Application Note

Instrument: Pegasus® BT

Characterization and Comparison of Citrus Aromas in Lemon and Lime Essential Oils with GC-MS

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Key Words: Essential Oil Analysis, Aroma Profile, Characterization, Comparison, Retention Index, GC, MS, TOFMS, Deconvolution

Introduction

Essential oils have a broad range of application, as they can be both a finished product and an ingredient or intermediate in the creation of other products. Due to this versatility, the analysis of essential oils is an important area of research with a variety of analytical objectives. Various goals may include quality control, authentication, or general characterization for better understanding the chemical constituents in the essential oil and how to best use them in a process or product. Gas Chromatography (GC) paired with Mass Spectrometry (MS) is an excellent tool for addressing these analytical needs. Essential oils are comprised of primarily volatile and semi-volatile analytes that are readily separated, identified, and quantified with GC-MS. The separation is achieved chromatographically and through the mathematical deconvolution of the full m/z range data, while the identification and quantification are achieved from library searching acquired mass spectral information and peak profile integration, respectively. The result of this type of GC-MS analysis is detailed chemical information on the constituents, which can help meet a variety of the analytical objectives. In this work, we use GC-MS for the characterization and comparison of two citrus essential oils: lemon and lime. The individual chemical components are determined and those with citrus odor notes are compared to better understand the similarities and differences in the citrus aroma profile of these materials. We demonstrate the benefits of full m/z range data, deconvolution, and retention index determinations for learning what else is in your sample.

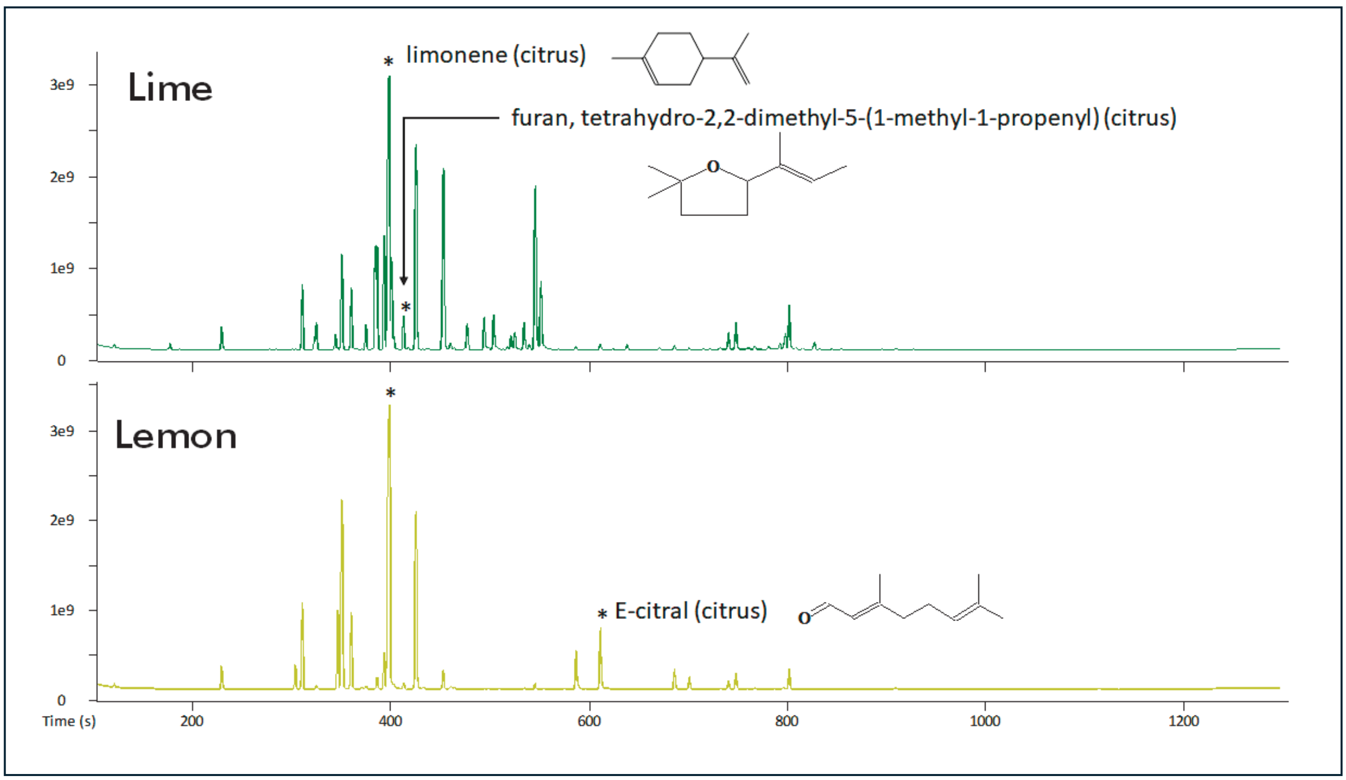


Figure 1. TIC Chromatogram for lemon and lime essential oils. Some key analytes with citrus odor types are highlighted.

Experimental

Lemon and lime essential oils were diluted to 1% in acetone and analyzed with GC-TOFMS, as described in Table 1. Data for an alkane standard (C6 through C24) were also collected with the same methods for Retention Index determinations.

Table 1. GC-TOFMS (*Pegasus* BT) Conditions

Gas Chromatograph	**Agilent 7890 with LECO L-PAL 3 Autosampler**
Injection	1 uL, split 100:1
Inlet	250 °C
Carrier Gas	He @ 1.4 mL/min
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm coating (Restek)
Temperature Program	40 °C ramp 10 °C/min to 280 °C
Transfer Line	300 °C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250 °C
Mass Range	33-500 m/z
Acquisition Rate	10 spectra/s

Results and Discussion

Representative GC-MS chromatograms for lemon and lime essential oil are shown in Figure 1. Many similarities and differences can be observed in these data. LECO's automated data processing software provides identification and relative quantification information for individual analytes and was helpful for better understanding the differences in the samples. Three specific analytes, all with citrus odor descriptors, are indicated in Figure 1 and described in Figures 2-5. The most intense peak for both lemon and lime essential oil is limonene, indicated with an asterisk on Figure 1 and shown in Figure 2. The identification was determined by comparing the observed spectral information to NIST library databases (similarity score = 936) and by comparing the observed retention index (1033) to NIST library information for limonene (1030). Limonene is present in both the lemon and lime essential oils at comparable levels. It has a citrus odor type that is further described as citrus, herbal, terpene, and camphor, and it is likely an important contributor to both lemon and lime essential oils.

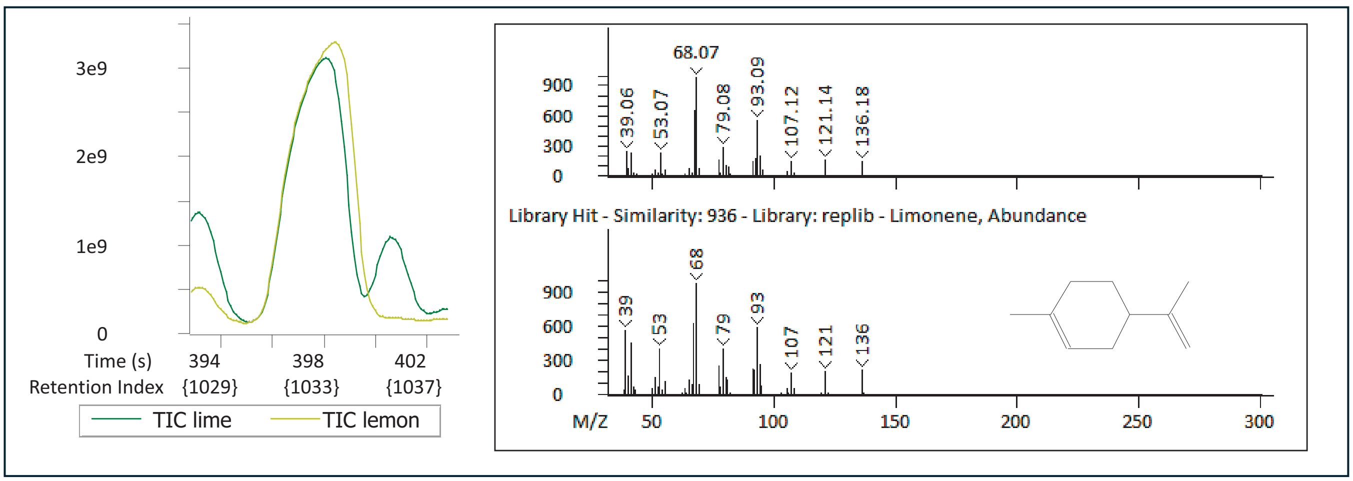


Figure 2. Limonene, with citrus odor characteristics, is present at comparable levels in both lemon and lime essential oils.

Other analytes with citrus odor types differ between the lemon and lime, for example (E)-Citral, shown in Figure 3, is observed at higher levels in lemon essential oil compared to the lime essential oil. The identification was determined by comparing the observed spectral information to NIST library databases (similarity score = 902) and by comparing the observed retention index (1274) to NIST library information (1270). (E)-Citral also has a citrus odor type and is further described as citrus and lemon. It is a larger contributor to the lemon essential oil than it is to the lime, and this difference likely contributes to the unique citrus characteristics of each oil.

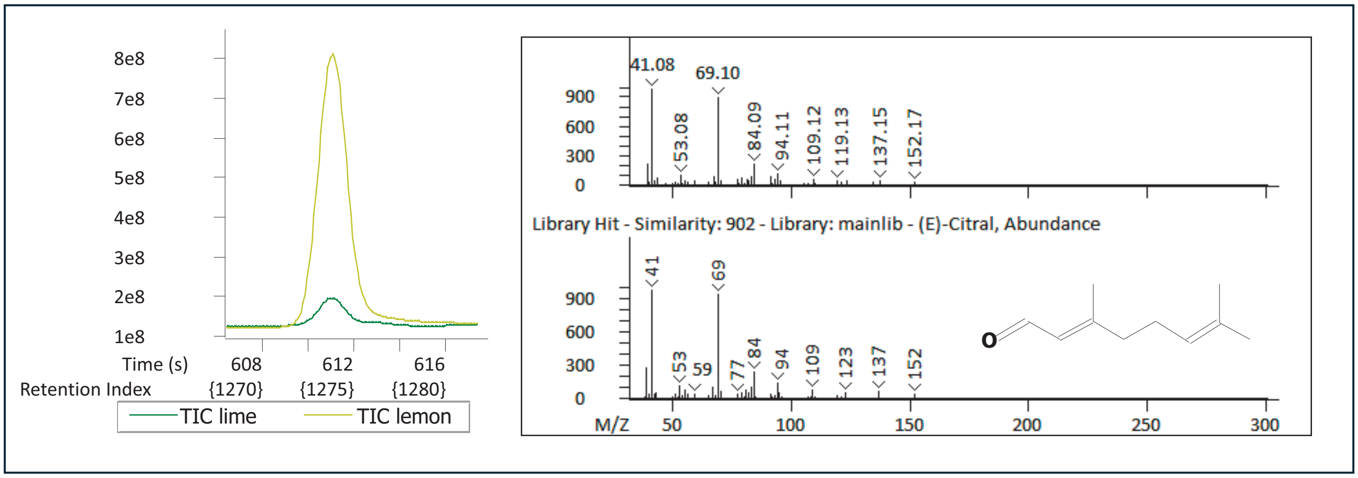


Figure 3. E-citral, with citrus notes, is observed at higher levels in lemon than lime essential oil

Both limonene and (E)-Citral and their relative amounts in the samples can be clearly observed in the TIC view of the data because the analytes are chromatographically resolved in both cases. In other instances where chromatographic coelution obscures analyte differences, the data processing tools in the software are helpful for understanding the samples. Deconvolution, in particular, helped to clarify a difference between the lemon and lime essential oils, as shown in Figures 4 and 5. The TIC view, shown in Figure 4, suggests that one analyte is higher in the lime essential oil compared to the lemon essential oil. However, the automated peak finding determined that there are actually two coeluting analytes. These two analytes and their distinct trends can be observed with extracted ion chromatograms (XICs) for m/z that are unique to each analyte. The TIC is displayed at 10% along with XICs for m/z that are specific to each analyte (m/z 139.16 and 93.10, for example) in Figure 4. This shows that there are clear chromatographic profiles for each analyte and it also shows that there are different relative trends for these two analytes. One is present in both samples, but at higher levels in lime while the other is only observed in the lime essential oil. Pure spectra for each of the analytes were also provided with deconvolution, resulting in the identifications of tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)-furan with citrus odor properties and trans-β-ocimene with herbal odor properties, as shown in Figure 5. The identification for the furan was determined by comparing the observed spectral information to NIST library databases (similarity score = 849) and by comparing the observed retention index (1049) to NIST library information (1047). The identification for the terpene was also determined by comparing the observed spectral information to NIST library databases (similarity score = 919) and by comparing the observed retention index (1049) to NIST library information (1049). The XICs are overlaid in Figure 5 showing the relative amounts of these analytes in each sample. Deconvolution was crucial for determining that there is a terpene that is higher in lime compared to lemon and a furan that is only present in the lime essential oil. This furan has citrus odor properties that are further described as sweet, citrus, herbal, green, celery, spicy, minty, and woody. It is likely important for the differences in the citrus profile between the essential oils, and it would have been obscured without deconvolution.

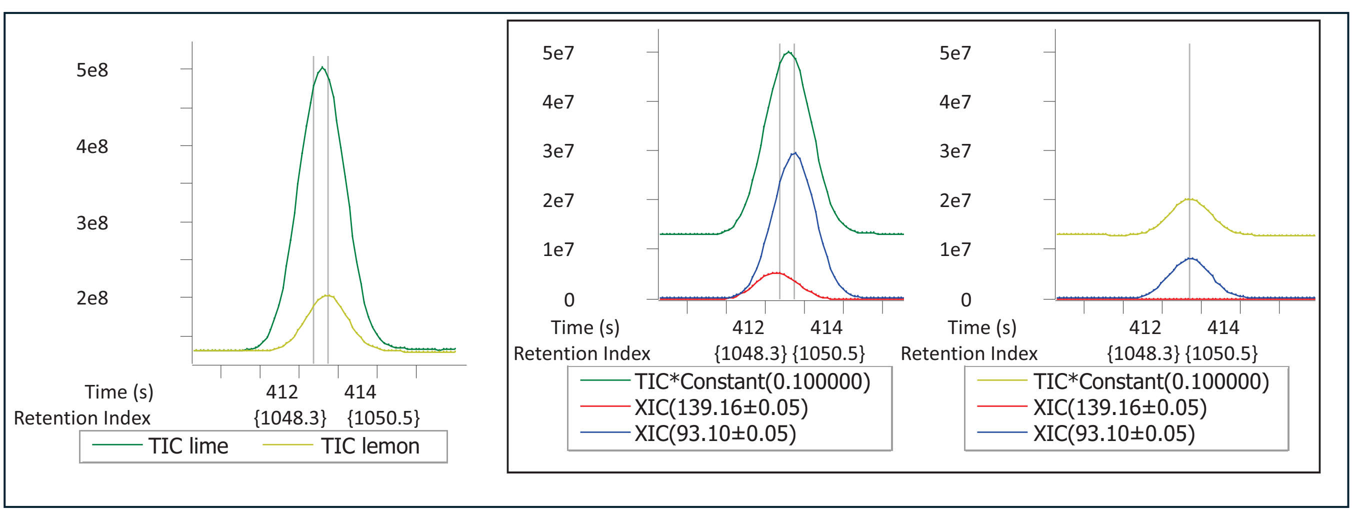


Figure 4. What appeared to be one analyte at higher levels in lime compared to lemon, was deconvoluted to two distinct analytes. One is higher in lime than lemon (m/z 93.10) and the other was only observed in lime (m/z 139.16).

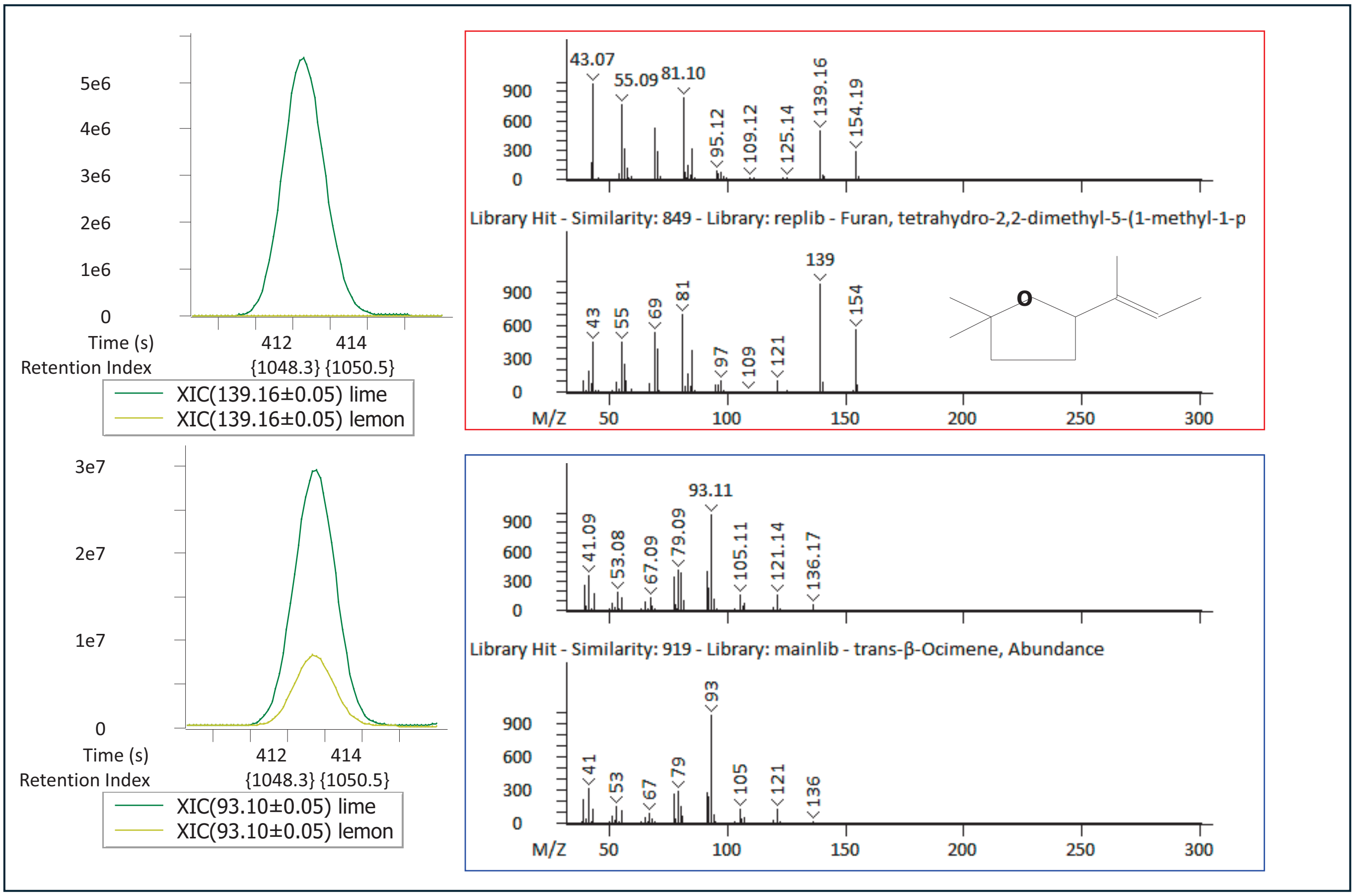
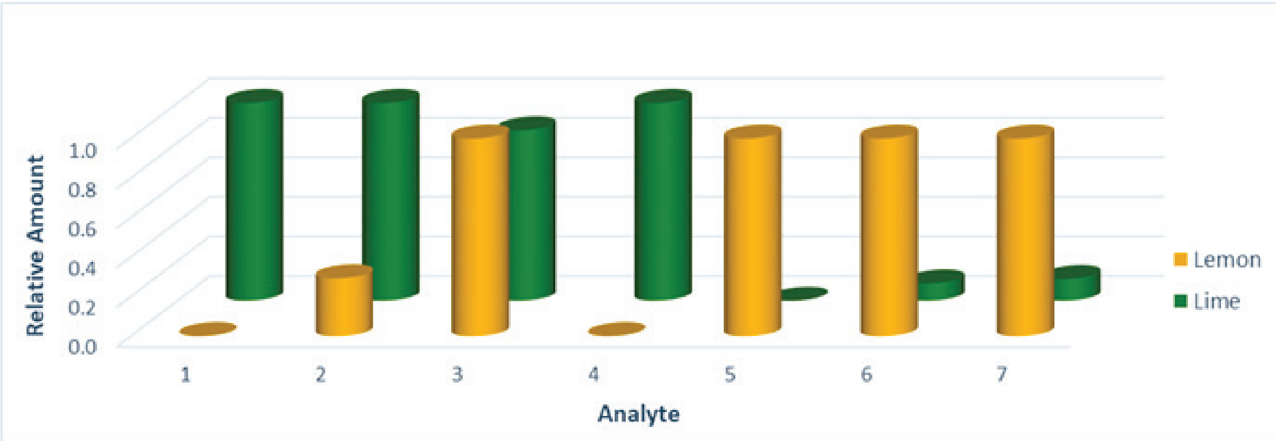


Figure 5. Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)-furan, with citrus notes, and trans-β-ocimene, with herbal notes), were deconvoluted in the essential oil samples and both observed higher or only in the lime essential oil.

While citrus is a key descriptor of both essential oils, the citrus notes of lemon and lime are not identical. This is consistent with the differences shown in the analytes highlighted in Figures 2-5. We further explored the citrus aroma by compiling information on other analytes in these samples that have a citrus odor type. This citrus aroma profile was determined by first identifying the analytes observed in these samples and then screening the identified analytes for those with citrus aroma types. Identifications were determined by spectral matching to library databases and by retention index verification when available, as previously described in Figures 2-5. Once identified, the odor types were determined with databases (www.thegoodscentscompany.com). Seven analytes with citrus odor type are shown in Figure 6. The associated table compiled the identification metrics (Similarity score and Retention Index information) and contains detailed and specific descriptions of the citrus odor notes. The relative amount of each analyte is shown in the associated bar chart with several differences clearly apparent. Limonene is observed at comparable levels in both samples, while all of the other analytes are higher in either lemon or lime. Of note, the analytes that are higher in lemon (trans-limonene oxide, (Z)-citral, and (E)-citral) have odor notes that are described as more lemony. The analytes observed at higher levels in the lime essential oil (D-limonene, 3-carene, and tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)-furan) have odor notes that are described as more herbal, woody, and orange. This citrus profile is helpful for better understanding the unique citrus characteristics of each essential oil.



#	Analyte	Similarity	CAS	Formula	tR (s)	RI Obs	RI Lib	Odor Notes
1	D-limonene	838	5989-27-5	$C_{10}H_{16}$	331	960		citrus orange fresh sweet
2	3-carene	909	13466-78-9	$C_{10}H_{16}$	380	1014	1011	citrus terpenic herbal pine solvent resinous phenolic cypress medicinal woody
3	limonene	936	138-86-3	$C_{10}H_{16}$	398	1033	1030	citrus herbal terpene camphor
4	tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)- furan	849	7416-35-5	$C_{10}H_{18}O$	412	1049	1047	sweet citrus herbal green celery spicy minty woody
5	trans-limonene oxide	852	4959-35-7	$C_{10}H_{16}O$	498	1143	1138	fresh citrus
6	(Z)-citral	848	106-26-3	$C_{10}H_{16}O$	587	1245	1240	sweet citral lemon peel
7	(E)-citral	902	141-27-5	$C_{10}H_{16}O$	611	1274	1270	citrus lemon

Figure 6. Citrus profile of lemon and lime essential oils.

Conclusion

In this work, we have demonstrated the application of GC-MS for the characterization and comparison of individual analyte components in lemon and lime essential oils. The analytical platform combines the chromatographic separation from GC with full m/z range non-skewed TOFMS detection, which allows for the optimal performance of deconvolution algorithms. Some key differences that were discovered in this data were obscured by chromatographic coelution and would have been difficult to realize without this deconvolution. This detailed chemical information on the essential oil provided characterization information and the ability to distinguish the specific chemicals contributing to the citrus aroma profile and how those differ between these two citrus essential oils.

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