EXPERIMENT
Oil of Wintergreen: Synthesis and NMR Analysis

Introduction: When salicylic acid reacts with methanol in the presence of an acid catalyst, methyl salicylate, or oil of wintergreen, is produced according to the following equation:

\[
\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{OH} \xrightarrow{H^+} \text{C}_6\text{H}_5\text{OCH}_3 + \text{H}_2\text{O}
\]

salicylic acid methanol methyl salicylate (oil of wintergreen)

If the organic product formed during a reaction remains in a reaction mixture containing impurities, such as in the case of methyl salicylate, performing an extraction will separate the product from the reaction mixture. In liquid-liquid extraction, equilibrium concentrations of a solute are established between two immiscible solvents. Usually one of the solvents is water and the other is a non-polar organic solvent; in this case, methylene chloride, CH\(_2\)Cl\(_2\). The solute of interest, methyl salicylate, is preferentially drawn into the organic solvent in which it is more soluble. Other components, particularly if ionic or very polar, are preferentially drawn into the water. When the two layers are separated, the organic compound in the organic solvent has been freed from most of the water-soluble impurities.

Fact Check 1: In liquid-liquid extraction, __________ __________ is used to remove the desired compound from the mixture based on polarity.

In the case of methyl salicylate, there will also be unreacted salicylic acid drawn into the organic solvent. To remove this unwanted starting reactant, a thorough washing with aqueous sodium bicarbonate, NaHCO\(_3\) (aq), will be performed. The sodium bicarbonate reacts with salicylic acid to form sodium salicylate, with water and carbon dioxide gas as byproducts:

\[
\text{C}_6\text{H}_5\text{OH} + \text{NaHCO}_3 \xrightarrow{} \text{C}_6\text{H}_5\text{O}^+\text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O}
\]

unreacted salicylic acid sodium bicarbonate sodium salicylate

The ionic sodium salicylate is now preferentially drawn into the aqueous layer and can be removed from the extraction mixture, leaving methyl salicylate in the organic layer free from most of the reaction mixture impurities and ready for analysis.
Thin Layer Chromatography (TLC): In order to verify that product has been formed in the reaction, and to assess the relative purity of the isolated product, you will use a method called thin layer chromatography, or TLC.

In General Chemistry I, you learned that chromatography is an analytical method for separating and identifying components of a mixture according to their chemical structure. TLC is one such method and is based on the concept that compounds in a mixture can be separated by their relative attraction to two phases:

- The stationary phase (silica gel)
- The mobile phase (the chosen solvent)

Compounds are separated based on their attraction to the stationary phase and on the polarity of the solvent used. Silica gel is polar; thus polar compounds will be more strongly held by the stationary phase and will move more slowly than non-polar compounds under the same conditions.

**Fact Check 2:** A non-polar compound will move a __________ distance than a polar compound because it is __________ attracted to the stationary phase.

We should note that the solvent will affect the rate of travel for the compound as well. Polar compounds will interact more readily with polar solvents and will travel at a faster rate in their presence. Polar solvents will have the opposite effect on non-polar compounds. Similarly, non-polar solvents will decrease the rate of travel for a polar compound and increase the rate of travel for a non-polar compound. A mixture of solvents is often used to maximize the separation of the compounds being analyzed.

Polarity of Solvents Commonly Used in TLC:

<table>
<thead>
<tr>
<th>Most Polar</th>
<th>Least Polar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (CH₃OH)</td>
<td>Hexanes (C₆H₁₄ isomers)</td>
</tr>
<tr>
<td>Acetone (CH₃COCH₃)</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate (CH₃CO₂CH₂CH₃)</td>
<td></td>
</tr>
<tr>
<td>Methylene chloride (CH₂Cl₂)</td>
<td></td>
</tr>
<tr>
<td>Diethyl ether (CH₃CH₂OCH₂CH₃)</td>
<td></td>
</tr>
<tr>
<td>Toluene (C₆H₅CH₃)</td>
<td></td>
</tr>
</tbody>
</table>

**Fact Check 3:** Adding hexane to acetone will cause a polar compound to move a __________ distance than it does in pure acetone.
R_f Values: You should also recall the concept of Retention Factor (R_f). It is calculated by dividing the distance traveled by the compound by the distance traveled by the solvent. All R_f values will be between 0 and 1.

Nuclear Magnetic Resonance (NMR) Spectroscopy: In order to verify the structure of the product, we turn to spectroscopic methods of analysis. Spectroscopy is defined as an experimental process for determining the composition of a substance by examining its selective absorption of electromagnetic radiation (light waves). This absorption correlates with the energy required to excite a compound in some way from a lower to a higher energy state. This energy is expressed according to the equation:

\[ E = h \nu \]

where \( h \) is Planck’s constant (6.63 x 10^{-34} \text{ J} \cdot \text{s}), \( \nu \) is frequency (measured in s^{-1} or Hz); hence the energy is directly proportional to the frequency of radiation.

Radio waves and microwaves; infrared, visible, and ultraviolet light; and x-rays and gamma rays are all examples of electromagnetic radiation, each of which can be measured by a specific type of spectrometer. For this experiment, we will be using a spectroscopic technique known as nuclear magnetic resonance spectroscopy, which measures the selective absorption of nuclei in a strong magnetic field. Isotopes whose nuclei have an unequal number of protons and neutrons are observed to have a property called “spin.” In the presence of a magnetic field, these nuclei can be excited to a higher energy state by absorption of radio frequency radiation, thus giving a signal to be measured by the spectrometer. The isotopes we will be looking at are ^1\text{H} and ^13\text{C}. (The nucleus of an isotope such as ^12\text{C}, which an equal number of protons and neutrons—and thus no overall nuclear spin—will be unresponsive to the magnetic field and will not give signals or show up on a spectrum.) It is worth noting that the abundance of ^13\text{C} is only about 0.1% of all naturally occurring carbon, compared to 99.9% for ^1\text{H}. Because of its low abundance, when performing ^13\text{C} NMR we must do many additive scans, sometimes upwards of 500–1000, to obtain discernable peaks. This is in stark contrast to ^1\text{H} spectra, which show satisfactory signals with under 20 scans using the same sample.

The NMR Spectrometer: NMR spectrometers come in varying strengths, but the type you will be using is a 60 MHz spectrometer. This refers to the radio frequency that will be applied. As the
frequency increases, the strength of the magnetic field that is required ($H_0$ in the schematic) also increases. Therefore, a 200 MHz machine will require a stronger magnet than a 60 MHz machine.

The sample tube is lowered into a chamber that positions it between the poles of the magnet and within the radio frequency coils. The tube is spun to ensure that the magnetic field is applied equally to all parts of the sample. The absorption of radio frequency radiation by the sample as the magnetic field is varied is recorded in a spectrum.

Schematic of an NMR Spectrometer

![Schematic of an NMR Spectrometer](image)

**Interpreting NMR Data:**

**NMR Scale:** NMR spectra are scaled in units of parts per million. This measurement is used because there are such small differences in the applied magnetic fields required to excite each nuclei to a higher energy state. $^1$H NMR scale ranges from 0 ppm to 10 ppm while $^{13}$C scale ranges from 0 ppm to 200 ppm. These ranges are selected because they are where the $^1$H and $^{13}$C atoms are typically responsive to the magnetic field.

**NMR Chemical Shifts:** Chemical shifts are based on a comparison between the protons of a given organic compound and those of a compound known as tetramethylsilane (TMS), $(\text{CH}_3)_4\text{Si}$. The protons of TMS are all equivalent and are more shielded than those in nearly all organic compounds, making it ideal for use as a standard. The signal for the protons of TMS is given the value of 0 ppm and it is important to understand that the value we give a signal from an organic compound is based on the comparison to TMS and not an “absolute” value. Where a particular signal is observed on the spectrum depends upon the electronic environment around a given nucleus. We can say that an electron cloud “shields” the nucleus. If an electronegative atom is adjacent to a particular nucleus in the compound, it will attract the electrons away from that nucleus leaving it “deshielded”. The more “deshielded” a nucleus is, the farther “downfield” (to the left in the spectrum) that signal will be. The more “shielded” a nucleus is, the farther “upfield” (to the right) the signal will be seen. (Figure 1.)
**Fact Check 4:** The greater the amount of electron density around the proton or carbon nucleus that is exposed to the magnetic field the _________ the energy required to excite it to a higher energy state because it _________ the nucleus from the field.

**Functional Groups:** The organic functional groups (shown in blue) we will encounter in this experiment are exemplified by the following compounds:

- **CH₃OH**
  - methyl alcohol, an **alcohol**
- **CH₃COOH**
  - acetic acid, a **carboxylic acid**
- **CH₃COOCH₃**
  - methyl acetate, an **ester**

A functional group is an atom or a group of atoms that has certain chemical and physical properties, regardless of the hydrocarbon skeleton to which it is attached. Methyl alcohol, ethyl alcohol, and isopropyl alcohol, for example, all have some properties in common owing to the alcohol functional group.

The electronegative oxygen atoms in these functional groups cause deshielding of the nearby protons and carbons. In the $^1$H NMR spectrum, the protons on the methyl group in the alcohol are shifted downfield to ~3–4 ppm, as opposed to those on saturated hydrocarbons, which appear at less than 2 ppm. (See Figure 2.) The ester group is even more deshielding, with the protons on the methyl group attached to oxygen occurring at ~3.5–4.5 ppm. The methyl groups attached to the carbons in the acid and the ester appear at ~2–3 ppm. Protons that are attached to oxygen atoms themselves are considerably more variable, with alcohol protons in the range of ~1–5 ppm, and acid protons ~10–12 ppm.
Similar effects are seen in the $^{13}$C NMR spectrum (Figure 3). A carbon singly bonded to an oxygen is shifted downfield to $\sim$50–80 ppm, while those with multiple bonds to oxygen, as in the acid and ester functional groups, occur even further downfield at $\sim$160–180 ppm. The carbons in the methyl groups attached to carbon are further upfield at $\sim$30–50 ppm.

Atom Equivalence: Understanding and translating the spectral results of NMR can sometimes be challenging. This is due in part to the existence of equivalent atoms in a compound. Atoms are said to be equivalent when they share a common electronic environment. In the following examples we will see how equivalence in a compound affects its spectroscopic interpretation.
**Integration in $^1\text{H NMR}$:** The integrated area of a signal in $^1\text{H NMR}$ is proportional to the number of protons in a particular environment in the compound. The more protons there are in that environment, the larger the signal will be on the spectrum. You should understand that this is a relative number and not an exact value. Integrations may be displayed or not depending on how the spectrum is recorded, and if displayed, are shown on the spectrum as relative values. Integration in $^{13}\text{C NMR}$ is more complex due to the fact that it is not directly proportional to the number of carbons, and therefore is usually not done.

**Analyzing Spectra:** Let’s first examine the compound tert-butyl alcohol.

**Figure 4.** $^1\text{H NMR}$ spectrum of tert-butyl alcohol

Looking at this compound’s structure we can see that there are three methyl groups attached to the central carbon. They are equivalent and as such their collective protons will show up as only one signal in the spectrum. There is also the proton attached to the oxygen which will give another signal, and this accounts for the two peaks observed. How do we know which protons correspond to which peak? One way is to look at the chemical shift. As can be seen in the Figure 2, the signals for protons attached to a simple alkane (such as CH$_3$) and those attached to the oxygen of an alcohol overlap, but we can still use chemical shifts to identify them by understanding that in general the protons on a simple alkane will be seen further upfield than the proton attached to the oxygen due to shielding/deshielding effects. We could then assign the protons of the methyl groups to the peak at 1.3 ppm and the proton attached to the oxygen to the peak at 2.0 ppm. These assignments can be further confirmed using integration. The height of the peak at 1.3 ppm is far greater than that of the peak at 2.0 ppm, in an approximate 9 to 1 ratio. This is also consistent with our assignment.
Keeping in mind the equivalence of those three methyl groups, we realize that they will appear as only one peak in the $^{13}$C spectrum as well. Given the one other nonequivalent carbon in the molecule, we then see two peaks in the spectrum. We can use a similar method for assigning carbons as we did for protons. The central carbon will be the most deshielded since it is attached to the oxygen. This carbon will be assigned to the peak at 69 ppm and the methyl carbons will then be assigned to the peak at 31 ppm.

Let’s now consider the compound methyl benzoate:

In the $^1$H spectrum above we see one tall peak at 3.9 ppm, and two clusters of peaks at ~7.5 and ~8 ppm. Based on the structure of the compound, we should expect to see four signals: one for the methyl protons, a second for the equivalent pair closest to the ester group on the ring, a third for the next equivalent pair, and a fourth for the single proton opposite the ester group. Using
Figure 2, we note that the protons on the methyl group should be in the range from 3.5 ppm to 4.5 ppm; we do see that peak at 3.8 ppm. The other five protons are aromatic (i.e., attached to a benzene ring) and as such they are found in the range of 6.4 ppm to 8.2 ppm. Because these are not all equivalent, and because of another characteristic of $^1$H NMR called “splitting” (which we won’t go into further here), we get a rather complex set of signals for those protons. Integration of this spectrum would show a relative ratio of 2:3 for the areas under the peaks at ~8 ppm and ~7.5 ppm, respectively, corresponding to the pair closest to the ester group (therefore furthest downfield at 8 ppm), with the two signals from the remaining three protons overlapping together at ~7.5 ppm.

![Figure 7. $^{13}$C NMR spectrum of methyl benzoate](image)

In the $^{13}$C spectrum we observe a total of six peaks, which we know is expected based on equivalency. (Be sure you can see that!) Again using Figure 3, we find that the carbon of the methyl group should be in the range of 50–80 ppm, and it appears at around 52 ppm in the spectrum. Next we see a series of four peaks in the region around 130 ppm. These correspond to the carbons of the benzene ring and as such fall into the range for aromatics, ~100–160 ppm. We won’t go into a detailed assignment of those peaks, but we should understand that because there are two pairs of equivalent carbons in the ring, we see four signals. Finally, the peak at 168 ppm is the carbon of the ester group, being found within the range of 155–180 ppm.

**Fact Check 5:** For both $^{13}$C NMR and $^1$H NMR, __________ nuclei give the __________ signal.

**Objectives:** In this experiment you will synthesize oil of wintergreen from salicylic acid and methanol, isolate the crude product by extraction, determine the purity of the isolated oil of wintergreen by TLC, and verify its structure by $^1$H NMR.

**Pre-Lab Notebook:** Provide
- title
- purpose
- reference
- reaction
- table of reagents containing salicylic acid, methanol, concentrated sulfuric acid, and methylene chloride

and the procedure in two-column format in your laboratory notebook before coming to lab.

**Equipment:**

**Week 1:**

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gloves</td>
<td>125 mL Nalgene Drop Bottle</td>
</tr>
<tr>
<td>Ring Stand w/ Utility Clamp</td>
<td>50 mL Beaker</td>
</tr>
<tr>
<td>Thermometer</td>
<td>10 mL Beaker</td>
</tr>
<tr>
<td>125 mL Erlenmeyer flasks (2)</td>
<td>Small Stir Bar</td>
</tr>
<tr>
<td>400 mL Beaker (for hot water bath)</td>
<td>5¼-inch Pasteur Pipets w/ Bulb (3)</td>
</tr>
<tr>
<td>10.0 mL Graduated Cylinder (2)</td>
<td>Disposable Pipets (2)</td>
</tr>
<tr>
<td>Centrifuge Tubes and Cap (2)</td>
<td>Parafilm</td>
</tr>
<tr>
<td>20 x 150 mm Test Tube</td>
<td>Grease Pencil</td>
</tr>
<tr>
<td>Spatula</td>
<td></td>
</tr>
</tbody>
</table>

**Stock Solutions:**

- 10% aqueous Sodium Bicarbonate
- Methanol in 125 mL Nalgene Drop Bottles (1 per group)

**Week 2:**

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 mL Beaker</td>
<td>Spotting Pipettes (3)</td>
</tr>
<tr>
<td>110 mm Filter Paper</td>
<td>Pencil</td>
</tr>
<tr>
<td>10.00 mL Volumetric Pipet</td>
<td>Forceps</td>
</tr>
<tr>
<td>Pipet Bulb</td>
<td>10 mL Snap Cap Vial</td>
</tr>
<tr>
<td>Watch Glass</td>
<td>Scissors</td>
</tr>
<tr>
<td>TLC Plate</td>
<td>Ruler</td>
</tr>
</tbody>
</table>

**Stock Solutions:**

- TLC Solvent (1:4 mixture of ethyl acetate to methylene chloride)
- Snap cap vials of pure oil of wintergreen dissolved in TLC solvent
- Snap cap vials of salicylic acid dissolved in TLC Solvent

**In-Lab Experimental Procedure:** Work in pairs. Wear gloves for handling sulfuric acid in Part A and for all of Part B.

**Part A: Synthesis of Oil of Wintergreen**

1. **One partner can complete steps 2-5 while the other partner works on step 1.** Fill a 400-mL beaker with 250 mL of water for a hot water bath. Set the beaker on a hot plate and place a thermometer in the beaker with a ring stand and clamp. The thermometer should not be touching the bottom or side of the glass beaker. Raise the temperature of the water to 60°C and keep it steady at this temperature (Refer to step 7).
2. Place a 20 x 150-mm test tube in a 125-mL Erlenmeyer flask to hold it upright.
3. Place about 0.250 grams of salicylic acid into the test tube. Record the exact mass of the acid in your laboratory notebook.
4. Carefully add 4.0 mL of methanol and then 8 drops of concentrated sulfuric acid to the test tube (Caution!). Record the exact amounts in your laboratory notebook.
5. Carefully slide a magnetic stir bar into the test tube and have it rest at the bottom. Hold the test tube level on top of the lab bench and draw a line with a grease pencil around the solvent level. You will need to keep the solvent level at or slightly above this line during the heating phase.

6. Note the odor of the starting reactant mixture. Remember, the proper way to smell a chemical is to waft the air above the container toward your nose. Never smell or sniff a chemical directly with your nose!

7. Place the test tube in a hot water bath at 59–64°C and heat for 70 minutes. Turn the stir knob on to a low setting to begin a gentle stir of the magnetic stir bar. One partner should always be monitoring both the temperature and the methanol solvent level to ensure that any methanol boiled off is being replenished throughout the 70 minute reaction time and to adjust the heat setting accordingly to stay within the 59–64°C temperature range. Hint: Once the hot water bath is around 60°C, keeping the heat setting at or slightly above ‘3’ (or slightly less than one-third of the total knob if your knob is not numbered) will hold the temperature steady.

8. Remove the test tube from the hot water bath and cool the bottom of the test tube under running tap water. Remove the stir bar by placing a stir bar remover on the outside of the test tube and dragging the stir bar up the side of the test tube to the opening.

9. Transfer the contents of the test tube into a centrifuge tube resting upright inside a 125-mL Erlenmeyer flask.

10. Note the odor of the formed product.

**Part B: Isolation of Oil of Wintergreen**

1. Using a 10.0-mL graduated cylinder and a plastic disposable pipet, carefully measure out 4.0 mL of methylene chloride and add to the centrifuge tube, then add 4.0 mL of de-ionized water to the centrifuge tube. The centrifuge tube should now be about four-fifths full of liquid.

2. Cap the centrifuge tube, invert and shake to ensure the phases are thoroughly mixed. Vent frequently. Failure to do so could result in the cap being blown off and the contents strewn all over the lab bench. One way or another, the pressure buildup will be alleviated! Do not vent the centrifuge tube toward another person.

3. Remove the cap and allow the layers to separate. Which layer is the organic layer and which layer is the aqueous layer? Densities: methylene chloride: ________ g/mL; water: ________ g/mL

4. Place a bulb on a 5¼-inch Pasteur pipet. Squeeze the bulb and place the tip of the pipet at the bottom of the centrifuge tube. Draw up all of the bottom (organic) layer and transfer to a clean centrifuge tube. Set the remaining aqueous layer aside for later disposal.

5. Obtain a clean 10-mL beaker and weigh and record its mass, to 3 decimal places, in your laboratory notebook.

6. Perform a sodium bicarbonate wash of the organic layer in triplicate. Add 3.0 mL of a 10% aqueous sodium bicarbonate solution to the centrifuge tube. Cap the tube, invert and shake gently. (Caution! Vent the centrifuge tube after every inversion! CO₂ gas is a product of this reaction, the pressure will build up quickly while mixing the phases). After mixing thoroughly and allowing the layers to separate, add a second 3.0 mL portion of 10% aqueous sodium bicarbonate, invert and mix thoroughly while venting. Allow the layers to separate. If the centrifuge tube is more than two-thirds full, draw off around two-thirds of
the top aqueous layer with a Pasteur pipet and transfer to a waste beaker. Then perform the
third, and last, 3.0 mL 10% aqueous sodium bicarbonate wash.
7. At this point the Oil of Wintergreen is in the bottom methylene chloride layer and free from
most of the reaction mixture impurities. Using a clean Pasteur pipet, squeeze the bulb and
place the tip of the pipet at the bottom of the centrifuge tube. Draw up the entire bottom
layer and transfer it into a 10-mL beaker.
8. Add 1 boiling chip to the 10-mL beaker containing the organic layer and perform an
accelerated evaporation of the methylene chloride solvent by turning a hot plate on at a low
setting and swirling the bottom of the glass beaker along the edge of the hot plate.
9. Once the solvent has evaporated, record you observations of the oil, including any odor, in
your laboratory notebook.
10. Remove the boiling chip carefully with a spatula. Try not to remove any oil with the
spatula tip.
11. Once the beaker has cooled, weigh and record the mass of the beaker and product to three
decimal places. Calculate the mass of your obtained product.
12. Seal Parafilm over the beaker and label your beaker with both partner’s names and lab
section number. Save the oil for analysis during next week’s lab.

Part C: TLC Analysis
1. Obtain a 400-mL beaker and a watch glass. This will be your developing chamber. The
instructor will provide the silica gel coated TLC plate and spotting pipettes. Care should be
taken to avoid touching the face of the plate, as this will alter the results.
2. To maximize the saturation of the chamber with solvent vapors, place a piece of 110-mm
filter paper with the bottom trimmed straight across into the chamber.
3. Using a 10.00-mL volumetric pipette, measure out 10.00 mL of the TLC solvent and place
in your 400-mL beaker and cover with the watch glass. The solvent should be allowed to
travel all the way to the top of the filter paper before introducing the TLC plate into the
chamber. You should slide the watch glass on and off instead of lifting it, in order to
minimize solvent vapor loss.
4. Using a pencil, lightly mark the plate with a horizontal line approximately ½ inch from the
bottom. (Ink contains organic dyes that will alter the results) On this line lightly mark 3
hashes, evenly spaced. These will be the origin points for the spotted compounds.

Example:
5. Obtain a vial and dissolve ~3 mg of your isolated product in 5-6 drops of the TLC solvent. Salicylic acid and pure oil of wintergreen already dissolved in TLC solvent will be provided.

6. Using a different spotting pipette for each compound, spot the TLC plate with the salicylic acid, the pure oil of wintergreen, and the isolated product, in that order. Touch the pipette lightly to the TLC plate at the hash mark to transfer some of the liquid to the plate. The spots should be no larger than about ⅛ inch. You should touch the pipette to the plate several times, pausing for the solvent to evaporate between each, to transfer enough compound to be able to see it once the plate is developed.

7. Place the TLC plate in the developing chamber. Make certain that the level of the solvent is below the level of the spots on the plate. Prop the plate against the inside of the container. Be careful not to slosh the solvent around in order to avoid uneven development. Replace the watch glass on top. The solvent will rise by capillary action.

8. Allow the plate to develop until the solvent front is approximately ½ inch from the top (or until it stops moving). Remove the plate and immediately mark the solvent front.

9. Allow the plate to dry and then examine it under UV light. Circle the spots as they are seen and be sure to mark the center. This should also be done lightly with a pencil only.

10. Discard the TLC solvent in the appropriate container as per your instructor.

**Part D: NMR Analysis**

Remove the CDCl₃ solvent bottle from the dessicator (as demonstrated by the instructor). The solvent contains a small % of tetramethylsilane (TMS), a reference compound. Using an unused, new, clean, dry Pasteur pipet, remove about 0.5 mL of the solvent and mix with 20-40 mg of the oil of wintergreen product to dissolve in a small, clean, dry beaker or Erlenmeyer flask. Transfer the solution to a clean, dry NMR tube using a filter pipet. (Find the NMR tube inverted in the beaker labeled “Clean NMR tubes”.) Add a drop or two of additional CDCl₃ to achieve the desired solution height in the NMR tube. Cap the solvent bottle and place it back into the dessicator (as demonstrated by the instructor). The solution in the tube should be clear and free of any particles. Carefully cap the tube. (The tubes are very fragile.) The sample is now ready for analysis. Follow directions as found by the instrument.

When finished with the analysis, empty the solution from the NMR tube into a bottle labeled “recovered CDCl₃ solution”. Do not wash the tube. Place it in the beaker labeled “used NMR tubes”.

In the event that time does not allow for you or your partner to obtain an NMR spectrum hands-on, there will be a lab discussion about the spectrum during the next lab period. You should obtain a copy of a student-run spectrum from the instructor and analyze it prior to the discussion.
Lab Report Outline for Synthesis of Oil of Wintergreen

<table>
<thead>
<tr>
<th>Graded Sections of Report</th>
<th>Percent of Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>(The “percent of grade” is an estimate only and may be changed by the instructor.)</td>
<td></td>
</tr>
<tr>
<td>Pre-Lab</td>
<td>10</td>
</tr>
<tr>
<td>In-Lab</td>
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</tr>
<tr>
<td>Oil of wintergreen synthesis</td>
<td>10</td>
</tr>
<tr>
<td>Isolation</td>
<td>10</td>
</tr>
<tr>
<td>TLC analysis</td>
<td>10</td>
</tr>
<tr>
<td>Post-Lab In your lab notebook post-lab section, show all calculations as indicated below, being sure to number each step.</td>
<td></td>
</tr>
<tr>
<td>Part A: Synthesis of Oil of Wintergreen</td>
<td></td>
</tr>
<tr>
<td>1. Find the limiting reagent and theoretical yield (in grams) for the oil of wintergreen product.</td>
<td>10</td>
</tr>
<tr>
<td>Part B: Isolation of Oil of Wintergreen</td>
<td></td>
</tr>
<tr>
<td>1. Calculate the percent yield of the isolated product.</td>
<td>5</td>
</tr>
<tr>
<td>2. Discuss any problems you encountered during the synthesis and isolation, and explain your resulting percent yields.</td>
<td>10</td>
</tr>
<tr>
<td>Part C: TLC Analysis</td>
<td></td>
</tr>
<tr>
<td>1. Calculate the ( R_f ) values for the starting material, the pure oil of wintergreen (provided), and your isolated oil of wintergreen.</td>
<td>10</td>
</tr>
<tr>
<td>2. Discuss the purity of the isolated product as evidenced by TLC.</td>
<td>10</td>
</tr>
<tr>
<td>Part D: NMR Analysis</td>
<td></td>
</tr>
<tr>
<td>1. Annotate the ( ^1H ) NMR spectrum by labeling the signals alphabetically from right to left (a, b, c…). Draw the molecule on the spectrum and label the hydrogens in the structure that correspond to the signals in the spectrum.</td>
<td>10</td>
</tr>
<tr>
<td>2. Discuss how you verified the product molecule’s structure. If there are any unexpected peaks present in the spectrum, what impurities might these peaks represent?</td>
<td>5</td>
</tr>
</tbody>
</table>