New York State Pollution Prevention Institute (NYSP2I)

Green Chemistry Module
Level: High School Regents

Spices and Perfumes

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Spices and Perfumes

In this lab experiment, students will be isolating the essential oil cinnamaldehyde from ground cinnamon. This technique is used commercially as an economically attractive technique for extracting cinnamaldehyde, used as a flavoring and in perfumes, as well as other applications.

This lab activity provides students with good practice in organic chemistry techniques, particularly distillation and separation via separatory funnel.

Two versions of the lab are provided. There is no difference in the procedure due to the advanced lab techniques included which will make its use limited in a Regents chemistry class. The main difference is in the lab write-up for the advanced level.

Basic Level Instruction: This lab would be suitable for an advanced Regents chemistry class. It involves rather advanced organic chemistry procedures and special equipment, which many high schools may not possess. It might be more suitable done as a teacher demonstration for a Regents class.

Advanced Level Instruction: For an advanced class (AP or Honors), the lab would be useful for practice in organic chemistry techniques. The quantitative application is very limited (calculation of percent yield). The laboratory write-up for the advanced level laboratory is a stand-alone report generated by the student.

Spices and Perfumes: Teacher's Guide

Intended Audience: High School Regents Chemistry Students
This experiment is aimed at students in high school learning about chemical changes and reaction types. The experiment would also be suitable for an introductory college laboratory.

Recommended Student Background: *To be completed the day before the lab.* Students read the introduction and complete the pre-lab questions.

Activity Timeline: *All times are estimates*

Setup	Distillation	Separation	Drying	Isolation	Cleanup	TOTAL TIME
5 min	30 min	15 min	10 min	5 min	10 min	75 min

Note that these times are estimates and may vary significantly. The 5 minute set-up time is very optimistic unless the instructor does most of the equipment set-up prior to lab. Distillation may take up to an hour to obtain at least 15-20 ml of distillate. The isolation step will likely take longer than 5 minutes for heat evaporation using a warm water bath.

Safety Issues: Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash hands well.
Both **ethyl acetate** and **cinnamaldehyde** are flammable irritants which are immiscible with water; **do not pour either down the sink.**
The vapors of ethyl acetate are flammable. Risk of fire exists when ethyl acetate and high temperatures mix. If the lab is completed over two days, a good break point would be between the distillation and separation steps.

Keys to Success:
It is suggested that students read through the procedure carefully before performing the experiment. Planning is essential to completing this experiment within the time allotted. This experiment could take one 75-minute session, though depending on distillation time, it may take two lab periods to complete.
It is recommended that students use heating mantles, if available. Sand baths work as well, but they take a long time to heat up and cool down.
Be sure that the ground glass joints are the same size and fit together properly.
This experiment requires a distillation, so it is necessary for each setup to be connected to a water source and sink. Be sure to have the proper nozzles installed on faucets for the tubing to be attached.

Advanced Preparation:
Depending on the level of experience students have with organic chemistry equipment and procedures, the instructor may wish to do a good portion of the equipment set-up prior to the start of the lab period, particularly if students must complete the lab in one lab period.

Be certain to have clearly labeled waste containers for the two waste streams. It may be advisable to post notices at the sinks warning not to dispose of any of the wastes down the sink.

Materials Check List: (per laboratory setup)

Chemicals:

50 mL Water
2.5 g Cinnamon (ground)
15 mL Ethyl Acetate
Anhydrous Sodium Sulfate (Na_2SO_4)
Silicone grease for ground glass joints
Ice for ice bath

Glassware:

- Distillation Setup
  - Heat Source (hot plate) and sand bath ***OR*** heating mantle
    - 250 mL Round Bottom Distillation Flask
    - Three Way Adapter
    - Alcohol Thermometer
    - Condenser
    - 2 lengths of rubber tubing (Each should be about 18 inches)
    - Bent Adapter
    - Receiving Flask (e.g. 250 Erlenmeyer)
    - Beaker for ice bath (big enough to fit receiving flask)
  - 125 mL Separatory funnel
  - 3 Ring-stands and clamps
  - Graduated cylinder
  - Spatula
  - 25 mL round bottom flask

Measurements:

Mass of cinnamon used
Volume of distillate
Appearance of distillate
Mass of empty receiving flask
Mass of cinnamaldehyde isolated
Smell of cinnamaldehyde

Recycling and disposal:

Have two large waste containers available for students to dispose of their waste. Label one "Aqueous Waste from Spices Lab" and the other "Hazardous Solid Organic Waste (Sodium Sulfate)". Place these receptacles in the fume hood. Dispose of the hazardous sodium sulfate waste according to state and local guidelines.

To dispose of the aqueous waste from spices, add sodium hydroxide until the pH is 13 or above, then reflux for one hour to destroy the ethyl acetate. Add acetic acid until the pH is 4-9, then wash down the drain with water. Alternatively, the mixture can be labeled as "water containing 4% ethyl acetate" and be disposed of as hazardous waste.

Green Chemistry: Making materials sustainably

Chemical manufacturing is as old as civilization and the discoveries of bronze and iron came to define the eras that ensued. In modern times, we take for granted a plentiful supply of metals, plastics, dyestuffs and medicines. We have come to depend on the chemical industry to provide us with all the materials we need for our "materialist" society.

But the supply of these materials is not infinite. As the human population grows, and demands an ever higher standard of living, the consumption of the Earth's materials is in danger of getting out of control. It is therefore essential that chemists become responsible stewards of the raw materials that remain. We need to develop methods for chemical processing that are both chemically and environmentally efficient, and which move us towards a sustainable society. We need new materials that can provide what we need without destroying the Earth.

Green chemistry is designed to help us meet these needs. It aims not just to treat waste, but to avoid producing waste in the first place. Products and processes should be "benign by design," but they must also be practicable.

In this lab manual, we will explore how we can this can be achieved in practice – how we can use chemistry to help solve our environmental problems. We will never be able to build a sustainable society if we don't understand the basic science of where our materials come from, and how they are produced. The goal of this manual is to provide that science, presented within the context of green chemistry.

The Twelve Principles of Green Chemistry

The basic principles of green chemistry were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice:"

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

It must be recognized that these represent a target, and we will not be able to satisfy every principle immediately with every process and product. Nevertheless, if we design our chemistry with these principles in mind, we will make great strides towards achieving sustainability.

Why should you teach about spices and perfumes?

Many flavorings and ingredients for consumer products are obtained through extraction from natural products. Often people do not have any idea where these substances originate. It is a good experience to discover the natural origins of many common ingredients. This laboratory experience allows students to practice one method of achieving this extraction – distillation.

Correlation of the experiment with Green Chemistry

Green Chemistry Principles: 4. Use renewable feedstocks

Curriculum alignment

Alignment to the NYS Regents Chemistry Curriculum:
VII.3 Organic acids, alcohols, esters, aldehydes, ketones, ethers, halides, amines, amides, and amino acids are categories of organic molecules that differ in their structures. Functional groups impart distinctive physical and chemical properties to organic compounds. (3.1hh)

This experiment correlates directly with the following sections of the New York State Core Curriculum:

Standard 4: The Physical Setting.

Key Idea 3: Matter is made up of particles whose properties determine the observable characteristics of matter and its reactivity.

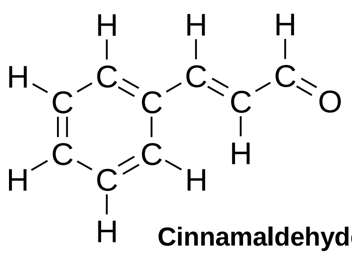
Performance Indicator 3.1 Explain the properties of materials in terms of the arrangement and properties of the atoms that compose them.

Major Understandings 3.1hh Organic acids, alcohols, esters, aldehydes, ketones, ethers, halides, amines, amides, and amino acids are categories of organic compounds that differ in their structures. Functional groups impart distinctive physical and chemical properties to organic compounds.

Background and Fundamentals for Basic Level Instruction:

Most living systems use the same chemistry to perform essential functions; all use DNA/RNA, glucose and the essential amino acids. But a handful of species also produce specific compounds, known as "secondary metabolites". These compounds often find uses in food or medicine, and indeed some plants may be cultivated principally to produce them.

For those secondary metabolites found in food, many are in the form of herbs and spices. Cinnamon is a well-known example, and the plant *Cinnamomum verum* has been used as a source of this spice for thousands of years. The major component in cinnamon oil is cinnamaldehyde, which has the structure shown:



Cinnamaldehyde

This compound is responsible for the characteristic smell of cinnamon. Cinnamaldehyde is a good example of a highly *unsaturated* compound. It contains an aromatic ring, as well as two double bonds outside the ring.

The cinnamaldehyde (boiling point 248 ^{o}C) is isolated using steam distillation. In this method, steam is used to carry cinnamaldehyde vapors over into the condenser, where the vapors condense back to liquid. The use of steam allows the distillation to be performed at temperatures close to the boiling point of water, well below 248 ^{o}C, so the cinnamon and cinnamaldehyde are not exposed to excessive heat.

In this experiment, we will start with cinnamon bark. In modern times, several species related to *Cinnamomum verum* are often sold as cinnamon, so you are likely to be working with *Cinnamomum aromaticum* (cassia, Chinese cinnamon) or *Cinnamomum burmannii* (Indonesian cinnamon). These are considered to be inferior to "true cinnamon" for food use, but they contain a higher proportion of cinnamaldehyde and are therefore *more* suitable for this experiment. *C. burmannii* is the most suitable, if available.

Guidance Notes:

Students may need assistance in setting up the distillation apparatus properly, including how to set up the water connections. It would be useful to have one station set up as an example for students to follow.

Students will likely not obtain very high yields of the cinnamaldehyde, especially if this is the first exploration of organic chemistry processes. Focus students' efforts on learning and practicing good lab separation techniques rather than trying to obtain a high yield of product.

Cleanup and disposal

Have two large waste containers available for students to dispose of their waste. Label one "Aqueous Waste from Spices Lab" and the other "Hazardous Solid Organic Waste (Sodium Sulfate)". Place these receptacles in the fume hood. Dispose of the hazardous sodium sulfate waste according to state and local guidelines.

To dispose of the aqueous waste from spices, add sodium hydroxide until the pH is 13 or above, then reflux for one hour to destroy the ethyl acetate. Add acetic acid until the pH is 4-9, then wash down the drain with water. Alternatively, the mixture can be labeled as "water containing 4% ethyl acetate" and be disposed of as hazardous waste.

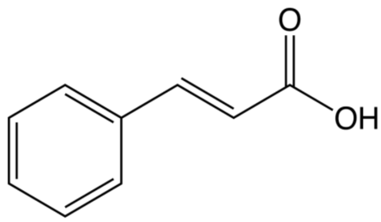
Background and Fundamentals for Advanced Level Instruction:

The background and fundamentals of the lab are the same as in the basic level instruction. All pre-lab questions, discussion questions and extension activities are the same as the basic level. The students will complete their own independent lab write-up for this level.

<u>Answers</u>

Pre-Lab (involves library/internet research)

1. Cinnamon contains other organic compounds besides cinnamaldehyde. Find out one other compound that is present in "true cinnamon" (*Cinnamomum zeylanicum*), and draw its structure in the space provided.



Cinnamic Acid is found in the oil of cinnamon and is used in flavors, synthetic indigo, pharmaceuticals, and in the making of compounds used in perfumes.

2. Traditionally, chloroform would have been used for the extraction in place of ethyl acetate. What problems are associated with chloroform that discourages its use today?
Chloroform is not used here because it has the potential to be extremely dangerous. The fatal oral dose may be as low as 10mL, and the vapors are known to depress the central nervous system. Small amounts of vapors can cause dizziness, fatigue, and headache. Basically it is not safe for the classroom environment.

Discussion points

1. Why did we need to use ethyl acetate?
Ethyl Acetate was used to attract the organic molecules within the solution, including the cinnamonaldehyde, and separate them from the aqueous molecules.

2. Cinnamon is brown, but the cinnamaldehyde/water distillate is colorless (as long as the mixture did not froth over). Why did the brown color not distil over?
The cinnamon aldehyde compound itself is a colorless liquid. The compounds within the cinnamon that give it its brown color were not compounds that boil at the temperatures reached, so they did not distill over with the cinnamon aldehyde.

3. When herbs and spices are steam distilled in this manner, the organic portion of the distillate (called the *essential oil*) nearly always exhibits the characteristic odor of the herb or spice. What characteristics about the structure of the cinnamaledhyde molecule allow it to be distilled out? (bonding, intermolecular interactions, boiling point)
The principle of steam distillation lies in the idea that a mixture of water and an organic compound, whose boiling point is higher than that of water, boils at a temperature below that of the organic compounds boiling point. This is because the pressures of the organic and the water increase nearly independently of one another and so the total vapor pressure exceeds the atmospheric pressure (this is what boiling is) at a temperature lower than it would for the organic compound on its own. In this way, the steam distills the organic molecule below its own boiling point, which is helpful because many compounds actually decompose rather than simply boiling.

Questions:

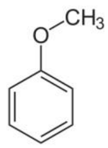
1. Explain the design and purpose of the following pieces of glassware:
    a. The condenser (used in the distillation)
    The Condenser is used to cool the hot steam and gases to return them to the liquid phase which can be collected.

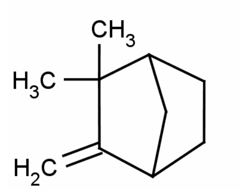
    b. The separatory funnel
    The separatory funnel is designed with a spigot at the bottom so that once the organic and aqueous fractions have separated within the funnel the bottom layer may be emptied out without disturbing the separation that has been achieved.

2. Calculate the percent yield of cinnamaldehyde extracted from the original sample of cinnamon.
    The answer should be calculated according to mass of cinnamaldehyde/mass of cinnamon x 100

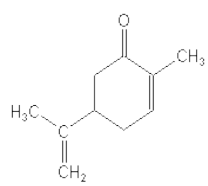
Extension Activities:
Research other essential oils that can be produced from natural substances. Give the name and structure of at least two essential oils, as well as the name of the material it is extracted from.

Other essential oils produced from natural products may include:

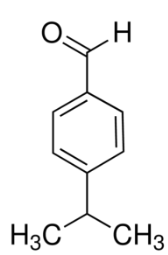
- anisole from anise, 



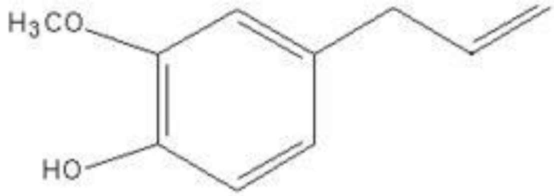
- camphene from nutmeg,



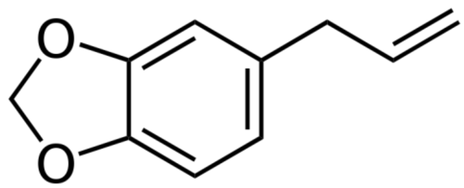
- carvone from caraway and spearmint,



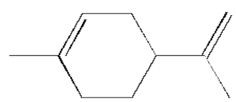
- cuminaldehyde from cumin,



- eugenol from cloves,



- safrole from sassafras,



- limonene from citrus peel.

Spices and Perfumes Laboratory Experiment # ______

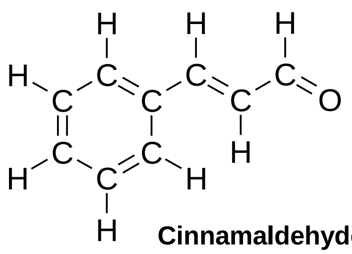
Name ________________________________ Date ________________________________

Partner ________________________________

Isolation of cinnamaldehyde from cinnamon

Most living systems use the same chemistry to perform essential functions; all use DNA/RNA, glucose and the essential amino acids. But many species also produce specific compounds (known as "secondary metabolites") which may only be found in a handful of species. These compounds often find uses in food or medicine, and indeed some plants may be cultivated principally in order to produce them.

For those secondary metabolites found in food, many are in the form of herbs and spices. Cinnamon is a well-known example, and the plant *Cinnamomum verum* has been used as a source of this spice for thousands of years. The major component in cinnamon oil turns out to be cinnamaldehyde, which has the structure shown:



Cinnamaldehyde

This compound is responsible for the characteristic smell of cinnamon. Cinnamaldehyde is a good example of a highly *unsaturated* compound. It contains an aromatic ring, as well as two double bonds outside the ring.

The cinnamaldehyde (boiling point 248 ^{o}C) is isolated using steam distillation. In this method, steam is used to carry cinnamaldehyde vapors over into the condenser, where the vapors condense back to liquid. The use of steam allows the distillation to be performed at temperatures close to the boiling point of water, well below 248 ^{o}C, so the cinnamon and cinnamaldehyde are not exposed to excessive heat.

In this experiment, we will start with cinnamon bark. In modern times, several species related to *Cinnamomum verum* are often sold as cinnamon, so you are likely to be working with *Cinnamomum aromaticum* (cassia, Chinese cinnamon) or *Cinnamomum burmannii* (Indonesian cinnamon). These are considered to be inferior to "true cinnamon" for food use, but they contain a higher proportion of cinnamaldehyde, and are therefore *more* suitable for this experiment. *C. burmannii* is the most suitable, if available.

What is Green Chemistry?

The goal of green chemistry is to design chemicals and processes that reduce or eliminate negative environmental impacts. This includes products and processes that use or generate less hazardous substances, reduced waste products, less or non-toxic components, and using substances more efficiently. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

Green chemistry provides a number of benefits, including:

- reduced waste, eliminating costly end-of-the-pipe treatments
- safer products
- reduced use of energy and resources
- improved competitiveness of chemical manufacturers and their customers.

There are twelve principles that green chemistry relies on that were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice”:

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
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12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

<u>Why is this experiment green?</u>
This experiment is green as it illustrates using a natural substance as the feedstock for a final product. In this case, cinnemaldehyde is used as a flavoring in gum, ice cream, candy and beverages, as well as in perfumes. It can also be used as a natural fungicide and insecticide. Recent research suggests it may even be useful as an anti-cancer agent.

Purpos: To isolate the essential oil cinnamaldehyde from the spice cinnamon.

Safety Issues: Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash their hands well.

Both **ethyl acetate** and **cinnamaldehyde** are flammable irritants which are immiscible with water; **do not pour either down the sink.**

Materials and Equipment

Chemicals:

50 mL Water
2.5 g Cinnamon (ground)
15 mL Ethyl Acetate
Anhydrous Sodium Sulfate (Na_2SO_4)
Silicone grease for ground glass joints
Ice for ice bath

Glassware:

- Distillation Setup
  - Heat Source (hot plate) and sand bath ***OR*** heating mantle
    - 250 mL Round Bottom Distillation Flask
    - Three Way Adapter
    - Alcohol Thermometer
    - Condenser
    - 2 lengths of rubber tubing (Each should be about 18 inches)
    - Bent Adapter
    - Receiving Flask (e.g. 250 Erlenmeyer)
    - Beaker for ice bath (big enough to fit receiving flask)
  - 125 mL Separatory funnel
  - 3 Ring-stands and clamps
  - Graduated cylinder
  - Spatula
  - 25 mL round bottom flask

<u>Experiment</u>

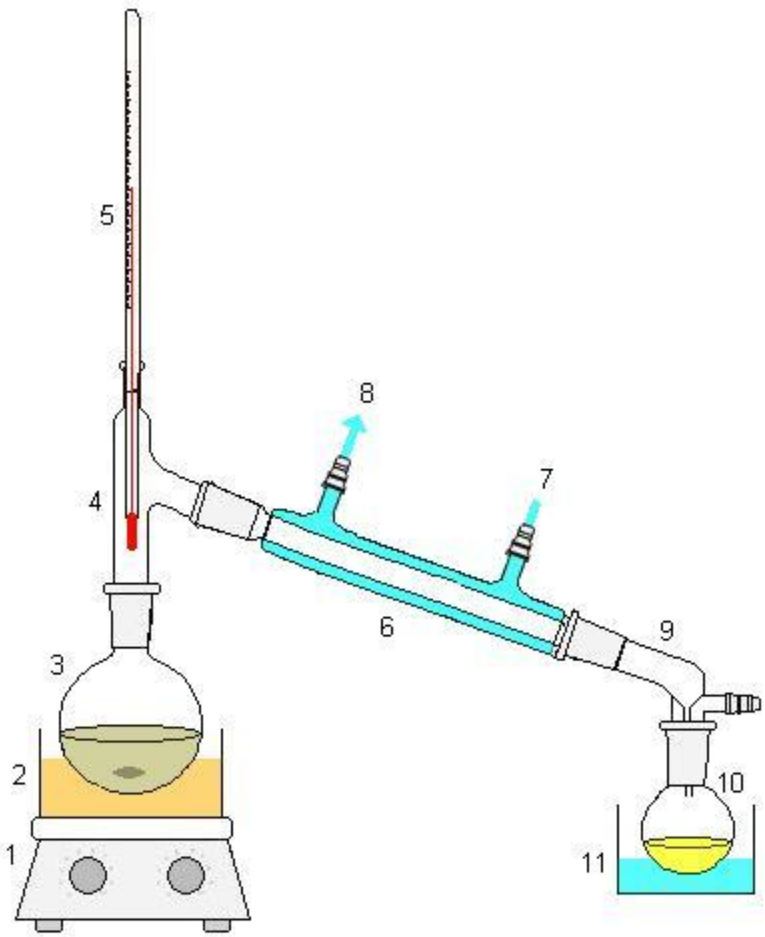
Pre-Lab (involves library/internet research)

1. Cinnamon contains other organic compounds besides cinnamaldehyde. Find out one other compound that is present in "true cinnamon" (*Cinnamomum zeylanicum*), and draw its structure in the space provided.

2. Traditionally, chloroform would have been used for the extraction in place of ethyl acetate. What problems are associated with chloroform that discourages its use today?

Procedure:

1. Partner 1 – Set up glassware for the distillation as show in Figure 1 (if not already set up). Be sure to clamp the condenser (6), the round-bottom flask (3) and the receiving flask (10) to three separate ring-stands. Also, secure the bent adapter (9) to the condenser (6) by placing a rubber band around the water-in spout of the condenser (7) and the spout of the bent adapter (9).



1) Heat Source (hot plate)
2) Sand Bath
3) Distillation Flask (cinnamon–water solutic
4) Three Way Adapter
5) Alcohol Thermometer
6) Condenser
7) Cool Water (in)
8) Water (out)
9) Bent Adapter
10) Receiving Flask (cinnamaldehyde- solution)
11) Ice Bath

Figure 1

2. Partner 2 – Measure approximately 2.5 g of ground cinnamon and record the mass. Place the cinnamon into a 250 mL round-bottom flask.

3. Partner 2 – Measure out and add 50 mL of water to the round-bottom flask. Mix thoroughly by gentle swirling.

4. Place the round bottomed flask into the distillation apparatus and begin water flow. The water should be trickling at a slow rate, not gushing like a fire hose. Using a heating mantle or sand bath, distil the cinnamon/water mixture until around 30-40 mL has collected at a rate of around 2 mL per minute, ***OR*** until 30 minutes has passed. <u>NEVER boil the solution in the distillation flask to dryness.</u> ALWAYS leave some liquid in the distillation flask.

5. Pour the distillate into a 125 mL separatory funnel for separation. The cinnamaldehyde/ water distillate should appear slightly cloudy with a distinct cinnamon smell.

6. Add 10 mL of ethyl acetate into the separatory funnel. GENTLY swirl the mixture for about 15 seconds to extract the cinnamaldehyde from the aqueous layer. [Note: Violently shaking the mixture will cause it to become extremely cloudy and difficult to separate.] The top layer consists of ethyl acetate/cinnamaldehyde,* and the aqueous layer is on the bottom (Figure 2). Allow 10 minutes for the layers to separate.

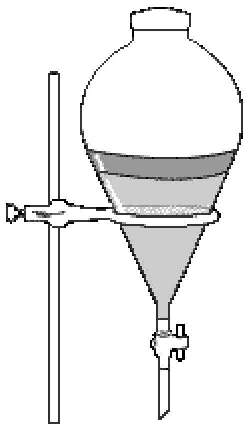


Figure 2

7. Once the two layers have separated, turn the stopcock to slowly remove the lower (aqueous) layer in portions into the round bottom flask used earlier. Take care not to allow drops of the organic layer to come out with the aqueous. Transfer the organic layer into a 125 mL Erlenmeyer flask labeled with your initials and the contents (cinnamaldehyde and ethyl acetate).

8. Transfer the aqueous layer back into the separatory funnel and repeat steps 6-7 using 3 mL of ethyl acetate.

9. Dry the organic fraction using a small amount (tip of a spatula) of anhydrous sodium sulfate. If the sodium sulfate clumps, then add more until clumping ceases and the sodium sulfate flows freely in the bottom of the flask.

10. Transfer the dried organic fraction to a clean, tared 25 mL round-bottomed flask. Rinse the sodium sulfate with 2 mL of ethyl acetate and combine this with the dried organic fraction.

11. Evaporate the ethyl acetate either by distillation from a warm water bath (~70°C), or (if available) using a rotary evaporator. Record the total mass, and calculate the mass of the isolated cinnamaldehyde – normally around 0.2 g. Note the smell of the remaining oil.

12. **WASTE DISPOSAL INSTRUCTIONS:** Pour the water used for the distillation into the waste container labeled "Aqueous Waste from Spices Lab". The instructor will dispose of this waste. Dispose of the sodium sulfate in the container labeled "Hazardous Solid Organic Waste (Sodium Sulfate)". Wash and dry all glassware.

Note: Ethyl acetate has a slight solubility in water, so you will see a smaller amount separating out.

References

Taber D., Weiss A., "Cinnamaldehyde by Steam Distillation," *Journal of Chemical Education*, 1998, 75(5), 633.

Measurements, Observations, and Results

Mass of ground cinnamon used (g)	
Volume of distillate (mL)	
Appearance of distillate	
Mass of empty 25mL round bottom flask (g)	
Mass of cinnamaldehyde isolated (g)	
Smell of cinnamaldehyde	

Discussion points

1. Why did we need to use ethyl acetate?

2. Cinnamon is brown, but the cinnamaldehyde/water distillate is colorless (as long as the mixture did not froth over). Why did the brown color not distill over?

3. When herbs and spices are steam distilled in this manner, the organic portion of the distillate (called the *essential oil*) nearly always exhibits the characteristic odor of the herb or spice. What characteristics about the structure of the cinnamaledhyde molecule allow it to be distilled out? (bonding, intermolecular interactions, boiling point)

<u>Questions:</u>

1. Explain the design and purpose of the following pieces of glassware:
    a. The condenser (used in the distillation)

b. The separatory funnel

2. Calculate the percent yield of cinnamaldehyde extracted from the original sample of cinnamon.

Extension Activities:

Research other essential oils that can be produced from natural substances. Give the name and structure of at least two essential oils, as well as the name of the material it is extracted from.

Spices and Perfumes Laboratory Experiment # ______

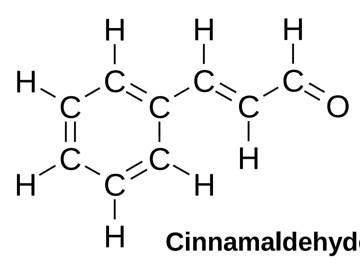
Name ________________________________ Date ________________________________

Partner ______________________________

Isolation of cinnamaldehyde from cinnamon

Most living systems use the same chemistry to perform essential functions; all use DNA/RNA, glucose and the essential amino acids. But many species also produce specific compounds (known as "secondary metabolites") which may only be found in a handful of species. These compounds often find uses in food or medicine, and indeed some plants may be cultivated principally in order to produce them.

For those secondary metabolites found in food, many are in the form of herbs and spices. Cinnamon is a well-known example, and the plant *Cinnamomum verum* has been used as a source of this spice for thousands of years. The major component in cinnamon oil turns out to be cinnamaldehyde, which has the structure shown:



Cinnamaldehyde

This compound is responsible for the characteristic smell of cinnamon. Cinnamaldehyde is a good example of a highly *unsaturated* compound. It contains an aromatic ring, as well as two double bonds outside the ring.

The cinnamaldehyde (boiling point 248 ^{o}C) is isolated using steam distillation. In this method, steam is used to carry cinnamaldehyde vapors over into the condenser, where the vapors condense back to liquid. The use of steam allows the distillation to be performed at temperatures close to the boiling point of water, well below 248 ^{o}C, so the cinnamon and cinnamaldehyde are not exposed to excessive heat.

In this experiment, we will start with cinnamon bark. In modern times, several species related to *Cinnamomum verum* are often sold as cinnamon, so you are likely to be working with *Cinnamomum aromaticum* (cassia, Chinese cinnamon) or *Cinnamomum burmannii* (Indonesian cinnamon). These are considered to be inferior to "true cinnamon" for food use, but they contain a higher proportion of cinnamaldehyde, and are therefore *more* suitable for this experiment. *C. burmannii* is the most suitable, if available.

What is Green Chemistry?

The goal of green chemistry is to design chemicals and processes that reduce or eliminate negative environmental impacts. This includes products and processes that use or generate less hazardous substances, reduced waste products, less or non-toxic components, and using substances more efficiently. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

Green chemistry provides a number of benefits, including:

- reduced waste, eliminating costly end-of-the-pipe treatments
- safer products
- reduced use of energy and resources
- improved competitiveness of chemical manufacturers and their customers.

There are twelve principles that green chemistry relies on that were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice”:

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Why is this experiment green?

This experiment is green as it illustrates using a natural substance as the feedstock for a final product. In this case, cinnemaldehyde is used as a flavoring in gum, ice cream, candy and beverages, as well as in perfumes. It can also be used as a natural fungicide and insecticide. Recent research suggests it may even be useful as an anti-cancer agent.

Purpos: To isolate the essential oil cinnamaldehyde from the spice cinnamon.

Safety Issues: Wear approved safety goggles and suitable clothing when working with or near all chemicals in this experiment. As they leave the laboratory, students should wash their hands well.

Both **ethyl acetate** and **cinnamaldehyde** are flammable irritants which are immiscible with water; **do not pour**

either down the sink.

Materials and Equipment

Chemicals:

- 50 mL Water
- 2.5 g Cinnamon (ground)
- 15 mL Ethyl Acetate
- Anhydrous Sodium Sulfate (Na_2SO_4)
- Silicone grease for ground glass joints
- Ice for ice bath

Glassware:

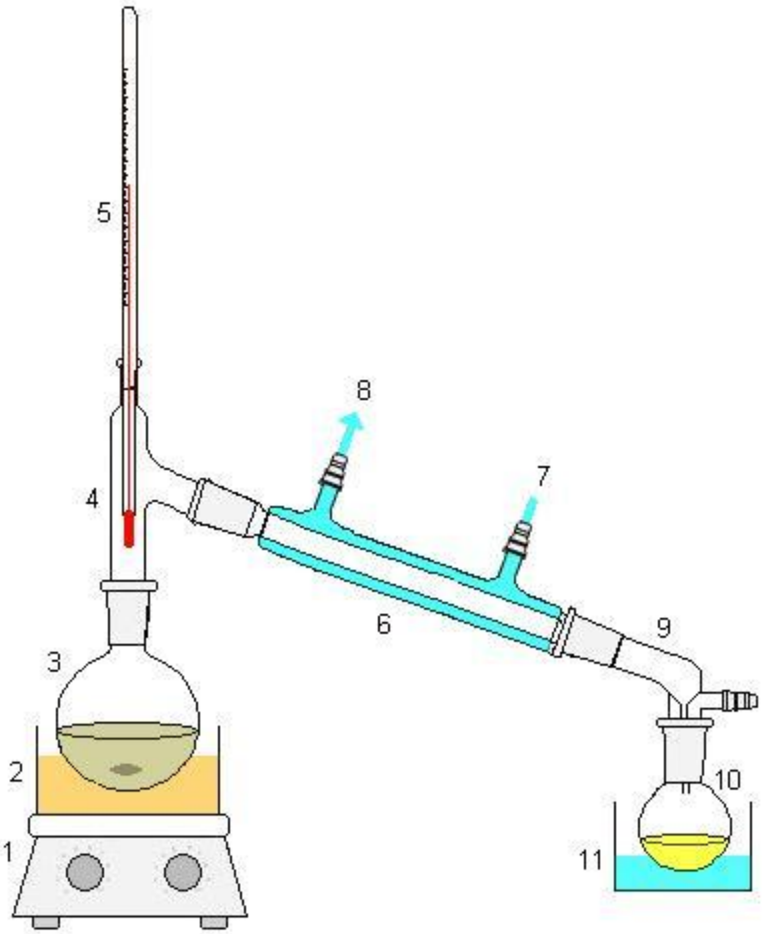
- Distillation Setup
  - Heat Source (hot plate) and sand bath ***OR*** heating mantle
    - 250 mL Round Bottom Distillation Flask
    - Three Way Adapter
    - Alcohol Thermometer
    - Condenser
    - 2 lengths of rubber tubing (Each should be about 18 inches)
    - Bent Adapter
    - Receiving Flask (e.g. 250 Erlenmeyer)
    - Beaker for ice bath (big enough to fit receiving flask)
  - 125 mL Separatory funnel
  - 3 Ring-stands and clamps
  - Graduated cylinder
  - Spatula
  - 25 mL round bottom flask

Pre-Lab (involves library/internet research)

1. Cinnamon contains other organic compounds besides cinnamaldehyde. Find one other compound that is present in "true cinnamon" (*Cinnamomum zeylanicum*), and draw its chemical structure.
2. Traditionally, chloroform would have been used for the extraction in place of ethyl acetate. What problems are associated with chloroform that discourages its use today?

Procedure:

1. Partner 1 – Set up glassware for the distillation as show in Figure 1 (if not already set up). Be sure to clamp the condenser (6), the round-bottom flask (3) and the receiving flask (10) to three separate ring-stands. Also, secure the bent adapter (9) to the condenser (6) by placing a rubber band around the water-in spout of the condenser (7) and the spout of the bent adapter (9).



1) Heat Source (hot plate)
2) Sand Bath
3) Distillation Flask (cinnamon–water soluti
4) Three Way Adapter
5) Alcohol Thermometer
6) Condenser
7) Cool Water (in)
8) Water (out)
9) Bent Adapter
10) Receiving Flask (cinnamaldehyde-solution)
11) Ice Bath

Figure 3

2. Partner 2 – Measure approximately 2.5 g of ground cinnamon and record the mass. Place the cinnamon into a 250 mL round-bottom flask.

3. Partner 2 – Measure out and add 50 mL of water to the round-bottom flask. Mix thoroughly by gentle swirling.

4. Place the round bottomed flask into the distillation apparatus and begin water flow. The water should be trickling at a slow rate, not gushing like a fire hose. Using a heating mantle or sand bath, distil the cinnamon/water mixture until around 30-40 mL has collected at a rate of around 2 mL per minute, ***OR*** until 30 minutes has passed. NEVER boil the solution in the distillation flask to dryness. ALWAYS leave some liquid in the distillation flask.

5. Pour the distillate into a 125 mL separatory funnel for separation. The cinnamaldehyde/ water distillate

should appear slightly cloudy with a distinct cinnamon smell.

6. Add 10 mL of ethyl acetate into the separatory funnel. GENTLY swirl the mixture for about 15 seconds to extract the cinnamaldehyde from the aqueous layer. [Note: Violently shaking the mixture will cause it to become extremely cloudy and difficult to separate.] The top layer consists of ethyl acetate/cinnamaldehyde,* and the aqueous layer is on the bottom (Figure 2). Allow 10 minutes for the layers to separate.

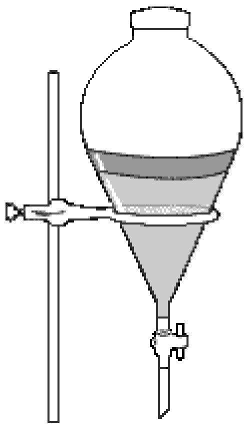


Figure 4

7. Once the two layers have separated, turn the stopcock to slowly remove the lower (aqueous) layer in portions into the round bottom flask used earlier. Take care not to allow drops of the organic layer to come out with the aqueous. Transfer the organic layer into a 125 mL Erlenmeyer flask labeled with your initials and the contents (cinnamaldehyde and ethyl acetate).

8. Transfer the aqueous layer back into the separatory funnel and repeat steps 6-7 using 3 mL of ethyl acetate.[*]

9. Dry the organic fraction using a small amount (tip of a spatula) of anhydrous sodium sulfate. If the sodium sulfate clumps, then add more until clumping ceases and the sodium sulfate flows freely in the bottom of the flask.

10. Transfer the dried organic fraction to a clean, tared 25 mL round-bottomed flask. Rinse the sodium sulfate with 2 mL of ethyl acetate and combine this with the dried organic fraction.

11. Evaporate the ethyl acetate either by distillation from a warm water bath (~70°C), or (if available) using a rotary evaporator. Record the total mass, and calculate the mass of the isolated cinnamaldehyde – normally around 0.2 g. Note the smell of the remaining oil.

12. **WASTE DISPOSAL INSTRUCTIONS:** Pour the water used for the distillation into the waste container labeled “Aqueous Waste from Spices Lab”. The instructor will dispose of this waste. Dispose of the sodium sulfate in the container labeled “Hazardous Solid Organic Waste (Sodium Sulfate)”. Wash and dry all glassware.

[*] Note: Ethyl acetate has a slight solubility in water, so you will see a smaller amount separating out.

References

Taber D., Weiss A., "Cinnamaldehyde by Steam Distillation," *Journal of Chemical Education*, 1998, 75(5), 633.

Discussion points

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Questions

1. Explain the design and purpose of the following pieces of glassware:
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Extension Activities

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Report

The lab report should consist of an introduction, answers to pre-lab questions, brief description of procedures, and a data table showing all measurements and observations. Be sure to include answers to the Questions (including calculation of percent yield) and the Extension activities.