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Research Article

Laser-Induced Fluorescence Studies on Some Edible Oils and Aromatic Frankincense Oil Excited by Blue and Violet Diode Lasers at 447 nm and 405 nm

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Laser-induced fluorescence (LIF) of certain edible oils (olive, mustard, sunflower, corn, sesame, peanut, rice bran, and flaxseed) and one unique aromatic oil (frankincense oil) have been studied using compact blue and violet lasers operating at 447 nm and 405 nm, respectively. LIF studies excited at these wavelengths have not been performed before, to our knowledge. The various features of the obtained spectra and their possible molecular origins have been discussed. The presence of vitamin E has been confirmed in corn, rice bran, peanut, sunflower, and frankincense oils, and the possible origin of the double peaks in the red region for olive oil has been explained.

1. Introduction

Laser-induced fluorescence (LIF) is a useful tool for the study and characterization of various materials, such as organic dyes, minerals, biological tissues, and edible oils [1–4]. In such studies, the choice of the excitation wavelength is an important parameter. In many cases, a UV or near-UV laser, such as the third harmonic of an Nd: YAG laser, or a nitrogen laser, is used for the excitation of the LIF spectra [2–5]. Edible oils and fats have been extensively studied by ordinary fluorescence spectroscopy [6–10]. To study edible oils, the second harmonic of the Nd: YAG laser at 532 nm [4], the fiber-coupled laser at 375 nm [5], and the helium-neon laser at 633 nm [11] has been used as excitation sources. There have been relatively few examples of using blue lasers for the excitation of LIF [12]. Use of compact and inexpensive blue diode lasers at 447 nm and 405 nm offers significant advantages for *in situ* practical applications of quick testing and characterization of oils by their LIF spectra, owing to their compact size, low cost, and ease of use. In contrast, other conventional and traditional lasers, such as Nd: YAG lasers, He-Ne lasers, or nitrogen lasers, are much heavier, bulkier, and more expensive and often require high voltages for operation. A typical diode laser used in this study costs only a few tens of dollars or even less and needs only a compact, low-voltage power source for efficient operation. It has no moving parts and hence is less prone to breakdowns, compared to conventional lasers.

On the other hand, diode lasers have some disadvantages as well. Only a limited number of wavelengths are available for diode lasers currently, and the power output is relatively limited in many cases. Their bandwidths, depending on the type of laser, can be large. The advantages and disadvantages of diode lasers as well as the other lasers are summarized in Table 1.

Besides the laser-induced fluorescence (LIF) method, various analytical techniques are available for the analysis of edible oils. The most important of these are high-pressure liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), HPLC-MS, and related techniques [13–16]. Most of these methods, though very useful, versatile, and effective, involve wet processing, sample preparation, and the use of chemicals. Some of them require relatively expensive equipment, such as GC-MS. On the

Table 1: Advantages and disadvantages of diode lasers as LIF excitation sources.

Types	Advantages	Disadvantages
Diode lasers	Compact, easy to use, low cost, no moving parts, relatively inexpensive	Only specific wavelengths available, limited output power, large bandwidths in case of multimode lasers
Other conventional lasers	Wider choice of wavelengths available, can be high power, narrow bandwidth	Bulky, expensive, often requiring high voltages for operation, may require maintenance

other hand, the LIF technique needs relatively simple instrumentation, does not require any sample preparation at all, and is relatively quick and easy.

In this paper, we report the use of compact blue and violet diode lasers at 447 nm and 405 nm for the excitation of various edible oils. In addition to the various edible oils, the studies here also include a traditional, aromatic, and nonedible oil from frankincense. To our knowledge, this has not been reported in the literature previously.

Frankincense is a plant-based aromatic resin derived from the *Boswellia* tree and has been produced in the Arabian Peninsula and adjacent regions since ancient times [17]. The plant grows in Yemen, southern Oman, and the adjacent regions, and the resin derived from the mature plants has been exported and traded as a valuable commodity for thousands of years due to its use as an incense, in perfumes, and in traditional medicine. An essential oil from frankincense can be derived by steam distillation of the resin and water mixture in a closed container kept still for several hours and by subsequent condensation [18]. The oil, known as frankincense oil, is used extensively in perfumes, skin treatments, and traditional medicine [19]. The oil contains a complicated mixture of molecules, mainly monoterpenes, sesquiterpenes, diterpenes, and esters [20]. The frankincense resin and the essential oil derived from it are shown in Figure 1.

2. Materials and Methods

Two semiconductor lasers operating at 447 nm (blue) and 405 nm (violet) wavelengths were used as the excitation sources. The schematic diagram of the experimental setup is shown in Figure 2(a). The blue laser uses a model M140 M laser diode with a heat sink and focusing lens. The maximum output power of the laser is 2 W, but about 80 mW was used for exciting the fluorescence. The violet laser used was a model LD-F405E04 laser diode emitting a maximum of 100 mW at 405 nm. The laser beams are incident on the liquid samples, contained in glass containers (cuvettes, size 10mmx10 mm) with flat faces. The emitted fluorescence is detected from the side (at roughly 90 degrees) by a fiber-optic probe with a NA of about 0.22. By adjusting the direction of the probe carefully, the direct reflection of the laser light from the glass surface could be minimized, so it was not necessary to use a long-pass cutoff filter.

A compact Thorlabs CCS200 spectrometer, connected to the fiber-optic probe, analyzes the fluorescent light. The spectrometer has a fixed grating of 600 lines/mm, allowing a wide detection range of 200–1000 nm and a spectral resolution of less than 2 nm. The spectrometer was connected to the PC using a USB cable. A complete fluorescence spectrum was acquired, typically in about 500 ms to 1 s. To avoid any possible influence of external light, all actual fluorescence data acquisitions were performed in a fully darkened laboratory.

The power spectrum of the blue exciting laser at 447 nm is shown in Figure 2(b). The peak power of the laser was observed at 447 nm, and the width (FWHM) of the laser was about 9 nm.

The edible oils were purchased from the local market and used directly without further purification. Frankincense oil, which was relatively expensive, was also procured from the local market. The acquired spectral data were saved as text files and plotted by the Origin software. Before plotting, some of the spectra were denoised with the Savitzky–Golay filter.

3. Results and Discussion

The superimposed laser-induced spectra of 4 edible oils (olive, mustard, sesame, and flaxseed) are shown in Figure 3(a). For olive oil, mustard oil, and sesame oil, we can observe strong fluorescence peaks with different intensities in the red and near-infrared regions of the spectrum (650–760 nm). Double peaks appear only for the olive oil in the red region. This fluorescence is much weaker for flaxseed oil. In addition, for sesame and flaxseed oils, a broad band of fluorescence can be seen in the green and orange regions of the spectrum (500–580 nm). This band is nearly absent for olive oil and only slightly present for mustard oil.

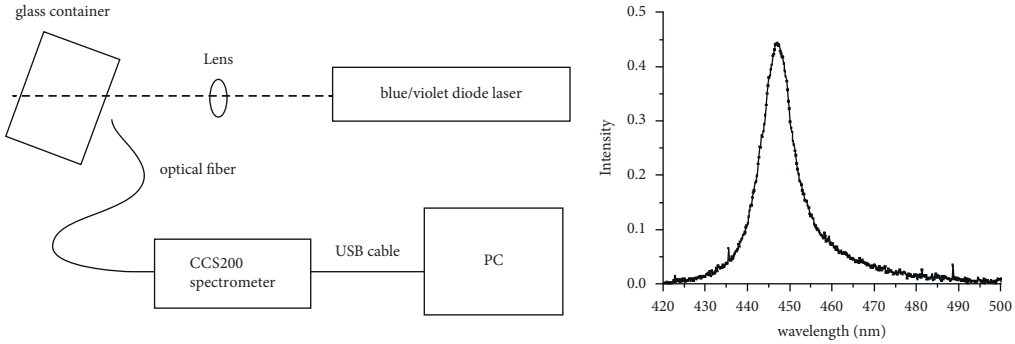
In Figure 3(b), laser-induced fluorescence spectra of rice bran oil, corn oil, peanut oil, and sunflower oil are shown. A broad, strong fluorescence band in the green, yellow, and orange regions (490–610 nm) for all these oils can be clearly seen, with a sharp peak at about 514 nm. For rice bran, corn, and peanut oils, the peaks are similar. For sunflower oil, this peak is of lesser intensity, but another very small peak can be discerned around 660 nm. The strong fluorescence peaks around 670 nm shown in Figure 3(a) have completely disappeared for the other three oils.

The LIF spectrum of the nonedible aromatic oil, frankincense oil, is shown separately in Figure 3(c). This oil exhibits a broad fluorescence band around the 470–600 nm region, with a distinct but sharp peak at 515 nm. No peak can be seen in the red or near-infrared region, as was observed for the edible oils in Figure 3(a). The fluorescence intensity was relatively weak compared to most of the edible oils but comparable to that of the sunflower oil.

For excitation by the 405 nm violet laser, the superimposed laser-induced spectrum of 4 edible oils (mustard, sesame, olive, and flaxseed) is shown in Figure 4(a). For all these oils, a single and prominent peak can be observed at

(a) (b)

Figure 1: (a) Frankincense resin and (b) frankincense oil.



(a) (b)

Figure 2: (a) Schematic diagram of the fluorescence experiment: blue/violet lasers of model M140 M/model LD-F405E04, a glass container of size 10 mm × 10 mm, and an optical fiber of NA = 0.22. (b) Power spectrum of the excited laser at 447 nm.

670 nm in the red region and the fluorescence extends to the near-infrared region up to about 760 nm. For olive oil, in contrast to the excitation by the 447 nm laser, no double peaks were observed in the red region. Little fluorescence can be observed for olive oil and mustard oil at shorter wavelengths (<650 nm). For sesame and flaxseed oils, a broad band can be observed at shorter wavelengths (420 nm to 650 nm), quite similar to the spectra produced by the 447 nm laser. The relative intensities of the broad band are smaller than the intensity in the red region. In general, the intensities produced at this excitation wavelength were higher than those produced by the 447 nm laser.

The above results, and a comparison of Figures 3 and 4, show that some features of the observed fluorescence spectra depend on the excitation laser wavelength. Hence, excitation by a laser of yet another wavelength, for example, a UV laser at $\lambda = 375$ nm, can be expected to produce significantly different spectra. This, however, should be verified by further experiments.

In Figure 4(b), the laser-induced fluorescence spectra of rice bran oil, corn oil, peanut oil, and sunflower oil are shown. The spectra are similar to those observed by using the excitation laser at 447 nm, but the light extends to shorter wavelengths up to 420 nm. For sunflower oil, the spectra are also similar to those observed before, i.e., the peak in the green is broader, but a small but distinct peak can be observed in the red region (around 660 nm) of the spectrum, which is not present in the other oils.

The LIF spectrum of frankincense oil, excited by the 405 nm laser, is shown in Figure 4(c). The spectra is also similar to that excited by the 447 nm laser (Figure 3(c)), but the intensity of the fluorescence is stronger and no sharp peak can be observed at 514 nm, but nevertheless, an intensity maximum can be detected near this wavelength.

We now discuss the main results obtained in this study. The main chemical components of edible vegetable oils are triacylglycerols (TG), free fatty acids, and a host of other minor compounds [21]. Among these minor compounds, phenolic derivatives, tocopherols (forms of vitamin E), and carotenes are the most important and significant ones, since they are characteristics of the particular oil and also responsible for their beneficial health properties. Of these

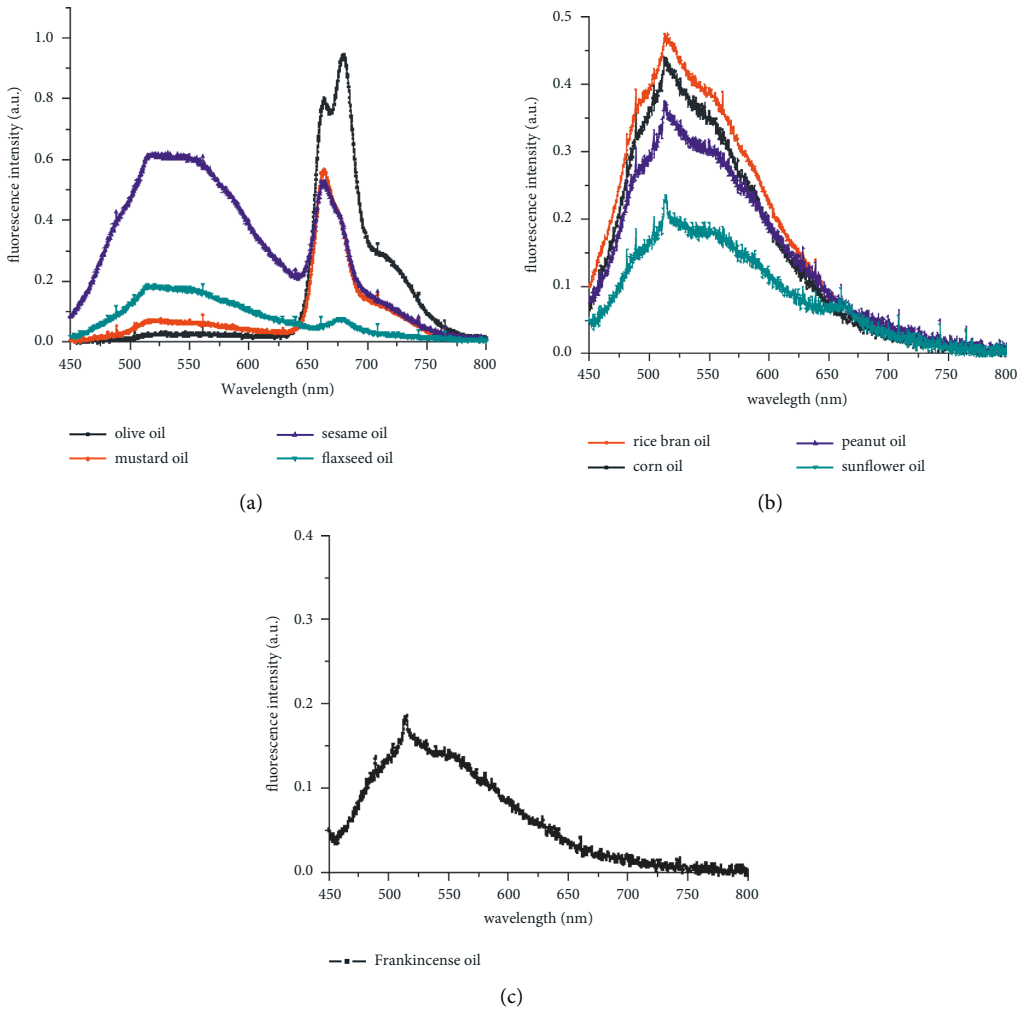


Figure 3: LIF spectra excited by laser at 447 nm: (a) olive, mustard, sesame, and flaxseed oil, (b) rice bran, corn, peanut, and sunflower oil, and (c) aromatic frankincense oil.

compounds, intense fluorescence is emitted by tocopherols, chlorophylls, and phenolic compounds. Chlorophylls (A and B) are known to emit fluorescence strongly in the red (>650 nm) [22]. The different types of tocopherols are known to emit at 445 nm, 475 nm, and 525 nm. Oxidation products in the oils emit in the region of 400–500 nm [4, 21].

In the present experiments with 447 nm blue laser excitation, we observed fluorescence mainly in the two bands: (a) in the broad blue-green, green, and orange regions (470–600 nm) with a sharp peak at 514 nm and (b) in the deep red and near-infrared regions (650–730 nm). The first band can be attributed to the presence of tocopherols and some oxidation products, and the latter can be attributed to the presence of chlorophylls.

From Figure 3(a), we can conclude the strong presence of chlorophylls in virgin olive oil, mustard oil, sesame oil, and, to a lesser extent, in flaxseed oil. These compounds are almost nonexistent in rice bran, corn, and peanut oils as shown in Figure 3(b). The presence of a small peak at around 660 nm for sunflower oil shows that chlorophylls are present in small concentrations in this oil. In addition, in Figure 3(c), the absence of any peaks in the red region for frankincense oil indicates the near absence of any chlorophylls.

The strong and broadband peaks in the region (470–610 nm) were observed in corn, peanut, and rice bran oils, and, to a lesser extent, in sunflower oil (Figure 3(b)), with a superimposed sharp peak at about 514 nm pointing to the common presence of tocopherols (a form of vitamin E) and possibly to some oxidation products. The relative weakness of this band observed in the spectra for olive and mustard oils indicates that tocopherol concentrations in these oils are much smaller than those of corn, rice bran, and peanut oils.

To test the above-mentioned point, we acquired fluorescence spectra of vitamin E excited by this laser. This is shown in Figure 5. In addition to a broad peak in the 460–600 nm region, we can observe a sharp peak at 514 nm. This can be considered as the characteristic peak of vitamin E, and it confirms the presence of this compound in corn, rice bran, peanut, and sunflower oils, and, in addition, in the aromatic frankincense oil as well. The presence of tocopherols (vitamin E) in edible oils (e.g., sunflower oil) has been

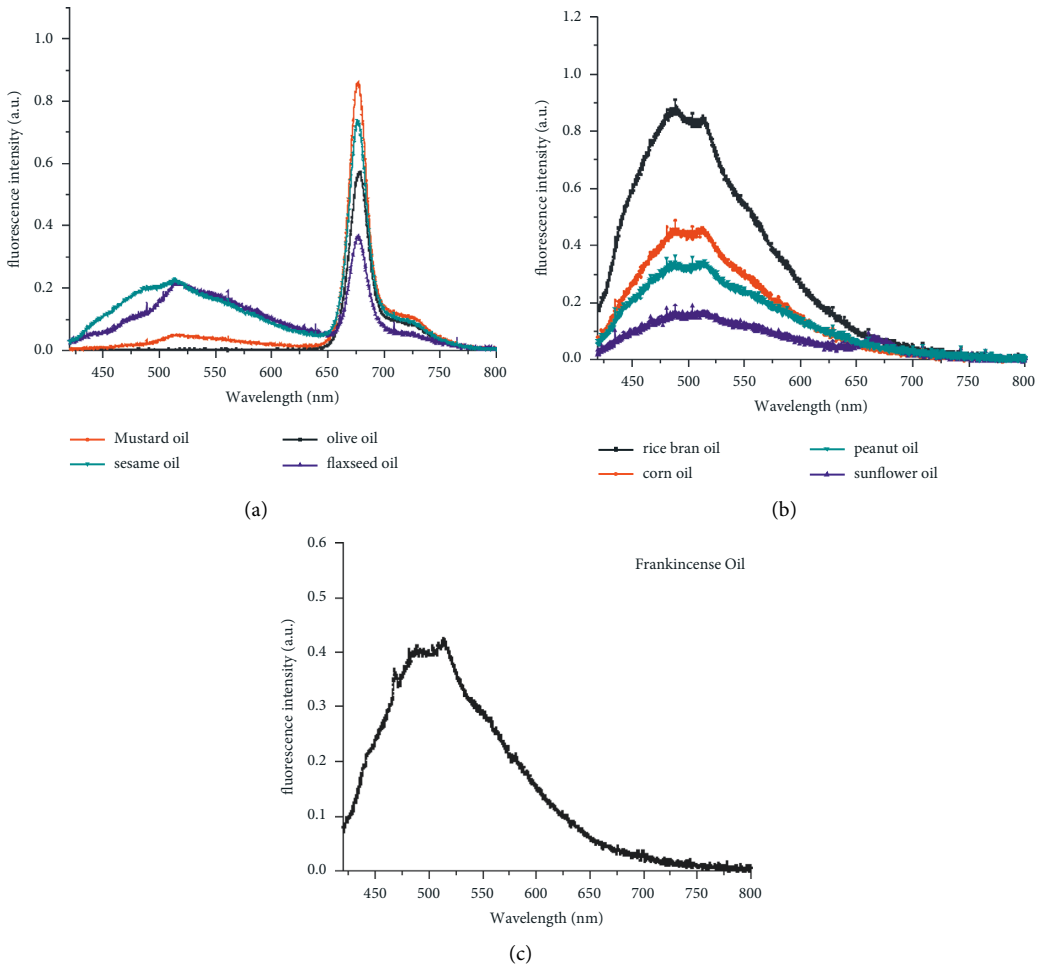


Figure 4: LIF spectra excited by laser at 405 nm: (a) mustard, sesame, olive, and flaxseed oil, (b) rice bran, corn, peanut, and sunflower oil, and (c) aromatic frankincense oil.

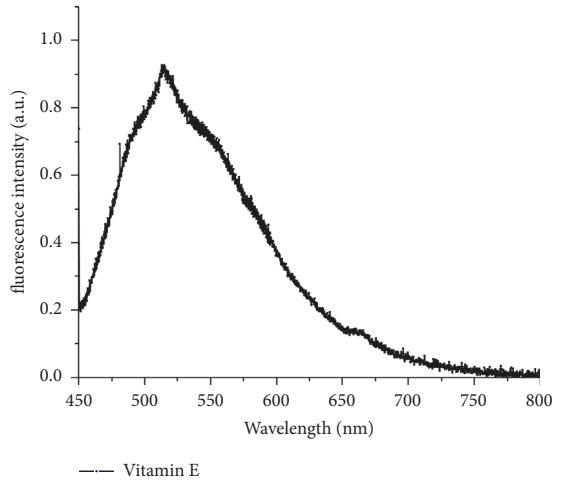


Figure 5: LIF spectra of vitamin E excited by laser at 447 nm. The sharp peak is at 514 nm.

previously confirmed by HPLC techniques [13]. More recently, Chen et al. have detected [23] the presence of tocopherols in various concentrations in sunflower oil, peanut oil, corn oil, extravirgin olive oil, and hazelnut oil by the HPLC technique. The exact quantitative detection of vitamin E concentrations in various oils, as well as the determination

Table 2: Areas under the peaks in the red region relative to olive oil.

Oil	Area under the peak in the red region (a.u.)	Area relative to olive oil
Olive oil	18	1
Sesame oil	12.5	0.69
Mustard oil	10	0.56
Flaxseed oil	5.35	0.29

of the detection limits, is however quite involved and is probably beyond the scope of this preliminary study.

The similar nature of the peak in the 470–610 nm region was observed in Frankincense oil as well as in corn, peanut, and rice bran oils, and this shows that similar chromophores are involved here, possibly tocopherols, including vitamin E. More study in this regard is needed in this case.

The double peaks clearly observed for virgin olive oil in the red region of the spectrum deserves a special mention in this context. It is known that chlorophylls A and B exhibit two distinct emission peaks, with the relative intensities of the two peaks dependent on the exact wavelength of excitation [22]. Both of these chlorophylls are known to be present in olive oil [24]. Excitation at 440 nm brings out the peak of chlorophyll A at 670 nm, while excitation at 460 nm brings out the peak of chlorophyll B at 655 nm [22]. In our experiment, we believe that the excitation at the 447 nm central laser wavelength, with light energy extending between 440 nm and 460 nm (see Figure 2(b)), brings out both peaks of chlorophyll A and B clearly and distinctly. This is only possible due to the unique wavelengths used for the excitation laser in our experiment, which actually lies roughly between 440 nm and 460 nm.

As an example of the quantitative information that can be obtained from the spectra, we estimated the area under the peak in the red region (650–700 nm) for violet laser excitation (Figure 4(a)) relative to the area under the peak for olive oil as shown in Table 2.

Since the peak in the red region results from the presence of the chlorophylls, it may be assumed that the quantity of the chlorophylls in the four edible oils shown, relative to olive oil, is roughly in the proportions shown in the last column of Table 2.

In general, the spectra excited by the two lasers (447 nm and 405 nm) are quite similar and the features of the different spectra excited by the 405 nm laser can be explained similarly. An important distinction is the spectrum of olive oil, where only a single peak is observed at 670 nm (Figure 4(a)), in contrast to the double peaks observed for 447 nm excitation (Figure 3(a)). We believe this is due to the fact that only one type of chlorophyll (Chlorophyll A) in olive oil is excited by the shorter wavelength (405 nm) excitation and the other type present (Chlorophyll B) is not. This is consistent with the explanation given earlier.

4. Conclusions

We have acquired LIF spectra of good quality from a variety of edible oils and the unique frankincense oil, by exciting them with a compact blue laser at 447 nm and a compact violet laser at 405 nm. These wavelengths are uncommon wavelengths of excitation, which have not been reported previously, to the best of our knowledge. Moreover, we also obtained the LIF spectra of the unique frankincense oil, which has valuable aromatic, medicinal, and cosmetic properties, for the first time to our knowledge. The various features of the spectra and their differences and similarities between the various oils have been discussed in detail. A possible origin of the unique double peaks of olive oil in the red region was explained, and the presence of vitamin E is confirmed in several edible oils, in addition to frankincense oil. Further studies of the oils are in progress. Furthermore, it is suggested that by using the fluorescence spectra of the frankincense oil, possible adulteration of frankincense oil [25] with alcohol or less-expensive oils could be detected by in situ real-time spectral analysis.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The author declares no conflicts of interest.

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