

Greener Synthesis of Jasminaldehyde via Cross Aldol Condensation Reaction Using Recyclable Phase Transfer Catalysis and its Cosmetic Application

Kishan Babu Velambath¹, Suraj N. Mali², Amit P. Pratap^{3,*} 

¹ Department of Dyestuff Technology, Institute of Chemical Technology, Mumbai, (University under Section 3 of UGC Act 1956; Elite Status and Centre of Excellence, Government of Maharashtra), Maharashtra, India

² Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, Mumbai, (University under Section 3 of UGC Act 1956; Elite Status and Centre of Excellence, Government of Maharashtra), Maharashtra, India; mali.suraj1695@gmail.com (S.N.M.)

³ Department of Oils, Oleochemicals and Surfactant Technology, Institute of Chemical Technology, Mumbai, (University under Section 3 of UGC Act 1956; Elite Status and Centre of Excellence, Government of Maharashtra), Maharashtra, India; ap.pratap@ictmumbai.edu.in (A.P.P.)

* Correspondence: ap.pratap@ictmumbai.edu.in (A.P.P.);

Scopus Author ID 57205354998

Received: 25.04.2022; Accepted: 3.06.2022; Published: 17.09.2022

Abstract: Jasminaldehyde or alpha amyl cinnamic aldehyde is a commonly used aroma molecule in perfume formulations. The aldol condensation of equimolar n-heptanal and benzaldehyde in NaOH using a surfactant catalyst cetyltrimethylammonium bromide to achieve high cross aldol product Jasminaldehyde selectivity was studied. The process is highly efficient due to the recyclability of the catalyst. The process was studied for four cycles of catalyst reusability. The selectivity of the cross product was dependent on the temperature, surfactant concentration, and mixing. The olfactive profile of Jasminaldehyde obtained with 0.1 M surfactant solution was identical to the standard. Jasminaldehyde formulation was created and applied to in-home care applications.

Keywords: surfactant; catalysis; phase transfer catalyst; cinnamic aldehyde derivatives; formulation; process optimization.

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

From a historical point of view, it has always been viewed those aromatic materials of a natural origin reign supreme over aroma chemicals. Before researching synthetics, natural materials were used in perfumery for millennia [1]. Because of their scarcity, aroma molecules are being synthesized to serve as alternatives to natural aromatic essential oils. To get the same quality of performance as the product of natural origin, synthetic aroma materials are required to be free from by-products. They have to be free of any non-characteristic odors. This translates back to its process of synthesis [2]. For instance, natural clove oil has a spicy, aromatic, balsamic, woody, phenolic, fruity, and powdery odor, and to mimic the same profile, primarily synthetic eugenol is used in perfumes which has a sweet, spicy, warm, clove, woody, phenolic and cinnamon-like odor. The eugenol must match the required standards to perform on par with natural eugenol. Jasminaldehyde or alpha amyl cinnamic aldehyde is a commonly used aroma molecule in perfume formulations. In perfumes, it is a highly tenacious raw material commonly used in floral compositions for soaps, detergents, and room fresheners.

Jasminaldehyde has a sweet, floral, oily, waxy odor with Jasmin, honey, fruity, herbal nuances, and some metallic, green, aldehydic character. It is a cinnamic aldehyde derivative and thus is highly tenacious in its formulations and behaves like a good fixative. Jasminaldehyde on dosing in soap gives a strong floral, waxy, Jasmin, honey, fruity character and is quite stable on its own. On exposure to heat, it gets oilier and rancid in profile. Formulations prepared with Jasminaldehyde are strong, good in florals, and work well in products such as soaps, shampoos, and deodorants. They have good stability and good acceptability.

Surfactant promoted aldol condensation reactions by Kenneth C. S *et al.*, Union Carbide Corporation, 4,215,076, 1980 forms a basis of this study [3]. It consisted of a study comprising aldol condensations of different aldehydes using different QAS catalysts. The cross-aldol reaction between n-heptanal and benzaldehyde in NaOH with different surfactant catalysts studied by Manu Vashishtha *et al.*, 2013 [4] had a comprehensive comparison of the reaction with different QAS salts as a catalyst for the reaction and provided a good understanding on the factors affecting the reaction overall. An overall 99% conversion of n-heptanal with minimal by-products was obtained in their optimum process. Cetyltrimethylammonium bromide as a catalyst or aqueous micellar medium for forming C-C bond is well demonstrated by C. D. Mudaliar *et al.*, 1997 [5]. They highlight the ease, convenience, and simplicity of using this catalyst. Similarly, Bheru S. Kitawat *et al.*, 2013 [6], have used different QAS catalysts to highlight their efficiency to afford Claisen – Schmidt condensation reaction products with high yields at standard atmospheric conditions. N. Sudheesh *et al.*, 2010 [7] have devised a solvent-free technique for synthesizing jasminaldehyde by using modified chitosan (a polysaccharide of natural origin) in a hydrogel synthesis route for the condensation of n-heptanal and benzaldehyde. This gives it the benefit of green catalysis. They obtained a conversion of nearly 100% with 88% selectivity to jasminaldehyde at 160°C. Reusability of catalyst was also studied to observe the minimal deterioration of catalytic activity and product selectivity. Sumeet K. Sharma *et al.*, 2007 [8] have synthesized jasminaldehyde via cross aldol condensation of n-heptanal and benzaldehyde in an amine/diamine functionalized magnesium organo silicate (MOS) interlayer. Here they use MOS as a solid base catalyst for condensing the reactants in one step without the requirement of the acetalization of n-heptanal, which traditionally is the first step for the synthesis of jasminaldehyde. Sharma, S. K. *et al.* (2010) [9] synthesized jasminaldehyde with reconstructed Mg/Al as a solid base catalyst. Similarly, Yadav, G. D. *et al.* (2012) [10] with Mg-Al mixed oxide on hexagonal mesoporous silica catalyst. Various processes of aldol condensation to obtain Jasminaldehyde with different catalysts have been studied, out of which micellar catalysis has been more effective overall in terms of convenience and cost [11-26]. This research involves the study of the clean aldol condensation of benzaldehyde and n-heptanal in NaOH with cationic surfactant phase transfer catalyst cetyltrimethylammonium bromide. The conversion of raw materials and selectivity of the desired product is maximized. The catalyst is replenished in the process and reused for further batches. The overall process is green, convenient, and economical. The process is studied by a variation of parameters such as the molar ratio of n-heptanal and benzaldehyde, reaction temperature, the concentration of catalyst, addition time of heptanal, mixing speed, and water quantity.

Jasminaldehyde is the cross-aldol condensation product of n-heptanal (n-HA) and benzaldehyde (BA) in NaOH. The regular aldol condensation process synthesizing Jasminaldehyde is carried out in the water, that is, in a biphasic medium. The catalyst in the water phase can be reused for subsequent batches making it a sustainable process. However,

this process, although being clean by only using water and obtaining the product easily, has the problem of self-condensation by-product and slow reaction rate because of the poor hit rate of reactants. Use of surfactants is useful to tackle this problem. The research uses cetyltrimethylammonium bromide (CTAB) as a phase transfer catalysis for the cross-aldol condensation to obtain an overall green process with minimal by-products and a faster reaction rate. CTAB is a quaternary ammonium salt (QAS) and forms positively charged micelles in water. The OH⁻ ions get concentrated around the N⁺ sites where n-heptanal and benzaldehyde are also attracted because of their lone pairs on their respective oxygen (from –OH). Thus, there is a consistent hit rate for maximum selectivity and a faster reaction rate.

Varying different parameters of the reaction like reaction temperature, heptanal: benzaldehyde ratio, agitation speed, surfactant concentration, and addition order can help study the overall reaction dynamics to study the process. The most optimum process was found with equimolar quantities of benzaldehyde and n-heptanal in NaOH with 0.1M cetyltrimethylammonium bromide at 30 °C for 3 hours and 30 minutes to obtain a highly selective Jasminaldehyde product with a minimal 2-n-pentyl-2-nonenal. The catalyst in the process can be reused in subsequent batches with the addition of reactants n-heptanal and benzaldehyde, thus being a sustainable process overall. Our research group is also working on the green synthesis of hydrazides-hydrazones using greener catalysts [27-31].

2. Materials and Methods

2.1. Materials.

All necessary chemicals/materials were procured from renowned chemical vendors and used without purifications, and details are as follows:

2.1.1. For reaction.

N-Cetyl-N,N,N-trimethylammonium bromide (Molychem); n-Heptanal (Merck); Benzaldehyde Extra pure (Molychem); NaOH pellets Extra pure (Molychem); Jasminaldehyde (Amyl cinnamaldehyde alpha) (Symrise); Toluene AR (Molychem), etc.

2.1.2. For perfume formulating.

Benzyl acetate, Benzyl salicylate, Eugenol, Lylal, Galaxolide, Hedione, Hexyl cinnamaldehyde alpha, Indole (10% DPG), Lilial, Vanillin, Jasmolactone, Acetophenone, cis-3-hexenol, Citronellol, Dipropylene glycol (DPG), Isoamyl phenyl ether, Geraniol, Phenyl acetaldehyde dimethyl acetal, Phenyl ethyl alcohol, Alpha terpineol, Rose oxide, Butylated hydroxyl toluene (BHT), Dihydromyrcenol, Hydroxycitronellol, etc.

2.1.3. Bases for perfume application.

- 1) Standard soap base (Symrise)
- 2) Standard cream base (Symrise)
- 3) Standard shampoo base (Symrise)
- 4) Standard shower gel base (Symrise)
- 5) Standard talc base (Symrise)

2.2. Methodology.

2.2.1. General scheme for the synthesis of jasminaldehyde.

A general scheme of the reaction goes as follows - In a reaction flask containing an aqueous solution of N-cetyl-N,N,N, trimethyl ammonium bromide (Molychem), add equimolar amounts of benzaldehyde 99% purity (Molychem) and n-heptanal 98% purity (Merck) under stirring. To this mixture, NaOH pellets (Molychem) were added and stirred to dissolve at 30 deg C. The reaction is carried out for 4 hours. The reaction is monitored by spotting on TLC plate to study the progress of the reaction. The solvent system used for the TLC is toluene: ethyl acetate (both Molychem) in a 93:7 ratio. Once the reaction is complete, the reaction mixture is allowed to stand for about 15 minutes. The upper organic phase containing the product is extracted by layer separation with a separating funnel or a syringe. The remaining micellar solution containing the NaOH is taken for the next batch by adding benzaldehyde and n-heptanal to it by ensuring n-heptanal is added second with a controlled addition. The process is repeated again and again for a total of four cycles. Jasminaldehyde obtained in each batch is spotted on TLC plate to check for purity and also olfactively evaluated. The product obtained has to be stored in a dark-colored air-tight bottle as it is prone to oxidation and discoloration. This general scheme is then performed by varying parameters like temperature (20 deg, 30 deg, 40 deg, 50 deg, 60 deg); heptanal: benzaldehyde ratio (1:1, 1:1.3, 1:1.5); Agitation; Surfactant concentration (0.01M, 0.025M, 0.05M, 0.075M, 0.1M, 0.2M, 0.3M); addition order (adding n-heptanal first). Jasminaldehyde was applied in a standard soap base (Symrise) to test aroma stability in soap. Formulations containing Jasminaldehyde as a primary ingredient were prepared to study perfume profile in-home care applications.

2.2.2. Formulations of various cosmetic products.

The exhaustive details of methodology and composition followed for formulations are given in supporting information.

3. Results and Discussion

3.1. Aldol reaction.

The reaction scheme is shown below in Fig. 1.

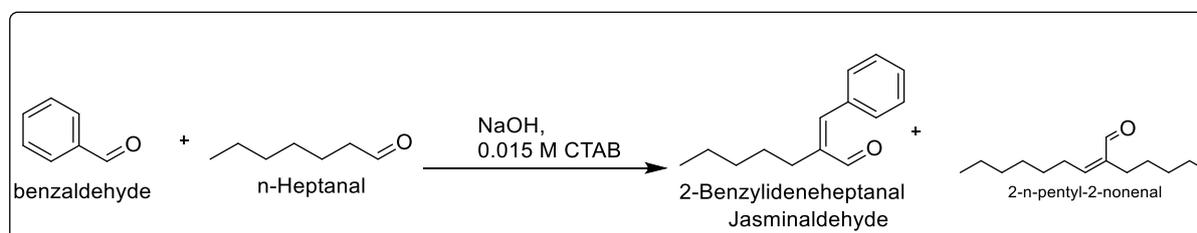


Figure 1. Reaction scheme for Jasminaldehyde synthesis.

The base used in the process is completely regenerated in the process. The 2-n-pentyl-2-nonenal is a -condensation product of n-heptanal, so it must be taken to add the benzaldehyde first and then a controlled addition of n-heptanal to it so that the n-heptanal only has benzaldehyde to react with. Adding the n-heptanal first cycle instead of benzaldehyde to the recycled NaOH - catalyst solution can lead to the formation of self-condensed products and is

to be avoided. At high concentrations of surfactant, high RPMs of the stirrer are to be avoided as it can cause foaming of the reaction mass.

3.2. Experimental results.

3.2.1. Catalyst reusability studies.

Batch 1 from the TLC analysis found that all reactants were consumed to obtain the product, along with a small amount of self-condensation by-product (Table 1). A similar result was found in batch 2, with almost complete conversion to Jasminaldehyde (Table 1). In batches 3 and 4, it was observed that there is a faint spot below benzaldehyde and n-heptanal, stating that there is a formation of benzoic acid and n-heptanoic acid, respectively, due to oxidation by exposure to air (Table 1). The product obtained had a very similar profile to the standard Jasminaldehyde. Therefore, it is quite evident that the catalyst reusability is good, and a consistent product is obtained.

Table 1. Catalyst reusability analysis for Batch 1-4.

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.015M
NaOH	40	0.02	0.8g	-	-

3.2.2. Optimization analysis for temperature variation.

At varying reaction temperatures, it was found that the reaction rate was highly affected by it. It was found that for the reaction at 60°C, the reaction was completed in 2 hours, while at 20°C (Table 2), it was found that the reaction was completed in around 5 hours; however, there was a self-condensation product higher in this case, therefore slower the reaction, the more likely it is for the n-heptanal molecules interact for self-condensation. The reaction time for the 60°C process was much lesser; however, it still requires energy for heating and maintaining the reaction temperature at 60°C, while the same results can be achieved at 30°C without any external factors to obtain the same conversions in 3 and a half hours. Also, it was found that the oxidation products are more in the case of 60°C conditions.

Table 2. Temperature variation- for 20°C.

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.015M
NaOH	40	0.02	0.8g	-	-

3.2.3. Optimization analysis for reactant molar ratio.

From Tables 2 and 3, where the n-HA:BA ratio was 1:1.3 and 1:1.5, respectively, it was found that the reaction was much more rapid as there is more contact between the n-HA and BA and thus more formation of cross condensation product Jasminaldehyde.

Table 3. Chemical Table: Batch 9 (Batch 9 : n-Heptanal : Benzaldehyde – 1 : 1.5).

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.03	3.18g	3.05ml	-
CTAB	364.45	-	-	40ml	0.015M
NaOH	40	0.02	0.8g	-	-

3.2.4. Optimization analysis for Surfactant concentration.

For batch 11 – 15 (Tables 4-7), where the surfactant CTAB concentration was varied, it was found that for concentrations of the surfactant below 0.1M, the conversion was consistently good. After the completion of the reaction, the product phase separates from the aqueous layer well and leads to easy separation of product. For batches 14 and 15, where the surfactant concentration was 0.2M and 0.3M, respectively, it was found that the layers were not separate, and a single-phase milky solution was obtained carrying the product. Thus, it is required to dilute the mixture so that the product is thrown out of the solution and can be separated with ethyl acetate and enriched by evaporation. This product is possibly contaminated from the ethyl acetate and is not as pure as the earlier batches. For surfactant concentrations of 0.015M and below, the number of micelles formed is less, so the reaction rate becomes slower as reason. Also, there is a likelihood of more contact between n-HA to form a more self-condensation product. There are also more oxidation products in this case.

Table 4. Chemical table: Batch 11 (Batch 11 : 0.01M CTAB concentration).

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.01M
NaOH	40	0.02	0.8g	-	-

Table 5. Chemical table: Batch 12.

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.05M
NaOH	40	0.02	0.8g	-	-

Table 6. Chemical table : Batch 13 (Batch 13 : 0.1M CTAB concentration).

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.1M
NaOH	40	0.02	0.8g	-	-

Table 7. Chemical table : Batch 15(Batch 15 : 0.3M CTAB concentration).

Compound	Mol. Wt.	No. of moles	Wt. in g	Amt. in ml	Conc. in M
n-heptanal	114	0.02	2.28g	2.82ml	-
Benzaldehyde	106	0.02	2.12g	2.03ml	-
CTAB	364.45	-	-	40ml	0.3M
NaOH	40	0.02	0.8g	-	-

3.2.5. Jasminaldehyde olfactive.

Jasminaldehyde obtained had a sweet, floral, oily, fruity, herbaceous, jasmine, honey-like, waxy, metallic, green, and aldehydic odor. It lasts upwards of 120 hours on the blotter and is very tenacious. Throughout exposure to air, it turns yellowish because of oxidation and gives out an oxidized, metallic, rancid oily smell that is quite harsh. The soap dosed with 1% Jasminaldehyde gave nice strong jasmine, honey, waxy, aldehydic, and green notes. The raw material on its own in a soap imparted quite a strong fragrance strength.

3.2.6. Formulations using synthesized Jasminaldehyde.

Jasmine infusion (Table S1): The overall profile is very strong with a nice jasmine character, with green, creamy, woody, aldehydic, and white floral nuances. The

jasminaldehyde promotes the jasmine character in the fragrance; benzyl acetate boosts the fruity jasmine nuances; benzyl salicylate acts as a fixative for the other raw materials and also adds to the jasmine character; galaxolide gives a clean musky feel; eugenol helps give a warm spicy carnation floral touch; hedione brings in the premium white floral, jasmine character; alpha-hexyl cinnamic aldehyde has a similar role to jasminaldehyde, helping with the jasmine, white floralcy; the indole in traces helps to give that slight animalistic touch to the jasmine to add more originality to it; to prevent the formula from coloring because of the oxidation of indole it is necessary to add BHT as an antioxidant; lilyal brings in the watery Muguet character which adds another dimension to the fragrance; lilyal also provides a Muguet touch along with some woody undertones; vanillin is added to give a smooth creaminess to the base; jasmolactone gives the jasmine a more lactony, coconutty, peachy touch, making it more robust.

Floral Muguet (Table S2): The profile is pleasant with a clean Muguet, jasmine, and white floral heart, with some rosy character for more complexity. Here citronellol is added to provide a nice citrusy, rosy touch; hedione enhances the jasmine character to make it more premium; jasminaldehyde for white floral jasmine notes; lilyal for the water, green, Muguet character; phenyl ethyl alcohol for a petally rose character; a touch of rose oxide for a metallic rose character for robustness; alpha-terpineol gives a piney, terpenic, citrus freshness to the profile; lilyal provides a nice Muguet, floral character with woody nuances and hydroxycitronellol gives a clean lily, green, rosy touch.

Fresh Floral Bouquet (Table S3): Nice floral bouquet with nice jasmine, rose, ylang-ylang, and fresh, fruity, sparkling nuances. Here the acetophenone imparts the strong jasminic, almondy, waxy, white floral notes enhancing the floralcy of the overall formula; cis-3-hexenol gives a green leafy apple fruity touch for more freshness; iso amyl phenyl ether provides a green touch to the fragrance; alpha-terpineol is for the piney, terpenic, citrus freshness; 2-methyl-4-phenyl-butan-2-ol gives a fresh rosy, violet, iris, lily character; citronellol, geraniol, and phenyl ethyl alcohol adds to the rosy character along with some freshness; indole provides the natural animalic jasmine, ylang-ylang character to the fragrance; phenylacetaldehyde dimethyl acetal gives a green, leafy, floral touch to the fragrance.

3.3. Discussion.

A general aldol condensation with equimolar concentration of n-heptanal and benzaldehyde with 0.01M surfactant solution for 4 hours afforded a lower selectivity of jasminaldehyde. On increasing the concentration of surfactant up to 0.1M it was found that there was close to no self-condensation product, and a highly pure jasminaldehyde was obtained. It was found that self-condensation was higher at lower RPMs due to improper mixing, and at higher RPMs, cross-product selectivity was nearly 100% (using 0.1M surfactant catalyst). On varying reaction temperatures, that is, 20°C, 30°C, 40°C, 50°C, and 60°C, it was found that the reaction rate was highly affected by it. It was found that for the reaction at 60°C (with 0.1M surfactant), the reaction was completed in 2 hours, while at 20°C, it was found that the reaction was completed in around 5 hours; however, there was a self-condensation product higher in this case, therefore slower the reaction, the more likely the n-heptanal molecules interact for self-condensation. The reaction time for the 60°C process was much lesser; however, it still requires energy for heating and maintaining the reaction temperature at 60°C, while the same can be achieved at 30°C without any external factors to obtain the same conversions in 3 and a half hours. Adding the n-heptanal first after the first cycle instead of

benzaldehyde in the recycled NaOH – catalyst solution leads to the formation of self-condensed products and is to be avoided. On varying surfactant concentrations, it was found that, at a low concentration of 0.01M, cross aldol product is less selective because of fewer micelles with less concentration of reactants at positively charged heads of the surfactant. Whereas, as predicted, the 0.1 M surfactant solution promoted nearly 100% selectivity of the cross product. However, at concentrations of 0.2M and 0.3M, it was found that after keeping the reaction mixture still after the reaction, the product layer does not separate and remains in one single phase. At higher RPMs, foaming of the reaction mass was also detected. Thus, it requires ethyl acetate to separate the product, which then requires another step to enrich the product, which is highly inefficient. The optimum process is equimolar benzaldehyde and n-heptanal in NaOH with 0.1M cetyltrimethylammonium bromide at 30deg C for 3 and 30 minutes to obtain highly selective Jasminaldehyde product with minimal 2-n-pentyl-2-nonenal.

Jasminaldehyde had a sweet, floral, oily, waxy aroma with Jasmin, honey, fruity, herbal nuances, and some metallic, green, aldehydic character. Being a cinnamic aldehyde derivative, it is highly tenacious and can be used as a fixative in formulations. On prolonged exposure to air, it oxidizes and gives out an oxidized, metallic, rancid oily smell that is highly repulsive. It performed extremely well in blotter evaluation and has a retentivity of upwards of 120 hours. It is highly stable in soap and detergent applications.

4. Conclusions

It was found that for the reaction at 60 deg C (with 0.1M surfactant), the reaction was completed in 2 hours, while at 20 deg C, it was found that the reaction was completed in around 5 hours; however, there was a self-condensation product higher in this case, therefore slower the reaction, the more likely the n-heptanal molecules interact for self-condensation.

Funding

This research received no external funding.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Krings, U.; Berger, R.G. Biotechnological production of flavours and fragrances. *Applied microbiology and biotechnology* **1998**, *49*, 1-8, <https://doi.org/10.1007/s002530051129>.
2. The Good Scents Company Information System, <http://www.thegoodscentscompany.com/>.
3. Stueben, K.C.; Deem, M.L. Union Carbide Corp. Surfactant-promoted aldol reactions. U.S. Patent 4,215,076, **1980**.
4. Vashishtha, M.; Mishra, M.; Shah, D.O. A novel approach for selective cross aldol condensation using reusable NaOH-cationic micellar systems. *Applied Catalysis A: General* **2013**, *466*, 38-44, <https://doi.org/10.1016/j.apcata.2013.06.015>.
5. Mudaliar, C.D.; Nivalkar, K.R.; Mashraqui, S.H. Michael reactions in aqueous micelles of cetyltrimethylammonium bromide. *Organic preparations and procedures international* **1997**, *29*, 584-587, <https://doi.org/10.1080/00304949709355237>.
6. Kitawat, B.S.; Singh, M.; Kale, R.K. Robust Cationic Quaternary Ammonium Surfactant-Catalyzed Condensation Reaction for (E)-3-Aryl-1-(3-alkyl-2-pyrazinyl)-2-propenone synthesis in water at room

- temperature. *ACS Sustainable Chemistry & Engineering* **2013**, *1*, 1040-1044, <https://dx.doi.org/10.1021/sc400102e>.
7. Sudheesh, N.; Sharma, S.K.; Shukla, R.S. Chitosan as an eco-friendly solid base catalyst for the solvent-free synthesis of jasminaldehyde. *Journal of molecular catalysis A: Chemical* **2010**, *321*, 77-82, <https://doi.org/10.1016/j.molcata.2010.02.005>.
 8. Sharma, S.K.; Patel, H.A.; Jasra, R.V. Synthesis of jasminaldehyde using magnesium organo silicate as a solid base catalyst. *Journal of Molecular Catalysis A: Chemical* **2008**, *280*, 61-67, <https://doi.org/10.1016/j.molcata.2007.10.013>.
 9. Yadav, G.D.; Aduri, P. Aldol condensation of benzaldehyde with heptanal to jasminaldehyde over novel Mg–Al mixed oxide on hexagonal mesoporous silica. *Journal of Molecular Catalysis A: Chemical* **2012**, *355*, 142-154, <https://doi.org/10.1016/j.molcata.2011.12.008>.
 10. Sharma, S.K.; Parikh, P.A.; Jasra, R.V. Eco-friendly synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde using hydrotalcite as a solid base catalyst. *Journal of Molecular Catalysis A: Chemical* **2008**, *286*, 55-62, <https://doi.org/10.1016/j.molcata.2008.01.039>.
 11. Arctander, S. *Perfume and flavor chemicals:(aroma chemicals)*. Allured Publishing Corporation. Volume 2, **1969**.
 12. Sudheesh, N.; Shukla, R.S. Investigations on different efficient strategies for the selective synthesis of jasminaldehyde over HRhCO (PPh₃)₃–hexagonal mesoporous silica and chitosan catalysts. *Reaction Kinetics, Mechanisms and Catalysis* **2022**, 1-18.
 13. Ekanayake, U.M.; Weerathunga, H.; Weerasinghe, J.; Waclawik, E.R.; Sun, Z.; MacLeod, J.M.; O'Mullane, A.P.; Ostrikov, K. Sustainable Claisen-Schmidt chalcone synthesis catalysed by plasma-recovered MgO nanosheets from seawater. *Sustainable Materials and Technologies* **2022**, *32*, <https://doi.org/10.1016/j.susmat.2022.e00394>.
 14. Rawat, S.; Singh, B.; Kumar, R.; Pendem, C.; Bhandari, S.; Natte, K.; Narani, A. Value addition of lignin to zingerone using recyclable AlPO₄ and Ni/LRC catalysts. *Chemical Engineering Journal* **2022**, *431*, <https://doi.org/10.1016/j.cej.2021.134130>.
 15. Bargujar S.; Ratnani, S. Aldol condensation: green perspectives. *Journal of the Iranian Chemical Society* **2022**, *19*, 2171-2190, <https://doi.org/10.1007/s13738-021-02464-w>.
 16. Wu, Z.; Li, Z.; Li, C. Cooperative catalytic effects between the penta-coordinated Al and Al₂O₃ in Al₂O₃-AlPO₄ for aldol condensation of methyl acetate with formaldehyde to methyl acrylate. *Chinese Journal of Chemical Engineering* **2022**, <https://doi.org/10.1016/j.cjche.2021.11.025>.
 17. Mohanty, A.; Borah, R.K.; Fatrekar, A.P.; Krishnan, S.; Vernekar, A.A. Stepping towards benign alternatives: sustainable conversion of plastic waste into valuable products. *Chemical Communications* **2021**, *57*, 10277-10291, <https://doi.org/10.1039/d1cc03705f>.
 18. Banerjee, M.; Panjekar, P.C.; Bhutia, Z.T.; Bhosle, A.A.; Chatterjee, A. Micellar nanoreactors for organic transformations with a focus on “dehydration” reactions in water: A decade update. *Tetrahedron* **2021**, *88*, <https://doi.org/10.1016/j.tet.2021.132142>.
 19. Chundawat, N.S.; Pathan, S.; Singh, G.P.; Deuri, A.S.; Zarrintaj, P.; Chauhan, N.P.S. Synthesis and characterization of chitosan pyridyl imine palladium (CPIP) complex as green catalyst for organic transformations. *Chemical Papers* **2021**, *75*, 2835-2850, <https://doi.org/10.1007/s11696-021-01526-w>.
 20. Harish, N.; Kathayini, N.; Baby, B.; Nagaraju, N. Investigation of active sites using solid state 27Al and 31P MAS NMR in ceramic amorphous aluminophosphate materials prepared from different potassium salts of phosphate for the synthesis of diphenyl urea derivatives. *Journal of Physics and Chemistry of Solids* **2021**, *154*, <https://doi.org/10.1016/j.jpcs.2021.110087>.
 21. Bai, Y.; Jian, J.; Liu, D.; Zhao, X. Synthesis, characterization and application of a new biomass-based antioxidant derived from vanillin and methyl ethyl ketone. *Journal of Cleaner Production* **2021**, *316*, <https://doi.org/10.1016/j.jclepro.2021.128315>.
 22. Di Fabio, E.; Incocciati, A.; Boffi, A.; Bonamore, A.; Macone, A. Biocatalytic Production of Aldehydes: Exploring the Potential of Lathyrus cicera Amine Oxidase. *Biomolecules* **2021**, *11*, <https://doi.org/10.3390/biom11101540>.
 23. Houssaini, J.; Naciri Bennani, M.; Ziyat, H.; Arhzaf, S.; Qabaqous, O.; Amhoud, A. Study of the Catalytic Activity of the Compounds Hydrotalcite Type Treated by Microwave in the Self-Condensation of Acetone. *International Journal of Analytical Chemistry* **2021**, *2021*, <https://doi.org/10.1155/2021/1551586>.
 24. Abdulridha, S.; Zhang, R.; Xu, S.; Tedstone, A.; Ou, X.; Gong, J.; Mao, B.; Frogley, M.; Bawn, C.; Zhou, Z.; Zhang, X. An efficient microwave-assisted chelation (MWAC) post-synthetic modification method to produce hierarchical Y zeolites. *Microporous and Mesoporous Materials* **2021**, *311*, <https://doi.org/10.1016/j.micromeso.2020.110715>.
 25. Ren, X.; Xu, D.; Yin, Y.; Zou, X.; Wang, Y.; Shang, X.; Wang, X. High Catalytic Performance and Sustainability of Zr Modified Aluminophosphate for Vapor-Phase Selective O-Methylation of Catechol with Methanol. *Catalysts* **2021**, *11*, <https://doi.org/10.3390/catal11060740>.
 26. Diwald, O.; Hartmann, M. Adsorption and Chemical Reactivity. In: *Metal Oxide Nanoparticles: Formation, Functional Properties, and Interfaces*. Volume 2, **2021**; pp. 593-636, <https://doi.org/10.1002/9781119436782.ch16>.

27. Desale, V.; Thorat, B.; Mali, S.; Ramesh, S.Y. Synthesis, admetSAR Predictions, DPPH Radical Scavenging Activity, and Potent Anti-mycobacterial Studies of Hydrazones of Substituted 4-(anilino methyl) benzohydrazides (Part 2). *Current Computer-Aided Drug Design* **2021**, *17*, 493-503, <https://doi.org/10.2174/1573409916666200615141047>.
28. Mali, S.; Pandey, A. Balanced QSAR and Molecular Modeling to Identify Structural Requirements of Imidazopyridine Analogues as Anti-infective Agents Against Trypanosomiases. *Journal of Computational Biophysics and Chemistry* **2021**, *21*, 83-114.
29. Thorat, B.; Mali, S.; Rani, D.; Ramesh, S.Y. Synthesis, In silico and In vitro Analysis of Hydrazones as Potential Antituberculosis Agents. *Current Computer-Aided Drug Design* **2021**, *17*, 294-306, <https://doi.org/10.2174/1573409916666200302120942>.
30. Mali, S.; Pandey, A. Molecular Modeling Studies on 2,4-Disubstituted Imidazopyridines as Anti-Malarials: Atom-Based 3D-QSAR, Molecular Docking, Virtual Screening, In-Silico ADMET and Theoretical Analysis. *Journal of Computational Biophysics and Chemistry* **2021**, *20*, 267-282.
31. Mali, S.; Pandey, A; Bapu, R. Thorat; Chin-Hung, L. Multiple 3D- and 2D-quantitative structure–activity relationship models (QSAR), theoretical study and molecular modeling to identify structural requirements of imidazopyridine analogues as anti-infective agents against tuberculosis. *Structural Chemistry* **2022**, 1-16, <https://doi.org/10.1007/s11224-022-01879-2>.

Supplementary Information

S1. Perfume formulation.

Fragrance raw materials were added to a beaker in the order of appearance on the table. It is ensured that the beaker is free from any odor. Care to be taken while the addition of RMs with the help of mandatory PPEs like gloves, face mask, safety goggles and lab coat. RMs were added with the help of paper strips. Entire formulation was stirred with the help of a magnetic stirrer, and the final compounded fragrance is evaluated with a paper blotter.

Table S1. Jasmine Infusion formulation.
Jasmine Infusion

Sr. No.	Raw Material	Percentage (%)	Amt. in g
1	Jasminaldehyde	30	3
2	Benzyl acetate	19	1.9
3	Benzyl salicylate	4	0.4
4	Eugenol	1	0.1
5	Galaxolide	4	0.4
6	Hedione	9.6	0.96
7	Alpha-hexyl cinnamic aldehyde	23	2.3
8	Indole (10% in DPG)	1	0.1
9	BHT	0.1	0.01
10	Lilial	3.5	0.35
11	Lylal	0.8	0.08
12	Vanillin (10% in DPG)	1	0.1
13	Jasmolactone (10% in DPG)	3	0.3
	Total	100	10

Table S2. Floral Muguet formulation.
Floral Muguet

Sr. No.	Raw Material	Percentage (%)	Amt. in g
1	Citronellol	10	1
2	Hedione	10	1
3	Jasminaldehyde	10	1
4	Lilial	10	1
5	Phenyl ethyl alcohol	10	1
6	Rose oxide (10% DPG)	2	0.2
7	Alpha-terpineol	20	2
8	Dipropylene glycol	15	1.5
9	Hydroxycitronellol	9	0.9
10	Lylal	4	0.4
	Total	100	10

Table S3. Fresh Floral Bouquet formulation.
Fresh Floral Bouquet

Sr. No.	Raw Material	Percentage (%)	Amt. in g
1	Acetophenone (10% in DPG)	3.4	0.34
2	Cis-3-hexenol (10% in DPG)	2	0.2
3	Citronellol	20	2
4	Dipropylene glycol	10	1
5	Isoamyl phenyl ether	0.7	0.07
6	Geraniol	12	1.2
7	Jasminaldehyde	20	2
8	Indole (10% in DPG)	1.5	0.15
9	BHT	0.1	0.01
10	Phenyl acetaldehyde dimethyl acetal (50%)	0.7	0.07
11	Phenyl ethyl alcohol	1	0.1
12	Alpha-terpineol	6.4	0.64
13	2-methyl-4-phenyl-butan-2-ol	20	2
	Total	100	10

S2. Fragrance application.

S2.1. Soap application.

100g soap noodles (Symrise standard soap noodles) are taken, and to it, add 1.5g of the fragrance. The noodles are well mixed and passed through the plodder as shown in Fig. S1 through a noodle stencil/mould/filter. This is repeated for 3 cycles to get uniform distribution of the fragrance.



Figure S1. Soap fragrance mixing.

After mixing, the noodles are passed through the plodder again, this time through a strip stencil/mould/filter as shown in Fig. S2 the strips are cut as they pass through the outlet. 2 strips obtained are put together, wrapped in butter paper, and are stamped in the soap mould to obtain the final soap as in Fig. S3.



Figure S2. Soap strip making.



Figure S3. Soap Stamping.

S2.2. Cream application.

10g of standard Symrise cream base is taken in a jar, and 1% of fragrance is added to it. The cream is mixed well with a glass rod. The resultant cream is allowed to stand for 1 day to ensure fragrance maturation

S2.3. Shower gel application.

10g of shower gel base is taken in a jar, and 1% of fragrance is added to it. The mixture is mixed well with the help of a glass rod for uniform distribution of the fragrance. The resultant shower gel is allowed to stand for 1 day to ensure fragrance maturation.

S2.4. Shampoo application.

10g of pearlescent shampoo base is taken in a jar, and 1% of fragrance is added to it. The mixture is mixed well with the help of a glass rod for uniform distribution of the fragrance. The resultant shampoo is allowed to stand for 1 day to ensure fragrance maturation.

S2.5. Talcum application.

10g of talcum powder base is taken in a jar, and 1% of fragrance is added to it. The mixture is mixed well with the help of a glass rod, and the jar is shut and shaken well. The resultant talcum powder is allowed to stand for 1 day to ensure that the fragrance is matured well.

S2.6. Thin-layer chromatography (TLC).

The two reactants benzaldehyde and n-heptanal, standard jasminaldehyde, and the product are spotted on the TLC plate. The eluent system used here is Toluene: Ethyl acetate 93:7.