Synthesis of Natural Carboxylic Acids and Alcohols from *Cinnamon cassia* Oil via Green Chemistry Approach

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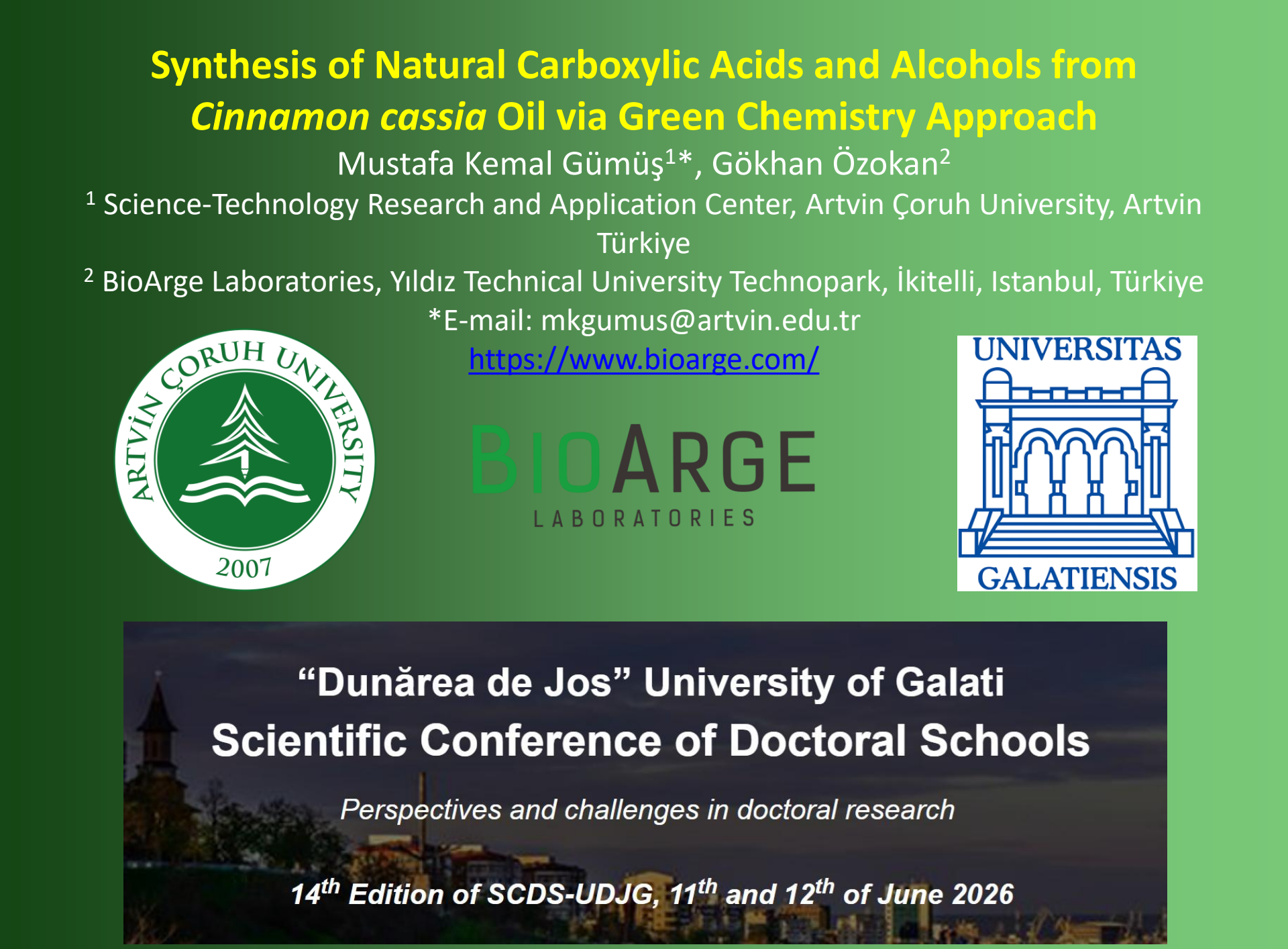
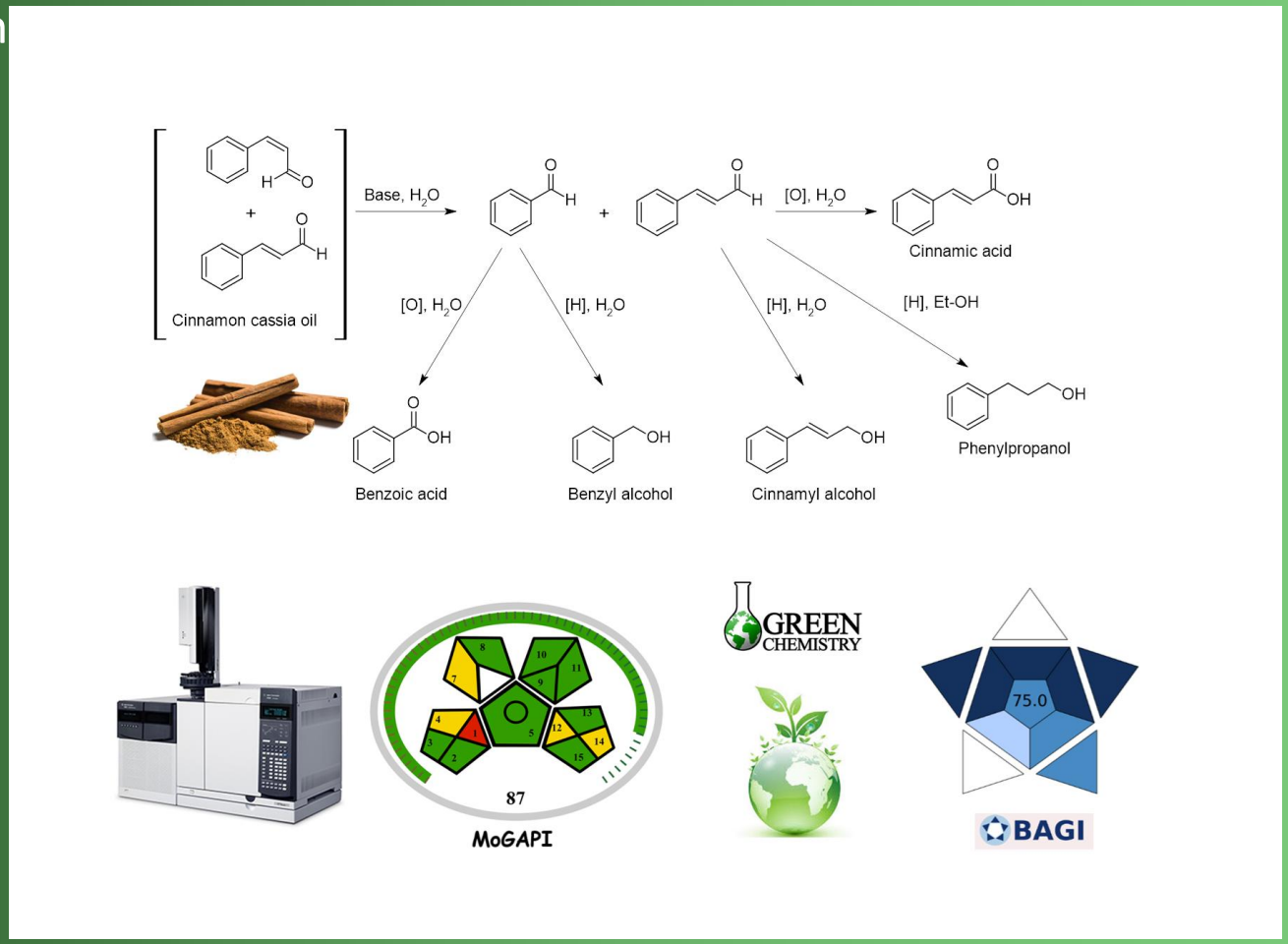


Synthesis of Natural Carboxylic Acids and Alcohols from *Cinnamon cassia* Oil via Green Chemistry Approach

• This study focuses on the synthesis of five industrially valuable organic compounds—benzoic acid, benzyl alcohol, cinnamyl alcohol, phenylpropanol, and cinnamic acid—using cinnamaldehyde and benzaldehyde, which naturally occur in *Cinnamomum cassia* oil, as starting materials.



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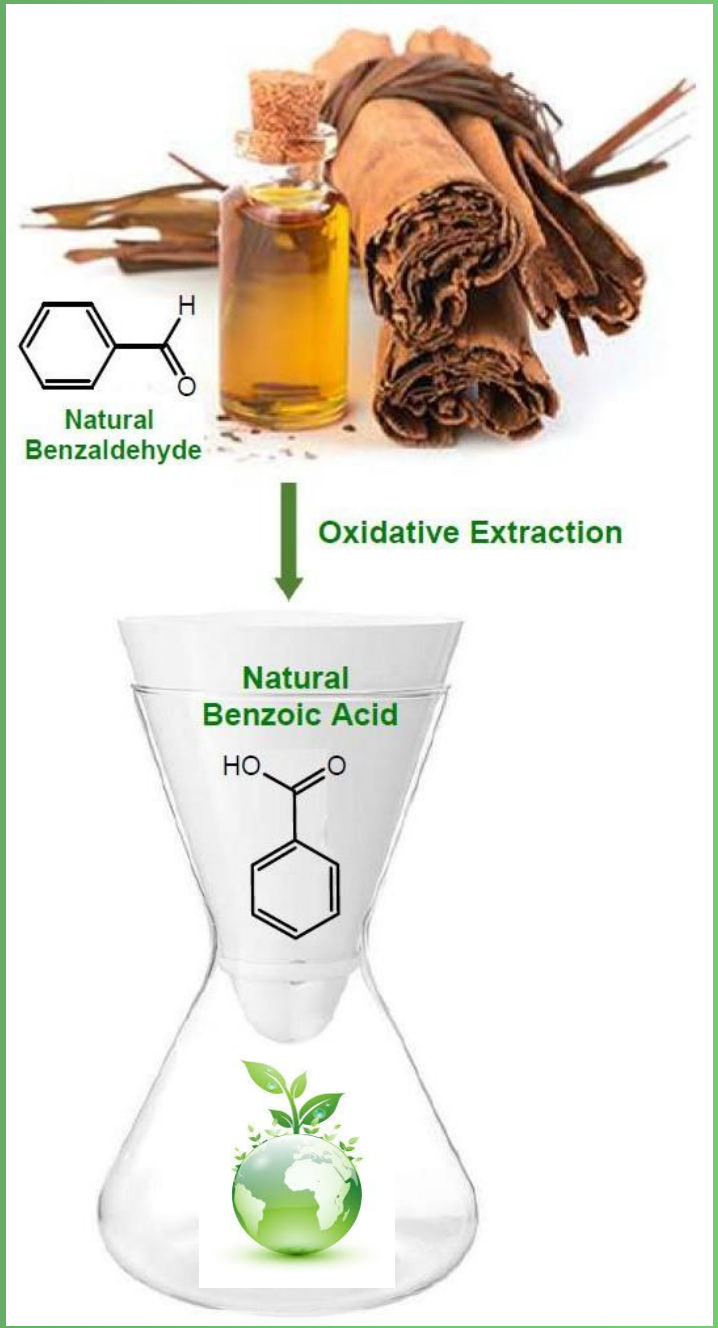
Motivation

The motivation for this research comes from two main needs. First, industries such as cosmetics, pharmaceuticals, and food manufacturing require large amounts of benzoic acid, benzyl alcohol, phenylpropanol, cinnamyl alcohol, and cinnamic acid. Second, traditional syntheses rely heavily on hazardous solvents, toxic oxidants, and processes that produce significant waste.

Green chemistry provides a clear opportunity to modernize these processes. Our aim was to design methods that reduce environmental impact while maintaining or improving efficiency and scalability.



What is Green Chemistry?

- • Minimizes hazardous waste
- • Safe solvents
- • Energy-efficient
- • High atom economy

- Before explaining our methods, it's helpful to revisit what we mean by "green chemistry." This approach seeks to minimize waste and avoid hazardous reagents, use safer solvents such as water or ethanol, operate at lower temperatures and pressures, and reduce energy consumption overall.
- For us, this meant avoiding harmful organic solvents, replacing strong oxidants with safer alternatives, and maximizing atom economy whenever possible.

Why *Cinnamon cassia* Oil?

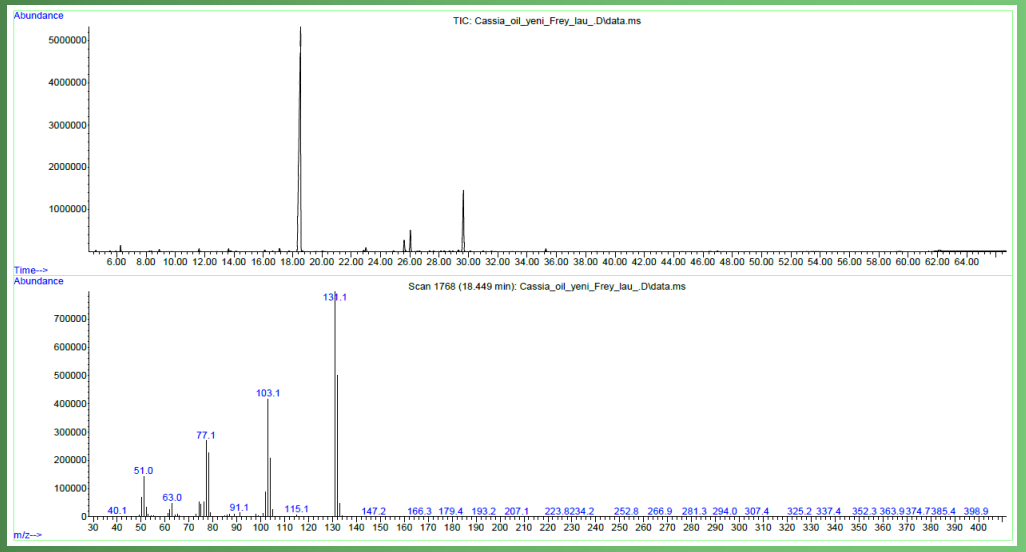
- • Rich in cinnamaldehyde (78–79%)
- • Natural benzaldehyde source
- • Sustainable and inexpensive
- • Ideal aldehyde feedstock

- *Cinnamon cassia* oil is an excellent starting material for green synthesis. It is inexpensive, renewable, and widely available. Most importantly, it contains very high levels of cinnamaldehyde—around 78 to 79 percent—and small but valuable amounts of benzaldehyde.

- These aldehydes are important intermediates for producing aromatic acids and alcohols, so they offer a perfect natural feedstock for our work.

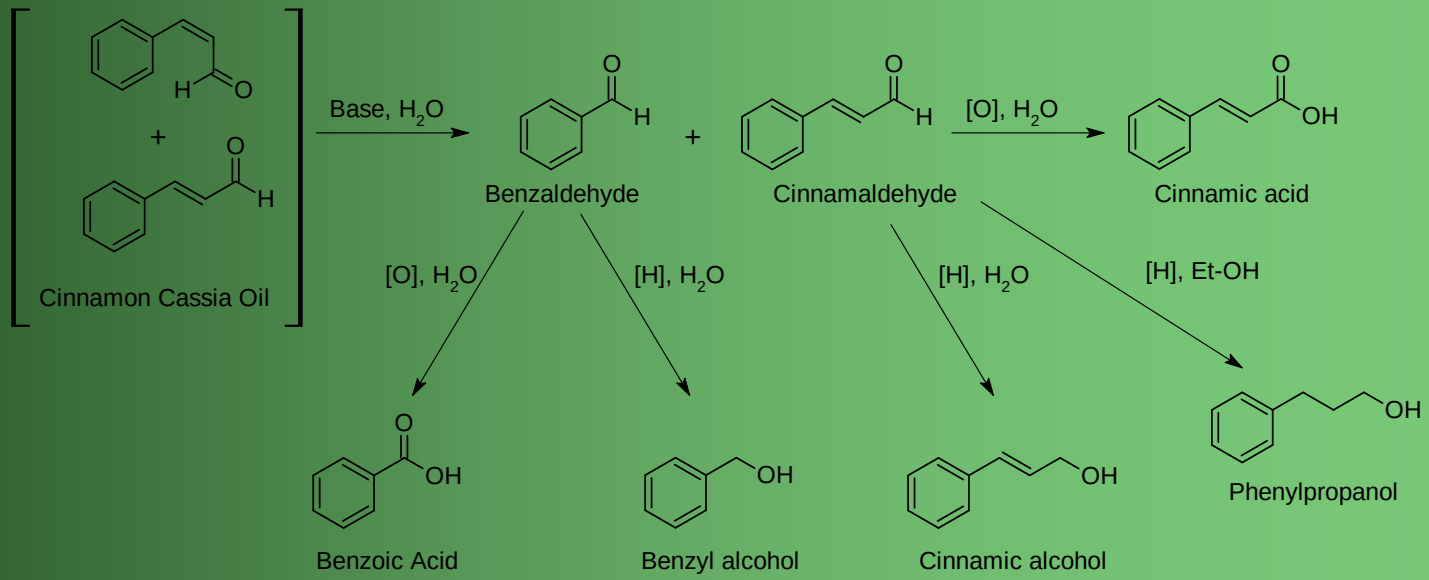
Oil Composition

- • Cinnamaldehyde: 78–79%
- • 2-Methoxycinnamaldehyde: 10–12%
- • Cinnamyl acetate: 2–3.5%
- • Benzaldehyde: 0.7–0.8%
- We began by characterizing the essential oil with GC-MS. The major components were cinnamaldehyde, 2-methoxycinnamaldehyde, cinnamyl acetate, and benzaldehyde. Knowing the precise composition allowed us to predict product yields and design efficient reaction pathways for all five target molecules.



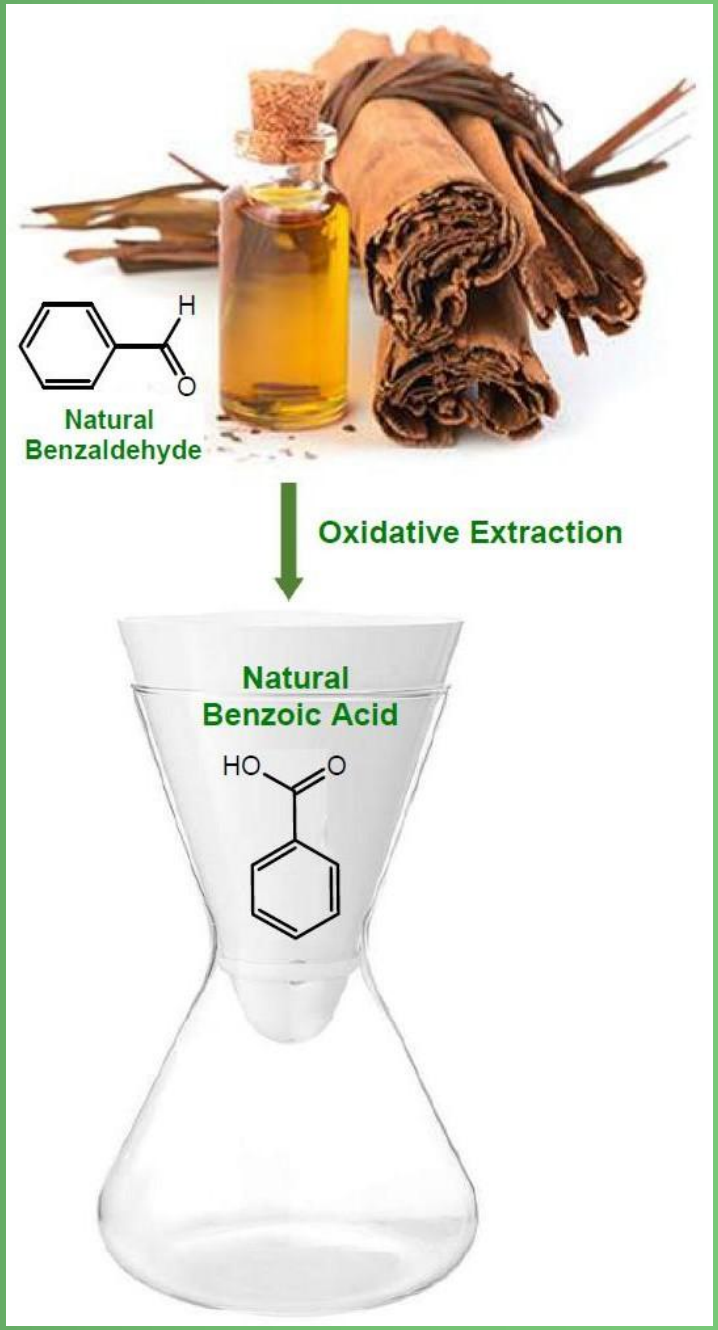
Research Goal

- Our goal was to produce five different compounds using only one natural starting material:
- 1. Benzoic acid
- 2. Benzyl alcohol
- 3. Cinnamyl alcohol
- 4. Phenylpropanol
- 5. Cinnamic acid
- All methods were required to follow green chemistry principles and be suitable for eventual industrial production.



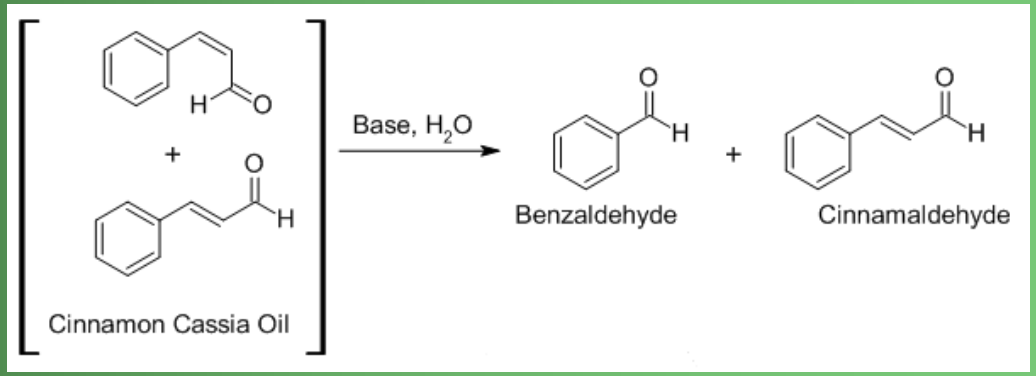
Synthetic Strategy

- • Oxidation → acids
- • Reduction → alcohols
- • Solvent: water (mostly)
- • Reagents: $KMnO_4$, $NaBH_4$, $LiAlH_4$
- The overall strategy relied on simple transformations: oxidation to obtain carboxylic acids and reduction to obtain alcohols. We used water for almost all reactions, except for phenylpropanol synthesis. Key reagents included potassium permanganate, sodium borohydride, and lithium aluminum hydride.
- Importantly, all reactions were carried out under mild conditions, and most produced very high yields.



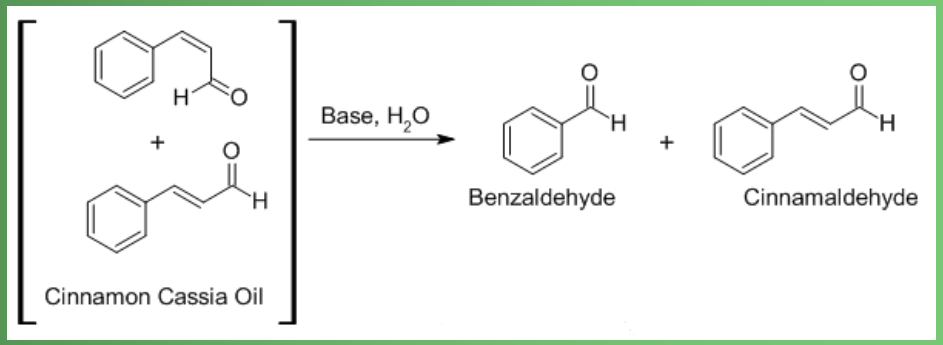
Isolation of Aldehydes

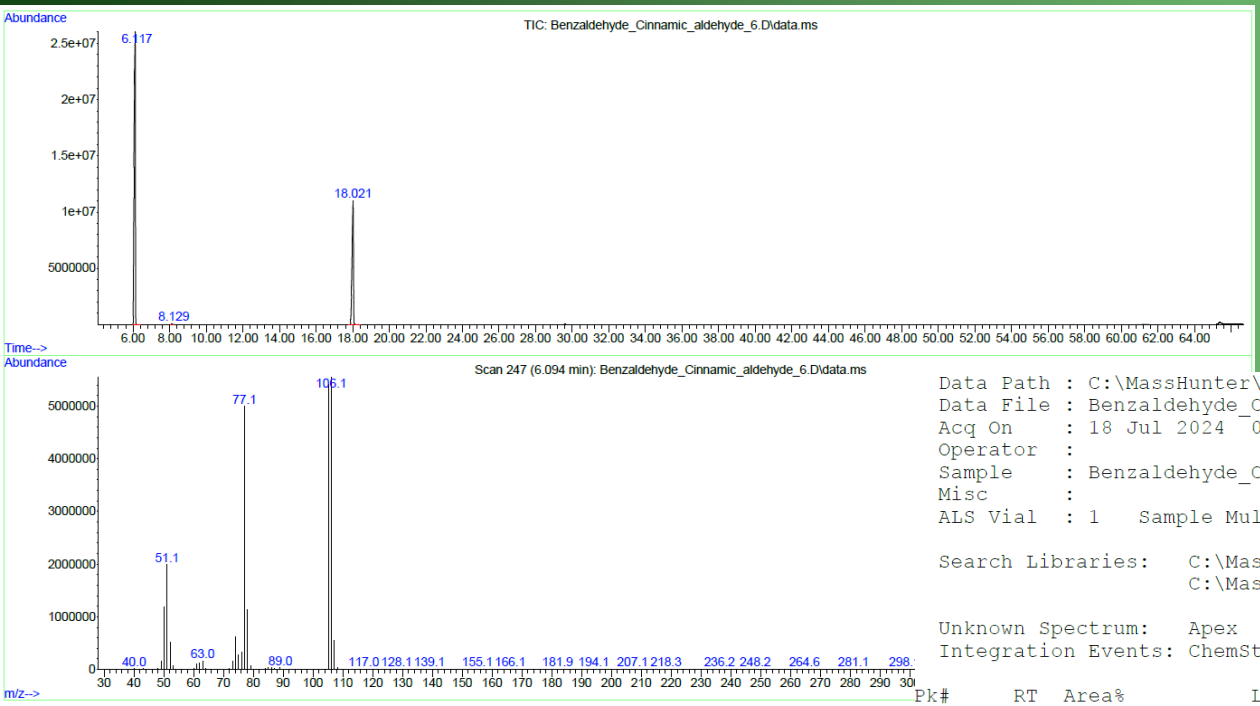
- • 3% Na_2CO_3 extraction
- • N_2 atmosphere
- • 7 h reflux
- • Purified via distillation



- The first step was isolating the aldehydes from the essential oil. We used a 3% sodium carbonate solution under nitrogen to prevent oxidation. After seven hours of reflux, we distilled the reaction mixture and obtained a purified aldehyde mixture with a 70/30 ratio of benzaldehyde to cinnamaldehyde. This mixture served as the precursor for all subsequent reactions.

Isolation of Aldehydes: Mixture



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Operator  :
Sample    : Benzaldehyde_Cinnamic_aldehyde_6
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\MassHunter\LIBRARY\NIST14.L    Minimum Quality:  80
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			Limonene	16032	000138-86-3	94
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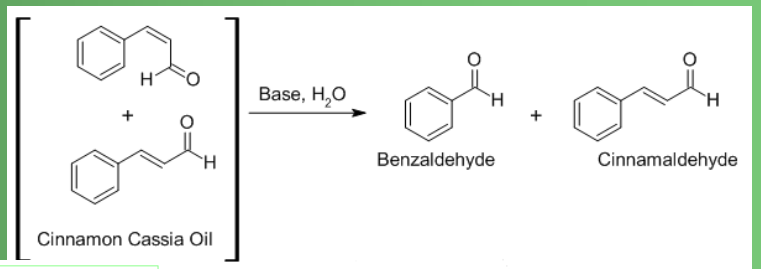
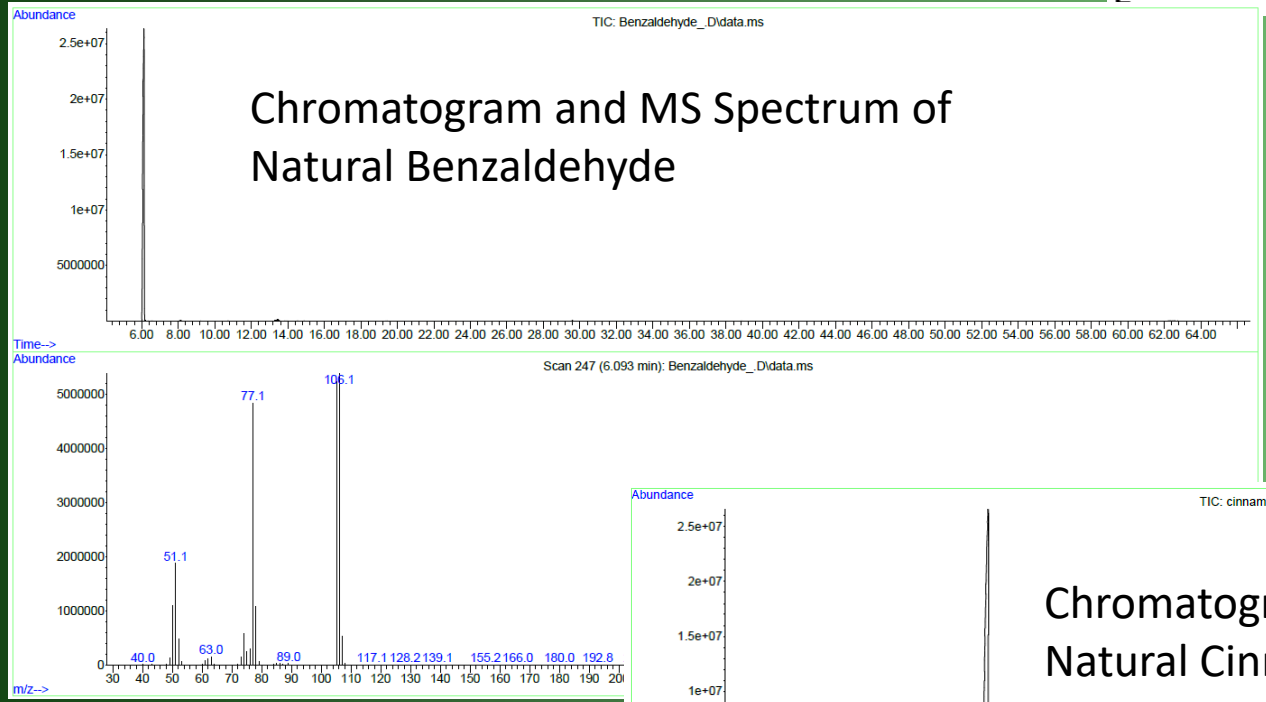
			2-Propenal, 3-phenyl-	14859	000104-55-2	97
			Cinnamaldehyde, (E)-	14849	014371-10-9	97

Chromatogram and MS Spectrum of Reaction Mixture: Natural Benzaldehyde and Natural Cinnamaldehyde (70:30%)

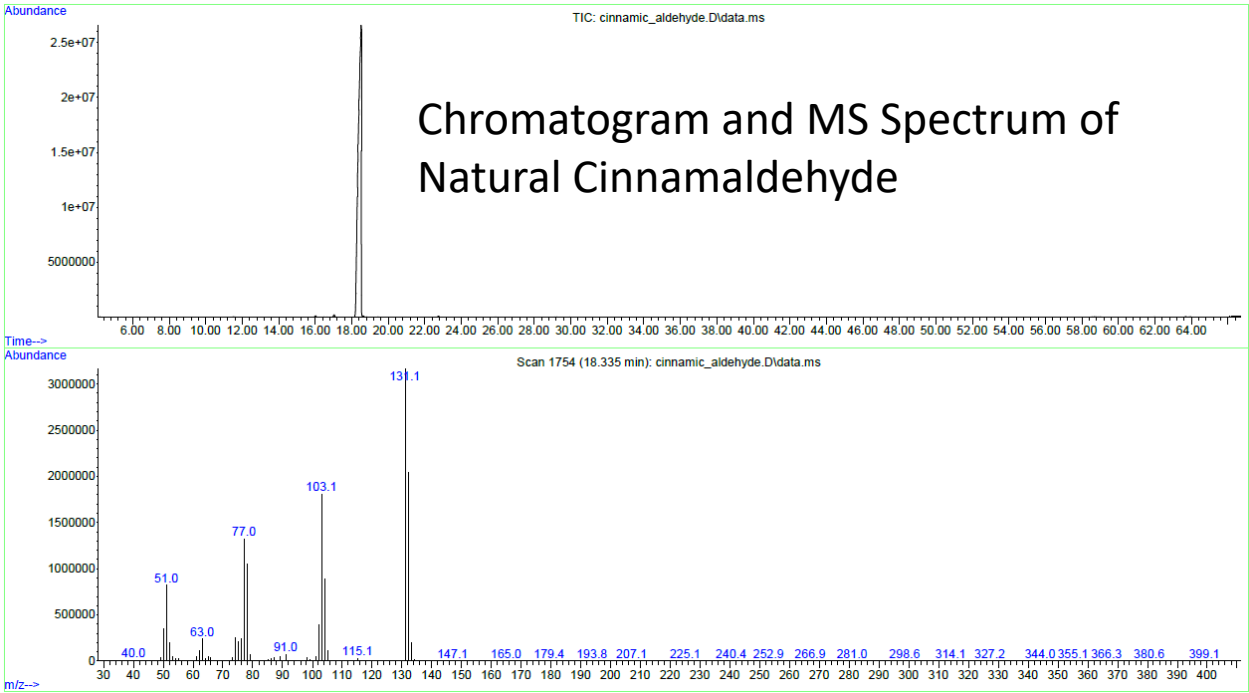
Purified Aldehydes:





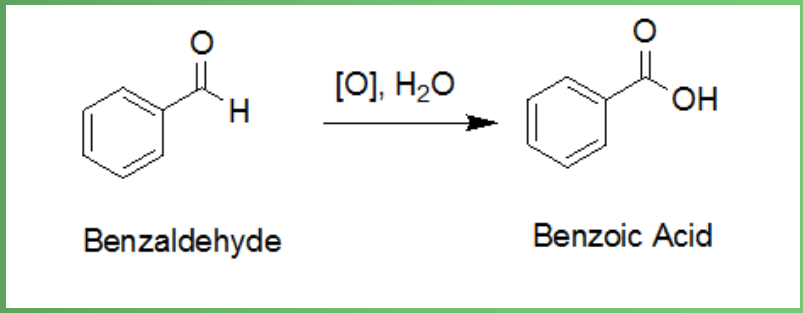
Chromatogram and MS Spectrum of Natural Benzaldehyde

Purified via distillation



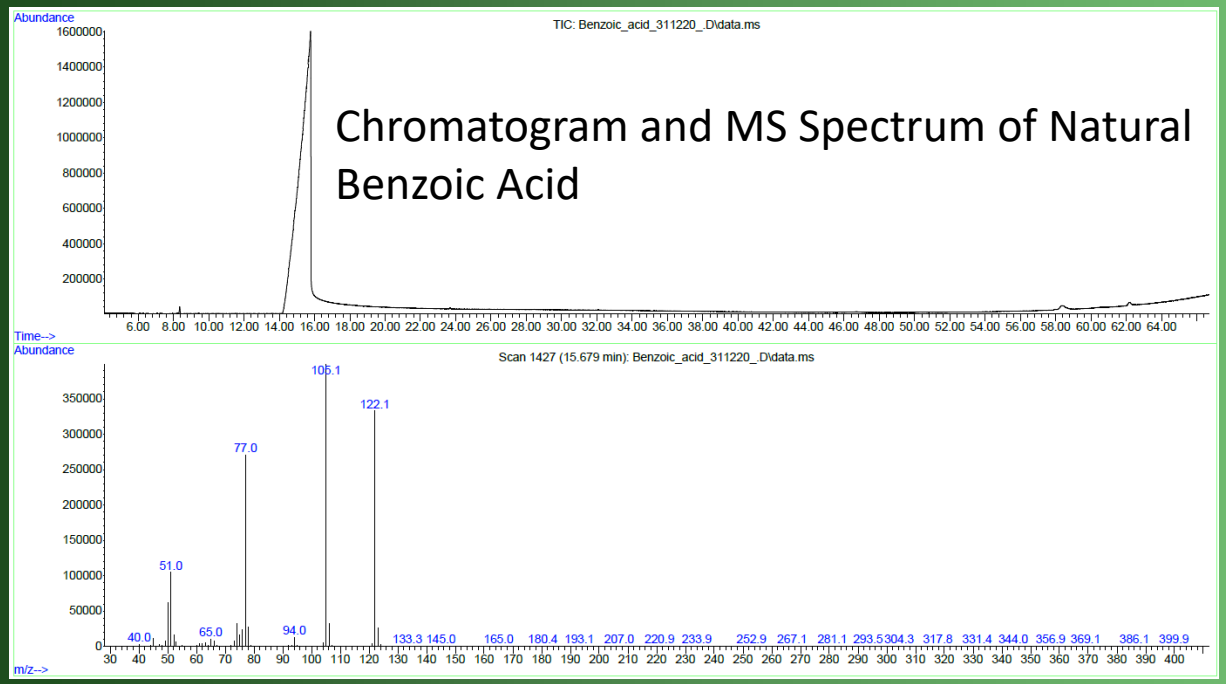
Chromatogram and MS Spectrum of Natural Cinnamaldehyde

Benzoic Acid Synthesis

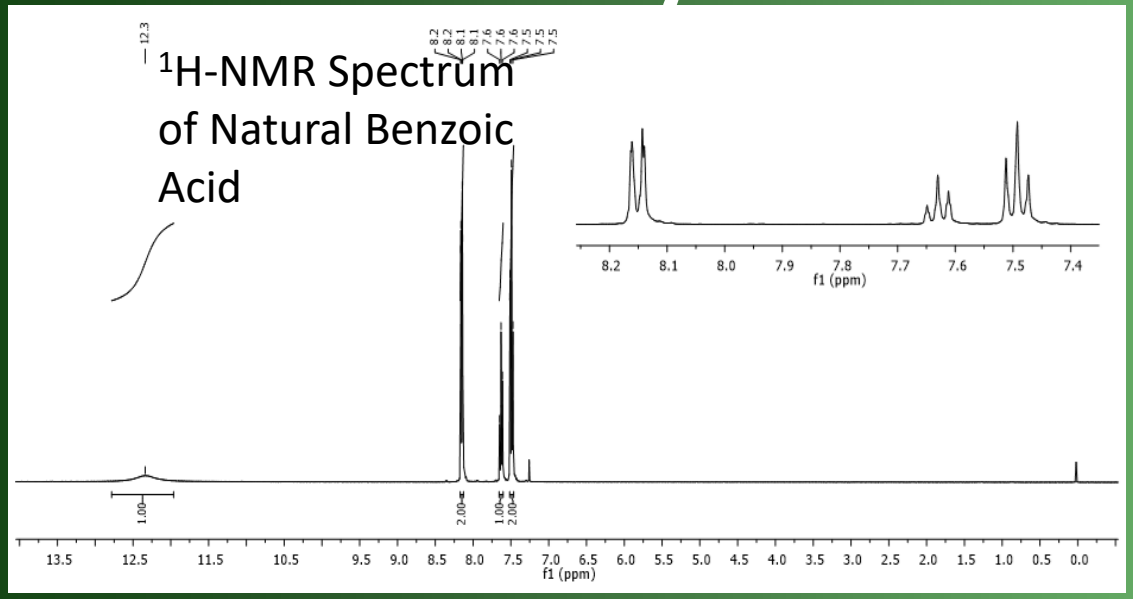


Benzaldehyde + $KMnO_4$ → Benzoic Acid

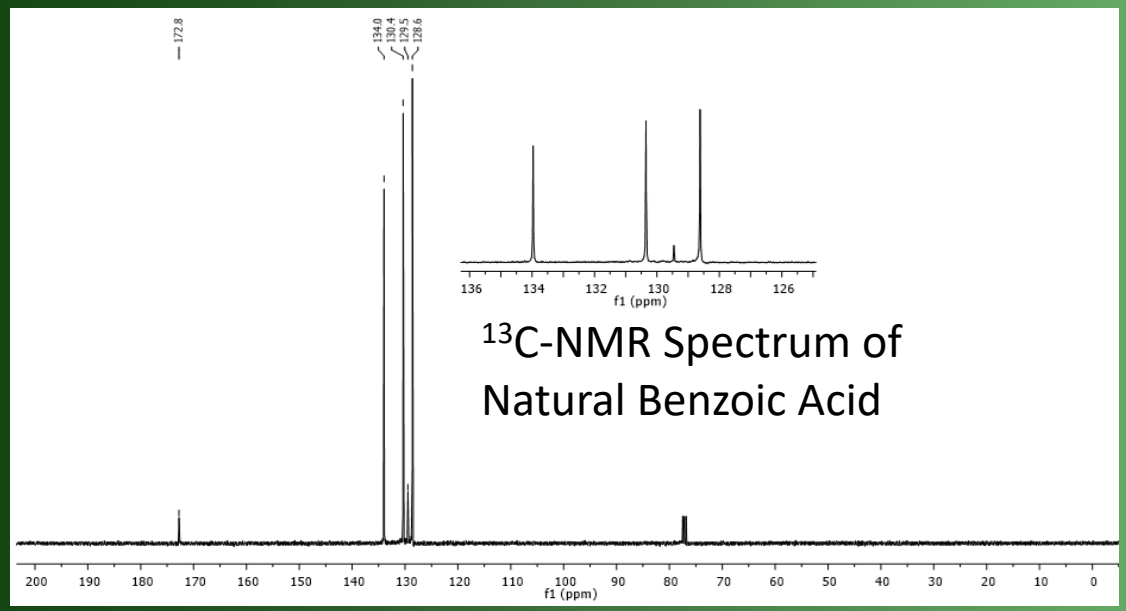
- • $KMnO_4$ oxidation
- • 90 °C, 45 min
- • 90–95% yield
- Our first target was benzoic acid. We performed an oxidation using potassium permanganate in pure water at 90 degrees Celsius for 45 minutes. This method produced benzoic acid crystals in yields between 90 and 95 percent.
- What makes this step significant is the complete absence of organic solvents and the simplicity of the purification process.



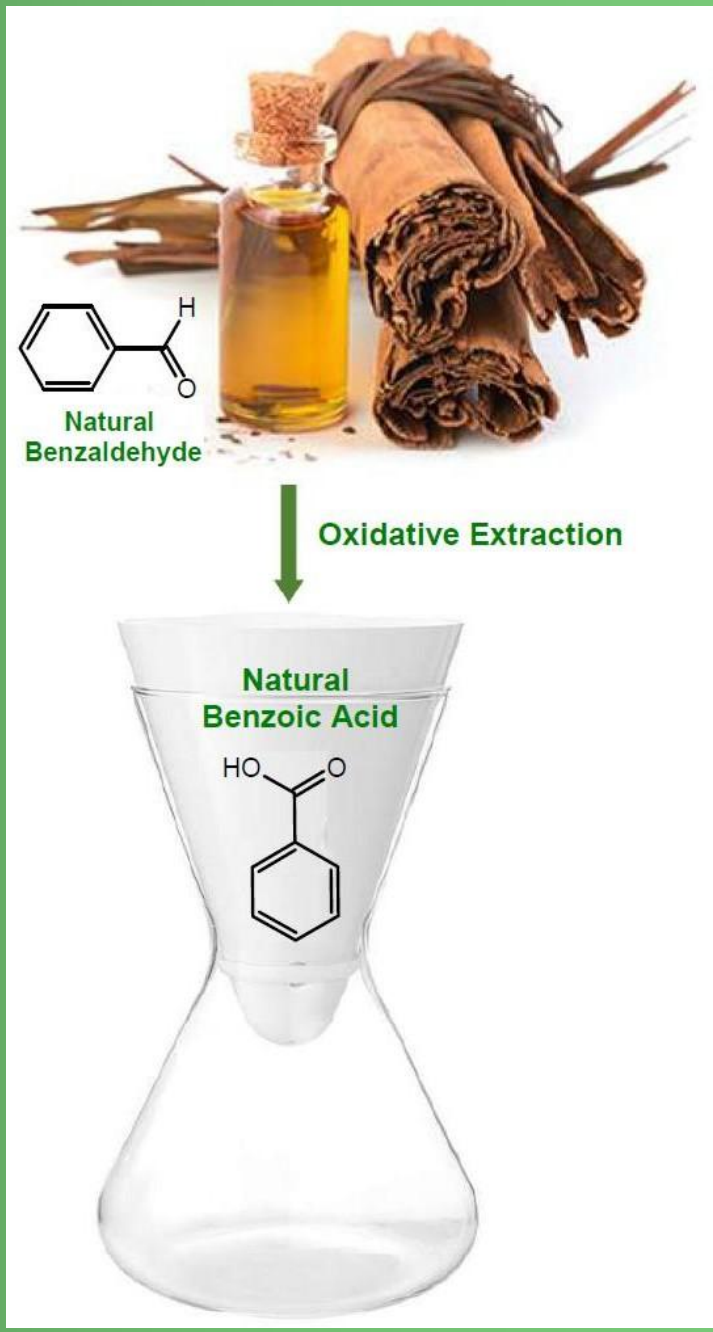
Benzoic Acid Synthesis



^{1}H-NMR Spectrum of Natural Benzoic Acid

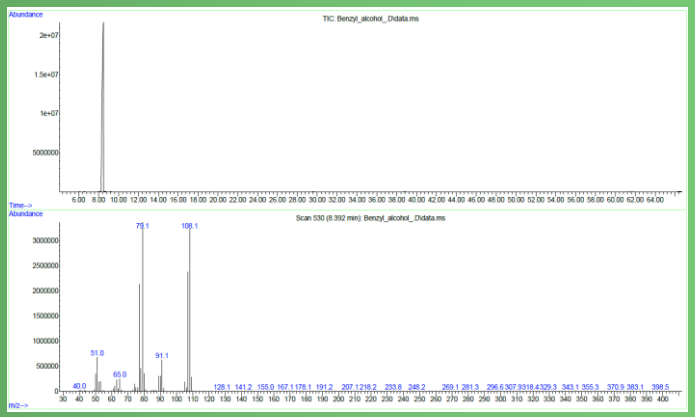


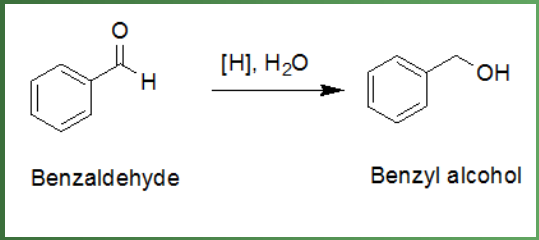
^{13}C-NMR Spectrum of Natural Benzoic Acid



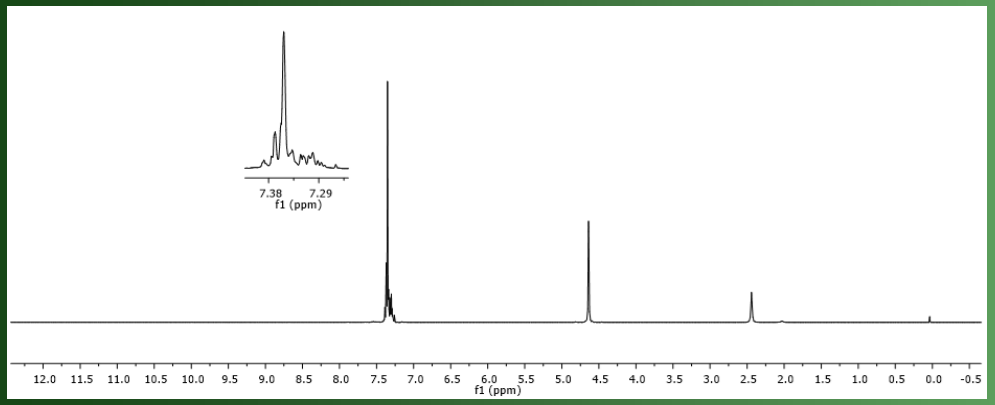
Benzyl Alcohol Synthesis

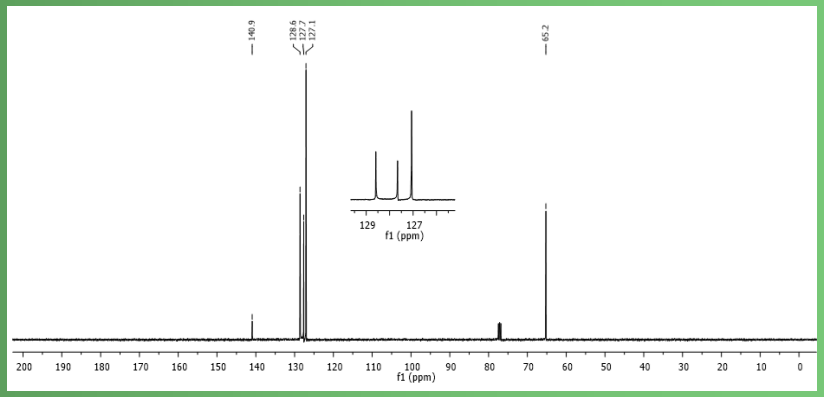
Benzaldehyde + $NaBH_4$ → Benzyl Alcohol





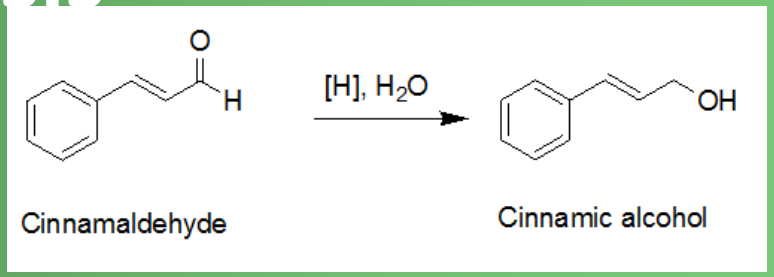
- • $NaBH_4$ in water
- • 1 h reaction
- • 90–95% yield
- Next, we reduced benzaldehyde to benzyl alcohol using sodium borohydride in water. Traditionally, $NaBH_4$ reactions are performed in anhydrous organic solvents because the reagent decomposes in water. However, with controlled addition, we achieved smooth reduction and high yields of 90 to 95 percent.
- This demonstrates that water can be used successfully, making the method far safer and more sustainable.



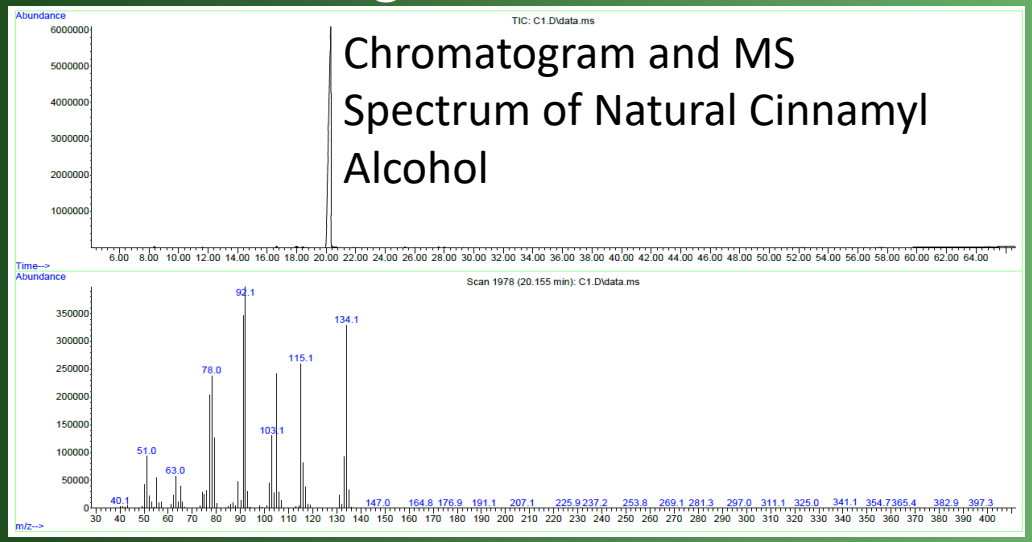


Cinnamyl Alcohol Synthesis

Cinnamaldehyde + $NaBH_4$ → Cinnamyl Alcohol



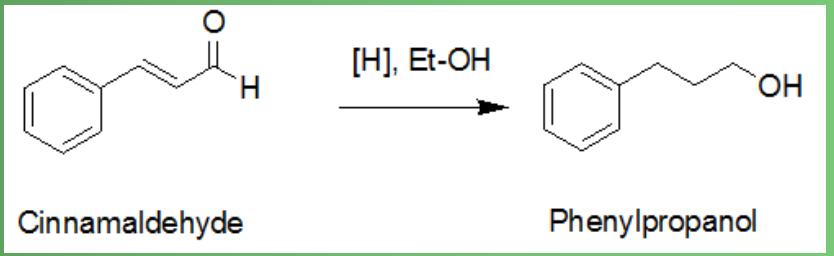
- • $NaBH_4$ reduction
- • ~95% yield
- We applied the same aqueous $NaBH_4$ method to cinnamaldehyde. The reaction again proceeded efficiently, producing cinnamyl alcohol in yields approaching 95 percent. This reinforced the idea that aqueous reductions can be both effective and green.



Chromatogram and MS Spectrum of Natural Cinnamyl Alcohol

Phenylpropanol Synthesis

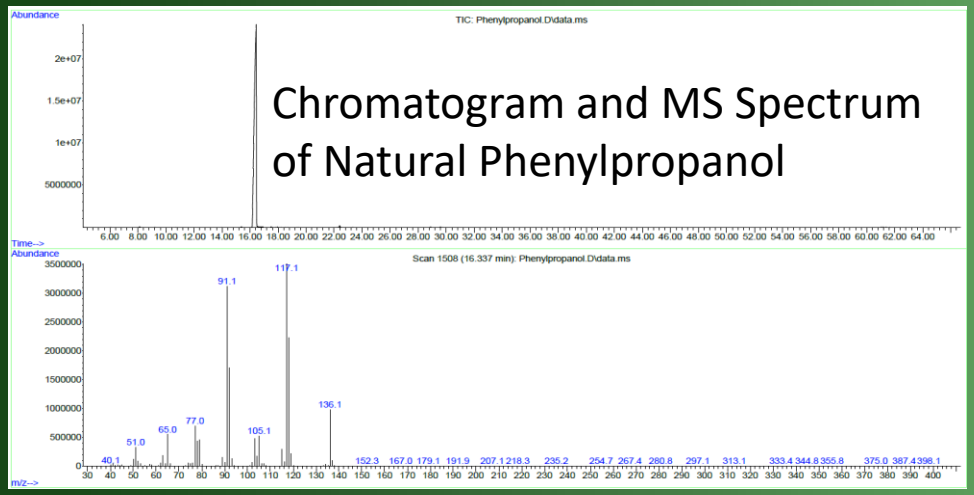
Cinnamaldehyde + $LiAlH_4$ → Phenylpropanol



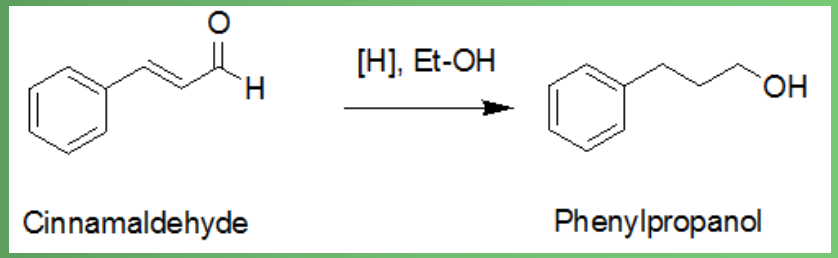
- • $LiAlH_4$ in ethanol
- • 60–65% yield
- • Reduces C=C + aldehyde
- The synthesis of phenylpropanol was more challenging because cinnamaldehyde contains both an aldehyde and an alkene. We needed a strong reducing agent capable of reducing both functional groups. We used lithium aluminum hydride in ethanol rather than water.
- Although this reaction is less green than the others, ethanol remains a relatively safe solvent. After distillation, we isolated phenylpropanol in 60 to 65 percent yield.

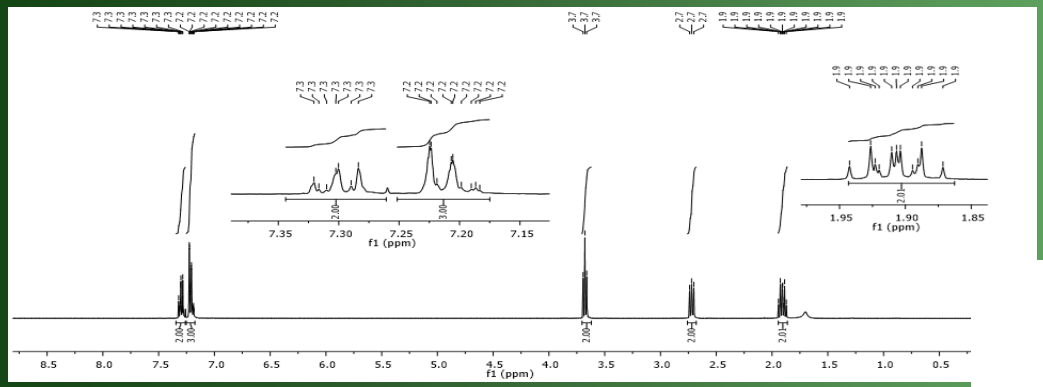
Phenylpropanol Synthesis

Cinnamaldehyde + $LiAlH_4$ → Phenylpropanol

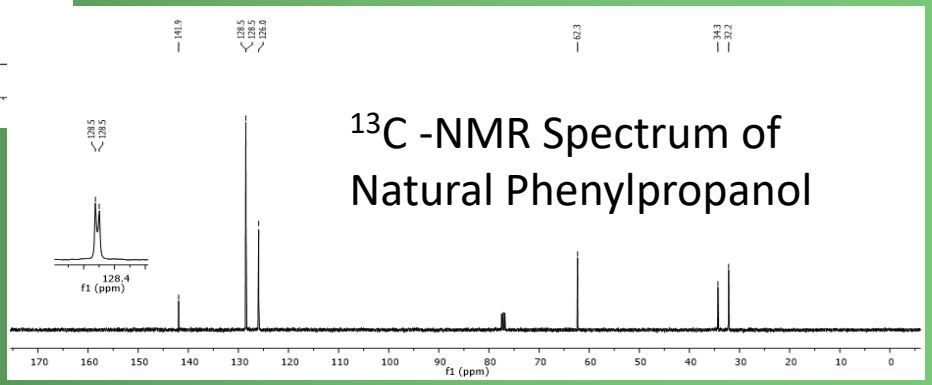


Chromatogram and MS Spectrum of Natural Phenylpropanol





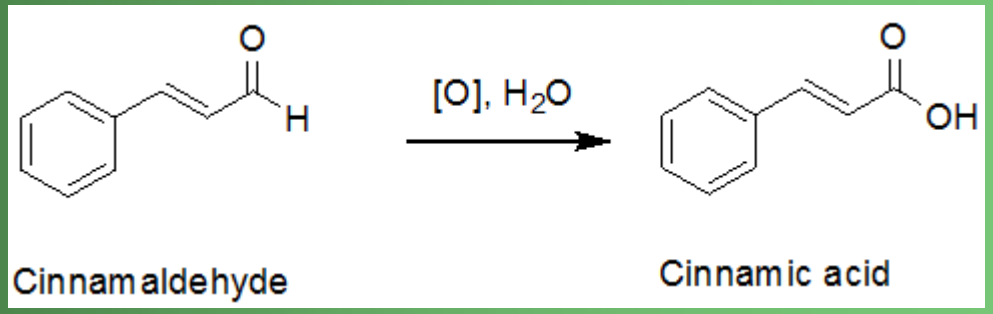
^{1}H-NMR Spectrum of Natural Phenylpropanol



^{13}C -NMR Spectrum of Natural Phenylpropanol

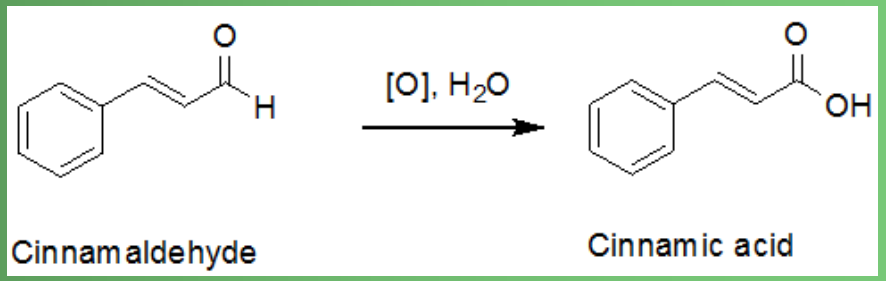
Cinnamic Acid Synthesis

Cinnamaldehyde + O2 → Cinnamic Acid

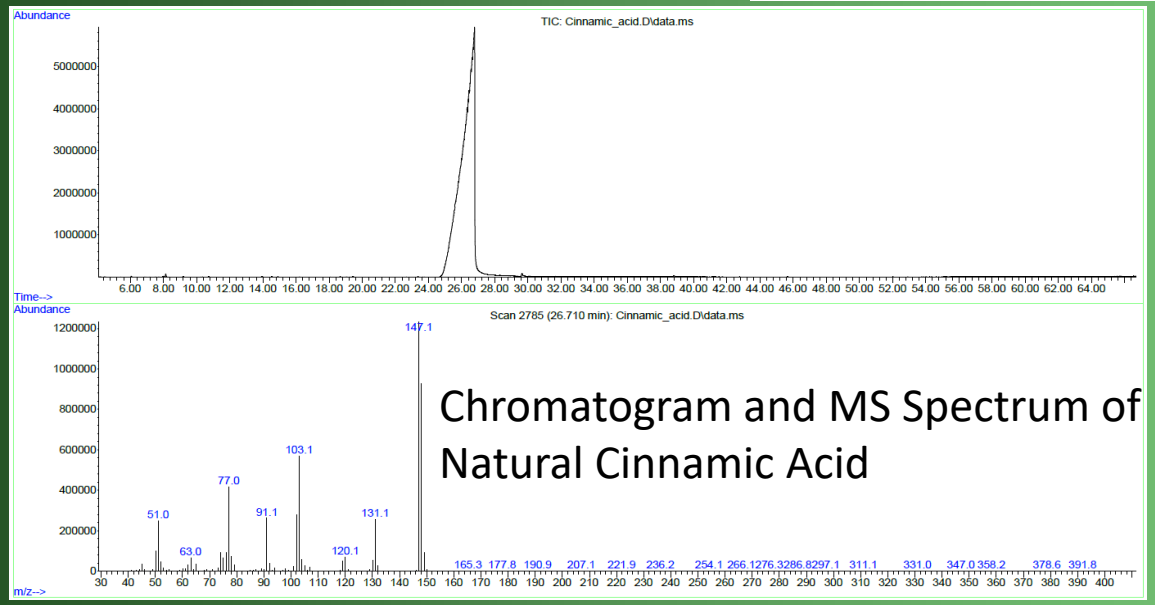


- • oxidation (O_2 gas)
- • 37 °C, 24 h
- • 75% yield
- Oxidation of cinnamaldehyde to cinnamic acid proved difficult because common oxidants caused degradation. Potassium permanganate, hydrogen peroxide, and sodium hypochlorite all produced unwanted by-products.
- Our solution was to use no oxidant at all. Instead, we exposed cinnamaldehyde to oxygen gas in water at 37 °C for 24 hours. This very mild method produced cinnamic acid in 75 percent yield, with excellent purity.

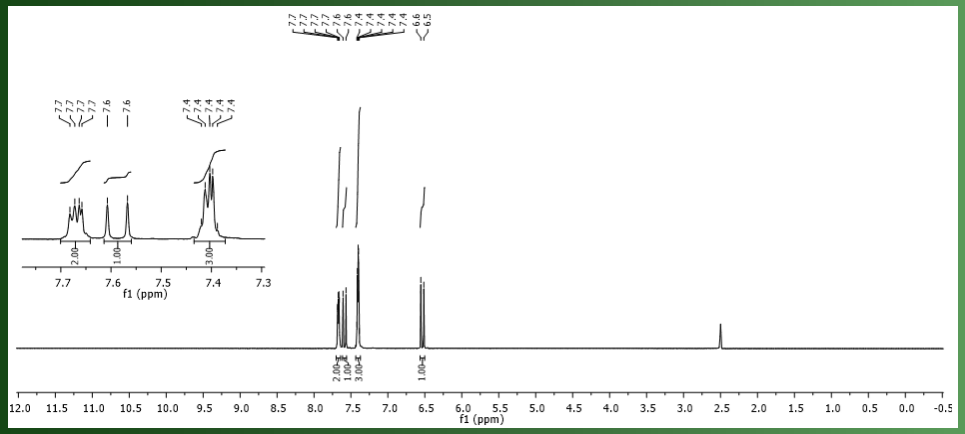
Cinnamic Acid Synthesis



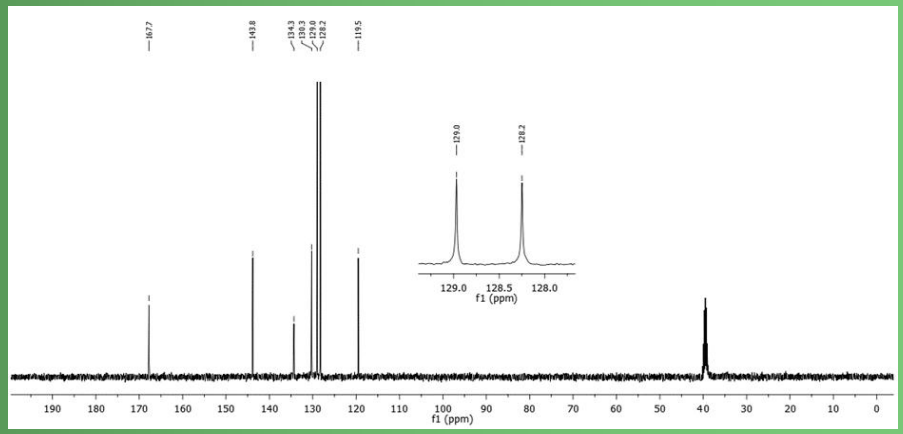
Cinnamaldehyde + O2 → Cinnamic Acid



Chromatogram and MS Spectrum of Natural Cinnamic Acid



^{1}H-NMR Spectrum of Natural Cinnamic Acid



^{13}C -NMR Spectrum of Natural Cinnamic Acid

Reaction Optimization

- 4 oxidants
- 5 reductant ratios
- 4 solvents
- 6 reaction times
- Water consistently gave best results
- Organic solvents lowered yield & complicated purification
- To ensure high efficiency, we systematically tested many parameters: different solvents, reagent quantities, and reaction times. Water consistently produced the best outcomes. Organic solvents not only reduced yields but also complicated purification.
- This reinforced our commitment to using green, safe solvents throughout.

Analytical Confirmation

- GC-MS: purity 99–100%
- NMR confirmation
- MoGAPI/BAGI green metrics
- High greenness scores
- Low solvent toxicity
- Simple sample preparation
- All final products were analyzed using GC-MS, ^{1}H-NMR, and ^{13}C-NMR. Purity levels were extremely high. We also evaluated our methods with the MoGAPI and BAGI indexes, which confirmed strong compliance with green analytical chemistry principles.

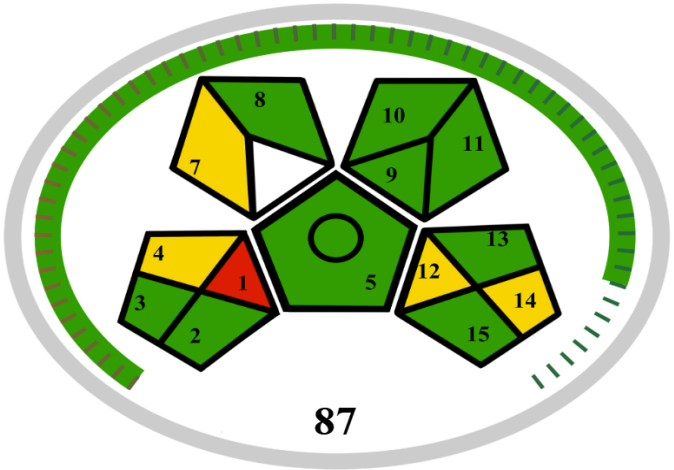
MoGAPI/BAGI green metrics

- High greenness scores
- We evaluated our methods with the MoGAPI and BAGI indexes, which confirmed strong compliance with green analytical chemistry principles.

MoGAPI

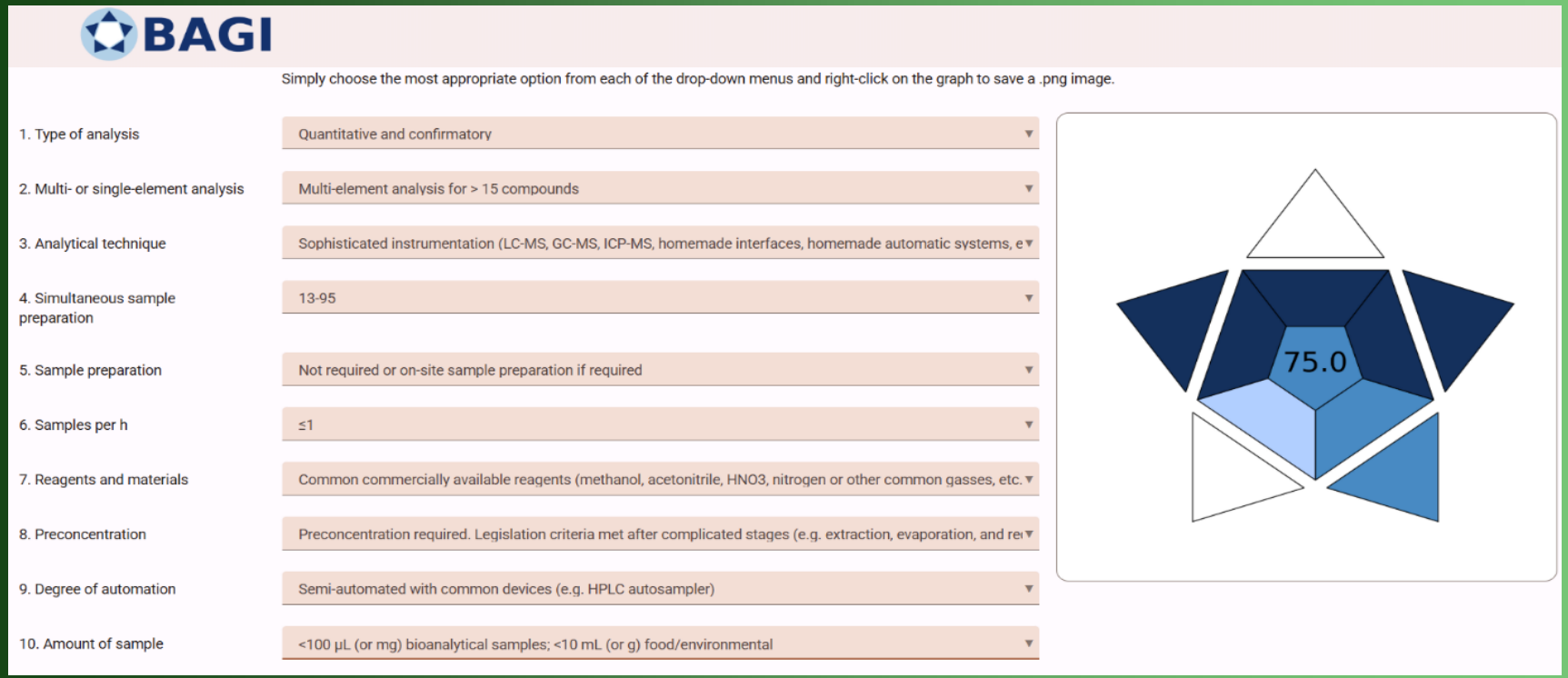
Questions

SAMPLE PREPARATION	
1 - Collection:	Off-line
2 - Preservation:	None
3 - Transport:	None
4 - Storage:	Under normal conditions
5 - Type of method:	No sample preparation
6 - Scale of extraction:	Not applicable
7 - Solvents/reagents used:	Green solvents/reagents used
8 - Additional treatment:	None
REAGENT AND SOLVENTS	
9 - Amount:	< 10 mL (< 10 g)
10 - Health hazard:	Slightly toxic, slight irritant; NFPA health hazard score = 0 or 1



MoGAPI/BAGI green metrics

- High greenness scores
- We evaluated our methods with the MoGAPI and BAGI indexes, which confirmed strong compliance with green analytical chemistry principles.



Scale-Up Experiments

- • Benzoic acid: 65% yield (5 kg)
- • Benzyl alcohol: 96% yield (5 kg)
- A major goal was industrial feasibility. We scaled up the benzoic acid and benzyl alcohol reactions to 5 kilograms. Benzoic acid yielded around 65 percent due to solubility losses, but benzyl alcohol produced an excellent 96 percent yield. Importantly, no safety hazards occurred during scale-up.

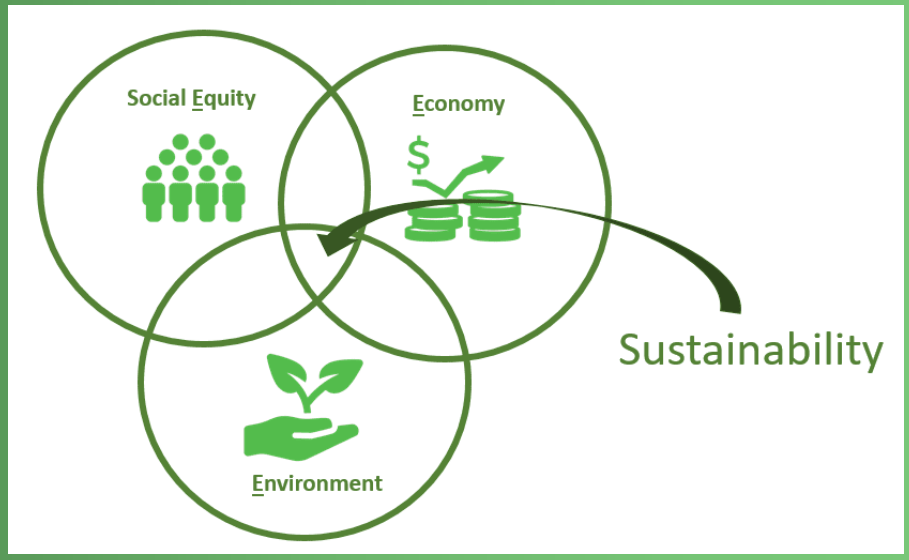
Environmental Impact (E-Factor) Results

https://doi.org/10.1039/C6GC02157C

- Benzoic acid: 3.45
- Benzyl alcohol: 1.37
- Waste mainly water + Na_2SO_4
- No toxic solvent waste
- We calculated E-factors to assess waste generation. Benzoic acid had an E-factor of 3.45, and benzyl alcohol had an E-factor of 1.37, both of which are quite favorable. The waste consisted mainly of water and sodium sulfate—no toxic organic solvents.

Advantages of the Method

- Single natural starting material
- Benign solvents
- (primarily water)
- Low-cost reagents
- High atom economy
- Energy-efficient
- High product purity
- Easily scalable



- Overall, our approach offers multiple advantages: use of a single natural starting material, green solvents, low-cost reagents, high atom economy, mild reaction conditions, excellent product purity, and straightforward scalability.

Applications of Products

- Cosmetics: preservatives, fragrances
- Pharmaceuticals: anesthetics, antimicrobial uses
- Food industry: flavoring agents
- Fragrances: floral & sweet aromas
- All five synthesized compounds have broad industrial applications. They are used in cosmetics as preservatives and fragrances, in pharmaceuticals as intermediates, in the food industry as flavoring agents, and in perfumery due to their aromatic properties.

Conclusion

- Successfully synthesized 5 valuable natural compounds
- Green chemistry approach throughout
- High yields (60–95%)
- Scalable and industrially feasible
- Demonstrates the power of natural, sustainable feedstocks
- We have demonstrated a green, scalable, high-yielding method for producing five valuable compounds from a single natural feedstock. Our approach reduces environmental impact, simplifies purification, and offers strong industrial potential.

Thank you

- “Our work demonstrates that a single natural and renewable material—Cinnamon cassia oil—can serve as an efficient platform for producing five high-value organic compounds through green, scalable, and economically viable methods. These processes minimize waste, avoid hazardous solvents, and maintain excellent yields and purity, showing real potential for industrial application. We believe this approach can inspire broader adoption of sustainable practices in chemical manufacturing. Thank you for your attention, and I look forward to your questions.”