Extraction and Characterization of D-limonene oil from orange peels using different solvents

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Abstract

D-Limonene essential oil was extracted from orange peels by soxhlation method using different solvents like ethanol,methanol, n-hexane, 1-propanol and distilled water in order to compare the yield percentage. The percentage of yield was in the order of ethanol > 1-propanol>hexane > distilled water>methanol. The study on variation of percentage yield with extraction time and weight of the peels showed a linear trend. The extracted oils were characterized by UV-Visible, FT-IR and ^{1}H NMR analysis.

Key words:D-Limonene, soxhlation, UV-Visible, FT-IR , ^{1}H NMR

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Introduction

D-limonene is one of the most common terpenes in nature. It is a major constituent in several citrus oils (orange, lemon, mandarin, lime, and grapefruit). D-limonene is listed in the Code of Federal Regulations as generally recognized as safe (GRAS) for a flavoring agent and can be found in common food items such as fruit juices, soft drinks, baked goods, ice cream, and pudding. D-limonene is considered to have fairly low toxicity[1] Limonene is common as a dietary supplement and as a fragrance ingredient for cosmetics products. As the main fragrance of citrus peels, D-limonene is used in food manufacturing and some medicines, such as a flavoring to mask the bitter taste of alkaloids, and as a fragrance in perfumery, aftershave lotions, bath products, and other personal care products.D-Limonene is also used as a botanical insecticide.[2] Limonene is used as a solvent for cleaning purposes, such as adhesive remover, or the removal of oil from machine parts, as it is produced from a renewable source (citrus essential oil, as a byproduct of orange juice manufacture).[3] It is used as a paint stripper and is also useful as a fragrant alternative to turpentine. Limonene is also used as a solvent in some model airplane glues and as a constituent in some paints. Commercial air fresheners, with air propellants, containing limonene are used by philatelists to remove self-adhesive postage stamps from envelope paper.[4]Limonene is also used as a solvent for fused filament fabrication based 3D printing.[5] Printers can print the plastic of choice for the model, but erect supports and binders from HIPS, a polystyrene plastic that is easily soluble in limonene. As it is combustible, limonene has also been considered as a biofuel.[6]In preparing tissues for histology or histopathology, D-limonene is often used as a less toxic substitute for xylene when clearing dehydrated specimens. Clearing agents are liquids miscible with alcohols (such as ethanol or isopropanol) and with melted paraffin wax, in which specimens are embedded to facilitate cutting of thin sections for microscopy[7]

In the present study we have extracted D-Limonene from orange peels by using various solvents and compare their percentage of yield against the solvent used and characterize it by UV-Vis, FT-IR and NMR analysis.

Experimental:

Materials

Oranges were purchased from the local market.Ethanol, Methanol, n-hexane, 1 – Propanol were reagent grade chemicals purchased from merck and used without further purification. Distilled water was collected from the distillation plant installed in the University's Chemistry Laboratory**.**

Extraction of D-Limonene

Orange peels were separated from the orange by means of a sharp blade and knife.Then cut into small pieces. 100,110,120 and 130 gms of the extracted peels were put in a 500 mL RBF along with 150 mL of ethanol, methanol , 1-propanol, n-hexane and distilled water and heated upto their boiling point under soxhlation for 4,5,6 and 7hrs. Then the collected volume fractions of the extraction were fractionally distillated in rotary evaporator to separate the essential oil D-Limonene and the solvents.The pure D-Limonene extracted with various solvents were labelled in vials and kept for further analysis.The percentage of yield of the oil was calculated by the following formula

$$\% \text{ Y} = \frac{\text{Weight of the Oil}}{\text{Weight of the Peel}} \; x \; 100$$

Characterizations:

UV-Vis absorption study of the extracted D-Limonene oils were carried out by double Beam UV-VIS Spectrophotometer – 2375(EI). IR Spectra of the extracted D-Limonene oils were recorded on a perkin Elmer spectrometer(Spectrum RX1,Perkin Elmer, Singapore)using KBr pellet technique, in the range 4000-500 cm^{-1} with a resolution of 2cm-1 using 4 scans per sample. The 1H-NMR spectra of the extracted products were collected on a Bruker WM-400 spectrometer, operating at 300 MHz for proton. All the chemical shifts were reported in parts per million (ppm) using tetramethyl silane (TMS) as internal standard and DMSO-d^6 as solvent for the samples.

Results and Discussion

The yield percentage of D-Limonene with various solvents have been recorded in table-1 goes on increasing with increase in weight of the peels .The yield percentage is more in case of ethanol and propane as evidence from figure-1. Yield percentage in distilled water as well as methanol was nearly same. Though extraction in hexane is better next than water but due to toxicity ,the oil can't be used for medicinal purpose. Extraction of the may not be economical in water but due less yield. The results shows that methanol is not a suitable solvent for extraction of D-Limonene as it is toxic as well as gives lower yield. So extraction is more feasible in ethanol though some less economical compared to distilled water. The variation of time yield percentage has been recorded in table-2.In all cases it is clear that yield percentage has a linear relationship with extraction time as proved from figure-2.But

one thing is very clear that there is no much variation in percentage of yield with time as all the extraction is collected within 4 to 5 hrs.

Table -1: Percentage yield of D-Limonene with various solvents of 150 mL at their boiling points.

Solvent –Methanol				
Weight of the peels (g)	**Temperature(^{0}C)**	**Time (h)**	**Weight of the oil collected (g)**	**% Y**
100	65	4	3.8	3.8
110	65	4	4.5	4.09
120	65	4	5.0	4.16
130	65	4	5.6	4.3
Solvent –Hexane				
100	68	4	4.1	4.1
110	68	4	4.7	4.27
120	68	4	5.4	4.5
130	68	4	6.0	4.61
Solvent –Ethanol				
100	78.5	4	4.6	4.60
110	78.5	4	5.4	4.90
120	78.5	4	6,0	5.0
130	78.5	4	6.7	5.15
Solvent –Distilled Water				
100	100	4	3.7	3.7
110	100	4	4.3	3.9
120	100	4	5.0	4.16
130	100	4	5.6	4.3
Solvent –Propanol				
100	97	4	4.3	4.30
110	97	4	4.9	4.45
120	97	4	5.5	4.58
130	97	4	6.0	4.61

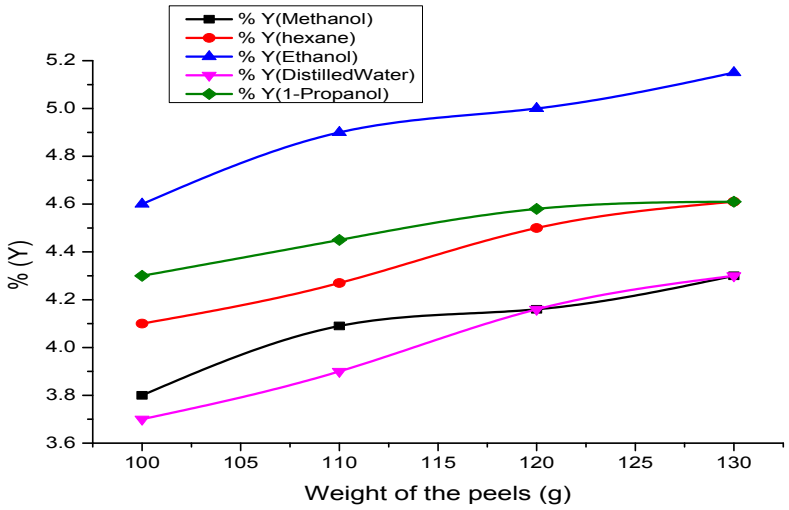

Figure-1: comparison of yield percentage with weight of peels in different solvents

Table-2 : Variation of percentage yield of D-Limonene with time

Solvent –Methanol				
Weight of the peels (g)	**Temperature(^{0}C)**	**Time (h)**	**Weight of the oil collected (g)**	**% Y**
100	65	4	3.8	3.8
100	65	5	4.0	4.0
100	65	6	4.5	4.5
100	65	7	5.0	5.0
Solvent –Hexane				
100	68	4	4.1	4.1
100	68	5	4.5	4.5
100	68	6	5.0	5.0
100	68	7	5.4	5.4
Solvent –Ethanol				
100	78.5	4	4.6	4.6
100	78.5	5	5.1	5.1
100	78.5	6	5.6	5.6
100	78.5	7	5.9	5.9
Solvent –Distilled Water				
100	100	4	3.7	3.7
100	100	5	4.0	4.0
100	100	6	4.5	4.5
100	100	7	5.0	5.0
Solvent –Propanol				
100	97	4	4.3	4.3
100	97	5	4.6	4.6
100	97	6	5.0	5.0
100	97	7	5.4	5.4

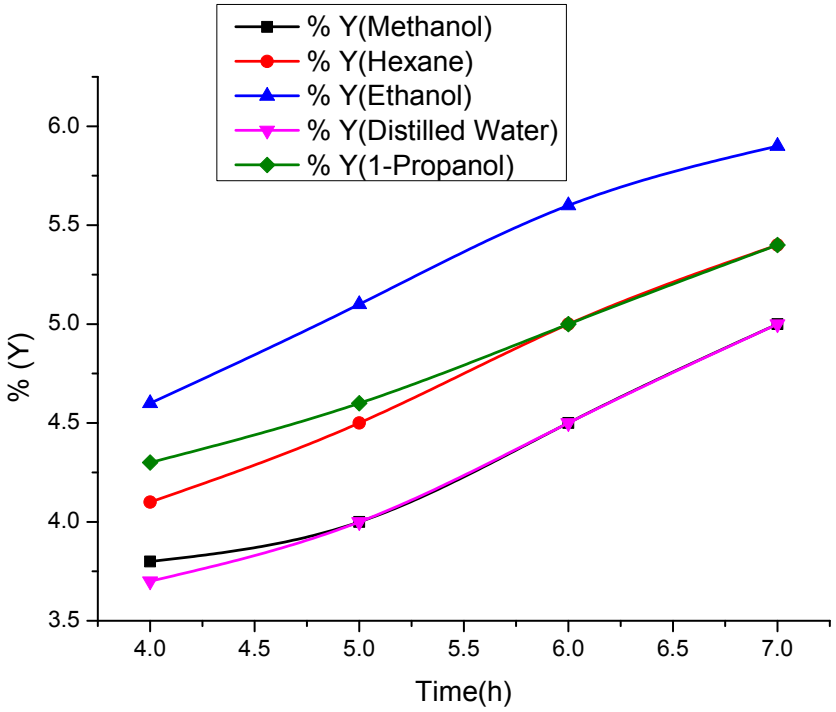

Figure-2: Comparision of percentage yield with extraction time in different solvents

UV-Visible

UV-Vis spectral analysis of all the oils extracted from different solvents were shown in figure-3.All the individual spectrum showed absorption in the range of 200 nm to 360 nm due to $\pi \rightarrow \pi^*$ transitions of the C=C bonds present in cyclohex-1-ene ring and prop-1-en-2-yl group. Another absorbance from 380nm to 500nm confirmed the orange colour of the solution.

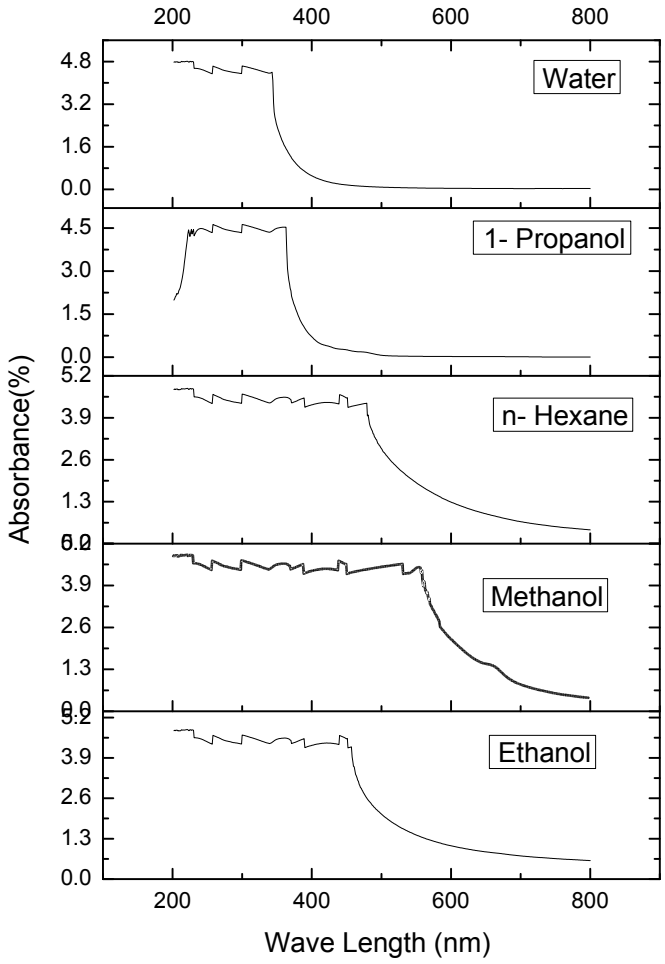

Figure-3:UV-VIS Spectra of D-Limonene oils extracted in various solvents

FT-IR

FT-IR spectrum of D- limonene extracted with various solvents have been shown in Figure 4[(a)-(e)]. It is observed that the peaks at 1309, 1217, 956, 913, and 885 cm^{-1} corresponding to the double bonds in limonene[8]. It should be noted the presence of characteristic band corresponding to the stretching

band of C=C at 1640 cm-1 in the spectra of limonene and also an intense band at 2930 cm^{-1} corresponding to the valence vibration of the methylene C–H bond in all FT-IR spectrum confirming the presence of D-limonene in the solution.

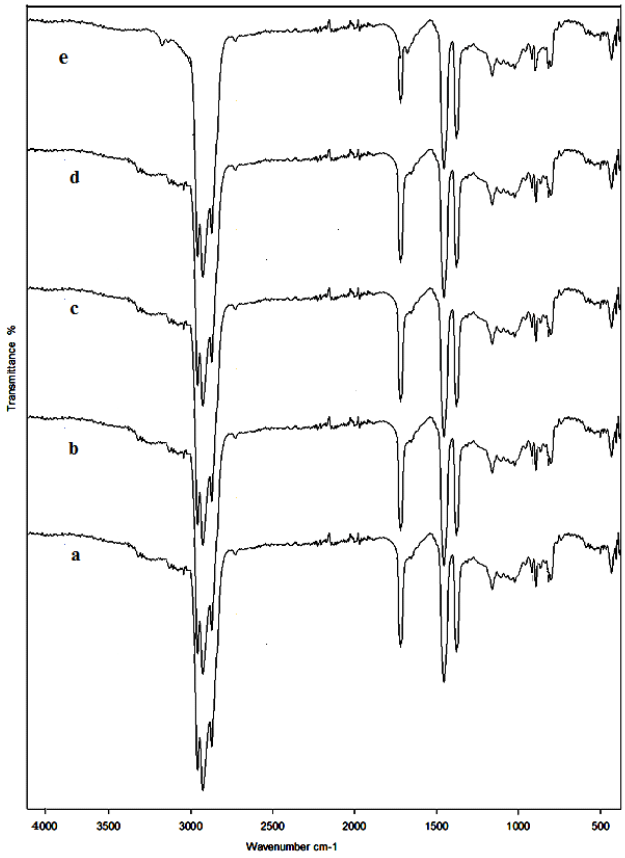

Figure-4:FT-IR Spectra of D-Limonene oils extracted in a) ethanol b)n-hexane c) methanol d) 1-propoanol e) distilled water

NMR

The nuclear magnetic resonance of all extracted D-limonene samples were shown in figure 5(a) to 4(e) in different solvents. All the spectrum showed similar peaks at 5.5 ppm due to the double bonded CH protons present in the cyclohex-1-ene ring.A singlet at 4.75 ppm for terminal double bonds of prop-1-en-2-yl group. A triplet in the range of 2.25 to 1.80 ppm is due to the CH_2 protons located in the cyclohexene ring.two singlets at 1.75 and 1.60 ppm appears due to the terminal methyl protons and protons of the methyl group present in prop-1-en-2-yl group. So the NMR data proved D-limonene is there in the sample.

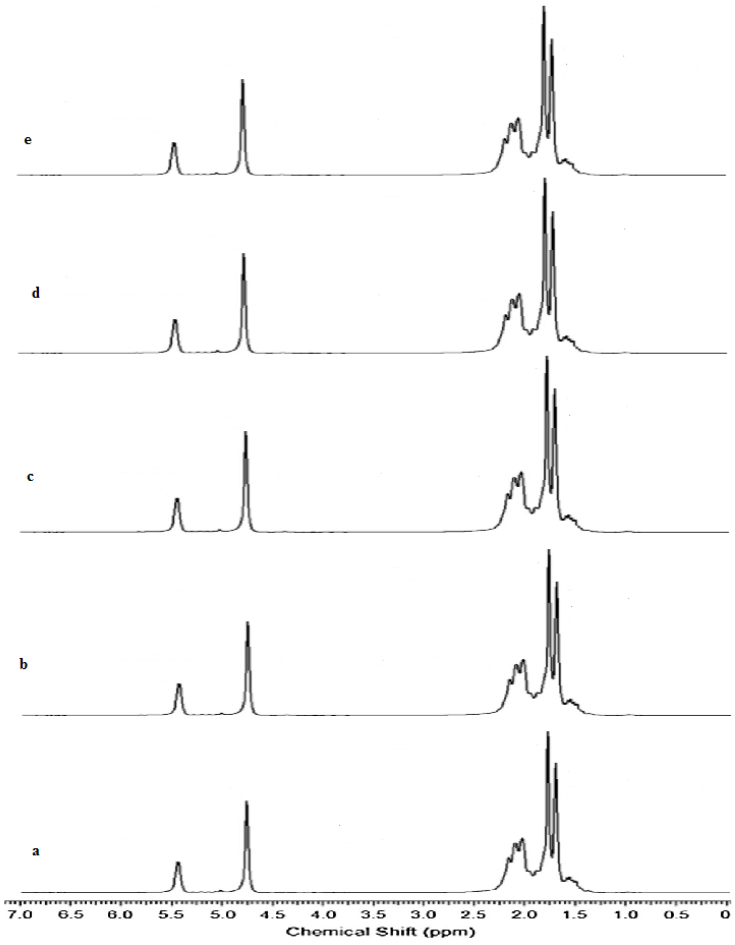

Figure-5:NMR Spectra of D-Limonene oils extracted with extracted in a) ethanol b)n-hexane c) methanol d) 1-propoanol e) distilled water

Conclusion:

It is summarised that D-limonene was successfully extracted from the orange peels by using ethanol, methanol, 1-propanol, n-hexane and distilled water as evidenced from different spectral analysis of the samples by UV-Visible, FT-IR and NMR Spectroscopic Techniques .Though extraction percentage is more in n-hexane but it's use wouldn't be suitable due to toxicity of the solvent. Similarly methanol extracted limonene is also not suitable for medicinal use as it may contain toxic methanol.But ethanol, 1-propanol and distilled water are suitable solvents through which limonene can be efficiently extracted and used for different applications in the field of medicine and other industrial purposes.

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