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# Type and magnitude of non-compliance and adulteration in neroli, mandarin and bergamot essential oils purchased on-line: potential consumer vulnerability

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1 Type and magnitude of non-compliance and adulteration in neroli, mandarin and  
2 bergamot essential oils purchased on-line: potential consumer vulnerability

3  
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17  
18 **Abstract**

19  
20 Thirty-one samples of essential oils used both in perfumery and aromatherapy were  
21 purchased to business-to-consumers suppliers and submitted to standard gas  
22 chromatography-based analysis of their chemical composition. Their compliance with ISO  
23 AFNOR standards was checked and revealed, although ISO AFNOR ranges are relatively loose,  
24 that more than 45% of the samples analyzed failed to pass the test and more than 19% were  
25 diluted with solvents such as propylene and dipropylene glycol, triethyl citrate, or vegetal oil.  
26 Cases of non-compliance could be due to substitution or dilution with a cheaper essential oil,  
27 such as sweet orange oil, blending with selected compounds (linalool and linalyl acetate,  
28 maybe of synthetic origin), or issues of aging, harvest, or manufacturing that should be either  
29 deliberate or accidental. In some cases, natural variability could be invoked. These products  
30 are made available to the market without control and liability by resellers and could expose  
31 the public to safety issues, in addition to commercial prejudice, in sharp contrast with the  
32 ever-increasing regulations applying to the sector and the high demand of consumers for safe,  
33 controlled and traceable products in fragrances and cosmetic products.  
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## 37 Introduction

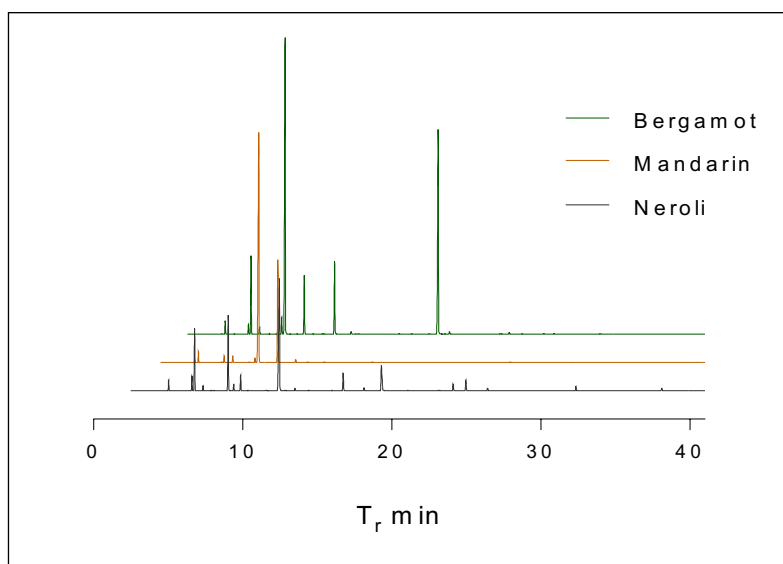
38 Essentials oils (EOs) are complex natural substances obtained by physical treatments of selected parts  
39 of plants. In most instances, distillation is used, either through hydro-distillation techniques or, for  
40 more sensitive materials, by steam distillation. In the particular case of the *Citrus* genus, cold pressure  
41 is generally applied to the pericarp to obtain the EO.

42 The fraction of the metabolome of plants as observed in EOs is mostly composed of terpenes,  
43 terpenoids, and phenylpropanoids. Sometimes, linear hydrocarbons are also observed as in rose EOs,  
44 or other compounds with sulphur-containing functional groups such as thiols or thiocyanates.  
45 Considering the method of obtention, EOs are almost exclusively volatile materials, although in the  
46 case of cold-pressed EOs, a non-negligible fraction can be non-volatile.

47 As volatile material, the analytical technique of choice for EOs is gas chromatography (GC) which allows  
48 for, when conducted with adequate and validated methods, both qualitative and quantitative  
49 characterization.<sup>1</sup> Typically, identity of analytes is obtained by coupling mass spectrometry (MS) with  
50 gas chromatography (GC-MS), determining retention indexes and co-injecting pure compounds if  
51 necessary, while their proportion in the mixture is determined by using a stable and universal detector  
52 such as a flame ionization detector (GC-FID) using the corrected response factor method.<sup>2,3</sup> The  
53 chemical composition of EOs thereby obtained is reproducible, and only subjected to natural variation  
54 that could occur depending on geographical, seasonal, or agricultural factors and manufacturing  
55 processes.<sup>4</sup>

56 For centuries EOs have attracted the attention of mankind for their biological properties, either as  
57 odoriferous material for religious or pagan practice, and perfumery, or for therapeutic applications,  
58 either in folk medicine, aromatherapy or pharmaceutical activities.<sup>5,6</sup> As potentially biologically active  
59 material, EOs sometimes contain significant quantities of toxic compounds such as methyleugenol  
60 (suspected carcinogen),<sup>7,8</sup> safrole (weak hepatocarcinogen among other adverse effects), estragole  
61 (suspected carcinogen and genotoxic),<sup>9-13</sup> furocoumarins (dermatitis inducers),<sup>14,15</sup> and allergenic  
62 compounds, among others.<sup>16</sup>

63 In the particular case of *Citrus* EOs, the chemical composition features mostly monoterpenes and  
64 monoterpenoids, the prominent metabolite being limonene, either as the *R* or *S* enantiomer  
65 depending on the genus, species or even cultivar.<sup>17,18</sup> *Citrus* EOs such as bergamot (*Citrus bergamia*),  
66 mandarin (*Citrus reticulata*), or neroli (*Citrus aurantium* ssp *Amara* or *Bigaradia*, from which only the  
67 flowers are steam distilled) EOs play an important role in fine perfumery for their delicate scents; while  
68 sweet orange (*Citrus sinensis*) EO, which is almost entirely constituted of (*R*)-limonene, has very little  
69 olfactory interest (Figure 1).



70

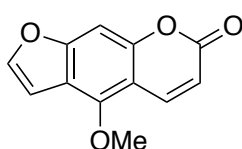
71 **Figure 1.** Examples of total ion chromatograms, offset by 1 minute each, of *Citrus* essential oils  
 72 (bergamot, mandarin, and neroli essential oils). Chemical compositions are detailed below.

73

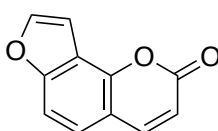
74 *In vitro* and *in vivo* biological activities for *Citrus* EOs have been reported such as antimicrobial, antiviral  
 75 and antioxidant properties, insect repellent activities,<sup>19</sup> as well as effects on central nervous system  
 76 (anxiety, attention, relaxation, sleep, mood, stress ...) <sup>20</sup> and should be used as natural preservatives.<sup>21-  
 77 <sup>23</sup></sup>

78 On a darker side, toxicity issues arise in the presence of furocoumarins, present in the non-volatile  
 79 fraction of some *Citrus* EOs obtained by cold-pressure along with the EO (*vide supra*), and  
 80 hydroperoxides, such as limonene hydroperoxide due to aging and auto-oxidation under air and light  
 81 exposure.<sup>24</sup> Furocoumarins and hydroperoxides can induce skin disorders such as contact dermatitis  
 82 and other allergenic reactions, and in worse cases exhibit photogenotoxicity for the former (Figure  
 83 2).<sup>14</sup> Furocoumarins total content should not exceed 1 ppm in cosmetic products in Europe.<sup>25</sup>

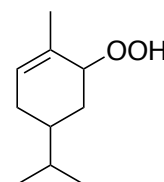
84



85 **Bergapten**



85 **Angelicin**



85 **Limonene 2-hydroperoxide**

86

86 **Figure 2.** Chemical structures of some furocoumarins and limonene 2-hydroperoxide.

87

88 EOs can be obtained from various part of most plants (flowers, leaves, steams, buds, roots, bark ...)  
89 resulting in a large diversity of EOs. However, because of the similarities in the early steps of plant  
90 metabolism, individual compounds such as monoterpenes are found in the essential oils of many  
91 plants. In the case of sweet orange EO, huge quantities are available on the market because it is a co-  
92 product of orange juice manufacture resulting in low cost and large availability (30 000 tons in 2004  
93 and increasing).<sup>26</sup> At the same time, rare EOs of high demand and/or of limited offer such as those  
94 obtained from rose (*Rosa damascena*), agarwood (*Aquilaria malaccensis*), orris (*Iris germanica*) or  
95 ylang ylang (*Cananga odorata*) are difficult to find and their value can reach several thousands of euros  
96 per kilogram. This contrast has resulted in economically motivated adulteration (EMA), a fraudulent  
97 practice consisting in adding cheap material to an expensive one to increase profit.<sup>27</sup> Adulteration of  
98 essential oils is typically observed in four different types:

- 99 - Dilution with a solvent featuring similar physico-chemical properties than EOs such as vegetal  
100 oils, or organic solvents (triethylcitrate, (di)propylene glycol, alkyl phthalates, ...);
- 101 - Addition of a cheaper EO more or less close in terms of origin (same genus) or chemical  
102 composition (e.g. sweet orange EO (*Citrus sinensis*) in other *Citrus* EOs or palmarosa EO  
103 (*Cymbopogon martini*) in rose EOs);
- 104 - Addition of individual compounds, either natural or synthetic, to mimic the olfactory  
105 properties, the composition or the chemotype (e.g. linalyl acetate to mimic lavender EO  
106 (*Lavendula angustifolia*) or neryl acetate to mimic immortelle EO (*Helichrysum italicum*));
- 107 - Substitution with another EO or mixture of EOs of low value (sweet orange oil, turpentine oil,  
108 ...) to which key compounds, either natural or synthetic, are added.

109 These types of deliberate practice should not be agglomerated with accidental events (errors of  
110 botanical authentication, inadvertent blending of vegetal material, sometimes handled as powders,  
111 contamination during manufacture, storage, labelling, ...) or natural variation that result in non-  
112 compliance. Trading of EOs is framed by normative references such as ISO and AFNOR providing  
113 industry accepted ranges of concentration for selected compounds in each EO.<sup>28</sup>

114 In all these cases, analytical chemistry is required to characterize adulteration both qualitatively and  
115 quantitatively.<sup>29</sup> Adulteration techniques have evolved continuously along with analytical  
116 countermeasures to reach a high level of sophistication. Indeed, besides sensory and physico-chemical  
117 properties such as density, optical rotation, or refractive index, R&D and QC labs have developed  
118 techniques and combinations of techniques to identify even the most subtle cases of adulteration.  
119 Worth mentioning but not limited to are isotopic approaches (<sup>13</sup>C/<sup>12</sup>C ratios or <sup>14</sup>C contents),<sup>30</sup>

120 enantioselective analyses,<sup>31</sup> multidimensional GC techniques,<sup>32</sup> or spectroscopic or spectrometric  
121 methods (NMR,<sup>33</sup> fluorescence,<sup>34</sup> IR,<sup>35</sup> Raman<sup>36</sup>) coupled with metabolomic approaches.

122 In contrast with these accurate, efficient, and sensitive techniques in constant evolution which enable  
123 professionals to detect most cases of adulteration, consumers in business to consumer (B to C)  
124 commerce have limited knowledge about issues of adulteration and no analytical capabilities and can  
125 only count on the fairness of their suppliers. The inherent risk for consumers handling concentrated,  
126 potentially biologically active, molecules with cases of overdose, misuse and intoxication in family  
127 practice is compounded upon when these products may not match their labels.<sup>37</sup>

128 In this context, we embarked into a study of the quality of EOs purchased on-line directly from EOs  
129 suppliers web sites or from global shopping platforms operating worldwide. We have chosen to focus  
130 on three *Citrus* EOs: mandarin (*Citrus reticulata*), bergamot (*Citrus bergamia*), and neroli (*Citrus*  
131 *aurantium* ssp *Amara* or *Bigaradia*).

132

### 133 **Results and discussion**

134 In the frame of a research program dedicated to the study of authenticity and naturality of essential  
135 oils, and considering the increasing interest of consumers for essential oils, natural products, home-  
136 made cosmetics and household products, we became interested in sampling essential oils purchased  
137 on-line to evaluate their quality. We thus purchased samples of EOs of mandarin (*Citrus reticulata*),  
138 bergamot (*Citrus bergamia*), and neroli (*Citrus aurantium* ssp *Amara* or *Bigaradia*). With 23 samples  
139 out of ca. 230 made available from a large platform operating on-line, the sampling size was deemed  
140 sufficient to have a first estimate ( $\pm 20\%$  at the 95% level of confidence, for a normal distribution). To  
141 these 23 samples were added 8 additional samples purchased from other retail sources, mostly online  
142 as well. To encompass the largest variability possible, we decided to simply start with checking the  
143 compliance of these samples with ISO norms using gas chromatography coupled with flame ionization  
144 detector (FID) and mass selective analyzer (MS).

145

#### 146 *Analysis of neroli essential oil (NEO)*

147 Nine commercial samples of NEO were analyzed and their peak areas were compared to ISO Norm  
148 3517.<sup>38</sup> Two samples were acquired from a reputable source and considered premium samples. Of the  
149 nine neroli samples, only one sample, N4, met all of the ISO chromatographic specifications. The ISO  
150 standard includes acceptable ranges for 13 compounds;  $\alpha$ -pinene,  $\beta$ -pinene, sabinene;  $\beta$ -myrcene,

151 limonene, (*E*)- $\beta$ -ocimene, linalool,  $\alpha$ -terpineol, linalyl acetate, neryl and geranyl acetate, (*E*)-nerolidol  
152 and (*E,E*)-farnesol.

153 Samples N6 and N9, were not compliant with all 13 compounds in the ISO range. N9 is low in  $\beta$ -pinene  
154 and high in linalyl acetate at  $16.19 \pm 0.02\%$  compared to the 3-15% range. N6 had  $21.42 \pm 0.02\%$  linalyl  
155 acetate, significantly outside the ISO range.

156 N1 and N2 were purchased online from two different labels but shared nearly identical compositions.  
157 Both had low values for  $\beta$ -pinene,  $\beta$ -myrcene, limonene, linalool and (*E*)-nerolidol. Linalyl acetate  
158 constituted over 26% of the oils' compositions; more than 10% higher than the ISO prescription.  
159 Sabinene and  $\alpha$ -pinene were not identified in either sample, however the standard range extends to  
160 traces of these compounds. Comparing the peak areas to the premium samples shows a gross  
161 adulteration by dilution, likely with a vegetal oil or propylene glycol type diluent.

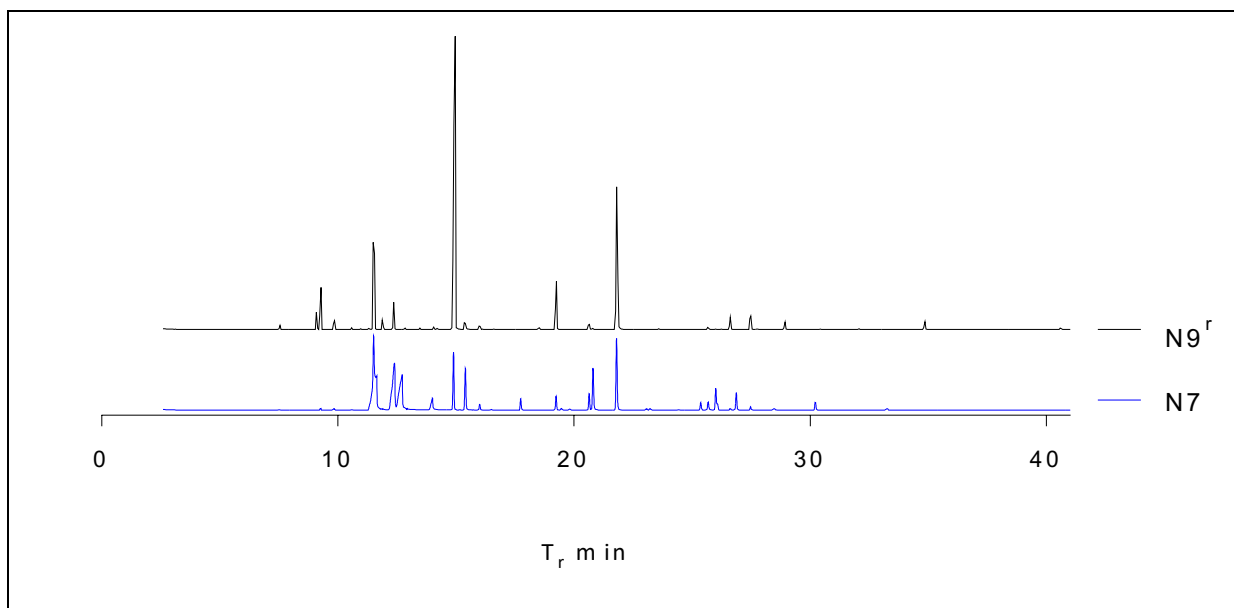
162 N3 and N4 were two of the best samples compared to the ISO requirements. N3 had low  $\beta$ -myrcene  
163 and (*E*)-nerolidol content. N4 met all of the prescribed values. N3's adherence is surprising due to its  
164 price point at less than \$1/mL compared to N4's \$5.32/mL. This is not to say there is no chance of  
165 adulteration in either of these samples, merely that these samples meet, or nearly meet, the advice of  
166 the ISO reference.

167 N5 fell out-of-range for 6 out of the 13 compounds.

168 N7 and N8 were severely adulterated with di-propylene glycol and propylene glycol, respectively. The  
169 chromatograms clearly show the adulterants as well as the resulting peak reduction of the compounds  
170 of interest (see S.I.). The coelution of the adulterant and the analyte peaks makes it difficult to even  
171 compare the samples to the ISO reference. This disregard toward the obviousness of adulteration is  
172 indicative of the fact that consumers have no real means of verifying the quality of the product. The  
173 business knows that the consumer has no access to GC and can adulterate without sophistication.

174 In addition, to boost olfactory properties, N7 contained 4-tert-butylcyclohexyl acetate (mixture of  
175 diastereoisomers), a well-known synthetic woody odorant, and N1, N2 and N7 contained nerolin and  
176 methyl- $\beta$ -naphthyl ketone, which are synthetic materials known for decades exhibiting neroli  
177 perfume.<sup>39</sup>

178 By comparing for example N7 and N9<sup>r</sup> (Figure 3), broad peaks in N7 are clearly visible and represent  
179 dipropylene glycol adulteration. There is a marked difference in linalool concentration at 15 min  
180 between the two samples. N7 also has significantly higher concentration of 2-phenylethanol, a  
181 naturally occurring compound in neroli found in the reference at about 1.1% but 5.24% in N7.



**Figure 3.** Sample comparison of two neroli samples as seen on GC-FID.

182  
183  
184  
185

186 N10, although considered reference for its olfactory quality, does not meet all specifications.

187

#### 188 *Analysis of mandarin essential oil (MEO)*

189 Mandarin oil is particular in the industry as the fruit is harvested in 3 stages of maturity; green, yellow  
190 and red mandarin oils can be sold as distinct oils, although the ISO norm only specifies Italian type  
191 mandarin. This range of harvest times affects the chemical composition of the oils but the three  
192 mandarin oils are not given individual ISO ranges. This increases the difficulty of determining if the  
193 variation of the composition is natural or the result of adulteration. Cold-pressed oils contain  
194 compounds too heavy or chemically unlikely to distill like waxes and furocoumarins. Citrus oils have  
195 characteristic furocoumarin compositions that can aid in the identification of adulteration. This  
196 approach was indeed successfully applied recently using either HPLC with columns with fused-core  
197 technology or UPLC-TOF-MS.<sup>40,41</sup>

198 Eleven commercial samples of MEO were analyzed and their peak areas were compared to ISO Norm  
199 3528.<sup>42</sup> Two samples were acquired from reputable sources and considered premium reference  
200 samples. Of the eleven MEO samples, only one sample, M4, met all of the ISO chromatographic  
201 specifications. The ISO standard includes acceptable ranges for 7 compounds;  $\alpha$ -pinene,  $\beta$ -pinene,  
202 myrcene,  $\gamma$ -terpinene, limonene, methyl-N-methylantranilate, and  $\alpha$ -sinensal.

203 The premium samples, M12 and M13 did not meet all 7 profiled compounds. M12 fell out of range for  
204 4 compounds. M13 was high for  $\beta$ -pinene at  $3.13 \pm 0.19\%$  rather than 2.0% max.



205 M1 and M2 were grossly out of specification in very similar fashion. Falling out of range for 6  
206 compounds, only passing the myrcene specification. Each have about 95% limonene content which  
207 would suggest the oil is actually sweet orange essential oil. Methyl N-methylantranilate was also not  
208 detected, an important odorant molecule for mandarin oil.

209 M3 poses an interesting question. Four of the regulated compounds are out of the ISO range, however,  
210 they are just slightly beyond the ranges. For example, ISO limits limonene to 65-75% area, this sample  
211 has  $76.15 \pm 0.04\%$ ; similarly,  $\gamma$ -terpinene is set from 16-22% with M3 containing  $15.35 \pm 0.005\%$ . The  
212 question then becomes, how hard are the limits of the ISO ranges? Is a sample really “bad” if it falls  
213 just beyond the prescribed ranges or should it be considered natural variability?<sup>43</sup> Besides the question  
214 of maturity of mandarins at the time of harvest mentioned above, linalool and linalyl acetate vary by  
215 several percent throughout a growing season of Egyptian neroli oil,<sup>44</sup> and  $\alpha$ -terpineol, terpinen-4-ol,  
216  $\alpha$ - &  $\beta$ -phellandrene and camphene change within growing seasons of bergamot crops, with  $\alpha$ -  
217 terpineol increasing consistently and dramatically throughout the season across different years.<sup>45</sup>

218 M4 and M10 came from the same company. M4 meets all requirements of the ISO mandarin reference.  
219 M10 was sold as tangerine and does not meet the requirements of the mandarin norm. There is no  
220 official ISO norm for tangerine but literature suggests that a limonene content greater than 90% and a  
221  $\gamma$ -terpinene content near 4% are characteristic.<sup>46</sup> M10 has a limonene content of 93.4% and  $\gamma$ -  
222 terpinene at 2.9% seemingly in agreement with other tangerine oils.

223 M5, M8, and M9 are all very nearly within the specification of the ISO standard. M5 met all specified  
224 ranges excluding  $\alpha$ -sinensal. M8 is just below the range for methyl N-methylantranilate and  $\alpha$ -  
225 sinensal was not identified, with all other compounds within the ranges. M9 had a limonene content  
226 of  $76.12 \pm 0.03\%$  and a  $\gamma$ -terpinene content of  $15.64 \pm 0.01\%$ . These minor deviations from the ISO  
227 profile could be considered natural variations within an oil.

228 M11 only met the specification for limonene, the other 6 compounds falling below the required ranges  
229 or not identified at all. Uncharacteristically, this oil also contained linalool and linalyl acetate at over  
230 10% each. This could be a sign of adulteration, potentially to improve the scent.

231 Furocoumarins contents were evaluated for the whole set of mandarin samples by reversed-phase  
232 HPLC-PDA analysis using 5-methylpsoralen<sup>47</sup> as analytical reference. M1, M2 and M10 showed the  
233 same furocoumarin pattern as sweet orange oil taken as reference. Most samples did not undergo  
234 furocoumarin removal process. Orange oil being sold with a label of mandarin oil can more than double  
235 the sale price (from \$0.20 to \$0.57 per mL from one source) to consumers that may not have a nose  
236 sensitive enough to smell the differences.

237

238 *Analysis of bergamot essential oil (BEO)*

239 Eleven commercial samples of bergamot essential oil were analyzed and their peak areas were  
240 compared to ISO Norm 3520.<sup>48</sup> Two samples were acquired from reputable sources and considered  
241 premium reference samples. Of the eleven BEO samples, only one sample, B6, met all of the ISO  
242 chromatographic specifications. The ISO standard includes acceptable ranges for 7 compounds:  $\beta$ -  
243 pinene,  $\gamma$ -terpinene, limonene, linalool, linalyl acetate, geranial, and  $\beta$ -bisabolene.

244 B1 and B2, purchased at 12.5 cents/mL, were subject to gross dilution. B1 had a large peak identified  
245 as triethyl citrate (TEC) comprising 60% of the total peak area. Excluding the TEC peak, B1 meets the  
246 relative peak area requirements of the ISO standard. B2 also meets the peak area requirements of the  
247 ISO standard, but is heavily diluted with a vegetal oil that is not visible by GC directly. These oils are  
248 likely genuine bergamot essential oils that have been diluted with a known perfumery solvent. <sup>1</sup>H-NMR  
249 analysis indeed showed in B1 characteristic signals of TEC with 2 quadruplets at 4.8-4.0 ppm, 2  
250 doublets with strong coupling constants and roof effect at 2.9-2.5 ppm, and 2 triplets at 1.3-1.2 ppm.  
251 In B2, a pattern consisting of ethylenic, allylic and aliphatic signals characteristic of soybean oil was  
252 observed (see S.I.).

253 The majority of the bergamot samples nearly met all of the ISO prescription except for either the  
254 geranial or  $\beta$ -bisabolene ranges. B3 was just over the range for  $\beta$ -pinene at  $9.58 \pm 0.00\%$  and below  
255 the 0.3% minimum  $\beta$ -bisabolene level, with all other compounds within the range. B4 and B10 also fell  
256 out of range for  $\beta$ -bisabolene. B4, B11 and B12, were lower than the 0.25% minimum geranial  
257 specification, B4 being nearly at the limit with  $0.24 \pm .004\%$ . B10 has a second compound out of range,  
258  $\gamma$ -terpinene, which is  $5.83 \pm 0.02\%$ , below the 6% AFNOR value. B9 falls just out of range for  $\beta$ -pinene  
259 at  $5.43 \pm 0.38\%$ , but this standard deviation would suggest the  $\beta$ -pinene can be considered within the  
260 range. B7 was in range for all compounds except geranial. B5 has 3 compounds out of range, but to a  
261 very small extent. These samples are all very close to being acceptable according to the AFNOR ranges.  
262 They are unlikely to be adulterated, but likely graded as lower odor quality by the perfume industry  
263 and sold to the essential oil industry.

264 B6 is entirely conformant to the ISO reference. B7, purchased from a French pharmacy, was fully  
265 compliant except for geranial again, possibly due to aging, aldehydes such as geranial and neral being  
266 lost upon oxidation to the corresponding carboxylic acids or cyclized and dehydrated to *para*-  
267 cymene.<sup>49,50</sup>

268 Reverse-phase HPLC-PDA analysis of bergamot samples revealed the presence of 5-methylpsoralen  
269 and a closely related peak, and at significantly lower concentrations in highly diluted samples B1 and

270 B2. Furocoumarin free (FCF) samples; B4, B10, B15, and B16 contained neither of these peaks, but had  
271 defaults in their composition in geranial and  $\beta$ -bisabolene.

272

273 *Graphical representation with heat maps*

274 Statistical manipulation follows a modified Z-score analysis. Standard Z-scores are calculated using the  
275 statistical mean and standard deviation.

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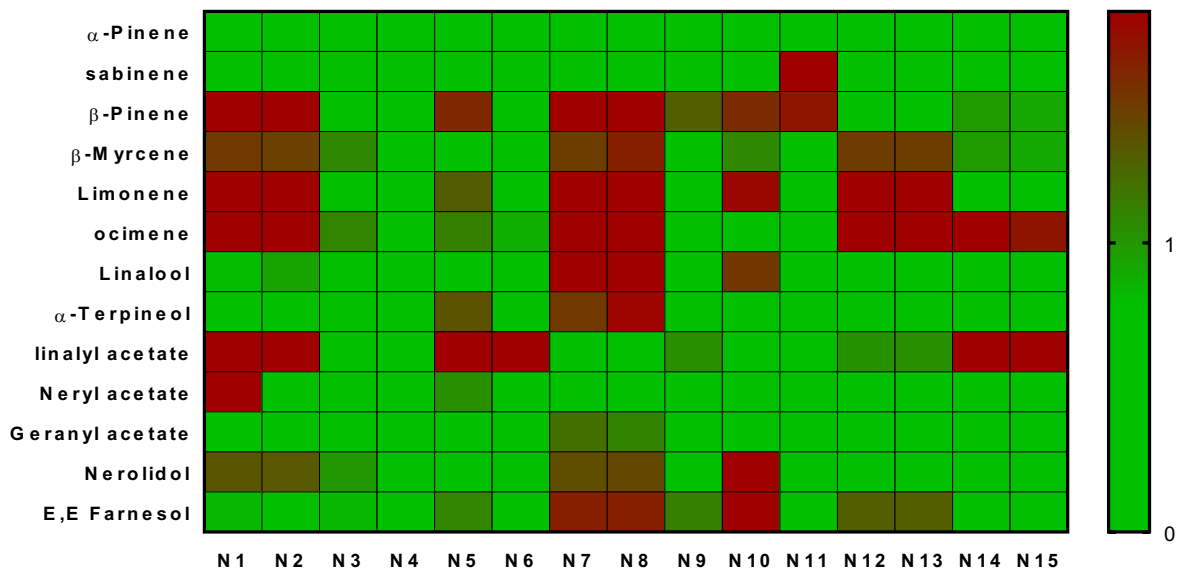
277 
$$z = \frac{x - \mu}{\sigma}$$

278 The score relays the relative distance of a data point to the mean, a Z-score less than one would place  
279 the data point within the first standard deviation of the data set.

280 In this analysis, the Z-score calculation was modified to reflect the AFNOR/ISO guidelines. The mid-  
281 point of the range replaces the statistical average ( $\mu$ ), and the distance between the mid-point and the  
282 edge of the range becomes the standard deviation ( $\sigma$ ). This results in a score of the distance of each  
283 compound from the accepted value, normalized to the magnitude of the range. This allows for easier  
284 comparison of compounds present at varying levels and with different specifications.

285 Heat maps are generated by applying the modified Z-score calculation to each sample's compounds of  
286 interested per the AFNOR standard. A score less than or equal to one is green, signifying the acceptable  
287 level of the compound. Scores over 1 are (gradient from green to red) with the intensity reflecting the  
288 severity of the distance from the accepted value. This visual representation shows quickly and  
289 intuitively if a sample is compliant or far from the AFNOR guidelines (Figures 4-6).

290

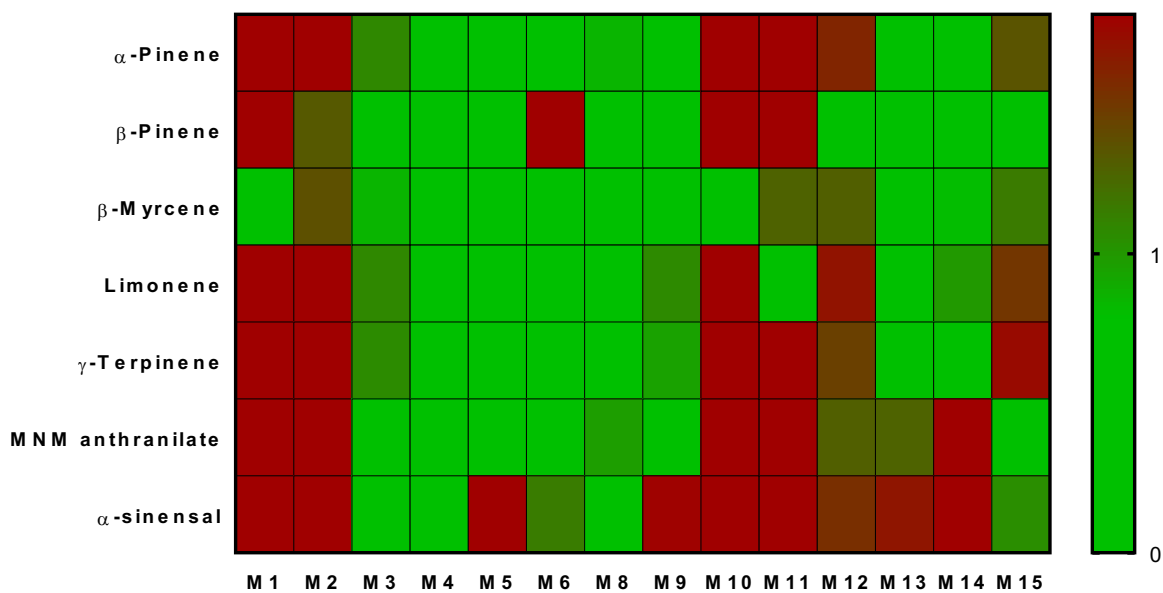


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**Figure 4.** Heat map of relative scores of neroli essential oils for relevant compounds according to ISO 3517. N9 and N10 were obtain from a reputable source.

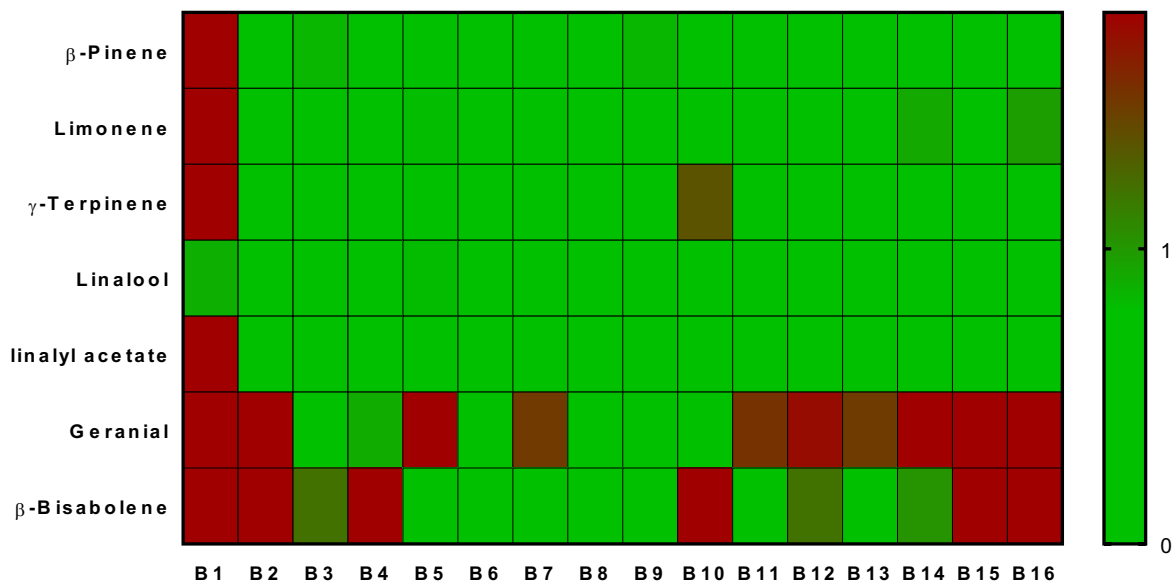


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**Figure 5.** Heat map of relative scores of mandarin essential oils for relevant compounds according to ISO 3528. M12 and M13 were obtain from reputable source.



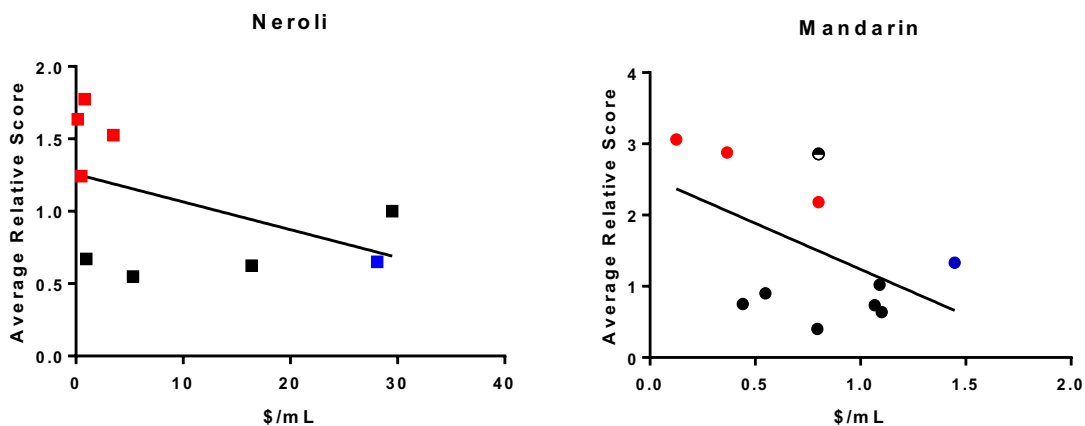
**Figure 6.** Heat map of relative scores of bergamot essential oils for relevant compounds according to ISO 3520. B11 and B12 were obtained from reputable sources.

### *Price/quality relationship*

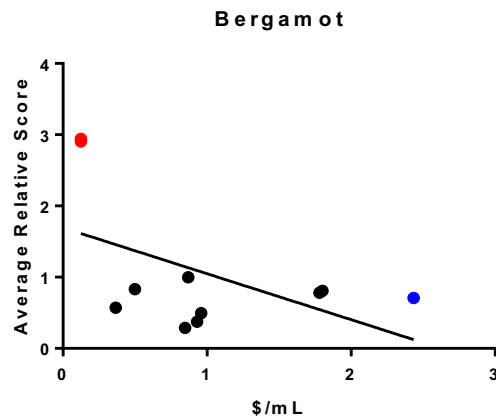
Price per milliliter of oil was calculated based on the purchase price in USD, excluding tax, and the container volume per label. Samples were chosen from online retailers with the intention of obtaining a range of price points. The hypothesis being that adulteration would be more prevalent in samples with a lower price/mL. Economically motivated adulteration is the unethical practice of adding material to a product to increase profits. To add diluent to an oil sold well below the market value would allow the seller to make a profit even at a reduced price, a buyer could predict that the quality of the product may be compromised when buying at a deep discount. To add diluent to an oil sold at or above market value would significantly increase the profits of the seller while falsely assuring the buyer that the oil is of the quality expected at the higher price point.

Because of neroli's high price, it is of particular interest in this study. Neroli is the steam distilled oil of bitter orange flowers, floral EOs are often expensive due to the delicate harvest procedures and low oil yields.<sup>51</sup> Additionally, because neroli blossoms become oranges if left to be pollinated on the tree, there is often a limit on neroli harvest in order to not impact the later bitter orange harvest. The price per milliliter of neroli in our sample set ranged from \$0.17/mL to \$29.50/mL. Sample N4, the only sample to meet all of the ISO guidelines for neroli EO was purchased at \$5.31/mL, falling about the median price of our sample list while the most expensive sample, N5, failed to meet 6 out of 13 of the requisite values (Figure 7).

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322

323 **Figure 7.** The average relative score of each sample is plotted against the price in USD per  
324 milliliter of essential oil (red: adulterated; black: acceptable; blue: reference).

325

326 Mandarin is a considerably less expensive oil. The price range of the samples analyzed here was \$0.12-  
327 \$1.45/mL, with the average price/mL equal to \$0.78.

328 This data does not give a clear prescriptive for purchasing a quality essential oil. The problem is not  
329 resolved by simply buying the most expensive oil. One could imagine that advice being quite dangerous  
330 to the market, flooding it with overpriced low-quality oils. The transparency and the quality control  
331 standards of businesses then become the consumers' guides for purchasing.

332 **Conclusion**

333 Regulatory bodies will struggle to police the online world of consumer products because of the  
334 magnitude of the industry. It would be impossible to test every essential oil in the online market the

335 way we have for these 31 products. Policing the market becomes even more difficult when a company  
336 that exists only online can change names or raw materials with little to no traceability. Label control  
337 seems non-existent with nearly all labels including some version of the words 100% pure, natural, or  
338 therapeutic grade essential oil. Most labels include verbiage to dilute essential oils as they are highly  
339 concentrated and can irritate skin, even on samples that had been heavily diluted already. There is  
340 also the question of who is at fault when an oil is sold adulterated. Is the adulteration happening at  
341 the raw material stage and the seller is only guilty of not verifying their raw materials? Or are the  
342 sellers buying quality raw materials and adulterating the products themselves? The surest choice for  
343 one consumer at the end of this complex value chain seems to be to purchase essential oils from known  
344 suppliers with a brand strategy, generally running rigorous quality control.

345

## 346 **Materials and Methods**

347 Commercial EO samples were obtained through internet retailers and French pharmacies. Premium  
348 samples were obtained from reputable fragrance houses. Nine (9) bergamot (*Citrus bergamia*)  
349 essential oil samples were purchased from online retailers, and 1 was purchased in a French pharmacy.  
350 Eight (8) mandarin (*Citrus reticulata*) essential oil samples were purchased online, 1 from a French  
351 pharmacy. One (1) Tangerine sample was also purchased online to compare to the mandarin samples.  
352 Eight (8) neroli (*Citrus aurantium*) essential oil samples were purchased from online retailers.

353 An Agilent Technologies gas chromatograph (6890) was used with a flame ionization detector (FID),  
354 and an Agilent J&W HP-5 column with dimensions 30m x 0.32mm ID, with 0.25µm film thickness. 1 µL  
355 of diluted essential oil (20 µL sample and 20 µL of 5mg/mL methyl octanoate internal standard diluted  
356 to 1.0 mL with ethyl acetate) was injected in split mode at 10:1. Oven temperature was programmed  
357 at 50 C for 3 minutes, then to 265 C at 3 C/min, a final ramp to 300 C at 15 C/min and 5 min hold.  
358 Injector and detector temperatures were set at 265 °C. Hydrogen was the carrier gas at a constant flow  
359 of 35 mL/min. Linear retention indices were calculated with reference to n-alkanes (C7-C30).

360 GC-MS analyses were performed on a 7890A GC system coupled to a 5975C VL mass spectrometer  
361 detector (Agilent Technologies) equipped with an Agilent J&W HP-5 column with dimensions 30m x  
362 0.32mm ID, with 0.25µm film thickness. 1 µL of diluted essential oil (20 µL sample and 20 µL of 5mg/mL  
363 methyl octanoate internal standard diluted to 1.0 mL with ethyl acetate) was injected in split mode at  
364 10:1. The GC-MS experimental conditions developed in the laboratory were the same as GC-FID  
365 analysis except for injector and detector temperatures (200 °C); carrier gas (helium); ionization voltage  
366 70 eV; electron multiplier, 1 kV. Compound identification was accomplished through comparison of

367 their mass spectra to NIST05 libraries as well as by comparison of their retention indices literature  
368 data. EOs compositions are given as relative area percentages. See SI for more details.

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495 **Author Contributions**

496 M.P. performed the analytical experimentation. M.P. and S.A. wrote the article. M.P., X.F. and S.A.  
497 participated in drafting the article. All authors designed the study, discussed the results and  
498 commented on the manuscript.  
499

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