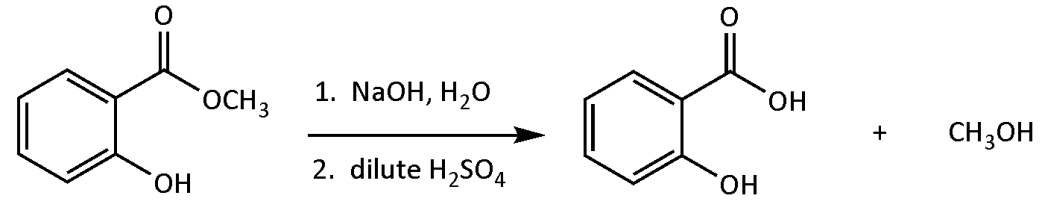
Saponification of Methyl Salicylate: Synthesis of Salicylic Acid

Reading The procedure below will be used, however you should review the following in Pavia: Technique 6 (Heating and Cooling); Technique 8 (Filtration); and Technique 11 (Crystallization). For a brief discussion on methyl salicylate and salicylic acid see Experiment 43 in Pavia, (pp 372-375). See the mechanism and discussion in Klein on saponification of esters, Sections 21.11 (2nd edition).

General

Methyl salicylate (from oil of wintergreen,) and salicylic acid (from Latin *salix*, willow tree) are both natural products. Methyl salicylate can be converted into salicylic acid using the saponification reaction. You will perform this reaction and will purify the product using crystallization.



methyl salicylate salicylic acid

Prelab

Include **Name**, **Date**, **Title** of the Experiment, **Purpose**, **Chemical Equation**, a **Reagent Table** (with theoretical yield) and an **Outline** of the procedure in your notebook. (For an example of a **Reagent Table** see, the **Laboratory Syllabus**.)

Procedure

Hazard Note: the following procedure involves the use of caustic hydroxide solution at the beginning and strong sulfuric acid solutions (H_2SO_4) during the work-up. Keep your goggles on at all times during the laboratory and wear gloves!

Clamp a 100-mL round-bottomed flask to a ring stand and add 2-3 boiling stones. Add 25 mL of 5.0 M sodium hydroxide solution to the flask using a plastic funnel. *Caution*: Do not let the hydroxide solution touch the ground glass joint! Add 2.0 mL of methyl salicylate to the flask and swirl the mixture slightly. A white gummy precipitate should form, which should dissolve later. Apply a very thin coat of stopcock grease to the bottom ground glass joint of a water-cooled condenser and then attach to the top of the flask and heat the flask with a heating mantle and temperature controller (never plug a heating mantle directly in the bench outlet!). Start the flow of water through the condenser, then heat the reaction mixture at reflux for 30 minutes. The start time of the reflux period is when the first amount of condensate returns to the flask – the reflux ring should be visible in the lower part of the condenser and no further than 1/4 up the length of the column (if the reflux ring is higher up than this, turn the heat down!). The initially formed solid should dissolve at this point.

After the reflux period, raise the flask out of the heating mantle and allow the flask to cool to room temperature. Keep the condenser water running until the flask has cooled down. Once the flask is cool enough to touch, you can lower the flask into a beaker of cold tap water to facilitate the cooling process.

Carefully add 3 M sulfuric acid solution to the flask in 2-mL increments until a heavy white precipitate of salicylic acid is formed. Swirl the flask between each addition to see if the precipitate remains. Continue to add 2-mL increments of the sulfuric acid solution, with intermittent swirling, until the supernatant liquid is at or below pH 2. To measure the pH of the mixture, touch the surface of the liquid in the flask with a clean glass stir rod, then touch it to a piece of pH paper (*Never add or insert pH paper into your flask or the liquid as the indicator dyes will leach from the paper and contaminate your*

product). You will need approximately 20-25 mL of sulfuric acid solution. Once the pH has been achieved, cool the flask in an ice-water bath for 5 min.

Collect the product by vacuum filtration using a Buchner funnel. (Save the filtrate from the filtration until you are certain that you have obtained the crude salicylic acid product.)

Recrystallize the crude salicylic acid from water. Use the following procedure as a guideline. Heat approximately 50 mL of deionized water in a 200-mL beaker that contains a boiling stone to near boiling on a hot plate. Transfer the crude salicylic acid to a 125-mL Erlenmeyer flask and add a wooden boiling stick (used to prevent bumping of the liquid when heating). Carefully add approximately 15 mL of the hot water to the crude salicylic acid then bring the contents of the flask to a boil. Add boiling water in 3-mL increments until the solid has completely dissolved – wait at least 30 seconds between additions to ensure that you add just enough and not too much water for the solids to completely dissolve. Record an estimate of the final volume of water used to dissolve the compound.

Remove the flask from the hot plate and allow the solution to cool slowly by placing it in a beaker lined with cotton. Once the flask has cooled to room temperature, crystals should be visible in the flask. If not, scratch the inside of the flask with a glass stir rod to induce crystal formation. Once crystallization is complete at room temperature, cool the flask in an ice-water bath for 5 minutes, then collect the product by vacuum filtration using a Buchner funnel. Rinse the solid with a few milliliters of ice-cold deionized water, then let the product air dry by pulling air over the sample for a few minutes using the vacuum.

Your purified salicylic acid is likely still wet with water and therefore takes time to dry sufficiently before you can get a final weight of the product and an accurate melting point. To facilitate this, transfer the purified salicylic acid to a tared 100-mL beaker, label it and put the sample in the oven at 100°C for approximately 10 minutes – dry the sample to constant mass. Obtain an accurate weight measurement and the melting point of the final product. Record this information in your notebook. Comment on the appearance of your final crystallized product. What does the solid look like? Is it colored? etc.

Disposal of wastes: All filtrates and aqueous solutions go in the Aqueous Wastes bottle; filter papers, boiling stones, and boiling sticks go in designated waste beaker.

To Complete the Experiment – Full Report
Turn in your final purified salicylic acid in a labeled vial (compound name, weight of product, mp, date, and your name). Calculate your percent yield – (grams of purified salicylic acid)/(grams theoretical yield) x 100. For your conclusion, summarize the results of your experiment and be sure comment on the quality of your product – melting point compared to literature and appearance of the product (look up the entry in the Merck Index for a description of the solid compound). See full report handout for more details on what to turn in.

Answer the following questions:

1. How many moles of hydroxide are required for each mole of methyl salicylate used in the saponification reaction? Explain.

2. What is the purpose of adding the sulfuric acid solution and why does the pH need to be adjusted to 2?