Fischer Esterification: Preparation of Banana Oil

Esters are an important functional group in organic chemistry. They are pleasant smelling molecules and are typically used in fragrances and as flavoring ingredients. They are also found in biological systems in the form of triacylglycerols (triglycerides). These make up fats and oils and, as such, are very important in biological metabolism.

There are a number of different reactions that allow you to prepare esters. One of these reactions is the Fischer esterification, which involves the reaction of a carboxylic acid with an alcohol to generate an ester and water. It is typically catalyzed by a strong acid, such as sulfuric or phosphoric acid.

In this experiment, you will prepare isopentyl acetate (the scent in banana oil) by a Fischer esterification of acetic acid and isopentyl alcohol, as shown in Figure 1. The reaction will be catalyzed by sulfuric acid. Following the reaction, isolation of the pure liquid ester will be obtained through distillation.

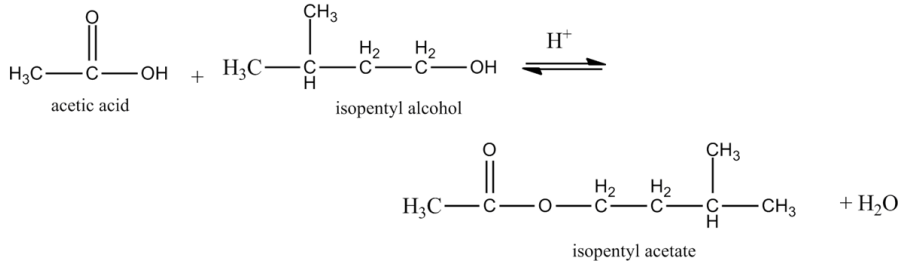

Figure 1

Gas chromatography will be used to characterize the ester product and monitor the reaction.

OBJECTIVES

- Perform a Fischer esterification to prepare isopentyl acetate, the scent in banana oil.
- Determine the major product using gas chromatography.

MATERIALS

Chromebook, computer, or mobile device
Instrumental Analysis app
Go Direct Mini GC
Go Direct Wide-Range Temperature and Graphical Analysis 4 app[1]
1 µL Hamilton syringe
paper towel or lint-free wipe
hexane
reflux apparatus
magnetic stir bar
two 25 mL round-bottomed flasks
simple distillation apparatus
heating mantle and stir plate
calcium chloride
isopentyl (isoamyl) alcohol
glacial acetic acid
concentrated sulfuric acid
5% sodium bicarbonate
separatory funnel
25 mL Erlenmeyer flask
anhydrous sodium sulfate
goggles and gloves
scale

PRE-LAB ACTIVITY

Complete Table 1. This information is a common starting point for understanding the behavior of a set of substances that may be found in a mixture being tested by gas chromatography.

Table 1

Compound	Boiling temperature (°C)	Molar mass (g/mol)	Chemical structure
isopentyl alcohol			
isopentyl acetate			

[1]Any temperature probe or thermometer that can measure temperature in the fractional distillation apparatus will work.

PROCEDURE

Part I Reflux, isolation, and purification

1. Put on safety goggles and gloves.

2. Assemble your reflux apparatus.
   a. Obtain a 25 mL round-bottom flask with a magnetic stir bar. Record the mass of the flask with stir bar.
   b. Attach a water condenser column for reflux. Attach the tubing to the condenser column so that the water enters the condenser column at the lower nipple and exits the upper nipple connector as shown in Figure 1.
   c. Top the water condenser column with a calcium chloride drying tube. Assemble the drying tube by first placing a small amount of glass wool into the tube in order to cover the bottom opening. Add enough anhydrous calcium chloride to fill the drying tube about half way. Insert the bottom nipple of the drying tube into a #1 one-hole rubber stopper, which is inserted into the top of the condenser. **WARNING**: *Do not eat or drink when using chemicals—harmful if swallowed. Causes serious eye irritation*.
   d. The apparatus will be heated using a heating mantle placed on top of a stir plate so that the mixture can be stirred continuously during the reaction. Secure the reaction setup to a ring stand using a three prong clamp attached to the condenser column, so that the reaction vessel can be easily elevated and cooled in the air, after the reaction is completed.

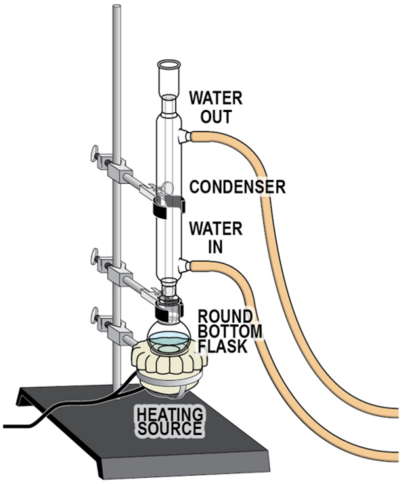

Figure 2

3. Assemble the reaction mixture.
   a. Disconnect the pre-weighed round bottom flask from the reflux apparatus and add 5 mL of isopentyl (isoamyl) alcohol to it. It should still contain the magnetic stirring bar. Record the mass of the alcohol in the data table. **DANGER**: *Flammable liquid and vapor. Skin and serious eye damage, corrosion or irritation. Acute toxicity, inhalation. Harmful if inhaled.*
   b. Add 7 mL glacial acetic acid to the flask with the alcohol and stirring bar. **DANGER**: *Glacial acetic acid,* CH_3COOH: *Keep away from heat, sparks, open flames, and hot surfaces—flammable liquid and vapor. May be harmful if swallowed. Causes severe skin burns and eye damage. Avoid breathing mist, vapors, or spray—toxic if inhaled*.

c. Using a graduated pipet, add about 0.5 mL of concentrated sulfuric acid to the flask. Do not try to measure sulfuric acid in a graduated cylinder. Immediately, swirl the flask to mix the contents. **DANGER**: *Sulfuric acid, concentrated,* H_2SO_4: *Causes severe skin burns and eye damage. Do not breathe mist, vapors, or spray. Maybe be harmful if inhaled. Harmful to aquatic life. Considerable heat generated when diluted with water.*

4. Start water circulating in the condenser and bring the mixture to a boil. Continue heating under reflux for 60–75 minutes. **Tip**: While waiting for reflux to complete, start Part III Gas Chromatography.

5. After the reaction is complete, turn off the heating mantle and allow the mixture to cool to room temperature. Disassemble the reflux apparatus.

6. Transfer the reaction mixture to a separatory funnel. Make sure the stir bar remains in the round bottom flask. Be sure that the stopcock is closed and, using a funnel, pour the mixture into the top of the separatory funnel.

7. Isolate your product.
   a. After adding the liquid reaction mixture to your separatory funnel, you will need to do washes to neutralize the sulfuric and acetic acid in the mixture. Add 20 mL of 5% sodium bicarbonate, stopper the funnel, and mix the phases by careful shaking and venting. Allow the phases to separate; the upper layer is isopentyl acetate and the lower layer is aqueous bicarbonate. Then, unstopper the funnel and drain the lower aqueous layer through the stopcock into a beaker; this will eventually be discarded in liquid waste. Repeat this wash two more times.
   b. Do a single wash with 20 mL of distilled water to remove any bicarbonate ions that may still be with the product. Remove the water layer (bottom layer).
   c. If you are doing Part III concurrently, prepare the Mini GC and inject 0.2 µL of the crude ester product with the 1.0 µL Mini GC syringe. If not doing it concurrently, set aside a very small amount of the crude ester product to be able to inject 0.2 µL with the 1.0 µL Mini GC syringe in Part III.
   d. Transfer the crude ester to a clean, dry 25 mL Erlenmeyer flask and add approximately 1.0 g of anhydrous sodium sulfate. Cork the mixture and allow it to stand for 10 to 15 minutes while you prepare the apparatus for distillation. If the mixture does not appear to dry (i.e., the drying agent clumps and does not "flow," the solution is cloudy, or drops of water are obvious), transfer the ester to a new clean, dry 25 mL Erlenmeyer flask and add a new 0.5 g portion of anhydrous sodium sulfate to complete the drying.

8. Purify your product by distillation.
   a. Assemble a simple distillation apparatus using your smallest round-bottom flask to distill from. Use a heating mantle to heat.

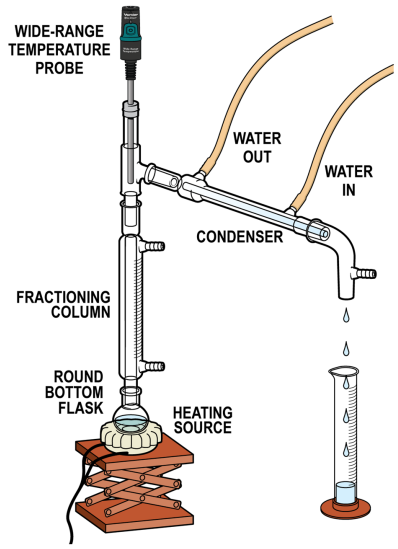

Figure 3

b. Pre-weigh and use another small round bottom flask to collect the product. Immerse the collection flask in a beaker of ice to ensure condensation and reduce odors. The isopentyl acetate will boil and then condense. It will be collected in the small round bottom flask.

c. Collect your material when you have a product at the appropriate boiling point of the isopentyl acetate. Record the boiling point range. Set this aside for measurement with the Mini GC.

9. Weigh the product and calculate the percentage yield of the ester.

Part III Gas chromatography

10. Set up the Go Direct Mini GC and Instrumental Analysis.
    a. Launch Instrumental Analysis.
    b. Connect the Mini GC to your Chromebook, computer, or mobile device via USB or Bluetooth wireless technology. If using Bluetooth, click or tap Connect an Instrument, connect to your Mini GC, and click or tap Done.
    c. Click or tap Gas Chromatography.

d. Set the temperature and pressure profile to the parameters listed in Table 2. Then, click or tap Apply to initiate the profile.

Table 2	
Start temperature (°C)	45
Hold time (min)	2
Ramp rate (°C/min)	5
Final temperature (°C)	95
Final hold time (min)	5
Pressure (kPa)	11

11. While the Mini GC is warming up, follow the procedure in this step to clean and flush the syringe with n-hexane. **Important**: The glass syringe is fragile. Be careful not to bend the needle or bend the plunger. Never pull the plunger back more than 50% of its total volume.
    a. Depress the plunger fully.
    b. Submerge the tip of the syringe needle into the vial of n-hexane. **DANGER**: *n-Hexane,* C_6H_{14}: *Keep away from heat, sparks, open flames, and hot surfaces—highly flammable liquid and vapor. Do not eat or drink when using. Avoid breathing mist, vapors, or spray. May be fatal if swallowed and enters airways. May cause damage to organs. Causes skin and eye irritation. May cause drowsiness or dizziness. Suspected of damaging fertility or the unborn child. Do not handle until all safety precautions have been understood*.
    c. Pull back the plunger to fill the barrel with 0.4 µL of n-hexane.
    d. Expel the liquid onto a lint-free wipe or a paper towel.
    e. Repeat Steps a–d at least two times, or until you are comfortable pulling up a liquid into the syringe and measuring the volume in the syringe barrel.

12. Follow the process in Step 11 to clean and flush the syringe with a 4:1 mixture of hexane and your starting material (isopentyl alcohol), the first sample to be injected into the Mini GC.

13. Once the Mini GC has reached the correct start temperature and pressure, the LED will turn green. Collect 0.2 µL of the first sample for injection. Insert the needle into the injection port of the Mini GC. Depress the syringe plunger; immediately following, press the button on the Mini GC to initiate data collection. Be careful not to bend the plunger as you press it down. Pull the needle out of the injection port immediately. Data collection will automatically stop after 17 minutes, or you can choose to end it early if you are satisfied that your species has eluted completely.

14. Name your sample appropriately. To do this, click or tap the y-axis label. Click or tap ⋯ next to the data set you wish to rename, and select Rename Data Set. Enter a name for the data set, and click or tap Rename.

15. To analyze the chromatogram, drag across the peak to select it, then click or tap Add Peak Integral, . Record the retention times in Table 3.

16. Test the crude product and the final product you collected.
    a. Click or tap Initiate Data Collection. Then, click or tap Apply; you will use the same parameters as before.
    b. While waiting for the instrument to warm up, follow the process in Step 11 to clean and flush the syringe with the crude product.
    c. Repeat Steps 13–15.
    d. Repeat this process to test the final product.
17. Save the file as directed by your instructor. Keep your test results open in Instrumental Analysis; you will need to refer to the various chromatograms to answer the Data Analysis questions.
18. When you are done with data collection, make sure to turn the Mini GC power switch to the off position and disconnect the Mini GC from AC power.

DATA TABLE

Table 3

Compound	Mass (g)	Retention time (min)	Peak area
isopentyl alcohol			
isopentyl acetate (crude)			
isopentyl acetate			

DATA ANALYSIS

1. What was the observed boiling point of the isopentyl acetate?
2. Determine the percentage yield of your ester.
3. Compare the odor of your ester product (isopentyl acetate) to that of the reactants (acetic acid and isopentyl alcohol).
4. How does your experimentally determined boiling point range compare to the literature value?