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Laboratory Experiment

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Extraction of Maltol from Fraser Fir: A Comparison of Microwave-Assisted Extraction and Conventional Heating Protocols for the Organic Chemistry Laboratory

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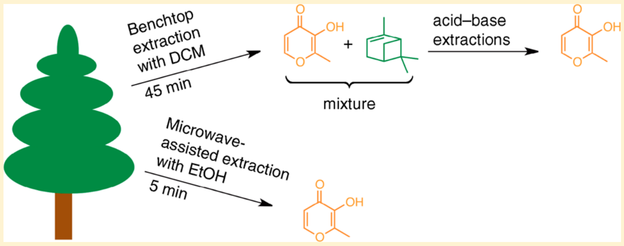
Ⓢ *Supporting Information*

ABSTRACT: Two methods for the extraction of maltol from Fraser fir needles are performed and compared in this two-week experiment. A traditional benchtop extraction using dichloromethane is compared to a microwave-assisted extraction using aqueous ethanol. Students perform both procedures and weigh the merits of each technique. In doing so, students see a trade-off between the ease of working with a highly volatile organic solvent and the selectivity that can be achieved with the greener solvent combination. This experiment combines multiple lab techniques, highlights the connections between chemistry and biology, and provides straightforward ^{1}H NMR spectra to support the introduction of spectroscopy in first-semester organic chemistry.



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Maltol (Figure 1) is found in many kinds of plant materials, including the needles of fir trees. It has a caramel-like odor and finds uses in foods, tobacco products, brewed beverages, cosmetics, and pharmaceuticals. A procedure featuring the extraction of maltol from Fraser fir needles has been adapted from published procedures of an analytical experiment to incorporate expanded use of NMR spectroscopy.[1] Students use ^{1}H NMR spectroscopy to confirm the structure of maltol. In the ^{1}H NMR spectral analysis, both chemical shift data and spin splitting data are used in the analysis. Needles of the Fraser fir contain approximately 1% maltol by mass.[2] The use of this natural source gives the experiment a biological and environmental connection that appealed to students.

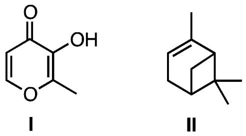

Figure 1. Structures of maltol (I) and α-pinene (II).

BACKGROUND

Microwave chemistry has been steadily making headway into the teaching laboratory curriculum as elsewhere in chemistry.[3−13] The development of dedicated laboratory instruments, which offer uniformity of heating, temperature profile control, and pressure-monitoring/relief, as well as explosion-safety features, has been central to the success of lab-based microwave techniques. Microwave instruments have been used most typically for organic synthesis, extraction, and digestion.

In this experiment, students are provided with an opportunity to perform extractions of the same compound via two distinct methods: Method A, a traditional benchtop extraction using dichloromethane at reflux, and Method B, a microwave-assisted extraction (MAE) using aqueous ethanol. Students consider the merits and drawbacks of both techniques and include such considerations in the discussion sections of their full written reports. The use of both extraction techniques allows for the greatest coverage of organic laboratory content. Learning goals include proper extraction techniques (solid−liquid, liquid−liquid, and acid−base extractions), as well as microwave heating techniques, and NMR spectral analysis.

This experiment is unique because it combines several desirable elements. The experiment catches the attention of students through a biological platform, which is attractive to them. The experiment utilizes a number of laboratory techniques, reinforces those already learned in previous experiments, and introduces new techniques. These techniques include the following: setting up a standard reflux, use of a separatory funnel, hot filtration, preparation of NMR samples, and use of a laboratory microwave reactor. The experiment demonstrates the relationship between structure and solubility. In addition, the experiment requires students to compare two

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extraction procedures directly and critically in their reports, thus encouraging reflective thinking.

This experiment elegantly highlights the structure−solubility relationship in organic molecules and can segue nicely into molecular modeling activities. The experiment also supports an earlier introduction to NMR spectroscopy in the lecture portion of the course. In its current form, this experiment has been successfully used for the last seven years by approximately 700 students and is one of the favorite experiments. The benchtop extraction experiment has been in constant use for over 10 years.

■ EXPERIMENT

Students work in pairs. The experiment requires two 3-h laboratory periods to complete.

Method A: Benchtop Extraction of Fraser Fir Needles in Dichloromethane at Reflux

In preparing for the experiment, students are given a handout that guides them through the sequence of operations with specific quantities of reagents. They are not given precise details of how the operations are performed, but develop a detailed procedure of their own prior to the start of experiment. They are assigned readings in the Zubrick text to aid them in the development of the procedures.[14]

Using dichloromethane (DCM) as a solvent results in a mother liquor that contains maltol, α-pinene, and small amounts of other nonpolar components (Figure 1). To isolate maltol from the co-extracted materials, a series of acid−base extractions are carried out using a separatory funnel (Scheme 1). ^{1}H NMR spectra of the crude extract and purified material are compared to determine if maltol has been successfully isolated from the co-extracted materials.

Method B: Microwave-Assisted Extraction of Fraser Fir Needles

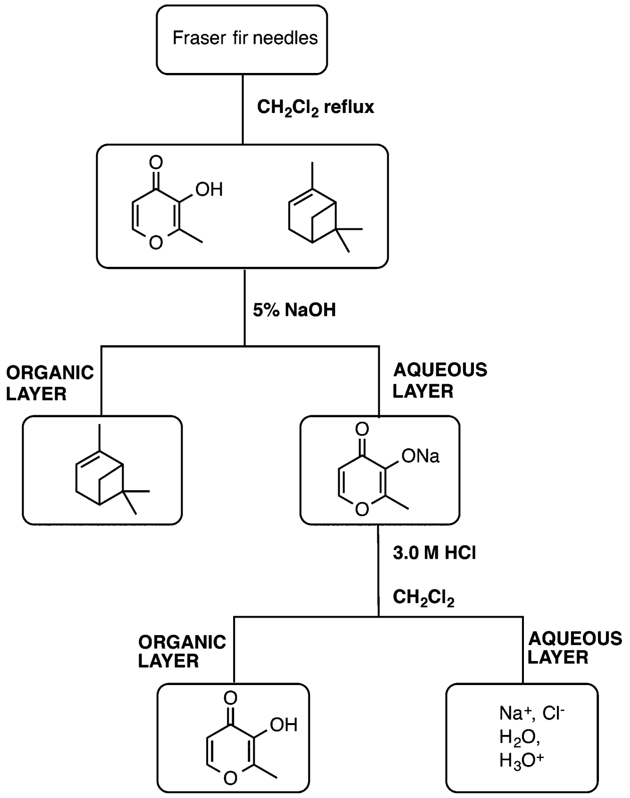
The MAE protocol is carried out while the benchtop extraction is at reflux. Aqueous ethanol is used as an extraction solvent that requires a shorter heating time, and does not co-extract α-pinene or other nonpolar components of the fir needles. Microwave samples are heated to 85 °C: ramp time 4.5 min, hold time 0.5 min, and cool down 10 min. Rotary evaporation of the aqueous ethanol affords a crude solid that students characterize by ^{1}H NMR spectroscopy. These results are compared to the results from the benchtop extraction procedure.

■ HAZARDS

Safety glasses must be worn at all times during the experiment. Gloves should be worn when handling solvents, and aqueous solutions of acid or base. Chemicals should be handled in a fume hood. Dichloromethane is an irritant, sensitizer and suspected carcinogen. Both sodium hydroxide and hydrochloric acid solutions will burn the skin and eyes. Pressure can build inside separatory funnels; be sure to vent frequently. Sodium sulfate has no significant warnings. Ethanol is volatile and flammable. Deuterated chloroform is a volatile suspected carcinogen, and irritant. Maltol and α-pinene do not have significant safety warnings. Both could be irritants; handle with gloves.

Microwave vessels should be correctly sealed to prevent chemical leakage. Read the entire operation manual for the microwave reactor that will be used. After heating, the microwave vessels are under pressure and quite warm to the touch; handle with care. Inside the microwave vessels, all solid material must be *completely* immersed in solvent to prevent hot spots and charring of material.

Scheme 1. Isolation Scheme for the Benchtop Extraction of Maltol



■ RESULTS

A ^{1}H NMR spectrum of purified maltol gave a readily interpretable example of spin coupling. Two aromatic doublets at 7.7 and 6.4 ppm and a methyl singlet at 2.3 ppm that integrate in a 1:1:3 ratio were easily interpreted (Figure 2). The hydroxyl signal was not generally seen without pretreatment of the NMR solvent, $CDCl_3$, with base.

For Method A, student recoveries typically ranged from trace amounts up to 20+ mg of material, which constituted a 0.05% recovery by mass out of a maximum theoretical recovery of 50 mg, or 1.0% of the Fraser fir needles by mass. Extraction times of up to 45 min were necessary in order to achieve a measurable amount of the desired compound. The crude extract contained a mixture of maltol and α-pinene, both of which were seen in a ^{1}H NMR spectrum (Figure 3 top). Following acid−base washes, signals due to α-pinene were absent from the ^{1}H NMR spectrum of purified material (Figure 3 middle), which appeared as a white or beige solid. Some aliphatic signals remained visible in the spectrum of the purified material and a water signal was often noticeable (Figure 3, top and middle).

For Method B, percent recoveries were typically not calculated. Instead, deuterated solvent was added directly to the round-bottom flask containing isolated maltol, and the resulting solution was transferred to an NMR tube. α-Pinene did not co-extract under these conditions. The ^{1}H NMR spectrum of the microwave extract (Figure 3, bottom) was noticeably simpler than the spectrum of the crude benchtop

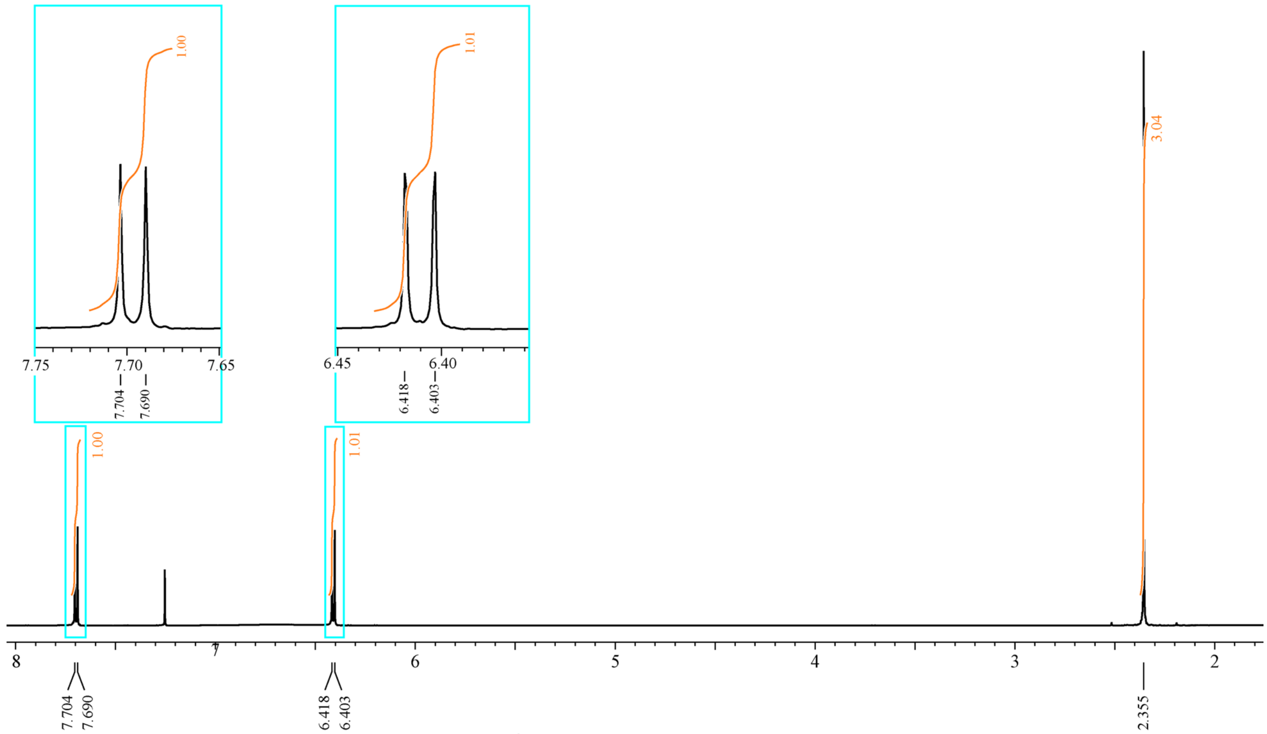


Figure 2. ^{1}H NMR spectrum of commercial maltol in $CDCl_3$.

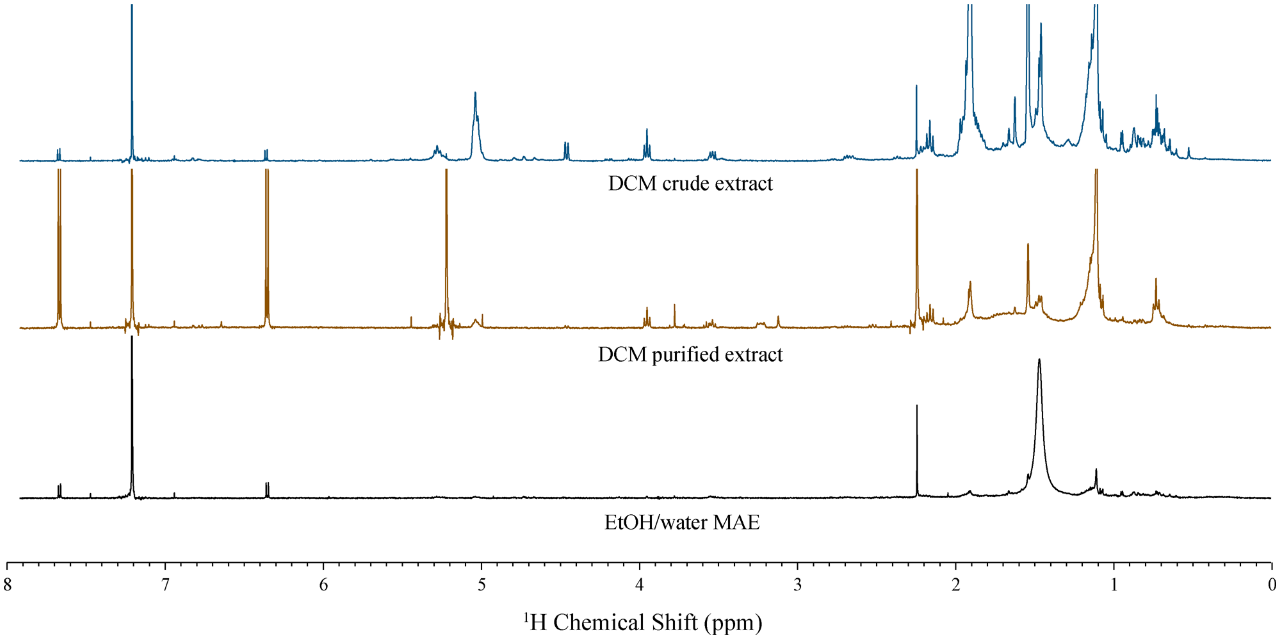


Figure 3. Typical ^{1}H NMR spectral data generated by students. (Top) The crude benchtop extract using DCM solvent. Peaks at 5.1 and 0.6–2.3 ppm are due to α-pinene. (Middle) The DCM extract after acid–base washes. The signal at 5.3 ppm is leftover DCM. Note the simplified aliphatic region. (Bottom) The crude MAE product using 50% aqueous ethanol solvent. The signal at approximately 1.5 ppm is water. No further purification was performed. Note the lack of signals due to α-pinene.

extract (Figure 3, top). A water peak was generally still visible at approximately 1.5 ppm.

■ DISCUSSION

Because this experiment occurred early in the first semester of introductory organic chemistry lab, students lacked confidence in the timely setup of a reflux. Students set up the reflux immediately and then set up a gravity filtration while the reflux was occurring in order to minimize downtime. The needles were rinsed with additional solvent after decanting the dichloromethane solution through filter paper to ensure a reasonable recovery of maltol.

Students noted the color and odor of the resulting solution. The solution should be colorless to pale beige and smell strongly of malt (beer, bread, etc.). A pale green solution, or a solution that smelled of pine, contained a relatively high amount of α-pinene. Students whose samples contained significant amounts of α-pinene needed to be diligent during the acid–base extractions in order to ensure that pure maltol was eventually isolated.

In the microwave procedure, the polarity difference between maltol and α-pinene was sufficient that, at elevated temperatures, maltol was much more soluble than α-pinene in ethanolic media. Aqueous ethanol evaporated in vacuo slowly. If time was a factor, the solutions were concentrated in vacuo and maltol was allowed to precipitate. The precipitate was filtered and dried before analysis.

The experiment has been quite successful despite generating very low recoveries by mass. Given that maltol constitutes only about 1% by mass of the Fraser fir needles, a fairly typical 20 mg recovery by mass constituted a 40% yield of the maximum amount recoverable (50 mg from 5 g of needles). The low yield has become a teaching moment to discuss the realities of harvesting chemicals from natural sources. All pairs of students were able to produce enough maltol from each extraction protocol for NMR analysis. In the case of Method B, the lack of signals other than those due to maltol in the crude extract highlighted the selective nature of the extraction.

The comparison of results from each procedure has always been an interesting and useful discussion with the students. In the benchtop procedure, a more volatile solvent was used, which simplified solvent evaporation. In the microwave procedure, students routinely commented that benefits included a greener solvent and a more selective extraction, which eliminated the need to use a separatory funnel. The drawback of the MAE procedure was that aqueous ethanol was more difficult to remove than dichloromethane, a trade-off that students were willing to pay for increased selectivity and increased environmental consciousness.

Analysis of the ^{1}H NMR spectrum for maltol provided a simple means to reinforce material presented very early in organic chemistry such as resonance, electron-donating effect, and electron-withdrawing effects and to connect those concepts with NMR spectral interpretation. These concepts were all covered in the specific assignment of the two aromatic signals at 7.7 and 6.4 ppm. The electron-withdrawing carbonyl functional group caused the beta proton to be more deshielded and to appear farther downfield in the spectrum. Likewise, the presence of the electron-donating pyran ring caused the proton α to the carbonyl to be more shielded and to appear farther upfield in the spectrum.

Students were assessed primarily on their written notebook entries, which included procedures, observations, and results, and their written discussion and conclusions, rather than on the percent recoveries obtained. Success was judged by the ability to write thorough observations, succinctly summarize results, and critically discuss those results. The complete discussion of these results included accurate assignment of ^{1}H NMR signals with reasoning, suggested explanations of low yields or lack of purity, and a rational examination of the benefits and drawbacks that each extraction method presented.

■ MODIFICATIONS TO THE EXPERIMENT

Modification 1

Over a two-week period, Week 1 could solely be spent on the benchtop extraction, Method A. In this scenario, students could finish the solid–liquid and liquid–liquid extractions by the end of the first week. Week 2 would then be dedicated to the MAE protocol and ^{1}H NMR analysis.

Modification 2

Molecular modeling using a program such as Spartan Student could be used to predict the dipole moments of maltol, α-pinene, dichloromethane, water, and ethanol. The predict values could then be compared to the observed relative solubilities of both maltol and α-pinene in the available solvents to further highlight the relationship between structure and physical properties.

■ CONCLUSION

The extraction of maltol from Fraser fir needles has routinely been a highly successful experiment. Typically, it has been the students' favorite experiment due to the high degree of success, the reinforcement of several lab techniques, and the simple, straightforward NMR data that were achieved. With the linking of typical organic laboratory techniques with a biological sample, higher levels of student interest have been observed, and students have appreciated the additional benefit of seeing one way in which organic chemistry fits into the world of biology. This experiment, more than any other, has fostered a curiosity about the connections between organic chemistry, biology, and sustainability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The written description of the experiment used by students, instructors' notes and sample NMR spectra obtained by students. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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