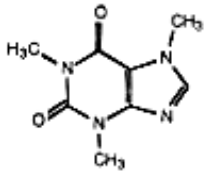
NS207 Lab 3 - ISOLATION OF CAFFEINE FROM TEA

Introduction

The use of tea as a stimulant dates back more than 2000 years. Its use became widespread in China around 700 A.D. and traders introduced it into Europe. The active ingredient in tea is caffeine (1).



1

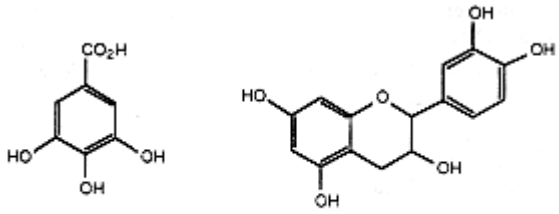
Caffeine belongs to a large group of natural products that contain nitrogen and have basic properties. They are thus based upon ammonia (NH_3), which is also basic and can be considered a parent structure for these compounds. This group of natural products is called alkaloids.

Many alkaloids like caffeine have profound effects on the central nervous system. Many are mild stimulants. Moderate consumption of coffee or tea appears to be relatively harmless even over a lifetime. The toxicity of caffeine is quite low and the lethal dosage required to kill 50% of test rats (LD_{50}) is in fact 200mg/kg of body weight. Heavier users of caffeinated products (greater than 5 cups/day) can develop a tolerance and dependence. Withdrawal symptoms include headaches and lethargy.

Caffeine occurs naturally in tea, coffee and kola nuts. The weight fraction of caffeine to tea or coffee can vary from between 2-5% depending on the source and quality. Decaffeinated coffee, prepared by extracting whole coffee beans with trichloroethylene, methylene chloride or supercritical carbon dioxide, generally contains much less than 1% caffeine. Caffeine can also be found in many headache remedies as a co-ingredient of acetylsalicylic acid (ASA). The ASA suppresses the headache, while the caffeine component acts as a mild stimulant to make the individual feel better. The active ingredient in NO-DOZE® is also caffeine.

Isolation of caffeine from tea

Tea contains many organic substances that give rise to its taste and aroma. The chemical components, which give various teas and coffees their characteristic taste and smells, are present in very small concentrations. These will not interfere with the isolation procedure of caffeine. Tealeaves also contain significant amounts of cellulose, which is not soluble in water and a variety of complex compounds called tannins (used to tan leather). These compounds contain hydroxyl groups attached to a benzene ring. Such compounds are called phenols. The tannins by virtue of the phenolic group are slightly acidic and can be converted into salts by treatment with bases such as $CaCO_3$ or Na_2CO_3. The resulting salts are no longer soluble in organic solvents and thus do not interfere with the caffeine isolation.



gallic acid catechin

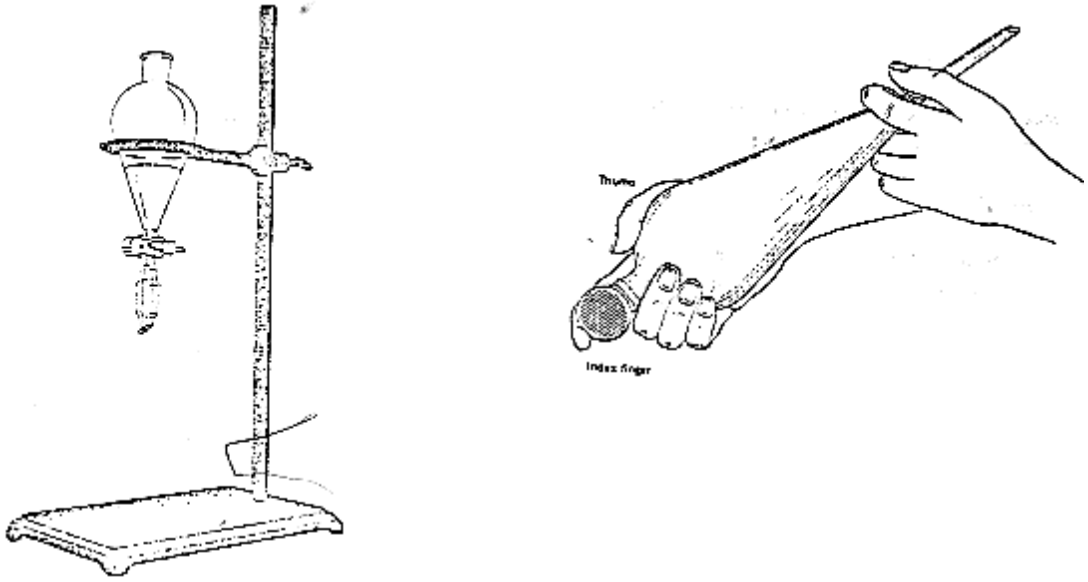
In the naturally occurring tannins the carboxyl group (COOH) of gallic acid is esterified with one of the hydroxyl groups of glucose.

EXPERIMENTAL PROCEDURE.

Dissolve 10g of $CaCO_3$ in 350ml hot water in a 500ml beaker and add 10 tea bags. Heat the mixture on a hot plate for about 20 minutes. Swirl the flask from time to time to promote the

Manipulations of a separatory funnel

a) supporting b) shaking



extraction of caffeine into the aqueous base. Filter the dark, still warm mixture through a Gooch-type filter and into a 500ml Erlenmeyer flask. Use a spatula to press as much of the liquid as possible out of the tea bags. Yani, you should end up with approximately 200ml of liquid. Cool the flask containing the filtrate in cold water to approximately room temperature. Add 25ml of methylene chloride to the dark solution and pour the mixture into a 500ml separatory funnel. If you are uncertain on the proper use of a separatory funnel, please inquire (yani, consult your demonstrator).

Gently swirl the contents of the funnel (30s) to extract the caffeine into the organic phase. Please note that we normally shake separatory funnels vigorously, however, in the case of this experiment, vigorous mixing as opposed to gentle stirring produces an emulsion. Emulsions are problematic, as they interfere with an efficient separation. In this respect, gentle stirring as opposed to vigorous shaking restricts the amount of emulsion formed to a manageable level. After swirling the contents for 30s, allow the layers to separate over a 5-minute period. Draw off (draw off = collect from the base) the methylene chloride layer (bottom, lightly colored layer) into a beaker. Try to avoid drawing off any residual parts of the emulsion.

Add 25ml of methylene chloride to the separatory funnel and repeat the extraction process. Combine the methylene chloride extracts. Repeat the extraction with a 3rd 25ml portion of methylene chloride and combine the methylene chloride extracts.

Add 2-5g of anhydrous sodium sulfate to the methylene chloride solution and swirl the beaker. This will remove any residual water from the organic phase. You can see that the solution becomes drier and drier (yani, you can tell when you've added enough drying agent) because some of the salt particles will float about loosely, giving the appearance of being non-sticky. Also, the solution becomes clear, while the original is hazy.

Take a conical funnel and plug its hole with a wad of cotton or glass wool. Alternatively, use some filter paper. Filter the dichloromethane solution through the funnel under the influence of gravity and collect the filtrate into a **previously** tared 100ml beaker or Erlenmeyer flask. Evaporate the solvent in the fume hood over a warm hot-plate (be careful! be conscious that organic solvents may be combustible!). Once dried, determine the weight of your crude caffeine. You should obtain 50-250mg of the slightly greenish solid.

Recrystallization
Dissolve the crude solid in a minimum amount of hot acetone (5-10ml). Cool the solution in an ice bath to induce crystallization. Collect the product by suction filtration through a Buchner funnel or Gooch funnel. Allow the colorless material to air-dry.

Analyses
Determine the weight and melting point. The literature melting point of caffeine is 238°C. Submit a portion (20mg) for ^{1}H-NMR and ^{13}C-NMR analysis (Room L022). Verify your caffeine sample against a commercially available standard caffeine sample using thin-layer chromatography. For this purpose, use a developing solvent of the composition ethyl acetate/methanol 19:1.

QUESTIONS
1. 1g of caffeine can be dissolved in 46ml of water at room temperature. In contrast, 1g of caffeine dissolves in 5ml of dichloromethane at room temperature.
a) Calculate the distribution coefficient of caffeine between water and methylene chloride.
b) How much caffeine would be extracted from 250ml of water containing 500mg of caffeine with one portion of 100ml of methylene chloride?
c) How much caffeine would have been extracted if two 50ml portions of methylene chloride had been used in part (b) above?
d) How much caffeine would be extracted using four 25ml portions?
Please note that several extractions using small amounts of solvent is more efficient than one single extraction using an equivalent total amount of solvent.

2. The solubility of caffeine in diethyl ether is 1g/530ml. How much caffeine can be extracted from 1L of water by a single extraction of 500ml of ether?

3. Suggest a reason why caffeine is much less soluble in a solvent such as hexane than in methylene chloride.