

## Isolation of essential oil from lauraceous leaves and Schiff's reaction based cinnamaldehyde derivatization

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### Abstract

The barks of Cinnamomum species found to contain essential oil, namely, *Cinnamomum zeylanicum*, *C. camphora*, *C. tamala* etcetra. The major component is Cinnamaldehyde. Essential oils from leaves of Lauraceae family have not yet been isolated. It was therefore thought to isolate essential oils from leaves of mentioned species and check presence of Cinnamaldehyde presence. It was found that Cinnaldehyde is found only in *C. zeylanicum*.

At same time, as Cinnamaldehyde is a chief constituent present in Cinnamomum species; it was observed that Cinnamaldehyde has been derivatized to make Schiff's bases for very few compounds. For example, Cinnamyl chitosan Schiff base was prepared by coupling chitosan with trans-Cinnamaldehyde -the main component of cinnamon oil- under acidic conditions to form cinnamyl chitosan Schiff base. Therefore, it was further thought worthwhile to derivatise Cinnamaldehyde with available Substituted amines available in the local market followed by physical characterization.

**Keywords:** *Cinnamomum zeylanicum*, *C. camphora*, *C. tamala*, Cinnamaldehyde, Essential oils, Clevenger Apparatus, LC-MS, Schiff's bases.

### Introduction

The odorous, volatile principles of plant and animal sources are known as volatile oils. As they evaporate when exposed to air at ordinary temperatures, they are also called as ethereal oils. They represent essence or active constituent of plant, hence they are also known as essential oils. Chemically they are derived from terpenes and their oxygenated compounds. They are made up of isoprene units (C<sub>5</sub>H<sub>8</sub>) and are usually mono, sesque and diterpene with empirical formulae as C<sub>10</sub>H<sub>16</sub>, C<sub>15</sub>H<sub>24</sub> and C<sub>20</sub>H<sub>32</sub> respectively.

They are soluble in alcohol and ether while insoluble in water. They are usually lighter than water. Most of them are optically active. They are present in entire plant or in any part of plant. They are commonly found in species of Lauraceae, Labiatae, Myrtaceae, Piperaceae, Rutaceae, Umbelliferae and Zingiberaceae. Essential oil is a product made by distillation with either water or steam, solvent extraction or by mechanical processes like Eculle or Enflourage. Following the distillation, the essential oil is physically separated from the water phase. In case of leaf drug, fresh material is subjected to hydro-distillation.

Schiff bases (also known as imine or azomethine), named after Hugo Schiff, and was reported in the 19<sup>th</sup> century by Schiff (1864). Since then variety of methods for the synthesis of imines has been described. The classical synthesis is when any primary amine condenses with a carbonyl compound, under specific conditions (for example, azeotropic distillation), according to the following equation:



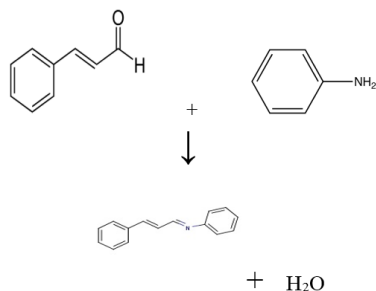
Structurally, a Schiff base is a nitrogen analog of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. An imine is a functional group or chemical compound containing a carbon–nitrogen double bond, with the nitrogen atom attached to a hydrogen atom or an organic group.

Aromatic aldehydes, especially with an effective conjugation system, form stable Schiff bases, whereas those aliphatic aldehydes are unstable and readily polymerize. Schiff base ligands with aldehydes are formed more readily than with ketones. Their chemical and physical properties in various fields such as preparative uses, identification, or protection, and determination of aldehydes or ketones, purification of carbonyl or amino compounds, or protection of these compounds in complex or sensitive reactions have been studied by various workers. Cinnamaldehyde occurs naturally in the bark of *Cinnamomum zeylanicum* family Laureaceae.

The important uses of cinnamaldehyde are fungicide, mild astringent, antimicrobial, anti-inflammatory, anti-septic etc. Cinnamaldehyde is an aromatic aldehyde. The main advantage of cinnamaldehyde is that direct contact is not required for being active as antimicrobial. Cinnamaldehyde has been shown to be active against a range of forborne pathogens bacteria. Cinnamaldehyde can be separated from commercial cinnamon sticks via steam distillation. Wash with aqueous NaOH should get rid of the eugenol. Distillation of the solvent should then give pure enough cinnamaldehyde to be used as starting material for the following synthesis.

An interesting imine can be synthesized from cinnamaldehyde by its condensation with aniline. The

formed imine is greatly conjugated and should have a bright orange colour.



The above scheme can be used for synthesis of various derivatives of Cinnamaldehyde with substituted aromatic amines.

### Objectives

1. To isolate essential oil from leaves from *C. zeylanicum*, *C. camphora* and *C. tamala*
2. To analyse oils by Liquid Chromatography and Mass Spectroscopy Method
3. To derivatize Cinnamaldehyde with substituted aromatic amines

### Materials and Methods

**Collection of Plant Material, Glasswares and Chemicals:** For present study, leaves of all three selected species of *Cinnamomum* (*C. zeylanicum*, *C. camphora* and *C. tamala*) from Oriental Herbal Garden. The leaves then identified, confirmed and authenticated by Prof. H.M. Pandit, Department of Botany, Khalsa College, Mumbai. The glasswares were purchased from Neha Enterprise, Mumbai. All the chemicals and reagents used in synthesis were of analytical grade and purchased from Camy Labs, Mumbai.

**Extraction of volatile oil:** About 100gms of fresh leaf sample of each species was accurately weighed and transferred to a 500 ml round bottom flask. Sufficient amount of water was added and the Clevengers Apparatus then attached to round bottom flask with the condenser and mixture was heated for six hours so as to isolate the volatile oil. The volatile oil of individual drug was then graduated tube of Clevenger Apparatus and separated and stored in vials. **Table 1.**

**Spectral Analysis of oils:** The three oils obtained then analyzed by LC-MS Method at IIT Pawai, Mumbai. The chemical constituents found in isolated oils are as follows.

*Cinnamomum zeylanicum* contains approximate components identified are 17 in numbers. The main chemical components of the essential oil are eugenol, eugenol acetate, cinnamic aldehyde and benzyl

benzoate. *Cinnamomum camphora* contains approximate components identified are 28 in numbers. Major components are camphor, caryophyllene, cymene, eugenol, linalool, methylamine ketone, phellandrene, pinene and many others. *Cinnamomum tamala* contains approximate components identified are 19 in numbers. Major components are linalool, 1, 8-Cineol, alpha-Pinene. List of constituent present in *Cinnamomum* species are mentioned in **Table 2.**

**Preparation of derivatives:** The synthetic route is represented in above Scheme

1. Synthesis of Phenyl-(3-phenyl-allylidene)-amine: Cinnamaldehyde (0.01 mol) and Aniline (0.01 mol) were refluxed in 50 ml of n-Hexane. Melting point-90 °C.
2. Synthesis of (4-Nitro-phenyl)-(3-phenyl-allylidene)-amine: Cinnamaldehyde (0.01 mol) and 4-Nitro aniline (0.01 mol) were refluxed in 50 ml of n-Hexane. Melting point-105 °C.
3. Synthesis of (4-Methyl-phenyl)-(3-phenyl-allylidene)-amine: Cinnamaldehyde (0.01 mol) and P-Toluidine (0.01 mol) were refluxed in 50 ml of n-Hexane. Melting point-85 °C.
4. Synthesis of (4-Chloro-phenyl)-(3-phenyl-allylidene)-amine: Cinnamaldehyde (0.01 mol) and P-Chloro aniline (0.01 mol) were refluxed in 50 ml of n-Hexane. Melting point-143°C.
5. Synthesis of (4-Carboxyl-phenyl)-(3-phenyl-allylidene)-amine: Cinnamaldehyde (0.01 mol) and Para Amino Benzoic Acid (0.01 mol) were refluxed in 50 ml of n-Hexane. Melting point-50 °C.
6. The structures with physical characters are mentioned in **Table 3.**

### Result and Discussion

It is found that all isolated oils from *Cinnamomum* species have pleasant agreeable odor. It is interesting to note that *C. zeylanicum* contains Cinnamaldehyde. The latter two species; *C. camphora* and *C. tamala* are devoid of Cinnamaldehyde. The absence of Cinnamaldehyde may be due climatic variation. A few common constituents found in these oils are 1-Spathulenol and 2- Terpeneol. One of the interesting points to note here is that *C. camphora*; does not found to contain Camphor. This may be due to climatic variation, or camphor could not have been biosynthesized at the time of collection of leaves. Schiff's base reaction was carried out using a simple refluxation method. All Schiff's bases synthesized were yellow to orange in color.

All results are mentioned in Table 1, Table 2 and Table 3.

**Table 1: Organoleptic characters and percent of Essential Oils**

Parameter	Cinnamomum zeylanicum	Cinnamomum comphora	Cinnamomum tamala
Amount	2.6 %	1.4 %	1.0 %
Color	Pale yellow	Colorless	Yellow
Odor	Aromatic	Camphory	Spicy
Taste	Irritant	Pleasant	Spicy

**Table 2: List of constituent present in Cinnamomum species**

S. N.	<i>C. zeylanicum</i>	<i>C. tamala</i>	<i>C. camphora</i>
1	1,2 Norpinene	o-Cymene	Pinene
2	Eucalyptol	Terpineol	Pseudopinene
3	Linalool	Eugenol	Eucalyptol
4	Terpineol	Bicyclo, undec-4 ene, 4, 11, 11 trimethyl, 8-methylene	$\beta$ -Terpineol
5	<b>Cinnamaldehyde</b>	1H-Cycloprop(e)Azulene-decahydro, 1,1, 7, trimethyl, 4-methylene	1,4-Isopropyl,1-methyl,2-cyclohexene,1-ol
6	Eugenol	Varideflorene	4-Terpineol
7	Caryophyllene	Acetoeugenol	Nerol
8	Cinnamyl acetate	Ledol	Kemitracin-50
9	Acetoeugenol	Spathulenol	1-methyl, 6-nonynoate
10	Caryophyllene oxide	Benzyl benzoate	Pinanediol
11	Spathulenol	Emersol	1,3-Allyl, 2-methoxy phenol
12	Ascabiol	Phytol	1-Methyl-4-[1-methyl ethyl]-2-cyclohexen-1-ol
13	3-(4-Dihydroxy,3-Methoxy Phenyl), 2-Propenal	Linoleoyl chloride	Geraniol
14	Cholestan-3-ol, 2-methylene	1-{2-carboxy, 4,4-dimethyl cyclobutenyl}-1-Butene-3-one	$\beta$ -Elemene
15	3-Acetyloxy, 6,16-Dimethyl, Pregn-5en-20-one	3-Acetyloxy, 6,16-Dimethyl, Pregn-5 en- 20-one	Bicyclo, undec-4 ene, 4, 11, 11 trimethyl, 8-methylene
16	Benzyl benzoate	3-Acetyloxy, 6,16-Dimethyl, Pregn-5 en- 20-one	Verbenol
17	Phenol, 2-methoxy, 4-{2-Propenyl} acetate	1H- 2, 8a methano cyclopenta (a) cyclopropa (e) cyclodecen-11-one	$\alpha$ - Caryophyllene
18		2-Octen-1-ol, 3,7-dimethyl isobutyrate	$\alpha$ -Selinene
19		Pregna-4,9 [11] diene, 20 – ol,3-on, 19-oic acid lactate	$\beta$ -Selinene
20			Eremophilene
21			Azulene
22			Elemol
23			Spathulenol
24			5-Azulene methanol
25			Cubenol
26			Alloaromadendrene oxide
27			Ledene oxide
28			Aromadandrene oxide

**Table 3: Structures with physical characters of Schiff Bases**

S. N.	Structures	Chemical Name	Melting Point	Color
1		Phenyl-(3-phenylallylidene)-amine	90 °C	Bright orange
2		(4-Nitro-phenyl)-(3-phenylallylidene)-amine	105 °C	Orange
3		(4-Methyl-phenyl)-(3-phenylallylidene)-amine	85 °C	Brown
4		(4-Chloro-phenyl)-(3-phenylallylidene)-amine	143 °C	Light Brown
5		(4-Carboxyl-phenyl)-(3-phenylallylidene)-amine	50 °C	Yellow

### Conclusion

In this study an attempt was made to isolate essential oils from three leaves *Cinnamomum* species, visibly, *C. zeylanicum*, *C. camphora* and *C. tamala*. The LC-MS Analysis showed that only *C. zeylanicum* oil contains Cinnamaldehyde. The different oils have shown presence of number of monoterpenes, diterpenes etc. A sincere attempt is made to prepare derivatives of Cinnamaldehyde with available substituted amines using Schiff's base formation scheme.

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