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CHEM 370-M

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Natural Products from Sandalwood Essential Oil

Introduction:

For centuries people have isolated and extracted essential oils found in the bark, seeds, roots, and leaves of plants. These oils, known as the “essence” of the plant, have been isolated by several methods including a solvent extraction, and more commonly by steam distillation. These oils, known as the “essence” of the plant, have uses varying from medicines to aromatherapy and perfumes. Some examples include the analgesic medication, Morphine, derived from the Opium Poppy, and the essence of dill seeds, limonene, used commonly in perfumes and other fragrances.

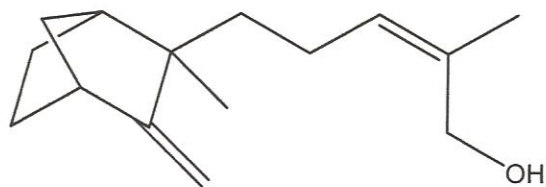
Sandalwood is a small evergreen tree with pink flowers found in East India, Taiwan, and Indonesia. The yellowish essence derived from Sandalwood has been used by several cultures for aromatherapy purposes, as a fragrance/incense, and even as a medicine for the immune system to aid in stimulating new growth of white blood cells. Sandalwood essence is typically isolated using steam distillation, where super-heated steam is forced through the wood chips liberating the oil from the wood and clutching the oil in vapor form up the distillation column. The overall yield of Sandalwood essence is dependent on both the duration of the distillation, and also the type of wood used. The heartwood, found either in the root or inner core of Sandalwood, is more essence rich than that of the outer wood or bark, therefore producing a higher yield.

As with other essential oils, after the steam distillation process the Sandalwood essence yields a mixture of several different compounds, which is why it is considered to be an unpurified crude oil. Both α -santalol, and β -santalol are known to contribute the majority of the essential oils aroma and character, so therefore the two compounds together are considered the target molecule. If given enough time, the target product (α -santalol and β -santalol) could be separated from the crude oil by flash column chromatography. The crude essence of sandalwood contains α -santalol, β -santalol, α -santalene, β -santalene, α -santalyl formate, and β -santalyl formate, as stated earlier. All of these compounds are similar in weight and structure, the major difference between them, however, is their polarity. In order to purify the crude essence and isolate the target compounds, a flash chromatography column containing silica gel must be used to separate the compounds based on each compounds polarity. Having almost identical polarities, α -santalol, and β -santalol will travel down the silica gel at a similar rate and therefore be collected and isolated.

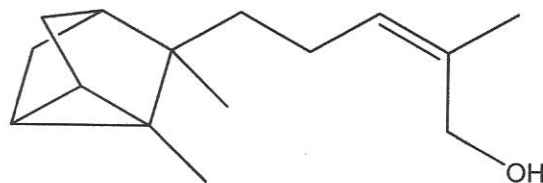
- α -santalol and β -santalol are the most polar molecules in the crude oil due to the alcohol substituent. The alcohol increases the molecules polarity since it is capable of being hydrogen bonding acceptor and donator. This high polarity will cause the molecules to travel down the polar silica gel the slowest and would come out last.
- α -santalene and β -santalene are almost identical in structure to the santalols, except the alcohol group is replaced with a another double bond. Without a alcohol substituent, the compound dramatically decreases in polarity. This non-polar molecule therefore travels down the flash column the fastest and also gives it the highest RF value.
- α -santalyl formate and β -santalyl formate are also similar in structure to the santalols except the alcohol substituent is replace with an aldehyde. Since aldehydes are only capable of being a hydrogen bonding acceptor, the polarity of this molecule decreases in comparison to the santalol groups but not as much as the santalenes. Therefore, the formate groups travel down the silica gel faster than the santalols but slower than the santalenes.

After all of the crude oil passes though the flash column and into separate test tubes, a TLC plate on every test tube is performed to ensure which contain compound. When the test tubes with compounds are isolated based on different RF values, a HNMR can be ran on the combined test tubes to detect which functional groups are present.

Experimental:



β -santalol



α -santalol

Heartwood Table of Reagents:

Compound	MW(g/mol)	Grams	Density (g/cm ³)	BP (°C)
Sandalwood		124.46		
Crude Essence		2.96-product	>1	>200

- Distilled for 150 min total.
- Percent crude product yield: $(2.96 \text{ g}/124.46 \text{ g}) \times 100 = 2.38\%$

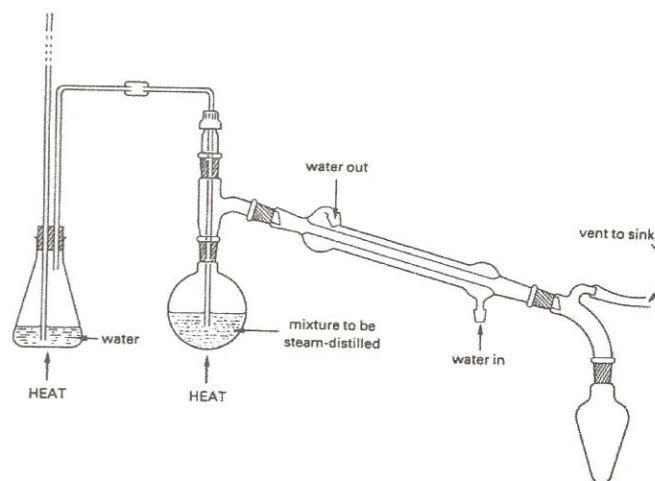
Outer wood Table of Reagents:

Compound	MW(g/mol)	Grams	Density (g/cm ³)	BP (°C)
Sandalwood		99.87		
Crude Essence		1.1-product	>1	>200

- Distilled for 150 min total
- Percent crude product yield: $(1.1 \text{ g}/99.87\text{g}) \times 100 = 1.10\%$

Procedure:

- 1) Pre-Weigh round bottom flask and funnel in sandalwood chips.
- 2) Construct a steam distillation apparatus (illustrated on right).
- 3) Begin distilling process for a long period of time monitoring the temperature and steam levels.
- 4) As the distillation continues, collect a portion of the distillate to confirm some sort of product.
- 5) Extract Product with hexanes in separatory funnel, then dry over MgSO_4 , and filter into a small round bottom flask.
- 6) Rotary Evaporate the solution to remove solvent, then perform H-NMR, Mass Spec, and TLC plate testing to crude product. (If product confirmed, go back to step 4 and repeat steps of the remainder product to maximize yield).
- 7) Set up and perform Flash Column Chromatography to separate the combination of compounds in crude product.
- 8) Based on RF values, separate target compounds, α -santalol and β -santalol, and put in round bottom flask to rotary evaporate solution.
- 9) Perform same analysis as in step 6, to confirm the target product.
- 10) Put all product in same pre-weighed RB flask as step one and record target weight.



(Procedure is the same for both outer and heartwood)

Spectroscopy Analysis:

Mass Spec: Received several peaks ranging from 7.067 to 15.555 minutes with the most abundant peaks occurring around 9.25 and 9.5 minutes

- Peak at 9.25 min: final peak at 220 m/z which confirms mass of either α -santalol and β -santalol. This accounts for 29.711% of the total oil based on the percent area report.
- Peak at 9.504 min: final peak at 220 m/z which confirms mass of either α -santalol and β -santalol. This accounts for 20.181% of the total oil based on the percent area report.

H-NMR: After multiple attempts at running an H-NMR sample of the crude essence, every sample came out imprecise and difficult to analysis. This is due to the fact that there is a total of six different molecules in the compound, making it hard to detect which peak belong to which molecule. The samples with the most defined peaks are defined:

- Peak at 10.2 ppm indicating the presence of a carbonyl group. This is assigned to the bond to aldehyde on α -santalyl formate, and β -santalyl formate.
- Several peaks ranging from 5 to 6 ppm which is typical for hydrogens bonded of carbon- carbon double bonds. There is at least one double bond on each of the six molecules in the compound each can be found in this region.
- Triplet peak at 4.3 ppm which is assigned to the hydrogen bonded beta carbon to both the alcohol and carbon-carbon double bond on α -santalol and β -santalol.
- Single peak at 3.5 ppm assigned to the alcohol group on α -santalol and β -santalol.
- Multiple peak found between 1 and 2.5 ppm which are typical of C-sp³ carbons assigned on each compound and the closer in proximity to either an alcohol, aldehyde, or carbon double bond, the higher the ppm.

TLC: Diluted crude oil in 5:1 Hexane/ EtOAc then placed in TLC jar with 5:1 Hexane/ EtOAc used as the solvent. After drying and heating, three elongated spots were shown. Each of these spots were slightly elongated which is due to the α and β version of each compound being similar but slightly different in polarity causing an almost smear look (Even after diluting the compound 10:1).

RF of first spot= $1.1 \text{ cm} / 5.35 \text{ cm} = 0.21$

- First Spot is assigned to α santalol and β -santalol since these compounds are the most polar, they dissolve in the silica gel the fastest giving the lowest RF.

RF of second spot= $1.9 \text{ cm} / 5.35 \text{ cm} = 0.35$

- Second Spot assigned to α -santalyl formate, and β -santalyl formate since these compounds are the next most polar giving the middle RF value.

RF of third spot= $3.1 \text{ cm} / 5.35 \text{ cm} = 0.58$

- Third spot is assigned to α -santalene and β -santalene since these compounds

Conclusion:

Although, the time necessary to isolate the target compounds was not provided, the crude essence of Sandalwood was successfully extracted. After steam distillation was performed on both the heart and outer wood, a total of 3.48% yield was extracted from 224.33 grams of wood chips. These low yields prove how inefficient the steam distillation process is, and provides an explanation to why sandalwood essence is so expensive. The low yield though steam distillation is accounted for by the fact that sandalwood essence has a slightly higher boiling point than water, so when steam vapor hits the sandalwood the majority of the vapor collected is water. In order to increase the percent yield of essential oil either a soxhlet or hexanes extraction could be performed on the wood chips. These methods, however, tend to be more tedious and consume a larger period of time.

After using the steam distillation method for identical amounts of time on both the heart and outer wood, the heart wood proved to be the greater contributor. Out of the 3.48% of the total yield of Sandalwood's crude essential oil 2.38% came from the heartwood, whereas only 1.1% was extracted from the outer wood. Not only was the yield much higher for the heart wood, the essence produced was much darker in color and had a more intense aroma to it. The increase in concentration of the heart wood could be explained by the fact that it contains a higher percentage of the santalol products; however these target compounds were not successfully isolated from the crude essence.

DATA ANALYSIS OF VOLATILE OIL OF SANDAL WOOD (WS HW7 TO HW9 18-1-11) ON THE BASIS OF GCMS POLAR COLUMN
S.NO. COMPONENT

	WS001 HW7	WS002 HW8	WS003 HW9
1 OIL YIELD %	0.0124	0.0484	0.047
2 SANTALENE <ALPHA>	0.0006	0.0017	0.0014
3 SANTALENE <EPI BETA>	0.0008	0.002	0.0016
4 SANTALENE <BETA>	0.0014	0.0032	0.0027
5 CURCUMENE <BETA>		0.0006	
6 CURCUMENE<AR>	0.0007	0.0008	0.0009
7 SANTALOL <Z> ALPHA	0.4547	0.4062	0.4159
8 BERGAMOTOL <Z> ALPHA TRANS	0.0538	0.0588	0.0664
9 FARNESOL	0.0075	0.0066	0.0083
10 CEDREN-13-OL	0.0035	0.0038	0.0038
11 SANTALOL <Z> EPI BETA	0.0358	0.0292	0.0297
12 SANTALOL <Z> BETA	0.1936	0.175	0.1894
13 LANCEOL	0.0257	0.0732	0.0913
14 NUCIFEROL	0.0713	0.0727	0.0859

Table 1: Essential oil Analysis of Hawaiian wood samples

	WS/11/005	WS/11/006	WS/11/007	WS/11/008	WS/11/009	WS/11/010
	Primary Heartwood	Secondary Heartwood	Whole Butt	Dark Root	Light Root	Sapwood
Percentage yield (%w/w)	3.19	1.77	2.22	0.87	0.94	0.18
<i>cis-α-trans</i> -bergamamol	0.37	0.37	0.49	0.45	0.83	0.53
<i>cis-α</i> -santalol	54.60	53.71	53.47	53.19	48.08	53.11
<i>epi-α</i> -bisabolol	4.48	6.41	5.11	6.67	7.24	7.11
<i>epi-β</i> -santalol	4.37	3.83	5.26	5.22	5.10	5.13
<i>cis-β</i> -santalol	23.94	24.13	24.01	24.45	20.50	24.67
<i>cis</i> -nuciferol	0.14	0.17	0.25	ND	0.76	0.21
<i>trans</i> , <i>trans</i> -farnesol	1.37	1.55	1.75	1.73	2.57	1.77
<i>cis-γ</i> -curcumen-12-ol	2.77	2.91	4.60	4.70	7.14	4.29
<i>cis-γ</i> -curcumen-12-ol	1.03	0.84	0.58	0.21	0.71	0.57
<i>cis</i> -lanceol	0.62	0.44	0.49	0.33	0.45	0.36

* ND – Not detectable (below the detectable range= <0.15%)