Isolation and Identification of Orange-Peel Oil

The roots of organic chemistry are embedded in the substances derived from natural sources. The eventual realization that these "natural products" could also be synthesized from nonliving materials led to the overthrow of the vital force theory and the creation of the discipline we still call "organic" chemistry. The experiment in this chapter is representative of the isolation and characterization approach that was used then and now. The choice of orange peel is simpler than most natural product isolations in that the volatile material is mostly a single substance. The experiment is also artificial in the sense that instead of an unlimited number of possibilities you will be given a short list of 10 candidates, one of which is the major constituent of orange oil. With a little imagination, you can picture yourself isolating a marvelous unknown substance. It is, after all, unknown to you.

Isolation of Orange-Peel Oil

Assemble a steam distillation apparatus shown in Figure 16.1 using a 1000 mL round-bottomed flask as the boiler. Steam distillations on this scale require a lot of heat, more than a small heating mantle can provide. As a heat source, we will use a hot plate equipped with a 6 in.-diameter heat concentrator (a fancy name for a ring of sheet metal that reflects the radiant heat back onto the walls of the flask). To assemble the apparatus, start with the heat concentrator, and then build up the equipment in order. Use a two-prong clamp around the neck of the flask and a three-finger clamp around the Claisen adapter. Place your distillation head with thermometer on the side arm of the Claisen adapter and a glass stopper in the central arm of the adapter. Next add the water-cooled condenser. The condenser must be clamped to avoid having it fall off and possibly break. When you tighten the clamp on the condenser, be careful not to apply excessive force to the ground joints. This may require that you use a separate ring stand to support the condenser. Use a supported 125-mL Erlenmeyer flask as a receiver. Be careful in clamping the apparatus to not stress the joints.

Cut or tear the peel of one orange into thin strips, determine the weight to the nearest 0.1 g, and place the material in a blender. Add about 250 mL of water and blend for 15-30 sec. Transfer the resulting mash to the boiler flask. This is conveniently done by temporarily removing the distillation adapter and slowly pouring the mash through a wide-mouth funnel into the side arm of the Claisen adapter. Reassemble the distillation apparatus and heat as rapidly as possible without charring the contents or having the foam reach the condenser.

Collect about 100 mL of distillate in the 125-mL flask. Chill the distillate in an ice bath and then extract three times with 5-mL portions of mixed "hexanes." Dry the extracts with anhydrous MgSO4, filter through an filter tube containing a wad of glass wool into a preweighed 25-mL round-bottomed flask, and remove the mixed "hexanes" by simple distillation. For the determination of boiling point, to be described in the next section, it is important that all of the solvent be removed. From the weight of the residue calculate the yield of steam volatile products.

Waste Disposal. Squeeze the water from the orange-peel mash and dispose of it in the waste basket. Wash the drying agents down the sink. The distilled mixed "hexanes" should be placed in the "nonhalogenated solvent" waste bottle.
Identification of Orange-Peel Oil

(A) Chemical Analysis

The major component of orange oil is a hydrocarbon analyzing for 88.2% carbon and 11.8% hydrogen. You can assume that there are 10 carbons in the unknown on the basis that numbers of carbons in all ordinary terpene natural products are a multiple of 5 and that the vapor pressure of your unknown is inconsistent with either 5 (too volatile) or 15 (not volatile enough). What is the molecular formula of the unknown? The number of double bonds in limonene (and alkenes, in general) can be determined by quantitatively measuring the amount of bromine taken up by the double bonds. The persistence of the bromine color serves as an end-point indicator. We won't actually do the titration because of the hazards in using bromine and the problems of disposal of the residual wastes. Instead, we will tell you what observation you would have made if you had done it. When a solution of 0.20 g of this oil in CC1₄ was brominated with 0.50 M Br₂ in CC1₄, 6.0 mL of the solution was required. How many double bonds are there in the unknown?

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\text{C} = \text{C} + \text{Br}_2 \rightarrow \text{C} - \text{C} \quad \text{(brown)} \quad \text{Br} \quad \text{(colorless)}
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Table 16.1 is a selected list of possible hydrocarbons. Use the analytic data to narrow down the list. The final identity of the unknown contained in this short list can be determined from the boiling point of the unknown.

(B) Determination of Boiling Point
Determine the boiling point of your sample using a 6-in. test tube as the boiler clamped at an angle with the bottom resting in the Thermowell heater. Add your extract to the tube and clamp a thermometer so that the bottom is about 114 in. above the liquid and does not touch the wall of the tube. Add a couple of small boiling chips and heat until the sample refluxes gently on the thermometer and the thermometer reading stops rising. You may wish to calibrate your thermometer by determining the boiling point of water before you tackle your orange-peel oil sample. Ideally, your boiling point should eliminate all but one of the compounds in the short list. If you have any orange oil left over, hand it in to your instructor in a small vial labeled "orange-peel oil".

Questions
1. In order for a compound to be steam distilled it must possess two physical properties. What are they?
2. The vapor pressures of hydrocarbons 1 through 10 are about 140 mm at 100'. Calculate the ratio of water to hydrocarbon that would be collected if the steam distillation process were 100% efficient. Why might the efficiency of this steam distillation be lower than normal?
3. Write a balanced equation for the bromination of an alkene. Calculate the volume of 0.24 M bromine solution that would react with 0.04 g of hydrocarbon having three double bonds and a molecular weight of 136.
4. Which of the hydrocarbons 1 through 10 obey the isoprene rule (i.e., can be thought of as formal combinations of two isoprene skeletal units)?