Synthesis of Sodium Myristate from Nutmeg

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Chem 213W, Spring 2018

Introduction:

Natural products are contained in many sources. These natural products have many uses, including treatment of diseases directly or as a starting point for the synthesis of particular drugs. In addition, natural products are used in colorants, food, flavors, fragrances, and preserving agents. The extraction of natural products is generally easier and cheaper than artificial synthesis, and is also generally more environmentally friendly than artificial synthesis, avoiding the use of potentially toxic catalysts or reagents. So, a major focus of organic chemistry is the extraction of natural products from their original sources.[1]

Nutmeg is a common spice made from the seed of the nutmeg tree. Aside from its use as a spice in a variety of cuisines, it is an important source of essential oils and nutmeg butter. In the interest of this experiment, it is a source of the natural product, trimyristin, a 13 carbon fatty acid chain triglyceride. Trimyristin can be extracted by heating ground nutmeg in an organic solvent, and then can be used to synthesize sodium myristate, a soap, by a simple saponification reaction. Sodium myristate has amphiphilic properties in that the carbon chain component makes it soluble in oils while the carboxylate component allows it to be soluble in water. Therefore, it acts as a surfactant, emulsifying oils so that they can be washed away with water. As a result, it is useful for household use in bathing or cleaning.[2]

In this experiment, trimyristin was extracted from ground nutmeg and purified by recrystallization. Then, the purified trimyristin was in a saponification reaction with sodium hydroxide, yielding the desired soap product, sodium myristate, and the byproduct, glycerol (Figure 1). It is known that esters undergo saponification into carboxylic acids when exposed to hydroxide. This reaction demonstrated the saponification of a triglyceride into three equivalents of the carboxylate salt sodium myristate.

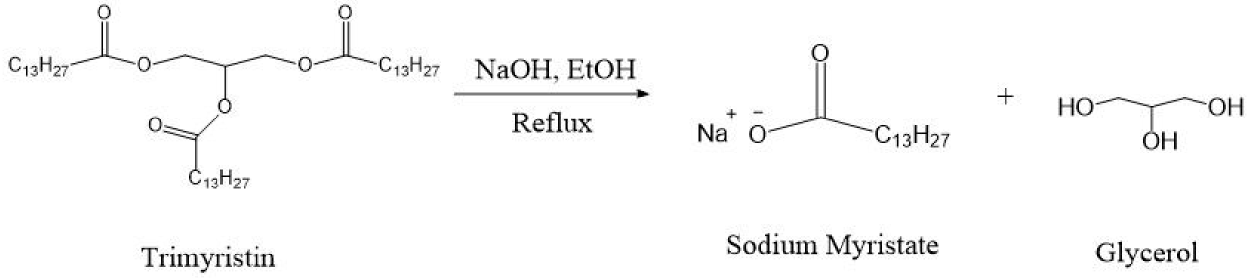

Figure 1. Reaction of trymyristin with NaOH

The mechanism for the formation of sodium myristate (Figure 2) begins with the nucleophilic attack of the hydroxide onto the carbonyl groups of trimyristin, forming a key tetrahedral intermediate. A lone pair on the carbonyl oxygen swings back into a π bond, cleaving the entire hydrocarbon chain. The same mechanism occurs on each of the three carbonyl chains of trimyristin, yielding three equivalents of the carboxylic acid. The carboxylic acid is deprotonated by the ethoxide anion from the deprotonation of ethanol to protonate the glycerol salt. The resulting two products are sodium myristate and glycerol.[3]

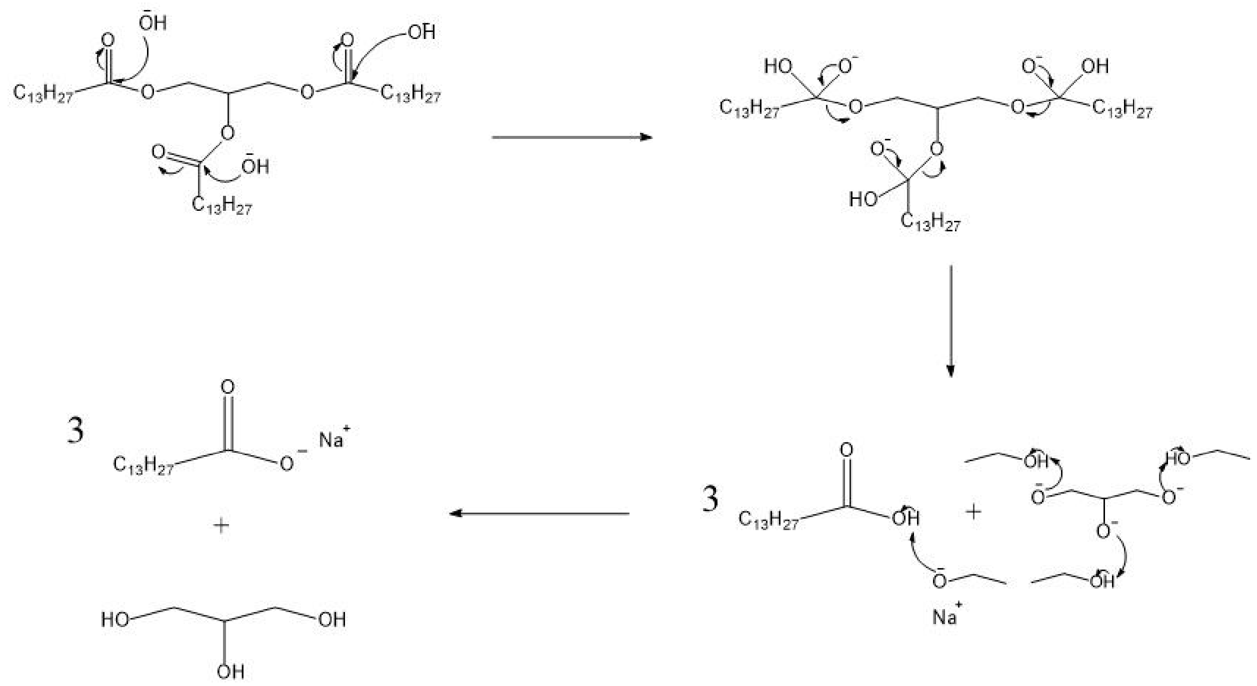

Figure 2. Mechanism of saponification of trymyristin with NaOH

Trimyristin was extracted from ground nutmeg by heating under reflux and purified by recrystallization. Then, the purified trimyristin was used to synthesize sodium myristate by saponification with sodium hydroxide. The product was characterized by qualitative tests with olive oil and iron (III) chloride as well as IR spectral analysis.

Results, Discussion, and Conclusion

The carboxylate product sodium myristate was synthesized via a saponification reaction between trimyristin extracted from ground nutmeg and sodium hydroxide. The extracted trimyristin was purified by recrystallization and the final carboxylate product was characterized by IR spectral analysis and qualitative experiments with olive oil and iron (III) chloride.

Extraction of the triglyceride trimyristin was a simple process. Ground nutmeg was simply heated under reflux in ether solvent. The heat released the trimyristin from the nutmeg, along with other compounds present in nutmeg. Ether was chosen as the solvent for the extraction because the polarity of the ether is similar to the polarity of the ester groups in trimyristin, therefore trimyristin was readily soluble in ether.

However, since nutmeg contains various other compounds other than trimyristin, the crude product from the extraction needed to be purified. Since the crude product was a yellow solid with small amounts of impurities, recrystallization was chosen as the purification method. The crude product melted at a low temperature, so care was taken to control the temperature of the recrystallization solvent. In addition,, excess solvent was used to dissolve the trimyristin, then some solvent was boiled off in order to ensure a better percent recovery. The percent recovery for the recrystallization of the trimyristin was calculated to be 52.3%, which still seems to be a very low recovery for recrystallization. Loss may have occurred from spillage during the recrystallization process, extra trimyristin sticking to the sides of recrystallization beakers, or still having excess solvent, meaning even more solvent needed to be boiled off before cooling. The percent recovery from the dried ground nutmeg was 22.36%. Typical trimyristin content in nutmeg is between 20-25%, so the percent recovery in this experiment seems to fit the expected percent recovery.[2] The melting point range of the purified trimyristin was determined to be 55.7 - 56.9 ℃, which is within the expected melting point range of trimyristin, which is 54 - 58 ℃. The accuracy of the melting range combined with the small melting point range supports the successful purification of trimyristin.[4]

IR analysis combined with the accurate melting range of the purified extract confirmed the identity. A very sharp and strong carbonyl peak was present at 1739.05 cm^{-1}, corresponding to the three carbonyl groups present in trimyristin.. In addition, strong scissor and aliphatic C-H peaks were present at 1450.78 cm^{-1} and 2916.44 cm^{-1}, respectively, which confirms the presence of long hydrocarbon chains. In the fingerprint region, carbon-oxygen peaks were visible at 1078.67 cm^{-1}, which correspond to the ester carbon-oxygen bond in trimyristin. These 4 peaks confirm the successful extraction and purification of trimyristin.

The saponification of the purified trimyristin involved the heating of trimyristin in the presence of sodium hydroxide. Solid sodium myristate was formed in a pasty white solid by the addition of sodium chloride, which allowed the myristate to precipitate as a solid by deprotonating the carboxylic acid product. The percent yield for the reaction was 164.7%. Typical percent yield for this reaction is greater than 100%, so the saponification seemed to be successful.[5] The high percent yield is accounted for by the side product, glycerol, which was not purified in any way.

IR analysis (Figure 1, supplemental information) of the product proved the successful formation of sodium myristate. Two strong C-H peaks are present at 2919.77 cm^{-1} and 2848.01 cm^{-1}. The intensity of these peaks confirms the presence of long hydrocarbon chains, which are present in sodium myristate. However, these peaks are present in almost all organic molecules, so they do not confirm the formation of sodium myristate. The key identifier is the salt carbonyl peak at 1558.04 cm^{-1}. The lower absorption than normal carbonyl peak indicates the presence of a carboxylate, since resonance on the carboxylate decreases the double bond character on the carbonyl and therefore decreases the absorption. Had there been leftover trimyristin reactant, the carbonyl peak would have been at a higher absorption, at around 1735 cm^{-1}. No peak was present in this IR spectrum, indicating pure sodium myristate was formed.[6] Umbrella bend peaks are also present at an absorption of 1443.42 cm^{-1}, which confirms the presence of methyl groups at the end of the hydrocarbon tails of sodium myristate.

Finally, qualitative experiments were performed on the sodium myristate. The first was to dissolve some sodium myristate in water, and add a few drops of olive oil. At first, since oil is immiscible in water, the oil simply sat on top of the water layer. However, after vigorous shaking, the oil broke up and no oil layer could be observed on top of the water layer. This qualitative experiment demonstrated the efficacy of soap as a surfactant, as the sodium myristate was able to emulsify the oil. By forming an emulsion, sodium myristate demonstrates the practical application of soaps, which can be used to clean stuck-on oils off of surfaces such as skin, dishes, or clothing. Normal oils that are immiscible in water are hard to wash off. The emulsion that forms upon the application of soaps such as sodium myristate is easily washed off with water. The next qualitative experiment was to use the same sodium myristate solution and add a solution of iron (III) chloride. Upon the addition of the solution, which was a dark yellow color, the solution became a dark and cloudy reddish brown color. The cloudy nature of the solution indicated the formation of iron myristate solid. This experiment demonstrated a pitfall with soap. When soap is mixed with hard water containing ions such as iron or calcium, the carboxylate precipitates, forming a hard solid precipitate that is known by the common name, soap scum. To counter this problem, households use water softeners that break up the soap scum. Water softeners contain anions that help dissolve the hard ionic precipitates.[7]

In conclusion, trimyristin was successfully extracted from ground nutmeg at a percent extraction of 22.36%. Crude trimyristin extract was purified by recrystallization with a percent recovery of 52.3% and then characterized by IR spectral analysis. The purified trimyristin was saponified with sodium hydroxide to form sodium myristate upon precipitation with sodium chloride. The percent yield for the saponification was 164.7%. Future experiments could target to improve the yield by purifying the sodium myristate of glycerol byproduct. Given the large amounts of impurities in the product, experiments with column chromatography could be attempted to separate the glycerol.

Experimental:

Ground nutmeg (10 g) was added to diethyl ether (30 mL) and stirred and heated under reflux for 30 minutes. The nutmeg was removed via vacuum filtration and washed with diethyl ether (2X 20 mL). The ether filtrate was evaporated under a stream of nitrogen, leaving yellow solid crude trimyristin. The crude trimyristin was purified by recrystallization (95% ethanol, 20 mL), and the purified trimyristin was collected with vacuum filtration and washed liberally with chilled ethanol (95%, 100 mL). IR ν_{max} (cm^{-1}) 2916.44, 1739.05, 1450.78, 1078.67. Purified trimyristin (200 mg, 0.276 mmol) and NaOH (40 mg, 1.0 mmol) were added to 95% ethanol and stirred and heated under reflux for 30 minutes. The warm solution was then transferred to distilled water (5 mL) and saturated NaCl solution (10 mL) and stirred to form sodium myristate, a thick paste. The solid sodium myristate was collected with vacuum filtration. Dried sodium myristate (0.25 g) was dissolved in distilled water (25 mL). Olive oil (5 drops) was added to the sodium myristate solution with vigorous shaking. Separately, iron (III) chloride solution (1%) was added with gentle agitation. IR ν_{max} (cm^{-1}) 2919.77, 2848.01, 1558.04, 1443.42, 1423.15.

References

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Supplemental Information

Figure 1. IR spectrum of sodium myristate

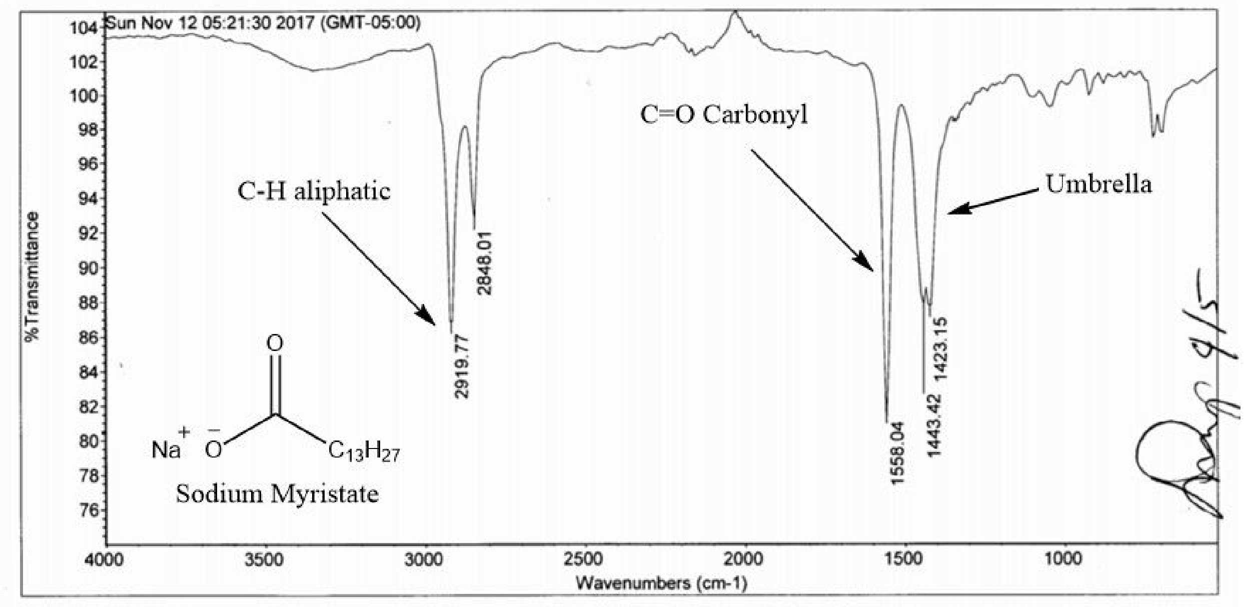

Figure 1