-methylethyl)- (cas), limonene, tripropylene glycol, linalool, linalyl acetate, alpha.-iso-methyl ionone, and lily aldehyde, present various potential hazards when used in perfume formulations. These compounds have been identified in different concentrations across the samples tested, indicating their widespread use in the fragrance industry. While their levels in the tested samples generally fall below exposure thresholds deemed unsafe, their cumulative effects and potential interactions warrant continuous monitoring and regulation by governmental authorities. Further research and comprehensive toxicological studies are necessary to fully understand the long-term health implications of these compounds in perfumes, ensuring consumer safety and regulatory compliance in the fragrance industry.

CONCLUSION

The perfume samples circulating in Gorontalo City contain chemical compounds that are relatively similar and potentially hazardous across samples A, B, C, D, and E, namely Alpha-Pinene, Dipropylene Glycol, Limonene, Linalool, and Linalyl Acetate. The concentrations of these compounds in each sample were as follows: Alpha-Pinene ranged from 0.0048 ppm to 0.0034 ppm, Dipropylene Glycol from 0.0322 ppm to 0.0465 ppm, Limonene from 0.0705 ppm to 0.1462 ppm, Linalool from 0.0092 ppm to 0.1233 ppm, and Linalyl Acetate from 0.0413 ppm to 0.1418 ppm. The exposure limits for these compounds are 1.053 ppm to 1.107 ppm for Alpha-Pinene, 200 ppm for Dipropylene Glycol, 450 ppm for Limonene, 2,790 ppm to 5,610 ppm for Linalool, and 12 ppm to 13.934 ppm for Linalyl Acetate. The concentrations of these compounds found in the samples are within exposure limits, suggesting their safe use. However, stringent governmental oversight is necessary for refillable perfume products available in Gorontalo City to ensure continued safety and regulatory compliance.

REFERENCE

G. Ohloff, W. Pickenhagen, P. Kraft, and F. Grau, *Scent and chemistry: the molecular world of odors*. John Wiley \& Sons, 2022.

J. Mensing, “Psychology of Perfume Choice: How We Smell, Who or What in the Brain Decides on the Scent, and Why Perfumes Do So Much Good,” in *Beautiful SCENT: The Magical Effect of Perfume on Well-Being*, Springer, 2023, pp. 53–80.

C. Barbieri, P. Borsotto, and others, “Essential oils: market and legislation,” *Potential Essent. oils*, pp. 107–127, 2018.

C. Wambolt, “Exposure to Toxic Chemicals in Consumer Products in the United States,” *Ballard Br.*, vol. 2021, no. 1, p. 1, 2021.

R. Asra, R. Rusdi, P. Arifin, and N. Nessa, “Analisis Senyawa Berbahaya Parfum Isi Ulang Yang Dijual Di Kota Padang Menggunakan Metode Kromatrografi Gas-Spektrometri Massa,” *J. Ris. Kim.*, vol. 10, no. 1, pp. 20–29, 2019.

L. Mondello, A. Casilli, P. Q. Tranchida, G. Dugo, and P. Dugo, “Comprehensive two-dimensional gas chromatography in combination with rapid scanning quadrupole mass spectrometry in perfume analysis,” *J. Chromatogr. A*, vol. 1067, no. 1–2, pp. 235–243, 2005.

I. Gavris, E. Bodoki, P. Verite, and R. Oprean, “Assessment of perfume ingredients with aphrodisiac potential by gas chromatography-mass spectrometry,” *Farmacia*, vol. 63, pp. 760–764, 2015.

A. F. Al-Rubaye, I. H. Hameed, and M. J. Kadhim, “A review: uses of gas chromatography-mass spectrometry (GC-MS) technique for analysis of bioactive natural compounds of some plants,” *Int. J. Toxicol. Pharmacol. Res.*, vol. 9, no. 1, pp. 81–85, 2017.

K. Gurning, H. A. Simanjuntak, H. Purba, and others, “Identification of the chemical compound of essential oil from ketumbar (Coriandrum sativum L.) leaves with GC-MS,” *Pharmacogn. J.*, vol. 12, no. 5, 2020.

J. Liu, M. Lin, P. Han, G. Yao, and H. Jiang, “Biosynthesis Progress of High-Energy-Density Liquid Fuels Derived from Terpenes,” *Microorganisms*, vol. 12, no. 4, p. 706, 2024.

N. T. Program and others, “NTP Technical Report on the Toxicity Studies of o-Phthalaldehyde

(CASRN 643-79-8) Administered by Inhalation to Sprague Dawley (Hsd: Sprague Dawley®SD®) Rats and B6C3F1/N Mice," 2018.

S. T. Cragg, "Glycol ethers: Ethers of propylene, butylene glycols, and other glycol derivatives," *Patty's Toxicol.*, pp. 789–878, 2001.

V. H. Adams, "Toxicology Report No. HEF-S. 0059709.14-19, October 2021 Toxicology Directorate Toxicology Assessment for Work Unit SAGE 16-01 Qualification of HAP-free Cleaners for Aircraft and Ground Vehicles October 2019-October 2021," *SAGE*, vol. 16, p. 1, 2021.

R. Soulimani, J. Bouayed, and R. K. Joshi, "Limonene: natural monoterpene volatile compounds of potential therapeutic interest," *Am. J. Essent. Oils Nat. Prod.*, vol. 7, no. 4, pp. 1–10, 2019.

S. Nikfar and A. F. Behboudi, "Limonene," 2014.

N. S. Dosoky and W. N. Setzer, "Biological activities and safety of Citrus spp. essential oils," *Int. J. Mol. Sci.*, vol. 19, no. 7, p. 1966, 2018.

L. Caputo *et al.*, "Lavender and coriander essential oils and their main component linalool exert a protective effect against amyloid-$β$ neurotoxicity," *Phyther. Res.*, vol. 35, no. 1, pp. 486–493, 2021.

S. C. Rastogi, S. Heydorn, J. D. Johansen, and D. A. Basketter, "Fragrance chemicals in domestic and occupational products," *Contact Dermatitis*, vol. 45, no. 4, pp. 221–225, 2001.

V. T. Politano, E. M. Lewis, A. M. Hoberman, M. S. Christian, R. M. Diener, and A. M. Api, "Evaluation of the developmental toxicity of linalool in rats," *Int. J. Toxicol.*, vol. 27, no. 2, pp. 183–188, 2008.

X. Guo and P. Wang, "Aroma characteristics of lavender extract and essential oil from Lavandula angustifolia mill.," *Molecules*, vol. 25, no. 23, p. 5541, 2020.

C. S. Letizia, J. Cocchiara, J. Lalko, and A. M. Api, "Fragrance material review on linalyl acetate," *Food Chem. Toxicol.*, vol. 41, no. 7, pp. 965–976, 2003.