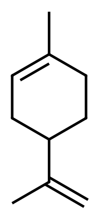
Analysis of (*R*)- and (*S*)-Limonene

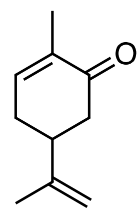
Reading *Pavia:* Essay on *Terpenes and Phenylpropanoids* (pg. 118), Essay on *Stereochemical Theory of Smell* (pg. 127), Techniques: 22 (especially 22.8), 23, Polarimeter instruction manual (Model SR-6), IR Sample Preparation Instructions

Introduction

Limonene is a naturally occurring chiral hydrocarbon found in the peel of citrus fruit as well as mint oils. Limonene is structurally similar to carvone, and like carvone, is produced in optically pure forms in nature and the two enantiomers have different odors.



limonene



carvone

Enantiomers cannot be separated by most common laboratory techniques including crystallization, column chromatography, and distillation. Chromatographic separation is possible if the stationary phase is composed of a single enantiomer of a chiral compound. Each enantiomer of the analyte will have a slightly different interaction with the chiral stationary phase—differing intermolecular attractions will cause one enantiomer to be retained by the stationary phase longer than the other, thus allowing for separation of the enantiomers. Most chiral GC and HPLC columns utilize a starch derived polysaccharide (cyclodextrin) as the chiral stationary phase.

Objectives

You will measure the optical rotation of pure samples of both the *R* and *S* enantiomers of limonene. As well, you will measure the rotation of a mixture (of unknown composition) of the two enantiomers. Using the optical rotation, you will calculate the enantiomeric excess of the mixture and percent composition of the mixture. The mixture will also be analyzed by chiral gas chromatography. You will compare the composition calculated from the optical rotation to the gas chromatography data. Finally, you will record infrared spectra of both enantiomers and you will be supplied with ^{13}C NMR spectra for both isomers.

Prelab

In addition to the usual **Title**, **Name**, and **Date**, include an **Objective Statement** (summary of the objectives of the experiment), structures of both enantiomers**,** a **Reagent Table** with all pertinent physical data for each of the enantiomers – especially the specific rotation - [α], and a **Procedure** (based on the text below).

Procedure

You should perform each of the test below – they can be performed in any order.

Odor—Carefully smell samples of pure *R* and pure *S* limonene. Use the wafting technique. Note your observations in your notebook.

Optical Rotation—Measure the rotation of ethanolic solutions of pure *R* and pure *S* limonene, as well as the rotation of the solution containing the mixture of enantiomers. The rotations should be measured to nearest 0.1^{o}. The solutions will be prepared by the instructors in advance and you will be provided with information that will allow you to calculate the concentration of the solutions. (You must read the manual to determine how to read the scale on our instrument to the nearest 0.1^{o}).

Gas Chromatography—Add five drops of the mixture of enantiomers to an autosampler vial. Fill the vial with methylene chloride to just below the threads at the top. Load the vial into the autosampler carousel and log your sample on the sheet.

Infrared Spectroscopy—Place one drop of either pure *R* or pure S limonene in the center of a salt plate then place a second salt plate on top. Record the infrared spectrum then repeat with the other enantiomer.

Completing the Experiment and the Report—A **Partial Report** will be collected for this experiment which includes the calculations described below. In addition to the calculations below, compare the IR and ^{13}C NMR spectra for the two enantiomers. Are there any similarities or significant differences?

Calculations

1. Calculate the specific rotation for both enantiomers, and the specific rotation of the mixture of enantiomers.
2. Calculate the optical purity (enantiomeric excess - %ee) of the mixture from the specific rotation values – use the value of the specific rotation for the enantiomer that is in excess for this calculation.
3. From the GC data, calculate the enantiomeric excess of the mixture.
4. Calculate the percent composition of the mixture from the enantiomeric excess.