*World Journal of Analytical Chemistry*, 2024, Vol. 9, No. 1, 1-9
Available online at http://pubs.sciepub.com/wjac/9/1/1
Published by Science and Education Publishing
DOI:10.12691/wjac-9-1-1

# Application of Molecular Spectroscopies for the Compositional Analysis of Short Chain Cinnamyl Ester Mixtures

**Ronald P. D'Amelia*, Evan H. Kreth**

Chemistry Department, Hofstra University, Hempstead, NY
*Corresponding author: ronald.p.damelia@hofstra.edu

*Received June 07, 2024; Revised July 08, 2024; Accepted July 15, 2024*

**Abstract** Short chain cinnamyl esters hold a multitude of applications within the food, cosmetic and pharmaceutical industries as flavor and fragrance compounds. However, due to high structural similarity, these compounds are difficult to differentiate from one another. Quantitative proton nuclear magnetic resonance ($^1$H NMR) and Fourier-transform infrared (FTIR) spectroscopies were utilized to not only distinguish between these compounds, but also to quantify their relative concentrations when present simultaneously. $^1$H NMR and FTIR spectra were first obtained for each cinnamyl acetate (CA), propionate (CP), and butyrate (CB) individually, followed by those for binary mixtures of weight percent ranging from zero to one hundred percent. Resolved $^1$H NMR methyl proton resonances $\delta$ 1.95 (s, 3H), 1.07 (t, 3H), and 0.88 (t, 3H) and unique peaks in the fingerprint region of the FTIR spectra were used to determine relative concentrations of CA, CP, and CB respectively in each of the binary mixtures. Strong, linear correlations were established between gravimetrically achieved weight percent and those ascertained by $^1$H NMR ($r^2 > 0.99$) and FTIR ($r^2 > 0.98$) spectra. These results confirm the use of fundamental spectroscopic techniques $^1$H NMR and FTIR in the identification, but more appreciably quantification, of organic compounds.

***Keywords:*** *Proton nuclear magnetic resonance spectroscopy ($^1$H NMR), Fourier-transform infrared spectroscopy (FTIR), short-chain cinnamyl esters, cinnamyl acetate (CA), cinnamyl propionate (CP), cinnamyl butyrate (CB)*

**Cite This Article:** Ronald P. D'Amelia, and Evan H. Kreth, "Application of Molecular Spectroscopies for the Compositional Analysis of Short Chain Cinnamyl Ester Mixtures." *World Journal of Analytical Chemistry* vol. 9, no. 1 (2024): 1-9. doi: 10.12691/wjac-9-1-1.

## 1. Introduction

Cinnamyl esters of short chain fatty acids have found many applications as flavor and fragrance compounds in the food, cosmetic and pharmaceutical industries [1,2,3,4,5,6,7]. For instance, cinnamyl acetate is utilized as a modifier in perfumes, as well as an intermediate in the synthesis of fine chemicals and drugs [3]. Figure 1 below shows the general structure of cinnamyl esters where *R* denotes alkyl substituents.

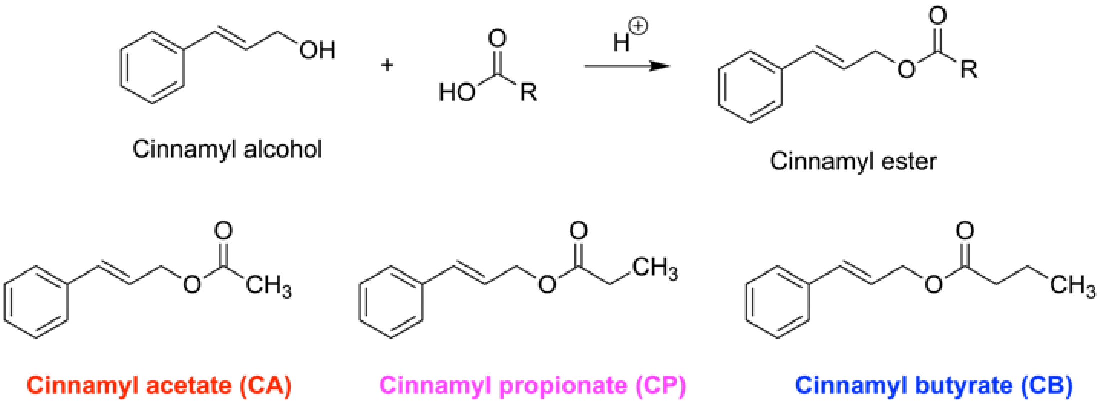

**Figure 1.** Acid-catalyzed, Fisher esterification of cinnamyl alcohol with a short-chain carboxylic acid to produce a generic cinnamyl ester, where *R* represents an alkyl substituent.

### 1.1. Experimental Objectives

1. To learn to prepare binary mixtures using volumetric and weight techniques. [8,9]
2. To determine chemical shift ( $\delta$ ), multiplicity, and integration values of the assigned peaks. [10,11,12,13,14]
3. To establish correlation curves between the integrated NMR peak heights and the calculated weight percent composition for a binary mixture. [15,16,17,18,19,20,21]
4. To record and analyze FTIR data on available CE and binary blends of various compositions. [22,23,24,25]
5. To prepare calibration curves plotting the absorbance ratio of specific peaks corresponding to unique peaks for each CE present versus the weight percent composition for each binary mixture. [26,27,28,29,30,31]

## 2. Materials and Methods

### 2.1. Experimental Materials

Cinnamyl acetate and butyrate were purchased as anhydrous liquids from TCI Chemicals with greater than 97.0% purity. Cinnamyl propionate was purchased also as an anhydrous liquid from Astatech Inc. with greater than 95.0% purity. All three reagents were pipetted directly from their containers and utilized without further purification.

### 2.2. Experimental Methods

A 400 MHz JEOL model ECS-400 NMR spectrometer was used to obtain HNMR spectra, while JEOL Delta NMR Processing and Control Software version 6.0.0 (Mac OSX) was used to analyze individual spectrum. Each sample was run neat, in the absence of solvent, and as a single pulse 1D proton NMR, with 0.25 Hz resolution, 24 scans, and a relaxation time of 8-10 seconds.

All CE samples were analyzed using a Bruker AlphaP FT-IR spectrometer with a Platinum® attenuated total internal reflectance (ATR) quick snap module with a diamond crystal. The Alpha-P had a Michelson Interferometer with a SiC globar as the IR source, and the time dependence of the IR intensity was measured with a pyroelectric DTGS detector. The data analyses were done using the Brucker OPUS® software version 7.0.122. Background measurements were conducted with 48 scans and a resolution of 2 $cm^{-1}$. Approximately 20-μL of each sample was analyzed by simply pressing the droplet between the anvil and diamond crystal. Each measurement represents the average spectrum of the aforementioned number of scans and resolution used for the background measurement. For qFT-IR measurements, five scans were conducted for each sample and their peak integrations were obtained using the built-in integration feature.

### 2.3. Experimental Preparation of Binary CE Mixtures

Twelve 5 ml binary mixtures of cinnamyl acetate, propionate, and butyrate were prepared as outlined by Table 1. All 7 ml. vials are labeled based on the volumetric ratio in the mixture and weighed before adding any CE.

**Table 1. Cinnamyl Ester Binary Mixtures**

| Volume Ratio | Gravimetric Weight Percent | |
|---|---|---|
| CA : CP | CA | CP |
| 0 ml: 5 ml | 0% | 100% |
| 1 ml : 4 ml | 20.61% | 79.39% |
| 2 ml : 3 ml | 40.67% | 59.33% |
| 3 ml : 2 ml | 60.35% | 39.65% |
| 4 ml : 1 ml | 80.40% | 19.60% |
| 5 ml : 0 ml | 100% | 0% |
| CA : CB | CA | CB |
| 0 ml : 5 ml | 0% | 100% |
| 1 ml : 4 ml | 20.96% | 79.04% |
| 2 ml : 3 ml | 41.43% | 58.57% |
| 3 ml : 2 ml | 61.13% | 38.87% |
| 4 ml : 1 ml | 80.34% | 19.66% |
| 5 ml : 0 ml | 100% | 0% |
| CP : CB | CP | CB |
| 0 ml : 5 ml | 0% | 100% |
| 1 ml : 4 ml | 20.54% | 79.46% |
| 2 ml : 3 ml | 40.56% | 59.44% |
| 3 ml : 2 ml | 60.35% | 39.65% |
| 4 ml : 1 ml | 80.34% | 19.66% |
| 5 ml : 0 ml | 100% | 0% |

Each CE was added using an Eppendorf series 2100 research 500-5000 $\mu$l pipette. After each addition of a CE into the vial their masses were recorded using an analytical balance with a 0.1-mg precision. These masses were used to calculate weight percent composition of a component in each binary mixture using equation 1:

$$percent\ composition = \frac{N_x}{N_x + N_y} \times 100 \qquad (1)$$

Where $N_x$ and $N_y$ are the gravimetrically determined masses of each component in a mixture. To serve as unknowns 50:50 and 70:30 mixtures of CA:CP; of CA:CB and of CP:CB mixtures were prepared as shown in Table 2.

**Table 2. Cinnamyl Ester Binary Mixtures Serving as "Unknowns"**

| Volume Ratio | Gravimetric Weight Percent | |
|---|---|---|
| CA:CP | CA | CP |
| 2.5 ml : 2.5 ml | 50.61% | 49.39% |
| 3.5 ml : 1.5 ml | 70.15% | 29.85% |
| CA:CB | CA | CB |
| 2.5 ml : 2.5 ml | 50.86% | 49.14% |
| 3.5 ml : 1.5 ml | 70.58% | 29.42% |
| CP:CB | CP | CB |
| 2.5 ml : 2.5 ml | 50.63% | 49.37% |
| 3.5 ml : 1.5 ml | 70.12% | 29.88% |

### 2.4. Hazards

Cinnamyl acetate (CAS 103-54-8), cinnamyl propionate (CAS 103-56-0), and cinnamyl butyrate (CAS 103-61-7 ). All these CE are liquids at room temperature. All the CEs have been used as fragrances and flavors ingredient and have been generally recognized as safe as a flavor ingredient by the USDA. No **major** health risks have been determined, however, the CEs can cause mild skin irritation, so wear gloves and work in the hood area as much as possible.

### 2.5. Statistical Analysis

Each of the binary mixtures were analyzed multiple times. The data reported is the average of the normalized peak heights. The average percent relative standard deviation for the analyzed samples ranged from 0.10% to 1.0%. Propagation of error analyses was conducted for all calibration plots and for calculating the experimental weight percent composition of a component in either the 50:50 or 70:30 mixtures. All gravimetric weight percent compositions were within the 95% confidence interval (CI) of the experimental results for three measurements.

## 3. Results and Discussion

### 3.1. Proton Nuclear Magnetic Resonance Spectroscopy

**Table 3. Summarization of Cinnamyl Ester $^1$HNMR Spectra**

| Cinnamyl Acetate (CA) | | | |
|---|---|---|---|
| Proton(s) | Chemical Shift, δ (ppm) | Normalized Integration | Multiplicity |
| Phenyl | 7.22 | 5.02 | multiplet |
| Less-shielded alkene | 6.53 | 0.95 | doublet |
| More-shielded alkene | 6.21 | 0.95 | doublet of triplets |
| Methylene | 4.64 | 2.00 | doublet |
| Methyl | 1.95 | 3.00 | singlet |

| Cinnamyl Propionate (CP) | | | |
|---|---|---|---|
| Proton(s) | Chemical Shift, δ (ppm) | Normalized Integration | Multiplicity |
| Phenyl | 7.22 | 5.01 | multiplet |
| Less-shielded alkene | 6.54 | 0.94 | doublet |
| More-shielded alkene | 6.22 | 0.94 | doublet of triplets |
| Methylene (Cinnamyl) | 4.65 | 1.98 | doublet |
| Methylene (Propionate) | 2.25 | 2.00 | quartet |
| Methyl | 1.07 | 3.00 | triplet |

| Cinnamyl Butyrate (CB) | | | |
|---|---|---|---|
| Proton(s) | Chemical Shift, δ (ppm) | Normalized Integration | Multiplicity |
| Phenyl | 7.22 | 5.12 | multiplet |
| Less-shielded alkene | 6.54 | 0.97 | doublet |
| More-shielded alkene | 6.23 | 0.97 | doublet of triplets |
| Methylene (Cinnamyl) | 4.67 | 2.01 | doublet |
| Methylene B | 2.23 | 2.02 | triplet |
| Methylene C | 1.60 | 2.02 | multiplet |
| Methyl | 0.88 | 3.00 | triplet |

Figure 2 through Figure 4 depict the $^1$H NMR spectra of cinnamyl acetate, propionate, and butyrate alone, respectively. Table 3 summarizes the chemical shift, multiplicity, and normalized integration values for the spectra of each cinnamyl ester.

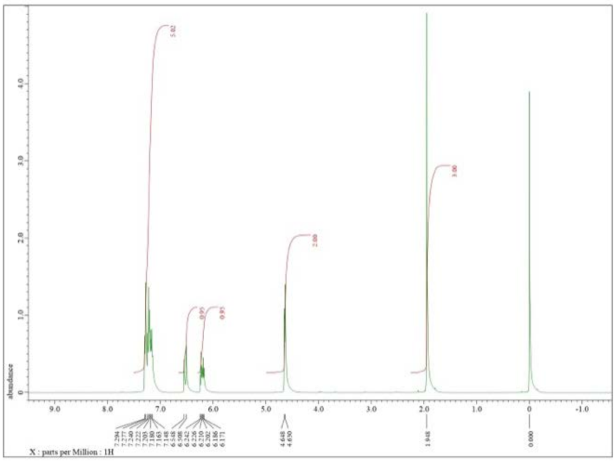

**Figure 2.** $^1$H NMR spectrum for cinnamyl acetate (CA)

All three spectra exhibited a multiplet correlating to five protons centered at 7.22 ppm, a doublet correlating to one proton centered at 6.53-6.54 ppm, a doublet of triplets correlating to an additional proton centered at 6.21-6.23 ppm, and a doublet correlating to two protons centered at 4.64-4.67 ppm. Collectively, these peaks correspond to the cinnamyl alkyl group shared by each of the cinnamyl esters, with slight variations in chemical shifts attributed to structural differences between each of the compounds.

The multiplet correlating to five protons centered at 7.22 ppm corresponds to the five phenyl protons found in each of the cinnamyl esters. Due to the electron withdrawing nature of the benzene ring, the protons located on the ring are highly deshielded, and therefore experience at much larger chemical shifts than any other proton in the molecule.

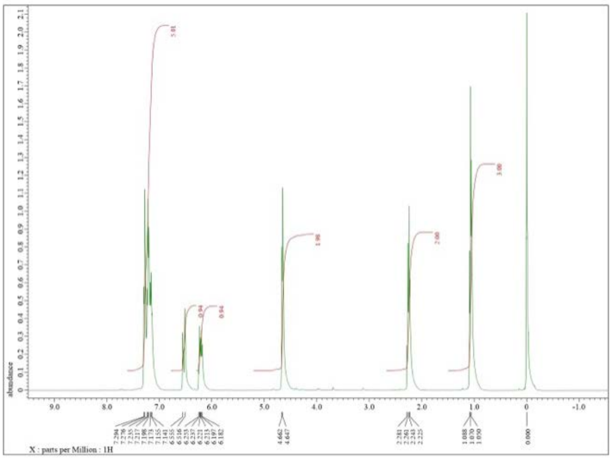

**Figure 3.** $^1$H NMR spectrum for cinnamyl propionate (CP)

As for the doublet centered at 6.53-6.54 ppm and the doublet of triplets centered at 6.21-6.23 ppm each correlating to a single proton, these peaks correspond to the protons of the alkene bond found in the cinnamyl group. The doublet centered at 6.53-6.54 ppm corresponds to the alkene proton located closer to the benzene ring, as the electron withdrawing effects of said benzene ring cause this peak to appear more downstream. Additionally, this peak appears as a doublet because it only possesses one neighboring proton, the other proton located on the alkene bond. As for the doublet of triplets centered at 6.21-6.23 ppm, this peak corresponds to the remaining alkene proton, that furthest away from the benzene ring. This peak appears at a chemical shift slightly lower than its counterpart because it is further away from the electron withdrawing effects of the benzene ring. Additionally, this peak appears as a doublet of triplets because it possesses two neighboring protons, producing a triplet peak as per the n + 1 rule, which is then J coupled into a doublet of triplets by the nearby vinylic alkene proton. Lastly, the doublet centered at 4.64-4.67 ppm correlating to two protons, shared by all three spectra, corresponds to the methylene hydrogens of the carbon directly bonded to the oxygen of the ester functional group. These protons appear as a doublet due to the fact that they only possess a single neighboring proton, the more-shielded alkene proton.

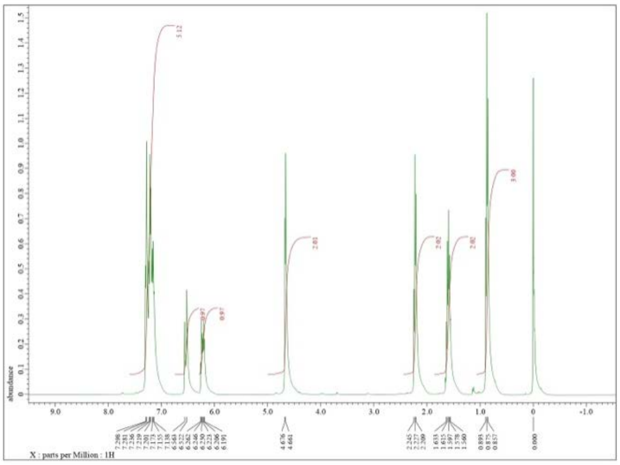

**Figure 4.** $^1$H NMR spectrum for cinnamyl butyrate (CB)

Aside from protons of the shared cinnamyl group, each cinnamyl ester also contains unique protons not found in the other compounds. Additionally, while all of the cinnamyl esters may have the same type of proton, such as methyl protons, their peaks on $^1$H NMR spectra appear at different chemical shifts due to structural differences between each of the esters. For instance, the peak correlating to the methyl protons for cinnamyl acetate occurs at a chemical shift of 1.95 ppm compared to 1.07 and 0.88 ppm for cinnamyl propionate and butyrate respectively. This large difference in chemical shift value can be attributed to the fact that the methyl group in cinnamyl acetate is closest to the oxygen atoms of the ester functional group than either of the other cinnamyl esters. Analogous to the benzene ring, these electronegative oxygen atoms pull electron density away from the methyl protons, deshielding them, and producing a peak that appears furthest downfield. Lastly, the peak corresponding to the methyl protons of cinnamyl acetate appears as a singlet because there are no neighboring protons and therefore experiences no peak splitting.

By contrast to cinnamyl acetate, the $^1$H NMR spectrum of cinnamyl propionate demonstrates its more-shielded methyl protons by its methyl proton peak appearing at 1.07 ppm, further upfield than that of cinnamyl acetate (1.95 ppm). These methyl protons are less affected by the electron-withdrawing effects of the ester oxygen atoms due to an additional carbon atom situated between the carbonyl carbon and the methyl group. Two methylene hydrogens are bonded to this carbon atom, represented by a quartet at 2.25 ppm on the $^1$H NMR spectrum of cinnamyl propionate. Lastly, the peak representing the aforementioned methyl protons of cinnamyl propionate exists as a triplet at 1.07 ppm due to the two neighboring methylene protons, which split the methyl proton peak according to the n + 1 rule.

Cinnamyl butyrate is unique in that it possesses the most shielded methyl protons of all the cinnamyl esters examined. These protons are represented by a triplet peak, due to splitting from two neighboring methylene protons as in cinnamyl propionate, at the smallest chemical shift of 0.88 ppm. In addition to its heavily shielded methyl protons, the $^1$H NMR spectra of cinnamyl butyrate also features peaks representing both sets of methylene protons. The peak regarding the first set of methylene protons (closest to the carbonyl carbon) exists as a triplet at 2.23 ppm while the second set (farther from the carbonyl carbon) exists as a multiplet at a chemical shift of 1.60 ppm. The difference in chemical shift values between the sets of methylene hydrogens can be explained by proximity to the ester functional group. Protons closest to the electronegative oxygen atoms experience their electron withdrawing effects most strongly, and therefore produce larger, downstream chemical shift values. By contrast, protons farthest from the ester functional group, or other electron withdrawing groups, are less susceptible to these effects and maintain low, upstream chemical shift values.

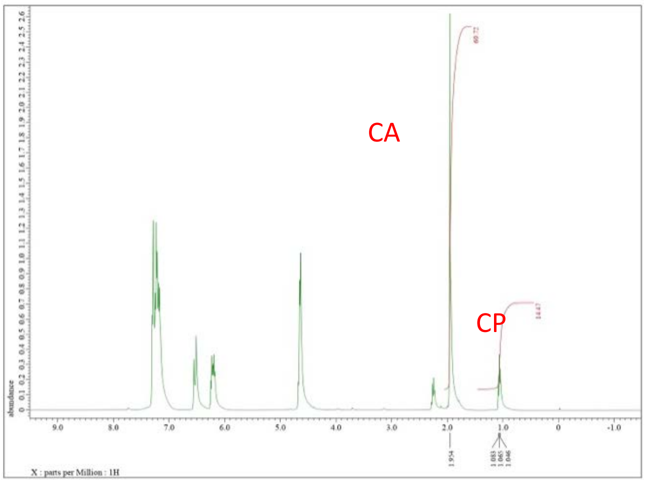

**Figure 5.** $^1$H NMR spectra of 4:1 CA:CP binary mixture

Figure 5 through Figure 7 depict $^1$H NMR spectra of select cinnamyl ester binary mixtures. They depict the $^1$H NMR spectra of 4:1 CA:CP, 4:1 CA:CB, and 4:1 CP:CB. For these spectra, only the peaks utilized in determining percent composition of each cinnamyl ester in the binary mixture (those of the methyl protons) are labeled with chemical shift and peak integration values.

Percent composition of each cinnamyl ester in each of the binary mixtures was determined by comparing the $^1$H NMR peak integration of one component, with that of the other component. The peak corresponding to the methyl protons of each cinnamyl ester (singlet peak at 1.95 ppm for CA, triplet peak at 1.07 ppm for CP, and triplet peak at 0.88 ppm for CB) were first integrated. Subsequently, the peak integration values were substituted into the equation below, where CE represents the peak integration value of the peak corresponding to the methyl protons for any of the cinnamyl esters.

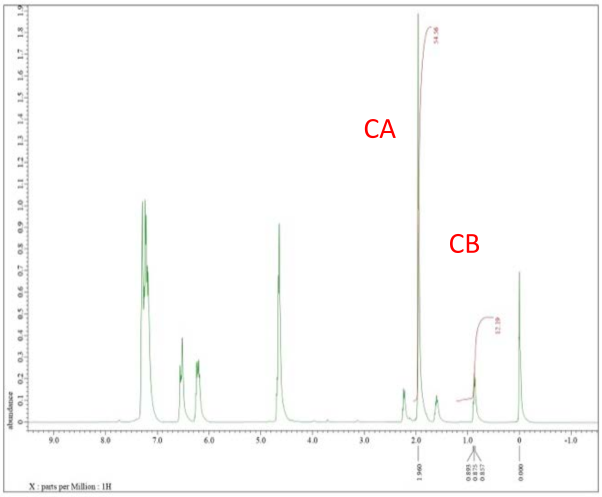

**Figure 6.** $^1$H NMR spectra of 4:1 CA:CB binary mixture

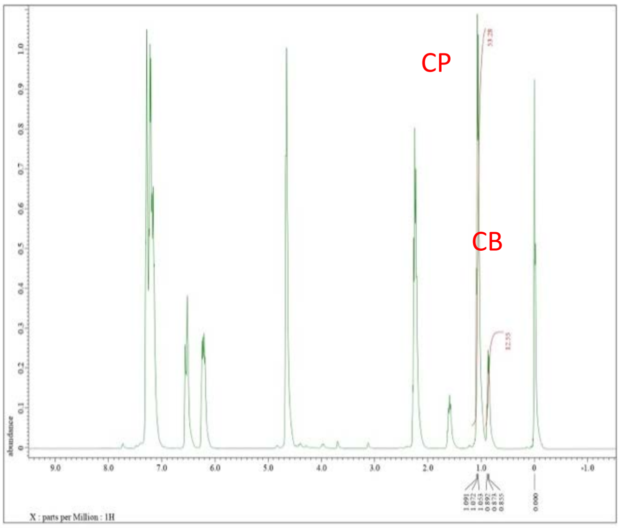

**Figure 7.** $^1$H NMR spectra of 4:1 CP:CB binary mixture

$$Percent\ composition\ of CE_1 = \frac{CE_1}{CE_1 + CE_2} \times 100 \qquad (2)$$

Percent composition was calculated for both cinnamyl esters in each of the binary mixtures according to the equation above. Figure 8 through Figure 10 display the calculated percent composition, or $^1$H NMR determined weight percent versus the gravimetrically determined weight percent, of CA in CA:CP, CA in CA:CB, and CP in CP:CB binary mixtures respectively.

Figure 8 through Figure 10 show linear correlations between the $^1$H NMR determined weight percent and gravimetric weight percent. In all cases, the experimental weight percent obtained via gravimetric analysis and the qHNMR weight percent align in a 1:1 relationship as shown by the slope in all cases being very close to 1. The qHNMR methodology is shown to be very accurate, as all calibration curves exhibit $r^2$ values greater than 0.99.

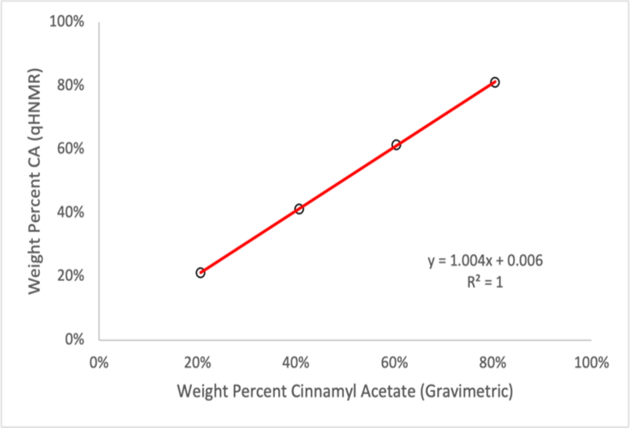

**Figure 8.** $^1$H NMR determined versus gravimetric weight percent CA in CA:CP binary mixtures

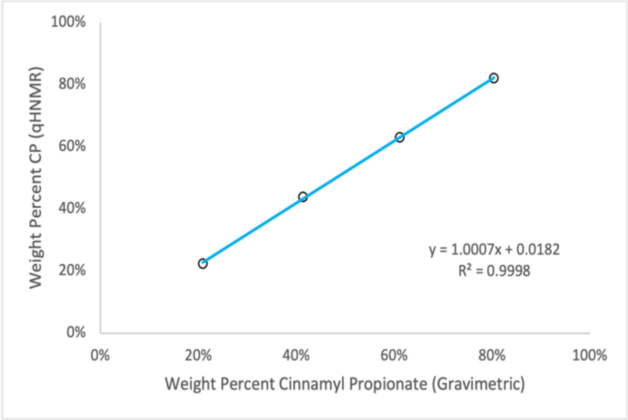

**Figure 9.** $^1$H NMR determined versus gravimetric weight percent CA in CA:CB binary mixtures

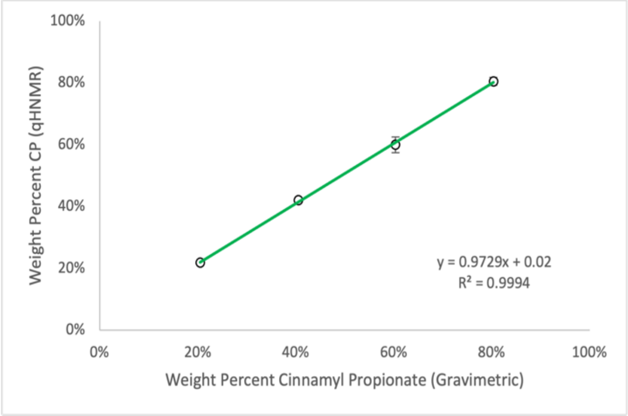

**Figure 10.** $^1$H NMR determined versus gravimetric weight percent CP in CP:CB binary mixtures

### 3.2.Fourier-Transform Infrared Spectroscopy

Figure 11 through Figure 13 show the ATR-FTIR spectra for CA, CP, and CB, respectively. All three cinnamyl esters exhibit weak aromatic stretching $\nu$ C-H peaks centered at 3028 cm$^{-1}$, two alkene stretching $\nu$ C=C peaks centered at 2875 and 2965 cm$^{-1}$, and multiple aromatic bending $\delta$ C-H and HC=CH peaks centered at 963 cm$^{-1}$, characteristic of the phenyl and alkene groups. All cinnamyl esters also exhibit very strong carbonyl stretching $\nu$ C=O peaks centered at 1733 cm$^{-1}$ and multiple stretching $\nu$ C=O peaks between 1220 and 1100 cm$^{-1}$, characteristic of the ester group, and multiple aliphatic $\delta$ C-H peaks between 1370 and 1250 cm$^{-1}$, characteristic of the methylene and methyl groups. CA has a unique aliphatic stretching $\nu$ C-H peak at 1023 cm$^{-1}$ in the fingerprint region, whereas CP and CB exhibit unique aliphatic stretching $\nu$ C-H peaks at 1081 and 1347 cm$^{-1}$, and 1098 and 1253 cm$^{-1}$, respectively.

Figure 14 displays all three cinnamyl ester ATR-FTIR spectra aligned with unique absorbance bands highlighted. The aforementioned absorbance bands unique to each of the cinnamyl esters are: CA, at 1023 cm$^{-1}$; CP, at 1080 and 1347 cm$^{-1}$; and CB, at 1100 and 1254 cm$^{-1}$; these were used to quantify each of the cinnamyl esters in the binary mixtures, and are shown shaded in red, magenta, and blue, respectively. Table 4 through Table 6 display the peak heights of the peaks used to identify each cinnamyl ester in the binary mixtures, as well as the calculated peak height ratios. Figure 15 through Figure 17 display the peak height ratios plotted against the gravimetric weight percent for one component in the binary mixtures, representing calibration curves for each set of binary mixtures. Colored points in each of the plots serve as "unknowns" to confirm the strength of the correlations.

**Table 4. Peak Height Ratios for CA-CP Binary Mixtures**

| Wt. % CA | Wt. % CP | Peak Height 1023 cm$^{-1}$ | Peak Height 1080 cm$^{-1}$ | Peak Height Ratio |
|---|---|---|---|---|
| 0 | 100 | 0.172 | 0.264 | 0.652 |
| 20.61 | 79.39 | 0.217 | 0.239 | 0.908 |
| 40.67 | 59.33 | 0.234 | 0.198 | 1.182 |
| 50.61 | 49.39 | 0.275 | 0.211 | 1.303 |
| 60.35 | 39.65 | 0.280 | 0.184 | 1.522 |
| 70.17 | 29.85 | 0.295 | 0.157 | 1.879 |
| 80.40 | 19.60 | 0.319 | 0.151 | 2.113 |
| 100 | 0 | 0.361 | 0.142 | 2.542 |

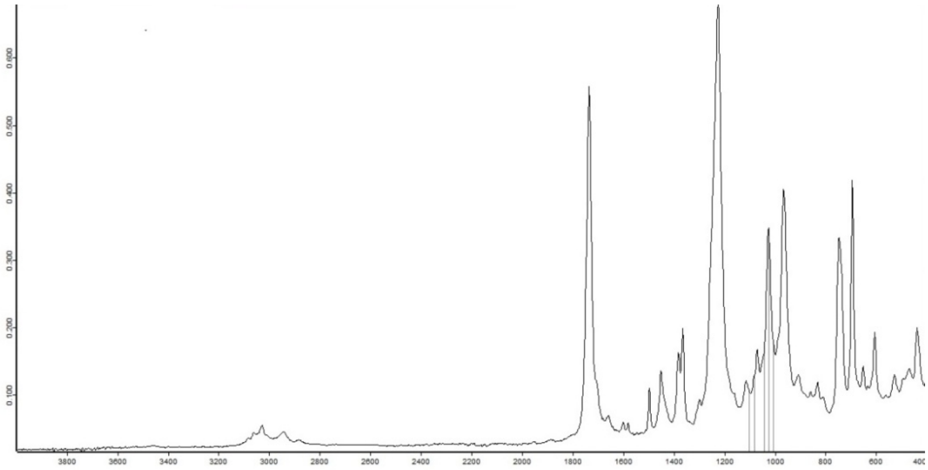

**Figure 11.** ATR-FTIR spectrum for pure cinnamyl acetate (CA)

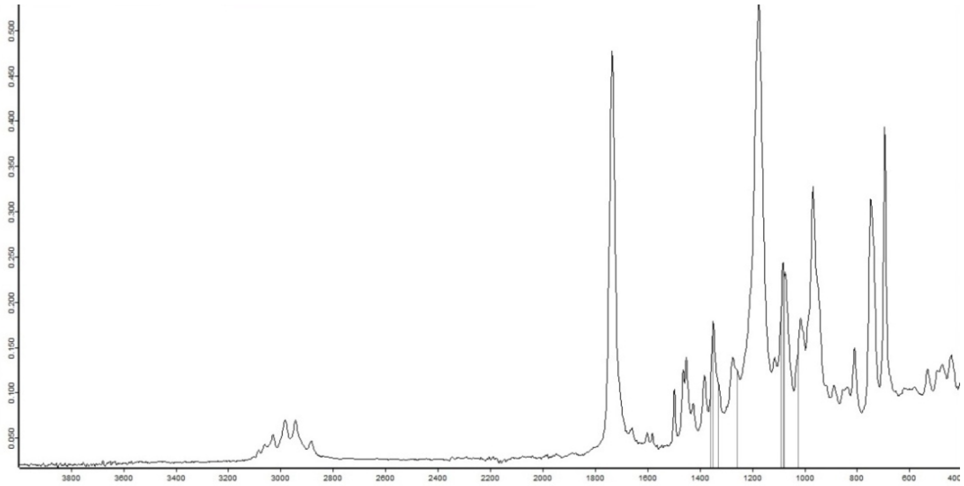

**Figure 12.** ATR-FTIR spectrum for pure cinnamyl propionate (CP)

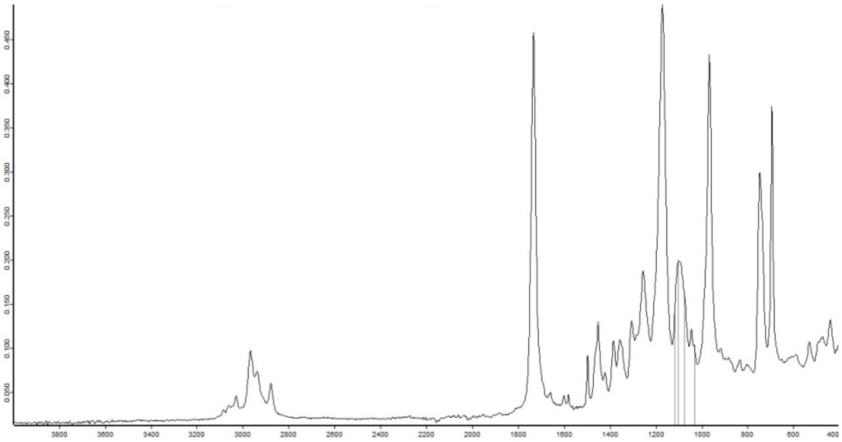

**Figure 13.** ATR-FTIR spectrum for pure cinnamyl butyrate (CB)

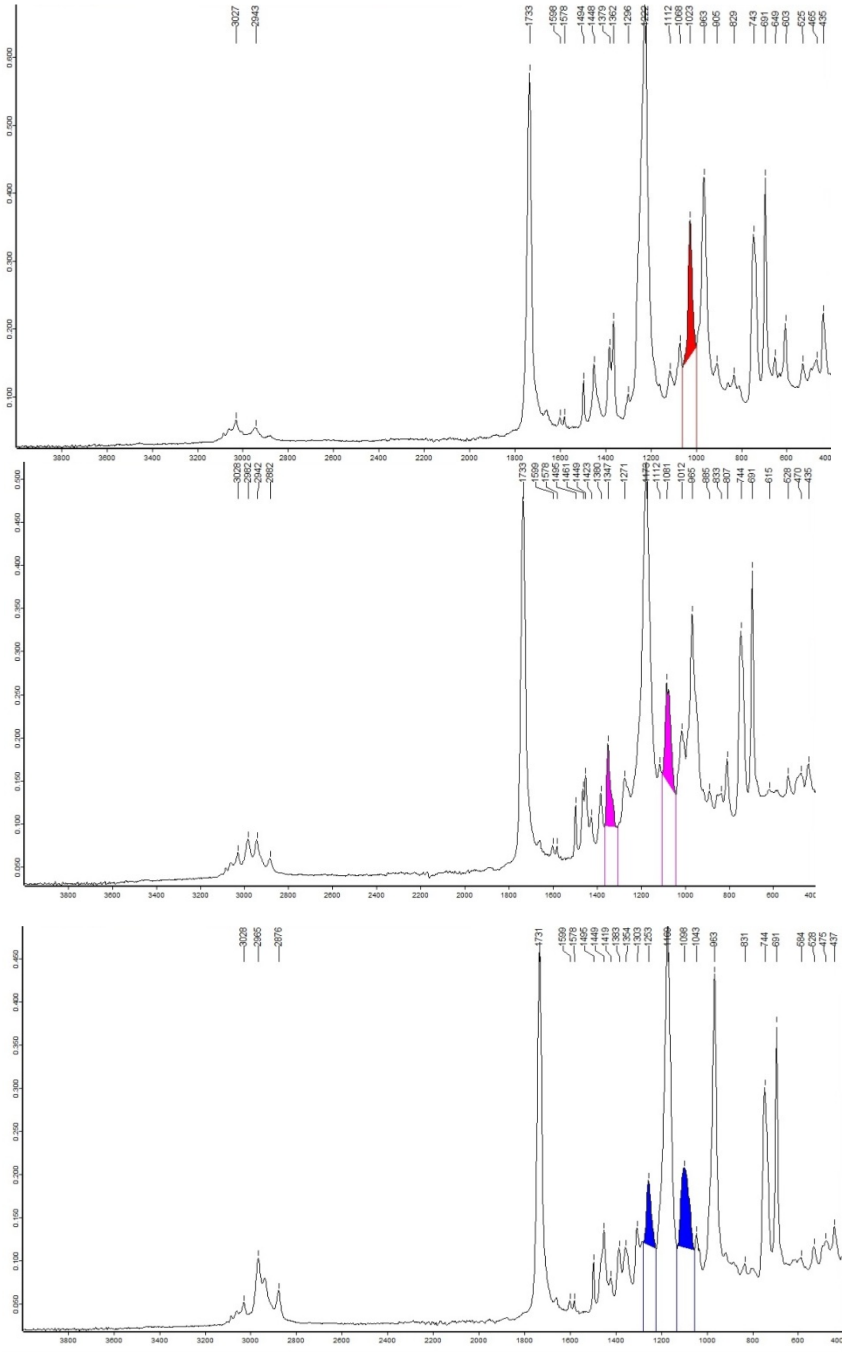

**Figure 14.** FTIR spectrum for cinnamyl acetate (CA), propionate (CP), and butyrate (CB), respectively. The absorbance bands unique to CA, at 1023 cm$^{-1}$; CP, at 1080 and 1347 cm$^{-1}$; and CB, at 1100 and 1254 cm$^{-1}$; used to quantify each of the cinnamyl esters in the binary mixtures, are shown shaded in red, magenta, and blue, respectively.

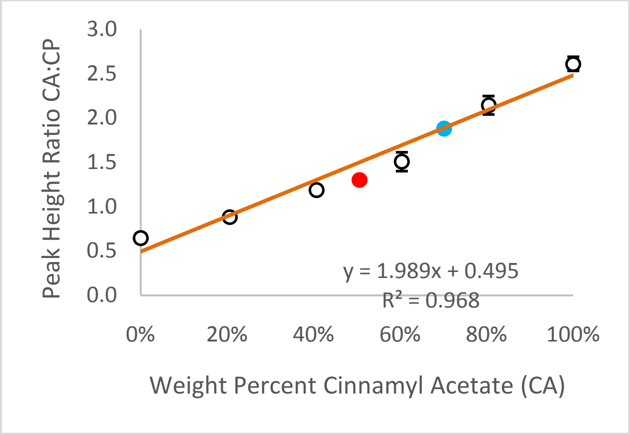

**Figure 15.** FTIR peak height ratios plotted against the gravimetric weight percent of cinnamyl acetate (CA) in CA:CP binary mixtures of various compositions. Error bars represent one standard deviation above and below the data points and the colored points represent unknowns

**Table 5. Peak Height Ratios for CA-CB Binary Mixtures**

| Wt. % CA | Wt. % CB | Peak Height 1023 $cm^{-1}$ | Peak Height 1100 $cm^{-1}$ | Peak Height Ratio |
|---|---|---|---|---|
| 0 | 100 | 0.100 | 0.208 | 0.481 |
| 20.96 | 79.04 | 0.187 | 0.192 | 0.974 |
| 41.43 | 58.57 | 0.217 | 0.168 | 1.292 |
| 50.86 | 49.14 | 0.248 | 0.165 | 1.503 |
| 61.13 | 38.87 | 0.273 | 0.159 | 1.717 |
| 70.59 | 29.42 | 0.289 | 0.139 | 2.079 |
| 80.34 | 19.66 | 0.315 | 0.141 | 2.234 |
| 100 | 0 | 0.361 | 0.125 | 2.888 |

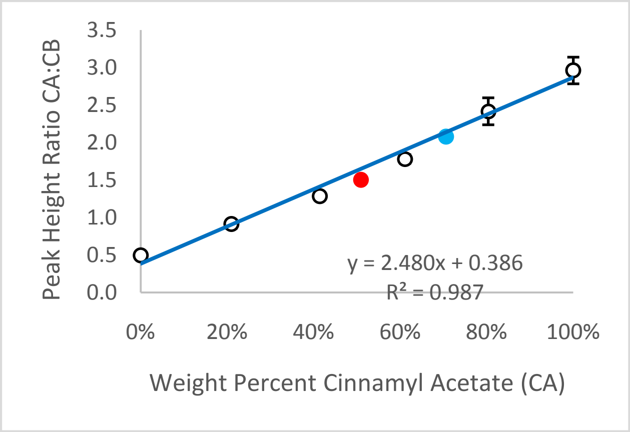

**Figure 16.** FTIR peak height ratios plotted against the gravimetric weight percent of CA in CA:CB binary mixtures of various compositions. Error bars represent one standard deviation above and below the data points and the colored points represent unknowns

**Table 6. Peak Height Ratios for CP-CB Binary Mixtures**

| Wt. % CP | Wt. % CB | Peak Height 1347 $cm^{-1}$ | Peak Height 1254 $cm^{-1}$ | Peak Height Ratio |
|---|---|---|---|---|
| 0 | 100 | 0.110 | 0.194 | 0.567 |
| 20.54 | 79.46 | 0.103 | 0.158 | 0.652 |
| 40.56 | 59.44 | 0.121 | 0.156 | 0.776 |
| 50.63 | 49.37 | 0.144 | 0.159 | 0.906 |
| 60.35 | 39.65 | 0.156 | 0.156 | 1.000 |
| 70.12 | 29.88 | 0.157 | 0.150 | 1.047 |
| 80.34 | 19.66 | 0.170 | 0.141 | 1.206 |
| 100 | 0 | 0.193 | 0.142 | 1.359 |

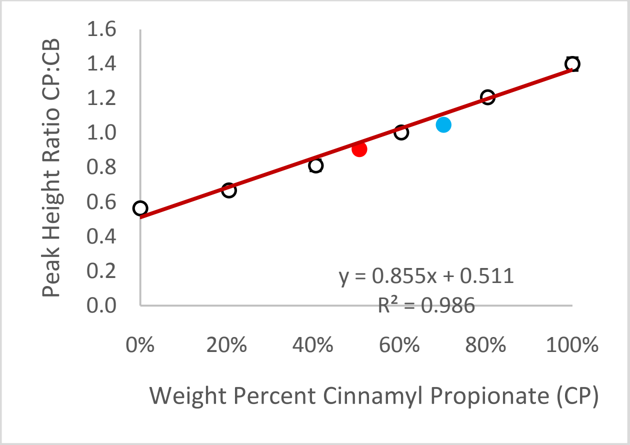

**Figure 17.** FTIR peak height ratios plotted against the gravimetric weight percent of cinnamyl propionate (CP) in CP:CB binary mixtures of various compositions. Error bars represent one standard deviation above and below the data points and the colored points represent unknowns

The above calibration curves were used to accurately determine the weight percent composition of a component in a binary mixture using different cinnamyl esters. There is a strong, linear correlation between the FTIR peak height ratio and the weight percent of one component determined gravimetrically ($r^2$ >0.98).

## 4. Conclusions

Each cinnamyl acetate, propionate, butyrate possessed unique H NMR methyl proton resonances of 1.95 (s, 3H), 1.07 (t, 3H), and 0.88 (t, 3H) and FTIR absorbance bands of 1023; 1080, 1347; 1100, and 1254 $cm^{-1}$ respectively. These peaks were used to not only identify but quantify relative concentrations of each of the cinnamyl esters when present in binary mixtures simultaneously. The use of these fundamental spectroscopic techniques quantitatively was supported by the strong linear correlations achieved between the gravimetrically and $^1$H NMR ($r^2$ > 0.99) and FTIR ($r^2$ > 0.98) determined weight percents.

## ACKNOWLEDGEMENTS

We acknowledge support from the Dr. Bruce and Doris Lister Endowed Fellowship in Chemistry Research, as well as funding from a Hofstra University HCLAS Research and Development Grant.

## List of Abbreviations and Symbols

CA = cinnamyl acetate
CP = cinnamyl propionate
CB = cinnamyl butyrate
NMR = nuclear magnetic resonance spectroscopy
$^1$H NMR = proton nuclear magnetic resonance spectroscopy
qHNMR = quantitative proton nuclear magnetic resonance spectroscopy
FTIR = Fourier-transform infrared spectroscopy
USFDA = United States Food and Drug Administration

$\nu$ = stretching vibrational mode
$\delta$ = bending vibrational mode

# References

[1] FDA (Food and Drug Administration). Code of Federal Regulations, 21 CFR 172.515. Title 21 – Food and Drugs, Volume 3, Chapter I – Food and Drug Administration, Department of Health and Human Services. Part 172 – Food Additives Permitted for Direct Addition to Food for Human Consumption. Subpart F – Flavoring Agents and Related Substances, 515 – Synthetic Flavoring Substances and Adjuvants.

[2] Belsito D, Bickers D, Bruze M, Calow P, Greim H, Hanifin JM, Rogers AE, Saurat JH, Sipes IG, Tagami H (2007). "A toxicologic and dermatologic assessment of related esters and alcohols of cinnamic acid and cinnamyl alcohol when used as fragrance ingredients". *Food and Chemical Toxicology*. **45** (Suppl 1): S1–23.

[3] Bhatia SP, Wellington GA, Cocchiara J, Lalko J, Letizia CS, Api AM (2007-01-01). "Fragrance material review on cinnamyl acetate". *Food and Chemical Toxicology*. 45 Suppl 1 (1): S53–7.

[4] Devulapelli, Venu Gopal; Weng, Hung-Shan (2009-07-25). "Synthesis of cinnamyl acetate by solid–liquid phase transfer catalysis: Kinetic study with a batch reactor". Catalysis Communications. 10 (13): 1638–1642.

[5] Cai X, Wang W, Lin L, He D, Shen Y, Wei W, Wei Dz (2017-04-01). "Cinnamyl Esters Synthesis by Lipase-Catalyzed Transesterification in a Non-Aqueous System". Catalysis Letters. 147 (4): 946–952.

[6] Geng, B. (August 2012). "Cinnamyl acetate synthesis by lipase-catalyzed transesterification in a solvent-free system." *Biotechnology and Applied Biochemistry*. 59 (4): 270–275.

[7] Luebke, William (2018-01-31). "cinnamyl acetate, 103-54-8". *www.thegoodscentscompany.com*. Retrieved 2018-03-23.

[8] D'Amelia, R.P., Huang, L., Nirode, W.F., Rotman, E., Shumila, J., and Wachter, N., "Application of $^1$H-NMR for the Quantitative Analysis of Short Chain Fatty Acid Methyl Ester Mixtures: An Undergraduate Instrumental Analysis Experiment", *World Journal of Chemical Education*, 3(2). 46-50. April 2015.

[9] D'Amelia, R.P., Mancuso, J., and Wachter, N., "Application of Quantitative Proton Nuclear Magnetic Resonance Spectroscopy for the Compositional Analysis of Short Chain Fatty Acid Benzyl Ester Mixtures", *World Journal of Chemical Education*, 7(3), 189-195. May 2019.

[10] Woodworth J.K., Terrance J.C., and Hoffmann M.M., "Using Nuclear Magnetic Resonance Spectroscopy for Measuring Ternary Phase Diagrams", *J. Chem. Educ.*, 83(7). 1065-1066. July 2006.

[11] Isaac-Lam M.F., "Analysis of Bromination of Ethylbenzene using a 45 MHz NMR Spectrometer: An Undergraduate Organic Chemistry Laboratory Experiment", *J. Chem. Educ.*, 91(8). 1264-1266. July 2014.

[12] McGregor, M.A., Euler, W.B., *Undergraduate NMR Laboratory Experiments. In NMR Concepts*; Traficante, D.D. Ed.; NMR Concepts: Warwick, RI, 1995.

[13] Gift A.D., Stewart S.M., and Bokashanga K.P., "Experimental Determination of pKa Values by use of NMR Chemical Shifts, Revisited", *J. Chem. Educ.*, 89(11). 1458-1460. August 2012.

[14] Dauner, B. and Pringle, D., "Proton NMR Analysis of Heat Exchange Fluids Containing Ethylene Glycol, Propylene Glycol, and Water: A Real-World Experiment for the Analytical Laboratory", *J. Chem. Educ*., 91(5). 743-746. April 2014.

[15] Hoffmann M.M., Caccamis J.T., Heitz M.P., and Schlecht K.D., "Quantitative Analysis of Nail Polish Remover using Nuclear Magnetic Resonance Spectroscopy Revisited", *J. Chem. Educ*., 85(10). 1421-1423. October 2008.

[16] Clarke, D., "Acetone and Ethyl Acetate in Commercial Nail Polish Removers: A Quantitative NMR Experiment using an Internal Standard", *J. Chem. Educ*., 74(12). 1464-1465. December 1997.

[17] Peterson, J., "$^1$H NMR Analysis of Mixtures using Internal Standards", *J. Chem. Educ*., 69(10). 843-845. October 1992.

[18] Phillips, J.S. and Leary, J.J., "A Qualitative – Quantitative $^1$H-NMR Experiment for the Instrumental Analysis Laboratory", *J. Chem. Educ*., 63(6). 545-546. June 1986.

[19] Podgorski, V.V., Milhalev, A. S., Kalabin, G.A., "Quantitative NMR Spectroscopy for the Quality control of Drugs and Pharmaceuticals", *Phar. Chem. J.,* 45(3). 194-197. June 2011.

[20] D'Amelia, R.P., Kimura, M.W., and Nirode, W.F., "Application of Quantitative Proton Nuclear Magnetic Resonance Spectroscopy for the Compositional Analysis of Short-Chain Fatty Acid Ethyl Ester Mixtures", *World Journal of Chemical Education*, 9(1), 8-13. November 2020.

[21] D'Amelia, R.P., Khanyan, B., and Mancuso, J., "Compositional Analysis of Mixtures of Oleate Esters of Short Chain Alcohols (C1-C4) by Quantitative Proton Nuclear Magnetic Resonance Spectroscopy (qPNMR)", *World Journal of Chemical Education*, 10(1), 1-7. December 2021.

[22] D'Amelia, R. P.; Kimura, M. W.; Villion, M.-C. "Qualitative and Quantitative Analyses of Synthesized Short-Chain Fatty Acid Phenyl Esters Using Fourier-Transform Infrared Spectroscopy". *World J. Org. Chem.* 2021, 9(1) 6-17.

[23] Schuttlefield, J. D.; Grassian, V. H. ATR–FTIR Spectroscopy in the Undergraduate Chemistry Laboratory. Part I: Fundamentals and Examples. J. Chem. Educ. 2008, 85 (2), 279.

[24] Robinson, J. W.; Frame, E. S.; Frame II, G. M. Chapter 4. In Undergraduate Instrumental Analysis; CRC Press: New York, 2014.

[25] Gebel, M. E.; Kaleuati, M. A.; Finlayson-Pitts, B. J. Measurement of Organics Using Three FTIR Techniques: Absorption, Attenuated Total Reflectance, and Diffuse Reflectance. *J. Chem. Educ.* 2003, 80 (6), 672.

[26] Lambert, J. B.; Gronet, S.; Shurvell, H. F.; Lightner, D. Organic Structural Spectroscopy, 2nd ed.; Prentice Hall: New Jersey, 2010.

[27] Bellamy, M. K. Using FTIR-ATR Spectroscopy to Teach the Internal Standard Method. J. Chem. Educ. 2010, 87 (12), 1399-1401.

[28] Tarhan, İ.; Ismail, A. A.; Kara, H. Quantitative Determination of Free Fatty Acids in Extra Virgin Olive Oils by Multivariate Methods and Fourier Transform Infrared Spectroscopy Considering Different Absorption Modes. Int. J. Food Prop. 2017, 20 (sup1), S790-S797.

[29] Ismail, A. A.; van de Voort, F. R.; Emo, G.; Sedman, J. Rapid Quantitative Determination of Free Fatty Acids in Fats and Oils by Fourier Transform Infrared Spectroscopy. J. Am. Oil Chem. Soc. 1993, 70 (4), 335-341.

[30] D'Amelia, R. P.; Gentile, S.; Nirode, W. F.; Huang, L. Quantitative Analysis of Copolymers and Blends of Polyvinyl Acetate (PVAc) Using Fourier Transform Infrared Spectroscopy (FTIR) and Elemental Analysis (EA). World J. Chem. Educ. 2016, 4 (2), 25-31.

[31] D'Amelia, R. P.; Huang, L.; Mancuso, J. Quantitative Analysis of Polyvinyl Alcohol-Polyethylene (PVOH-PE) Copolymers and Polyvinyl Pyrrolidone-Polyvinyl Acetate (PVP-PVAc) Copolymers and Blends Using Fourier Transform Infrared Spectroscopy and Elemental Analysis. World J. Chem. Educ. 2019, 7 (1), 1-11.