BOLETIN LATINOAMERICANO Y DEL CARIBE DE PLANTAS MEDICINALES Y AROMÁTICAS
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Articulo Original / Original Article

Extraction of geraniol from palmarosa oil using hydrotropic solvents

[Extracción de geraniol del aceite de palmarosa utilizando solventes hidrotrópicos]

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Section Phytochemistry

Received: 31 October 2022
Accepted: 22 April 2023
Accepted corrected: 26 August 2023
Published: 30 May 2024

Citation:
Rashma LJ, Presley SID, Prakash DG
Extraction of geraniol from palmarosa oil using hydrotropic solvents
Bol Latinoam Caribe Plant Med Aromat
23 (3): 382 - 389 (2024).
https://doi.org/10.37360/blacpma.24.23.3.26

Abstract: The extraction of geraniol from palmarosa oil using hydrotropic solvents was investigated. Palmarosa oil possesses an appealing rose aroma and properties like anti-inflammatory, antifungal, and antioxidant due to the presence of geraniol. The extraction of geraniol from palmarosa oil by using distillation methods like steam distillation and fractional distillation was a laborious process. So hydrotropes were tried for extraction. The geraniol yield and purity depend on parameters like concentration of hydrotrope, solvent volume ratio, and time period. Using the Box Benkhem Design (BBD), the extraction process was optimized. One of the major advantages of using hydrotropic solvents is that they were classified as green solvents, and recovery of solvents is also possible. To reduce the extraction time probe sonication is carried out. Different hydrotropic solvents with probe sonication are done on palmarosa oil by altering various process parameters to study the separation, yield, and purity.

Keywords: Geraniol; Hydrotropes; Response surface methodology; Box-Behnken design; Gas chromatography

Resumen: Se investigó la extracción de geraniol del aceite de palmarosa utilizando solventes hidrotrópicos. El aceite de palmarosa posee un atractivo aroma a rosa y propiedades antiinflamatorias, antifúngicas y antioxidantes debido a la presencia de geraniol. La extracción de geraniol del aceite de palmarosa mediante métodos de destilación como la destilación por vapor y la destilación fraccionada ha sido un proceso laborioso. Por lo tanto, se probaron los hidrotropos para la extracción. El rendimiento y la pureza del geraniol dependen de parámetros como la concentración del hidrotropo, la relación de volumen del solvente y el período de tiempo. Se optimizó el proceso de extracción usando el diseño Box Benkhem (BBD). Una de las principales ventajas de usar solventes hidrotrópicos es que se clasifican como solventes verdes y también es posible recuperar los solventes. Para reducir el tiempo de extracción, se lleva a cabo una sonda de ultrasonido. Se realizan diferentes solventes hidrotropos con sonda de ultrasonido en el aceite de palmarosa alterando varios parámetros del proceso para estudiar la separación, el rendimiento y la pureza.

Palabras clave: Geraniol; Hidrotrópicos; Metodología de superficie de respuesta; diseño de Box Benkhem (BBD); Cromatografía de gases.

INTRODUCTION

Geraniol is used as a fragrance ingredient in shampoos, soaps, toiletries, household detergents, and cleaners. Geraniol was found in many essential oils such as palmarosa oil, lemongrass oil, citronella oil, geranium oil, and cannabis and it can be found in abundant quantities in palmarosa oil. Palmarosa oil possesses an appealing rose aroma and properties like anti-inflammatory, antifungal, and antioxidant due to the presence of geraniol. Also, geraniol is used in the biosynthesis of the terpenes, myrcene, and ocimene (Thakker *et al*., 2016a). Palmarosa oil contains 70% - 80% of geraniol along with geraniol acetate (Kumaran *et al*., 2003). Geraniol has many uses, both as a safe natural additive to add taste or scent. The extraction of geraniol from palmarosa oil is done by using conventional distillation methods like steam distillation and fractional distillation even though these methods are well established it has some limitations like time, energy consumption and not environmental friendly (Mazaud *et al*., 2020). Geraniol has a boiling point of 230^{o}C and geranyl acetate has a boiling point of 245^{o}C, since the temperature difference is not high, it is difficult to separate geraniol from geraniol acetate by a fractional distillation process. To overcome the difficulties involved in distillation, we tried hydrotropic solvents compared to common organic solvents. Hydrotropic solvents are classified as green solvents. Hydrotropes are highly water-soluble organic salts similar to that surfactants but shorter in their molecular structure. These hydrotropes were used to increase the aqueous solubility of sparingly soluble organic compounds and it has wide industrial applications (Mehringer & Kunz, 2021). Many sparingly soluble organic compounds like amyl chlorides' solubility increased approximately 10-100 times using sodium xylene sulfonate hydrotrope solution. They also discussed the easy recovery of the dissolved solute by the addition of water in the hydrotrope solutions. Hydrotropes consist of both hydrophilic and hydrophobic parts, but the hydrophobic part is too small to cause self-aggregation. This self-aggregated assembly tends to form an aggregate with other water-insoluble or sparingly soluble compounds (Booth & Everson, 1948). Hydrotropy occurs when hydrotropic salt initiates the solubility of sparingly soluble or insoluble solutes in water. The mechanism involves the complex formation between solute and hydrotropes or self-aggregation takes place similar to that of surfactants. Hydrotropes can be ionic or non-ionic. Hydrotropes were effectively used in the extraction of bioactive compounds and also in the separation of close boiling mixtures (Mazaud *et al*., 2020). Sodium xylene sulfate, sodium salicylate, sodium acetate, sodium benzoate, urea, and resorcinol are some of the hydrotropes used for the extraction of geraniol. Hydropes are cheap, non-toxic, eco-friendly, non-flammable, and easily available. Our work focuses to improve the yield of geraniol by hydrotropic extraction. Hydrotropic extraction mainly depends upon the parameters like temperature, concentration, and volume ratio of the hydrotropic solvent. The introduction of sonication augments the extraction of geraniol. Sonication is a process in which sound waves are used to agitate particles in solution. Sonication can be used to speed dissolution by breaking intermolecular interactions of the mixture. The present work aims to develop an efficient technique for the extraction of geraniol from palmarosa oil by using hydrotropic solvents and to understand the role of each parameter in the extraction.

MATERIALS AND METHODS

Palmarosa oil (M/s.Ancient Herbs, India), sodium xylene sulphonate were purchased from Sigma Aldrich, France, Sodium benzoate were purchased from Sisco Research Laboratories Pvt. Ltd.Maharashtra India, Resorcinol, Sodium salicylate,Sodium carbonate and Sodium acetate were purchased from S D Fine-Chem Limited, Mumbai, India.

Sample analyses were performed using gas chromatography (GC 8860 Agilent Technologies, Santa Clara, USA) equipped with a 7693A auto-injector. The system was controlled and monitored by Chemstation software. Chromatographic separation was done by using the following condition.

Column - Agilent DB1, 60 m x 0.25 mm I.D., 0.25 μm

Oven - 60°C (2 min), 3°C/min to 230°C

Carrier gas - Nitrogen 1 mL/min

Sample - Neat

Detector - FID

Injection volume - 0.2 μL, 100:1 split

Our initial screening involves treating palmarosa oil with six different hydrotropes to find out the solubility of geraniol in hydrotropes. The solubility experiments were carried out in a cylindrical glass vessel with vigorous stirring for 6-8 hours at 30°C. Of the six hydrotropes, we observe solubility only in sodium xylene sulphonate (SXS). So SXS is chosen for further studies. The extraction procedure involves treating palmarosa oil with hydrotropic solvent and stirring for 6 to 8 hours, after stirring the layers were allowed to separate (Figure No. 1), then the separated aqueous layer is again diluted and allowed to extract geraniol. Since the extraction time is more we subjected the solution to sonication. Optimization of concentration, sonication time, and the oil-solvent ratio was done by trying out different trials. After the extraction of the extracted organic layer of geraniol, the extracted organic solution is additionally pre-conformed by the TLC method. In this TLC method, the sample is introduced into the reported mixture of the mobile phase (Figure No. 2) (Wany *et al*., 2014).

The yield is calculated by using the following equation.

$$y = \frac{m_1 * 100}{m_2}$$

Where y is the yield in % (v/v), m_1 is the volume of geraniol collected in mL and m_2 is the volume of the palmarosa oil taken.

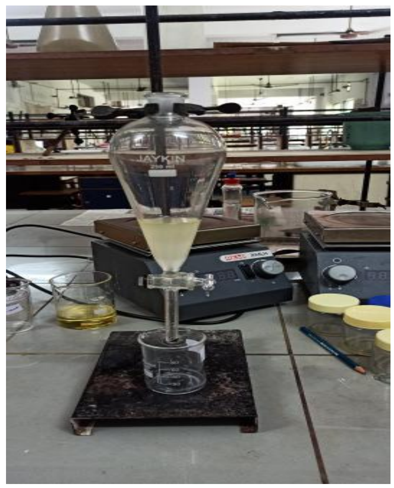

Figure No. 1
Separation of organic and aqueous layer

Figure No. 2
TLC for geraniol compound

RESULTS AND DISCUSSION

Optimization of oil extraction is obtained by adopting Box-Behnken design. The design of experiments involving reaction parameters such as sonication time, the concentration of hydrotropic solvents, solvent to oil ratio, and coded as A, B, and C respectively, are shown in Table No. 1. Optimization of the reaction parameters was done by using the response surface methodology and the counterplots and response surface were analyzed.

Table No. 1
The range for independent variables

Code	Name	Unit	Variable Range
A	Sonication Time	Minutes	5-20
B	Concentration	Mole	1.75 to 3.0
C	Solvent Volume ratio	mL	1 to 3

Using Design-expert software v13.0 the above parameters are entered which gives 14 runs and are tabulated in Table No. 2.

Table No. 2
Design of experiments based on Box-Behnken design

Std.	Run	Factor 1 A: Sonication Time	Factor 2 B: Concentration	Factor 3 C: Solvent Volume Ratio	Response 1 Yield
		Minutes	Mole	mL	%
11	1	12.5	2.375	2	53
14	2	12.5	2.375	2	60
10	3	12.5	2.375	2	58
1	4	5	1.75	2	40
3	5	5	2.375	1	33
8	6	12.5	3	1	60
5	7	5	2.375	3	68
2	8	20	1.75	2	18
12	9	12.5	2.375	2	56
7	10	12.5	1.75	1	14
6	11	20	2.375	3	68
9	12	12.5	1.75	3	70
4	13	20	2.375	1	40
13	14	12.5	2.375	2	56

The experimental data obtained were fitted in a second-order polynomial quadratic response equation. The below equation gives the link based on coded factors.

$$Y = 56.68 + 1.75A + 16.90B + 17.77C + 12.75AB - 8.22BC - 6.55A^2$$

The coded equation assists in evaluating the relative significance of the independent variables and are useful for identifying the relative impact of the factors by comparing the factor coefficients. The quadratic model and its statistical significance are evaluated from the ANOVA results, given in Table No. 3. The regression model has a high coefficient of determination (R^2=0.9658) and the impact of each term can be assed from the *p*-value. The *p*-values of less than 0.05 show that model terms are significant.

Here B, C, AB, BC, A^2 are significant model terms. In table 4 the statistical interpretations demonstrate a high coefficient of determination (R^2=0.9658) and also R^2 adj (0.9364) values explain the significance of the model. The difference between R^2 and R^2 adj is values insignificant which show the model is desirable. The coefficient of variation (CV) is 9.14, generally, a CV less than 10 indicates good consistency for the experiments that are carried out (Thakker *et al.*, 2016b).

The F-value for the lack of fit test is 5.71 and is not significant implying that the models sufficiently describe the obtained data. The Model F-value of 32.92 implies the model is significant.

p-values less than 0.0500 indicate model terms are significant. In this case, B, C, AB, BC, and A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Optimum value of each factor and their interactions can be obtained from a three-dimensional response surface and contour graph. The variables which influence the extraction were given in Figures No. 3A, No. 3B and No. 3C. Figure No. 3A and No. 3B give the interaction of sonication time and concentration. Figure No. 3C gives the interaction of concentration and solvent volume ratio. In Figure No. 3A the sonication time is 5 minutes and the concentration is 2.375 moles and the yield reported is 68%. Whereas in Figure No. 3B the sonication time is 12.5 minutes and the concentration is 1.75 moles and the reported yield is 70%. By decreasing the molar concentration and by increasing the sonication time we observe there is no much change in yield. Figure No. 3C gives the information of solvent volume ratio from the design of experients table we can conclude that 1:2 can be otimized for extraction.

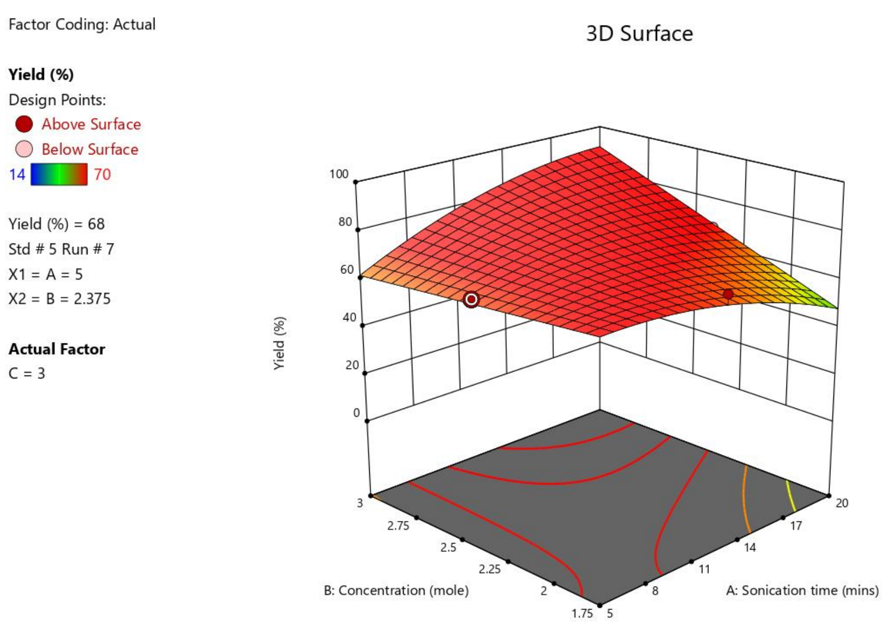

Figure No. 3A
Response surface plots for yield showing Sonication time vs Concentration

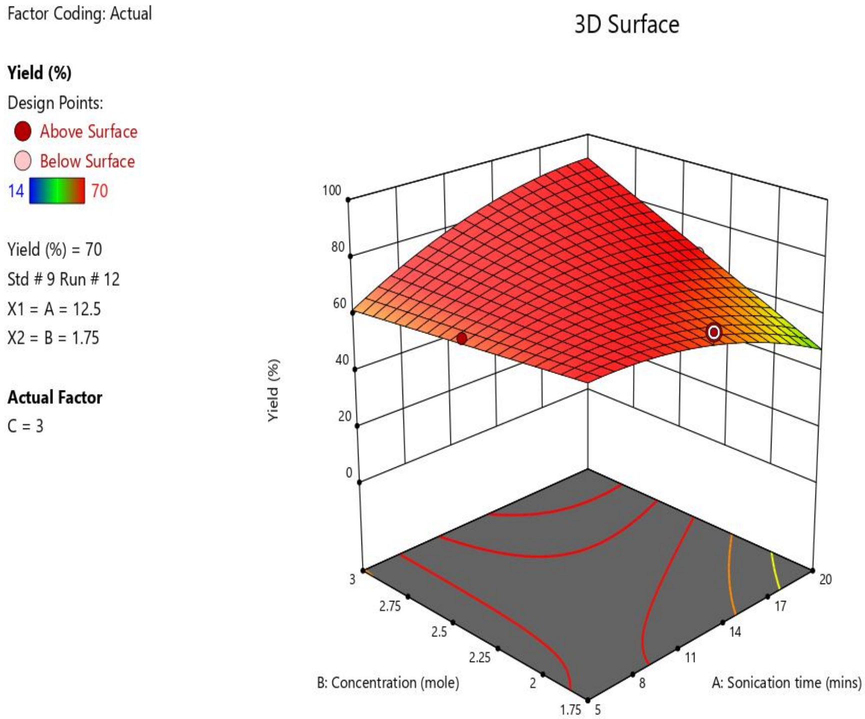

Figure No. 3B
Response surface plots for yield showing Sonication time vs Concentration

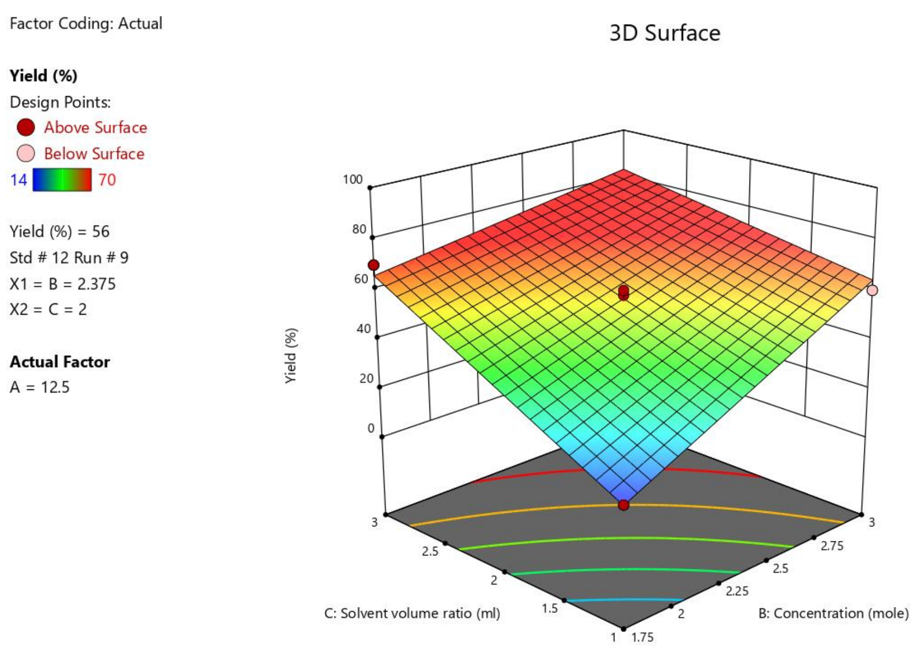

Figure No. 3C
Response surface plots for yield showing Concentration vs Solvent volume ratio

Sonication helps in breaking the cell wall of the plants since we are taking the oil higher sonication time doesn't have any impact on extraction. A higher concentration of the hydrotropes helps in better extraction of geraniol but on increasing the concentration to more than 3 mole the solution becomes colloidal and yield is decreased, below 1 mole concentration separation is not observed so the range of 1 M to 3 M concentration is fixed. The higher the solvent volume, the higher the yield since hydrotropes have an amphiphilic structure it increases the solubility of hydrotropic solvent and helps to solubilize less water-soluble molecules through weak van der Waals interaction (Neumann *et al*., 2007). We analyzed the purity for samples with higher yield and the purity varies from 78.14 to 81.87% from the original percentage of 76.91%. A 3 to 5% increase in the purity of geraniol shows that on further optimizing the conditions more improvement in purity can be achieved (Figure No. 4). When compararing the results with the conventional extraction techniques the yields were 54%, 65% and 70%, respectively.The yields using the hydrotropic solvents and conventional techniques were almost same but conventional techniques requires high energy and time consuming.

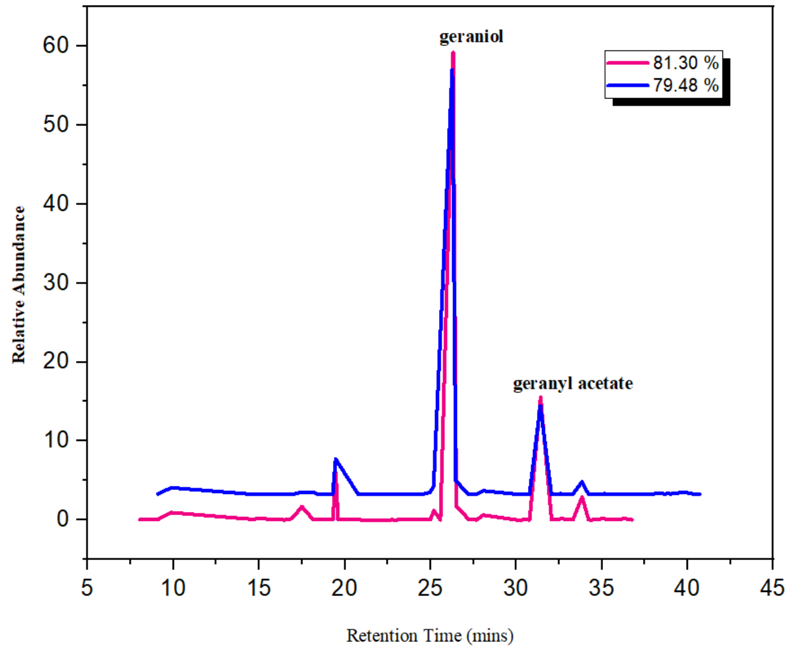

Figure No. 4
Chromatogram of geraniol and geranyl acetate

Table No. 3
Analysis of variance for response surface quadratic model

Source	Sum of Squares	Df	Mean Square	F-Value	*p*-Value	
Model	4055.68	6	675.95	32.92	< 0.0001	significant
A-Sonication time	12.25	1	12.25	0.5965	0.4652	
B-Concentration	967.35	1	967.35	47.11	0.0002	
C-Solvent volume ratio	1825.79	1	1825.79	88.91	< 0.0001	
AB	216.75	1	216.75	10.56	0.0141	
BC	152.98	1	152.98	7.45	0.0294	
A^2	140.18	1	140.18	6.83	0.0348	
Residual	143.74	7	20.53			
Lack of Fit	116.54	3	38.85	5.71	0.0627	not significant
Pure Error	27.20	4	6.80			
Cor Total	4199.43	13				

Table No. 4
Regression coefficients of the predicted second-order for extraction of geraniol

Factor	Regression Coefficient
Intercept	56.68
A	1.75
B	16.90
C	17.77
AB	12.75
BC	-8.22
A^2	-6.55
R^2	0.9658
Adj-R^2	0.9364
C.V.%	9.4

R^2 – coefficient of determination; C.V.- Coefficient of variance

CONCLUSION

Coefficeint of determination (R^2=0.9658) the second-order regression model and experimental observations are in good correlation. A maximum yield was observed at two conditions one when the sonication time is 12.5 minutes, concentration at 1.75 M, and solvent volume ratio at 3, and the other condition is when sonication is 5 minutes, concentration at 2.375 M, and solvent volume ratio at 3. Both the conditions the yields were around 68-70%. The response surface methodology clearly demonstrates the best operating conditions to maximise the yield. One of the major advantages of this extraction technique is that we were able to complete the process in less than 30 minutes with minimum setup. No heating or cooling is required as this extraction is done only at room temperature. The above extraction procedure can be scaled up for larger production.

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