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REVIEW ARTICLE

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Synthesis of (–)-menthol: Industrial synthesis routes and recent development

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Abstract

(–)-Menthol is one of the most popular aroma compounds worldwide. While in the past mostly extracted from mint plants, today (–)-menthol synthesis from other raw materials is becoming more relevant. Common starting materials for menthol synthesis are *m*-cresol, citral and myrcene, but also substrates like menthone, mono- and bicyclic terpenes and terpenoids have been used for this purpose in the past. As for many applications (–)-menthol of high purity is required, asymmetric syntheses and enantiomeric resolution of obtained raw products are applied for menthol production. This review gives an overview on the most important synthetic menthol production processes of the companies Symrise, Takasago and BASF and relevant literature in the field of menthol synthesis with a focus on the last 20 years.

KEYWORDS
asymmetric catalysis, heterogeneous catalysis, industrial chemistry, menthol

1 | INTRODUCTION

Essential oils of different mint species (lat. Mentha) were already used in ancient times for medicinal and cosmetical purposes. As one of the main components of the essential oils,[1–7] (–)-menthol is responsible for the well-known taste, smell and cooling sensation of mint. Currently, it is the worldwide most used aroma compound, with still growing demand.

Although mint oil has been used for many centuries, pure menthol was first characterized in 1862 by Oppenheim.[8] Menthol has three stereogenic centres, resulting in four pairs of optical isomers (Figure 1).

The physical properties of the pure enantiomers and the racemic mixtures vary slightly (Table 1). While the boiling point difference between the highest and lowest boiling isomer with around 4°C is small in comparison to the range of the melting points, fractional distillation is still the method of choice for separation of the isomers. Concerning the organoleptic properties, the absolute configuration of menthol has a great impact. While the isomers isomenthol, neomenthol and neoisomenthol have a rather unpleasant smell with earthy and musty notes, menthol is associated with the typical fresh minty aroma and has a subjective cooling sensation on the human mucosa.[1] As the chemoreceptors of the body can be highly shape sensitive, the fresh and cool aroma of the L-(–)-menthol enantiomer (Laevomenthol) is percepted much stronger than that of D-(+)-menthol, which in addition has some slightly unpleasant notes. The application of menthol as an aroma compound is therefore limited to (–)-menthol or the racemic mixture of the two enantiomers. Menthol is used commonly in sweets (e.g. chewing gum), oral care products (e.g. toothpastes, mouthwashes), cosmetical and medicinal products (e.g. creams, balms, inhalations, cough syrups) and as additive in tobacco. The biological properties of menthol have been reviewed by Kamatou et al. in 2013.[9]

For the longest time menthol has exclusively been extracted from natural mint or used directly in combination with other compounds as mint-oil. The extraction and usage on a large scale started in the second half of the 20th century. The common process consists

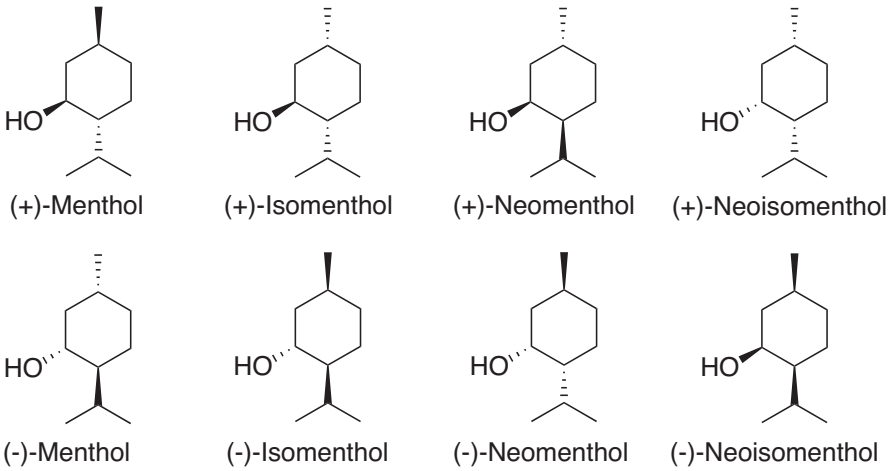


FIGURE 1 Isomers of menthol

TABLE 1 Physical properties of menthol isomers[10]

Isomer	Boiling point (°C)	Melting point (°C)	$[\alpha]_D^{20}$ (20% EtOH)
(−)-Menthol	216.5	43.0	−50
rac-Menthol	216.5	38.0	0
(−)-Isomenthol	218.6	82.5	−26
rac-Isomenthol	218.6	53.5	0
(−)-Neomenthol	211.7	−15.0	−20
rac-Neomenthol	211.7	52.0	0
(−)-Neoisomenthol	214.6	−8.0	−2
rac-Neoisomenthol	214.6	13.5	0

of the fast crystallization from cornmint oil at around −40°C and the purification of the obtained crude menthol by following slow recrystallization under strictly controlled conditions. A comprehensive overview on mint cultivation, production of mint oils or natural menthol and their properties is provided by Lawrence et al. in the monograph "Mint".[1]

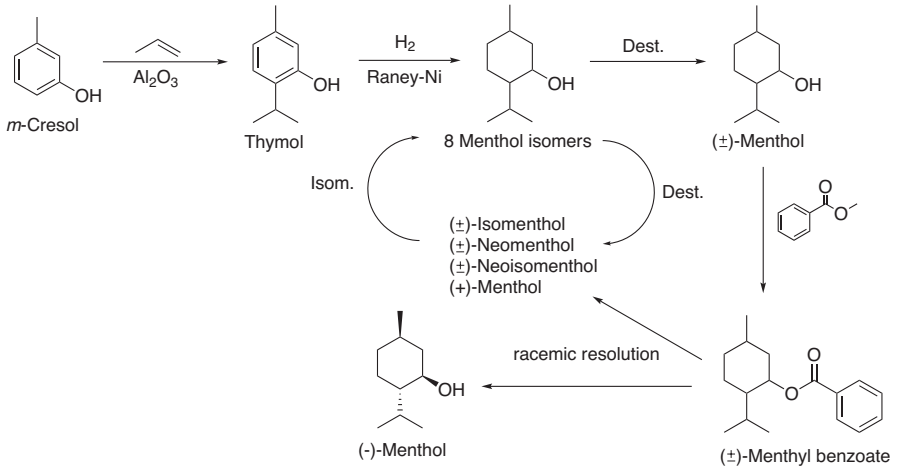
The increasing world demand and the price volatility of natural menthol has led to research on possible synthesis of menthol from other raw materials. In 1998, Clark estimated the annual worldwide menthol production to be 11 800 metric tons, of which around 80% were natural menthol and 20% synthetic menthol.[11] Currently, the worldwide production is around 34 000 metric tons per year, with the share of synthetic menthol now being about 60%. This gives a clear indication to the growing importance of synthetic menthol.

For menthol synthesis, the starting materials should be highly available and applicable in an efficient and cost-effective synthesis route. The most successful synthetic routes of the companies Symrise and Takasago (both developed in the 1970s), as well as BASF (started with menthol production in 2012) have been discussed in various textbooks (e.g. "Natural products in the chemical industry",[12] "Fundamentals of Fragrance Chemistry[13]) and most recently reviewed by Bernd Schäfer in 2013.[14] While our review also gives a short overview of this processes, the focus is on the peer-reviewed literature of the last 20 years dealing with synthesis of (−)-menthol from *m*-cresol, citral, myrcene and naturally occurring terpenoids with *p*-menthan structure and shall provide an overview of the most promising approaches.

2 | SYMRISE: MENTHOL FROM *M*-CRESOL AND PROPENE

The synthesis of menthol starting from *m*-cresol (Figure 2) was developed by the German company Haarmann & Reimer, which later became part of Symrise AG.[15] It starts with the Friedel-Crafts-alkylation of fossil-based *m*-cresol with propene to *p*-thymol over alumina[16] or acidic zeolites.[17] Hydrogenation of thymol over nickel- or cobalt-containing catalysts under conditions enabling isomerization results in a racemic mixture of the four menthol diastereomers with >50% of the thermodynamically preferred (±)-menthol.[15,18] (±)-Menthol is separated from the mixture by distillation. The racemic resolution of (−)- and (+)-menthol enantiomers is achieved by transesterification with benzoic acid methyl ester and enantioselective crystallization by seeding the mixture with enantiopure (−)-menthyl benzoate under strict crystallization conditions.[19] The transesterification is necessary, because (±)-menthol forms crystals with a racemic composition and therefore cannot be resolved by this method. The remaining fraction of iso-, neo- and neoisomenthol together with (+)-menthol (after hydrolysis from (+)-menthyl benzoate) is isomerized to an equilibrium mixture, consisting of 60% menthol, 30% neomenthol and 10% isomenthol.[20,21] The recycling process minimizes waste and maximizes the yield of the desired (−)-menthol isomer. The selectivity for the (±)-menthol diastereomer in the initial thymol hydrogenation step and the formation of racemates, resulting in the need for recycling steps and a rather complex enantiomeric resolution, are compensated by the high availability of the starting materials. While thymol could be recovered from natural sources like thyme oil,[22] currently its price is much higher than the synthetic product. This might change in future, but regarding availability and seasonal price fluctuations

FIGURE 2 Symrise (–)-menthol process



the raw material will have similar disadvantages as mint for natural menthol production.

2.1 | Recent publications on menthol synthesis from *m*-Cresol

Alternative versions of some of the reaction steps have been described in the literature. Continuous alkylation of *m*-cresol with propene in the gas phase has been accomplished over the acidic zeolite ZSM-5 by O'Connor et al. with selectivity (*S*) for thymol up to 90%.[23] Besides the directing effects of the hydroxyl and methyl group, the high selectivity is mostly attributed to the shape of the narrow pores of the catalyst, which allow the preferred diffusion of thymol. In contrast, the equilibrium mixture of the possibly formed isomers contained only 20% thymol and consisted mainly of 3-isopropyl-5-methylphenol. This and the preferred formation of thymol at lower temperatures indicate that the formation of thymol is kinetically controlled. Consistently the selectivity declined with increasing conversion (*X*).

Many publications relating to the isopropylation of *m*-cresol include the in situ generation of propene from isopropanol. The major drawback is the formation of water as byproduct, which can have negative effects through catalyst deactivation. With this approach, the highest selectivity for thymol formation was reported for the mesoporous catalyst Al-MCM-41.[24–26] Selvaraj and Kawi claimed 100% thymol selectivity at 91% conversion over Al-MCM-41 impregnated with zinc between 290°C and 350°C in continuous vapour phase isopropylation.[24] A isopropanol/m-cresol = 2 feed mole ratio provided the best results, with lower ratios leading to lower conversion, while higher ratios resulted in dialkylation. At lower temperatures (200–260°C) significant amounts of other thymol isomers and double C-alkylated products were produced. In contrast, mostly O-alkylated products were observed with not impregnated Al-MCM-41 at lower temperatures. Afreen et al. have reported the vapour phase alkylation of *m*-cresol with isopropanol over various zeolites[27–29] and zinc aluminates.[30] Good results were achieved with Zn-exchanged Y zeolite, as the catalyst with the highest acid density and Lewis acid strength, with up to 75% thymol selectivity. With progress of the reaction, the deactivation of the catalyst through coking led to falling thymol selectivity, while the formation of dialkylated products increased substantially. In contrast to the findings of O'Connor et al., the authors reported preferred formation of the O-alkylated product over H-ZSM-5 zeolite. Other reports for the alkylation of *m*-cresol with medium selectivity can be found for catalysts like H-BEA zeolite,[24,27,31] $ZnAl_2O_4$,[32] ionic liquids,[33,34] sulphated ZrO_2-TiO_2,[35] (sulphated) Al_2O_3,[36] heterogenized $AlCl_3$,[37] Fe_2O_3[38] and magnesium-aluminium hydrotalcites[39] (Table 2).

The hydrogenation of thymol can be achieved with most common heterogeneous hydrogenation catalysts like supported platinum-group metals,[40–44] copper chromite,[45,46] and supported nickel catalysts.[47,48] Menthol can be formed either by direct hydrogenation or via menthone/isomenthone, formed as an intermediate through keto-enol tautomerization. In the second pathway, the hydrogenation of menthone leads to the menthol and neomenthol isomers, while hydrogenation of isomenthone results in isomenthol and neoisomenthol formation. However, under hydrogenation conditions epimerization between menthone and isomenthone via the enol can occur. Table 3 shows selected results of selectivity for the hydrogenation of thymol.

Under reaction conditions suppressing the isomerization of the menthol isomers, neoisomenthol is being formed more readily in both pathways due to all-*syn* addition of hydrogen at the catalyst surface.[40,41,43,47,48] The highest selectivity was reported by Solladie-Cavallo et al. for hydrogenation with Ru/Al_2O_3 in ethanol at 40°C to a mixture of menthol isomers with 79% neoisomenthol and 10% isomenthol.[43] In hexane, the reaction was slower and resulted in a mixture with 48% neoisomenthol and 44% isomenthol, indicating an increased *anti* addition of hydrogen to thymol in the non-polar solvent.

Different selectivity has been achieved with several Pd/C catalysts.[44] Under basic conditions, up to 84% of the menthol diastereomer was formed, while in aqueous acetic acid the selectivity for neomenthol was higher with up to 56%. While the authors identified the hydrogenation via menthone as the main pathway, they did not

TABLE 2 Overview of selected catalysts for the isopropylation of *m*-cresol

Catalyst	T [°C]	Substrate ratio	Space velocity/ Residence time	*X* (*m*-cresol) [%]	*S* (thymol) [%]	Ref.
ZSM-5 *(Si/Al = 110)*	200	propene/*m*-cresol = 1	WHSV = 0.4 h^{-1}	55	90	23
Zn-Al-MCM-41 *(Si/[Al + Zn] = 75)*	350	i-PrOH /*m*-cresol = 2	WHSV = 1.45 h^{-1}	91	100	24
Al-MCM-41 *(Si/Al = 21)*	350	i-PrOH /*m*-cresol = 2	WHSV = 1.45 h^{-1}	76	88	
ZnY *(Si/Al = 2.4)*	250	i-PrOH /*m*-cresol = 2	WHSV = 2.8 h^{-1}	92	75	27
H-BEA zeolite *(Si/Al = 20)*	290	i-PrOH /*m*-cresol = 2	WHSV = 1.45 h^{-1}	47	60	24
H-BEA zeolite *(Si/Al = 19)*	200	i-PrOH /*m*-cresol = 2	W/F = 0.3 h	57	47	31
$ZnAl_2O_3$ *(ZnO/Al_2O_3 = 0.5)*	270	i-PrOH /*m*-cresol = 5	WHSV = 0.5 h^{-1}	86	80	30
$ZnAl_2O_3$ *(ZnO/Al_2O_3 = 1)*	255	i-PrOH /*m*-cresol / water = 5:1:1	WHSV = 0.5 h^{-1}	78	88	32
$ZnCl_3^-$ - ionic liquid[a]	120	i-PrOH /*m*-cresol /ionic liquid = 2:1:1	5 h	96	24	33
	150	i-PrOH /*m*-cresol /ionic liquid = 2:1:1	n.s.	68	54	
HSO_4^- - ionic liquid[b]	190	i-PrOH /*m*-cresol /ionic liquid = 2:1:1	6 h	78	49	34
Sulfated ZrO_2-TiO_2 *(2:1)*	220	i-PrOH /*m*-cresol = 3	WHSV = 6.72 h^{-1}	73	75	35
γ-Al_2O_3	250	i-PrOH /*m*-cresol / water = 5:1:1	LHSV = 0.5 h^{-1}	74	90	36
$AlCl_3$-SiO_2	250	i-PrOH /*m*-cresol = 3	n.s.	78	48	37
Fe_2O_3	420	i-PrOH /*m*-cresol / water = 5:1:1	WHSV = 0.5 h^{-1}	17	60	38
MgAl-hydrotalcite	400	i-PrOH /*m*-cresol = 4	WHSV = 8.6 mole h^{-1} kg^{-1}	36	80	39

Abbreviations: LHSV, liquid hourly space velocity; n.s., not specified; *S*, selectivity; W/F, residence time; WHSV, weight hourly space velocity; *X*, conversion.

[a]N,N,N-triethyl-4-sulfobutan-1-aminium trichlorozincate (II).

[b]N,N,N-trimethyl-4-sulfobutan-1-aminium hydrogensulfate.

TABLE 3 Overview of selected catalysts for the hydrogenation of thymol

					S [%]				
Catalyst	p(H_2) [bar]	T [°C]	solvent	*X* [%]	NIML	NML	ML	IML	Ref.
Pt/C	30	40	c-Hex	100	64	25	9	2	40
	30	100	c-Hex	100	52	29	16	3	
Ru/Al_2O_3 (5%)	20	40	n-Hex	100	48	5	3	44	43
	20	40	EtOH	100	79	5	6	10	
Pd/C (10%)	35–40	125–130	H_2O (+NaOH)	100	n.s.	n.s.	78	n.s.	44
RuO_2/C	40	80	*i*-PrOH	n.s.	n.s.	n.s.	n.s.	87	49
Co/SiO_2	50	150	*t*-BuOH	n.s.	n.s.	n.s.	n.s.	71	50

Abbreviations: IML, isomenthol; ML, menthol; n.s., not specified; NIML, neoisomenthol; NML, neomenthol; *S*, selectivity; *X*, conversion.

rule out the possible isomerization of menthol diastereomers as the source of this selectivity.

With ruthenium oxide supported on pine needle char, Kumar et al. reported the formation of isomenthol with 87% yield in isopropanol.[49] Similar results were achieved by Murugesan et al. with 92% yield for menthols and 71% selectivity for isomenthol with cobalt nanoparticles supported on silica in *tert*-butanol.[50] Ravi and Divakar reported a high selectivity towards formation of (±)-menthol as main isomer in a solid state hydrogenation with Rh/Al_2O_3 and ß-cyclodextrines.[51]

While the isomerization over nickel-catalysts or copper chromite via dehydrogenation-hydrogenation of the menthol isomers obtained from thymol hydrogenation results in mixtures rich in the thermodynamically preferred (±)-menthol,[18,20,52] the separation of (−)-menthol remains challenging. In this context, racemic resolution of menthol under enzymatic catalysis could give a powerful alternative to physical processes. Vorlova et al. reported the racemic resolution of the menthyl benzoate enantiomers by *candida rugosa* lipase. The (−)-menthyl benzoate was selectively hydrolysed, resulting in (−)-menthol with an enantiomeric excess (ee) >99%.[53] Symrise claims similar selectivity,[54] while >97% ee have been achieved by Gao-Wei Zheng et al.[55] for hydrolysis of (−)-menthylacetate with esterase from *B. subtilis* even for high substrate concentrations. A different approach found in the literature is the enantioselective transesterification of (−)-menthol with vinyl acetate[56–59] or carboxylic acids.[60,61] Sun et al. reported an excellent 99% ee for continuous transesterification of (−)-menthol with vinyl acetate over immobilized *Thermomyces lanuginosus* lipase with retention of activity over a prolonged period of time.[59]

3 | SYNTHESIS ROUTES INCLUDING CITRONELLAL

Most of the publications in the field of menthol synthesis have been published for syntheses starting from citronellal or containing the cyclization of citronellal as the key step (Figure 3). In this chapter, the industrial menthol processes of Takasago and BASF, both with (+)-citronellal as the main intermediate, will be presented. Next, recent literature for one-pot synthesis of menthol, starting from citronellal or citral will be reviewed, followed by an overview of literature on the cyclization of citronellal to isopulegol.

3.1 | Takasago: Asymmetric synthesis from myrcene

The Japanese company Takasago started to produce menthol in the 1950s. While their starting materials and processes varied with time, they achieved a breakthrough in the 1980s by developing the first asymmetric (−)-menthol synthesis (Figure 4), which is still used nowadays.[62–65]

It starts with myrcene, which can be isolated from gum rosin and other renewable sources, but is mainly synthesized by pyrolysis of ß-pinene from wood turpentine.[62,66] The first step is a telomerization of myrcene with diethylamine, catalysed by *n*-butyllithium, to N,N-diethylgeranylamine.[67] In the following crucial step, N,N-diethylgeranylamine is isomerized with a chiral organometallic rhodium-BINAP catalyst,[68–70] giving (+)-citronellal enamine.[71–73] Through the shift of the double bond, chirality is induced in the molecule with high selectivity. The enamine is then hydrolysed to give (+)-citronellal with >98% ee, which is then selectively cyclized to (−)-isopulegol with aluminium tris(2,6-diphenylphenoxide) (ATPH).[62] Originally, $ZnBr_2$ was used in this step. Subsequent hydrogenation gives (−)-menthol.

While the myrcene used in the Takasago process is a naturally abundant and cheap substrate, the lack of chirality poses a great disadvantage. To overcome it, Takasago chose a chirality-inducing isomerization step instead of enantiomeric resolution (see Symrise process), which requires rather expensive homogeneous catalysts. Therefore, the optimization of catalyst recycling and lifetime is crucial for the cost-efficiency of the process. Takasago claims high turnover numbers of around 200 000 for this process. This, together with the high intrinsic selectivity in the following cyclization step, makes this approach feasible and results overall in a high (−)-menthol yield.

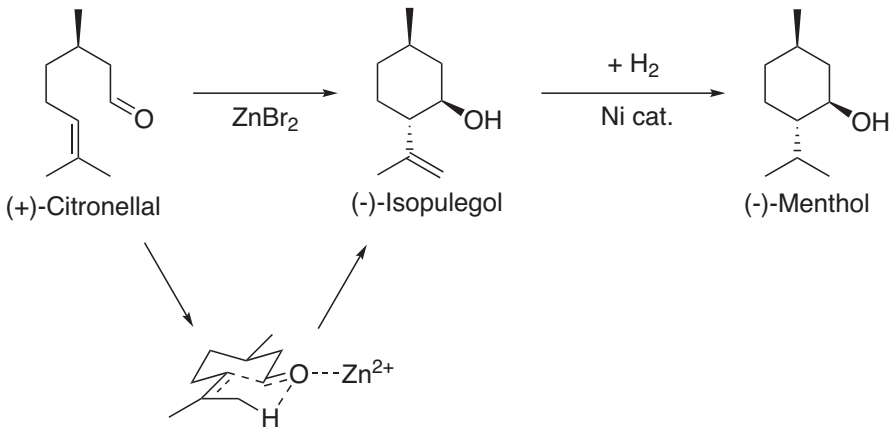


FIGURE 3 Transformation of citronellal to menthol

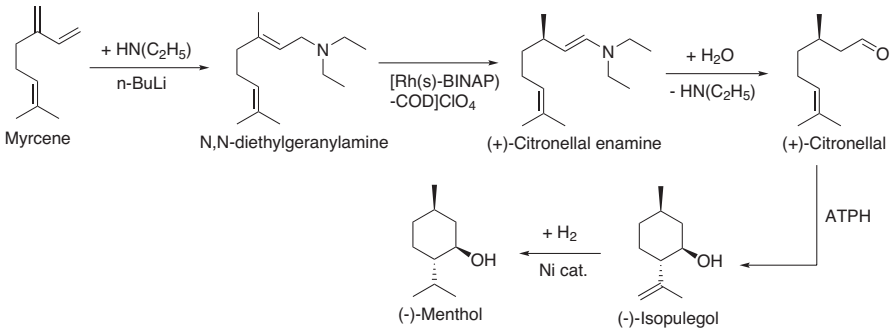


FIGURE 4 Takasago (−)-menthol process

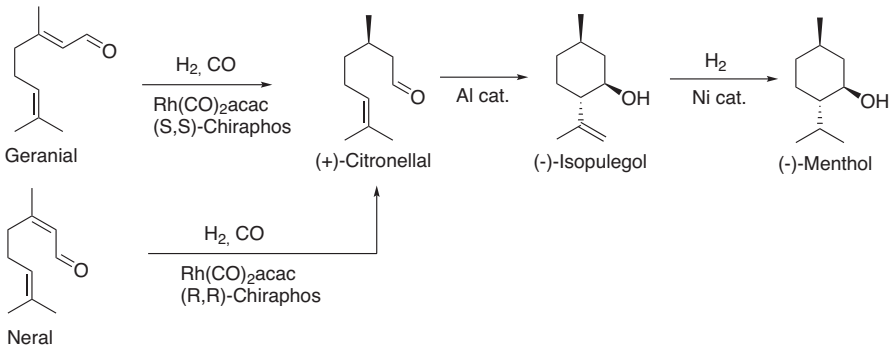


FIGURE 5 BASF (−)-menthol process

3.2 | BASF: Synthesis from Citral

Recently BASF has developed a menthol synthesis based on citral as a starting material (Figure 5). Citral is produced on a large scale by BASF from relatively cheap isobutene and formaldehyde via isoprenol, yielding nearly equal amounts of the two isomers geranial and neral.[74–76] The hydrogenation of geranial over a chiral rhodium-(S,S)-Chiraphos catalyst or neral over a rhodium-(R,R)-Chiraphos catalyst both lead to (+)-citronellal with >87% ee.[77] This remarkable chemo- and enantioselectivity can be achieved by pairing the Chiraphos-ligand with CO-ligands, which supresses the hydrogenation of the carbonyl group and the trisubstituted double bond and also prevents the undesired *cis/trans*-isomerization between the geranial and neral isomers, which can occur under hydrogenation conditions. An extensive literature survey on selective hydrogenation of citral to citronellal has been published by Stolle et al. in 2012.[78] Similar to the Takasago route, the next steps include the cyclization of citronellal to (−)-isopulegol, catalysed by diarylphenoxy aluminium compounds[79] or tris(aryloxy)aluminium compounds[80] and hydrogenation to (−)-menthol.[81,82]

Another approach patented by BASF includes the enantioselective hydrogenation of geraniol or nerol to citronellol over a chiral ruthenium-BINAP catalyst, followed by dehydrogenation to citronellal over mixed $ZnO/CaCO_3$ catalysts.[83] It is not clear if this route has been used on an industrial scale.

Similar to the Takasago process, the lack of chirality in the substrate makes the use of expensive rhodium-based catalysts necessary. While the citral produced by BASF is fossil-based, its synthesis has the potential of including renewable feedstocks in the future, making its menthol synthesis more attractive from a sustainability viewpoint.

3.3 | Recent publications on the cyclization of citronellal to isopulegol

As the most important step in the synthesis of (−)-menthol from citronellal, the cyclization to isopulegol has been studied extensively. Various homogeneous and heterogeneous catalysts showed good selectivity for formation of a diastereomeric mixture of isopulegols (isopulegol, isoisopulegol, neopulegol, neoisopulegol), but only few reports for formation of the (±)-isopulegol diastereomer with high selectivity can be found (Table 4).

The cyclization of citronellal with $ZnBr_2$, first reported by Nakatani and Kawashima in 1978, yields (±)-isopulegol with a high diastereoselectivity up to 94%.[84] It is induced by the most stable transition state (see Figure 3). However, equimolar amounts of the catalyst had to be used and partial dissolution of $ZnBr_2$ in the reaction medium posed a problem for reusability of the catalyst. Imachi et al. tried to overcome these disadvantages by loading $ZnBr_2$ on mesoporous silica.[85] The resulting heterogeneous catalyst gave isopulegols with 94% yield and 88% diasteroselectivity for (±)-isopulegol. No significant leeching of the $ZnBr_2$ was observed. However, the lifetime of the catalyst was not investigated by the authors.

Corma et al. reported Sn-BEA zeolite as an effective catalyst for the continuous cyclization of citronellal.[86] Selectivity for isopulegols >98%, with a diastereoselectivity for (±)-isopulegol of 83% were achieved for continuous operation, without significant deactivation

TABLE 4 Overview of selected catalysts for the cyclization of citronellal to isopulegol

Catalyst	T [°C]	*Y* (isopulegols) [%]	*DS* ((±)-isopulegol) [%]	Ref.
$ZnBr_2$	5–10	70	94	84
$ZnBr_2$/C16-HMS	25	94	87	85
Sn-Beta zeolite	80	97	83	86
K-10 (montmorillonite)	80	41	90	87
Zr-montmorillonite	80	98	90	
Zr-Beta zeolite	80	98[a]	93	88
Al/Fe-pillared montmorillonite	25	98	80	89
AlF_3	60	92[a]	92	90
ACPP[b]	−10	95	99	91
Scandium triflate	−78	95	94	93

Abbreviations: *DS*, diastereoselectivity; *Y*, yield.

[a]GC-yield.

[b]Tris(2-cyclohexyl-6-phenylphenoxy) aluminium complex.

of the catalyst. Zr-exchanged montmorillonite was successfully used by Tateiwa et al. with 98% yield for isopulegols and 90% diastereoselectivity for (±)-isopulegol.[87] In comparison, non-exchanged montmorillonite (H^+-form) showed the same diastereoselectivity, but a lower yield of 41% for isopulegols. Yongzhong et al. used Zr-BEA zeolite with an overall selectivity for isopulegol formation of 98% and a selectivity for (±)-isopulegol of 93%.[88] The catalyst was reused several times with constant selectivity but decreasing activity. The initial activity was fully restored by calcination at 550°C. The authors demonstrated a significant poisoning of the catalyst with rising conversion without solvent and in acetonitrile, possibly because of preferred adsorption of isopulegols at the active sites. In *tert*-butanol no poisoning was observed due to higher solubility of reaction products in the solvent. Al/Fe-pillared clays were successfully used by Cramarossa et al. with remarkable yields of 98% of isopulegols and up to 80% selectivity for (±)-isopulegol at room temperature.[89] For reactions at 80°C, initially isopulegol was formed, which after 24–45 h was isomerized to menthones with a yield of 70% and 60% selectivity for formation of (±)-menthone. Coman et al. reported the cyclization of citronellal over heterogeneous metal fluoride catalysts.[90] With AlF_3, synthesized by sol–gel method, the selectivity for formation of isopulegols in toluene was 92%, with (±)-isopulegol formed also with 92% selectivity.

Diastereoselective cyclization of (+)-citronellal, catalysed by homogeneous aluminium complexes, was explored by Itoh et al. from the company Takasago.[91,92] They reported an excellent diastereoselectivity for (−)-isopulegol of 99.5%, with an overall yield of 95% with the 2-cyclohexyl-6-phenylphenol ligand on a 100 g scale.[91] After hydrogenation with Raney-Nickel, (−)-menthol was obtained with 91% yield and 99.5% diastereomeric purity. High diastereoselectivity of 94% for (±)-isopulegol, with >95% yield for isopulegols has been reported with scandium triflate as homogeneous catalyst.[93] However, a temperature of −78°C was required to maintain selectivity.

Mostly medium selectivity for the cyclization of citronellal to isopulegol was reported with various metal oxides[94–100] and metal sulfates,[95] supported heteropolyacids,[101–104] transition metal chlorides,[105,106] zeolites and mesoporous silicates,[107–112] saponite clay modified with Zn,[113] sulphated zirconia,[114,115] dialuminium-substituted silicotungstate,[116] ion exchange resins and sulfonated polystyrene waste,[117] in situ generated triphenylcarbenium ions[118] and oxidized carbon nanotubes.[119]

3.4 | One-Pot Synthesis of Menthol from Citronellal

The one-pot synthesis of menthol from citronellal including cyclization to isopulegol and subsequent hydrogenation has gained interest in recent years. The catalysts need to be bifunctional with acidic sites for cyclization as well as metallic centres for hydrogenation. Under hydrogen atmosphere, the isomerization and hydrogenation reactions proceed simultaneously, resulting in the formation of undesired acyclic by-products (Figure 6). This disadvantage can partly be overcome by choosing suitable catalysts and reaction condition, which minimize the citronellal hydrogenation or by a two-stage approach, with cyclisation of citronellal performed under inert atmosphere, followed by reduction under hydrogen atmosphere.

The first approach is particularly interesting in regard to continuous processes,[120] with platinum group metals supported on H-BEA zeolites proven especially useful. With Pt/H-BEA in dioxane, selectivity up to 85% yield for the desired menthol diastereomer could be achieved.[121] The choice of the solvent had a pronounced effect on selectivity, with solvents like cyclohexane, tetrahydrofurane and toluene promoting the undesired hydrogenation of citronellal to 3,7-dimethyloctan-1-ol. Similar results were reported by Plößer et al. with yields of menthol isomers of 93% with a selectivity of 79% for (±)-menthol with Ru/H-BEA in 1,4-Dioxane at 373 K.[122,123] Besides the solvent influence, the selectivity was also affected by reaction temperature, with undesired hydrogenation of citronellal taking place at lower temperatures, while higher

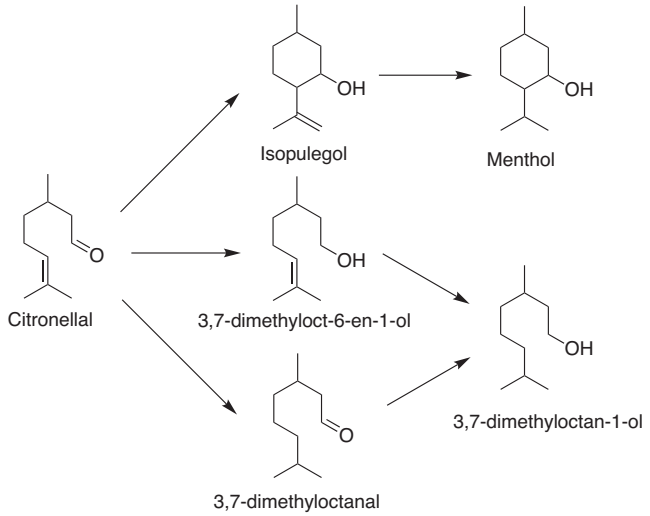


FIGURE 6 Possible reactions in the one-pot transformation of citronellal under hydrogen atmosphere with bifunctional catalysts

temperatures led to formation of defunctionalized olefins. In addition, reduction of catalyst in hydrogen prior to the reaction at elevated temperatures significantly improved activity and selectivity for menthol formation due to partial dealumination of the zeolite structure. In comparison to ruthenium, Pd/H-BEA showed a strong tendency for defunctionalization and dimerization. Neatu et al. and Iosif et al. found, that for Ir/H-BEA the solvent with the lowest dielectric constant (cyclohexane) gave the highest yield of menthol isomers.[124,125] Consistently with the other reports, high hydrogen pressure led to acyclic hydrogenation product formation, while low hydrogen pressure resulted in isopulegol not being fully hydrogenated to menthol. With phosphotungstic acid and palladium supported on silica, da Silva Rocha et al. achieved a yield of 92% for menthols with a selectivity of 85% for (−)-menthol when starting from (+)-citronellal.[126] The authors did not observe hydrogenation of citronellal even at high hydrogen pressures, which could be explained by the higher acidity of phosphotungstic acid in comparison to H-BEA zeolite, resulting in a higher cyclization rate. The selectivity towards menthols was highest at low initial concentrations of citronellal, with significant formation of dimeric products up to 34% at higher substrate concentration. A remarkable yield of 93% for (±)-menthol was reported by Negoi et al. with ionic gold supported on hydroxylated MgF_2.[127] While the acidic support catalysed different side reactions like dehydration and etherification of isopulegol on its own, the impregnation with gold nanoparticles seemed to suppress these reactions completely. Additionally, no acyclic hydrogenation products were observed. However, long reaction times (22 h) and regeneration of the catalyst by reoxidation of Au^{I} to the active Au^{III} by air were required.

For a two-stage approach, a variety of bifunctional catalysts can be used. Nie et al. reported the transformation of (±)-citronellal over nickel-impregnated Zr-BEA zeolites and mixtures of Zr-BEA and Ni/MCM-41 with (±)-menthol yields up to 89%.[128,129] The higher diastereoselectivity towards the desired isopulegol isomer of the alumina free Zr-BEA was attributed by the authors to the size difference between Al^{3+} and Zr^{4+} in the zeolite framework. The impregnation of nickel on the zeolite resulted in partial pore blockage and reduced selectivity. The application of a mixture of Ni/MCM-41 and Zr-BEA resulted in faster hydrogenation of isopulegols and higher selectivity for menthols because higher metal loadings were possible without impairment of the cyclization activity of the Zr-BEA. Up to 96% menthol isomers were obtained by Dam et al. with the mesoporous silicate TUD-1, containing tungsten trioxide and platinum.[130] The recycling of the catalyst showed a strong deactivation through agglomeration of WO_3 particles. Cirujano et al. incorporated palladium nanoparticles into a chromium MOF (MIL-101) by impregnation.[131] With the resulting bifunctional catalyst an overall yield of 81% of (±)-menthol was attained when racemic citronellal was used in a two-stage reaction. With simultaneous isomerization and hydrogenation in one stage, the yield was only 21%, with hydrogenation of citronellal to 3,7-methyloctanol being the dominant reaction.

Other catalysts reported for the one-pot transformation of citronellal with medium selectivity were, e.g. Ni supported on or incorporated into ZrS,[132] Ru-$ZnBr_2$/SiO_2,[133] Ru/H-MCM-41,[134] metal nanoparticles supported on perfluorinated superacid polymers,[135] Cu/SiO_2[136] and scrap catalytic converters modified with Fe.[137]

3.5 | One-Pot synthesis of menthol from citral

A few examples in the literature have described the one-pot synthesis of menthol from citral combining the hydrogenation to citronellal, the cyclization to isopulegol and the hydrogenation to menthol. Compared to the one-pot synthesis from citronellal, the additional step increases the risk of side reactions. With nickel supported on Al-MCM-41 and constant hydrogen pressure, Trasarti et al. reported a yield of 94% menthol isomers, with 71% being (±)-menthol.[138,139] A preliminary screening of hydrogenation catalysts (metals supported on SiO_2) showed that only Pd and Ni have a high initial selectivity for the hydrogenation of the conjugated C=C bond, while Co, Cu, Pt and Ir produced significant amounts of geraniol/nerol. In the tested support materials, SiO_2-Al_2O_3, Al-MCM-41 and zeolite H-BEA showed the highest cyclization activity. The resulting bifunctional catalysts all promoted the decarbonylation and cracking of citral and citronellal to some extent, but on Ni/Al-MCM-41, as the catalyst with the lowest acidity, these side reactions were reduced to around 6%. Nie et al. have achieved a remarkable yield of 89% for (±)-menthol with the dual catalytic system of Zr-beta zeolite and Ni/MCM-41 described in the previous chapter. By using low initial hydrogen pressure and rising the pressure after most of the isopulegol was cyclized, the authors were able to maintain high selectivity, while shortening the reaction time.[140]

Medium yields for menthol in the one-pot transformation of citral were achieved with nickel and platinum group metals supported on H-MCM-41 and H-Y zeolites,[141] BEA zeolite[142] or ionic liquid catalysts containing Pd.[143]

4 | SYNTHESES FROM OTHER RAW MATERIALS

In this chapter, other possible starting materials for the synthesis of menthol will be presented. Some of the syntheses were commercialized in the past, others are only of theoretical importance due to low availability of the starting material or uneconomical synthesis routes. The older synthesis routes were reviewed by Lawrence et al.[1] and Leffingwell and Shackleford.[144]

Menthone and many terpenoids occurring in nature (see Figure 7) can be transformed to menthol by simple hydrogenation. This group contains, e.g. pulegone, piperitone, piperitol and piperitenol. An important source is the dementholized cornmint oil, being the residue of natural menthol production. However, the selectivity suffers from the fast isomerization via keto-enol tautomerism under hydrogenation conditions, resulting in mixtures of menthol diastereomers. For transfer hydrogenation of menthone with Raney-nickel with overall selectivity for menthols close to 100%, Phillipov et al. reported a fast isomerization to the equilibrium ratio of 72/28 menthone/isomethone in 2-propanol.[145,146] The isomerization was fastest in secondary alcohols and negligible in primary alcohols like 1-propanol, which is consistent with the overall hydrogen donor properties of alcohols in transfer hydrogenation. Interestingly, the transfer hydrogenation of menthone was also successfully conducted by the authors in supercritical alcohols under non-catalytic conditions. Here, secondary and primary alcohols showed similar activity for transfer hydrogenation as well as the isomerization to isomenthone.

Vetere et al. reported the hydrogenation of menthone (80% (−)-menthone, 20% (+)-isomenthone) over supported platinum catalysts.[147] Pt/SiO_2 showed a selectivity of 50% for (−)-menthol and 39% for (+)-neomenthol at 80% conversion. However, significant deactivation of the catalyst was observed. Higher conversions were achieved by modification of the catalyst with tin, which unfortunately reduced the selectivity for (−)-menthol to 44%. Under the same conditions, the hydrogenation of pulegone resulted in a mixture of menthone and menthols, with neoisomenthol as the main isomer. Hydrogenation with supported copper catalysts was investigated by Ravasio et al.[148,149] Cu/Al_2O_3 gave 52% (−)-menthol and 39% (+)-neomenthol. Hydrogenation of pulegone under the same conditions resulted in neomenthol as the main isomer. Initially predominating neoisomenthol was converted to the more stable isomers in the course of the reaction. Other catalysts reportedly used for hydrogenation of menthone to menthol were osmium complexes,[150] $B(C_6F_5)_3$ in combination with cyclodextrines,[151] Raney-nickel,[152–156] boron-containing frustrated Lewis pair catalysts[157] and Pt/Al_2O_3.[158]

With chiral homogeneous ruthenium catalysts, Ohshima et al. demonstrated a stereoselective menthol synthesis from pulegone.[159] In the first step, (+)-pulegone was hydrogenated to (−)-pulegol using a $RuCl_2(PPh_3)_2$(propanediamine) complex with 97% selectivity. In the second step with a $Ru(OCOPh)_2$(dppe) complex, (−)-menthol was obtained with 96% selectivity. Bogel-Łukasik investigated the hydrogenation of pulegone in supercritical CO_2 as a potential green solvent with platinum metals supported on alumina.[160] The hydrogenation over Pd/Al_2O_3 gave menthone with 98% selectivity. Interestingly,

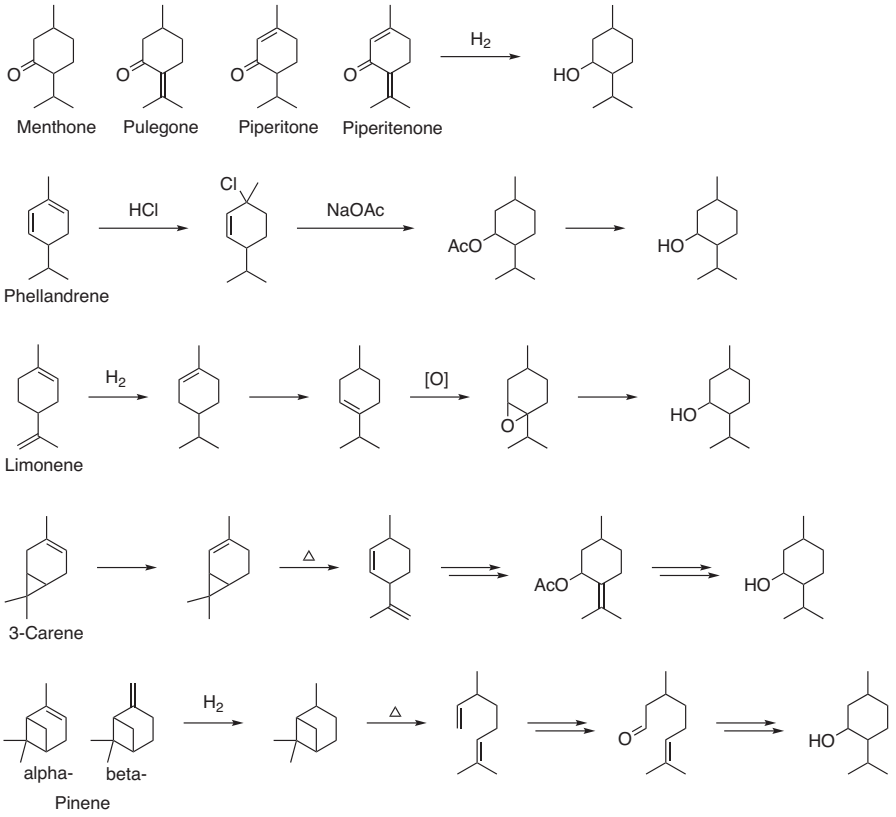


FIGURE 7 Examples for transformation of terpenes and terpenoids into menthol[144]

hydrogenation over Ru/Al_2O_3 gave carvone and hydrogenation over Rh/Al_2O_3 gave thymol with high selectivity. The hydrogenation of pulegone has also been reported with catalysts like nickel nanoparticles,[161] palladium and cobalt supported on carbon[162,163] and via electrocatalytic hydrogenation.[164]

Unsaturated *p*-menthane analogues like α-phellandrene and limonene, as well as bicyclic terpenes like α-pinene and 3-carene have been used for commercial menthol synthesis in the past (see Lawrence et al.,[1] Leffingwell and Shackleford[144]). Especially pinene and carene, as the main components of crude sulphate turpentine generated in large amounts as waste in wood pulp production, are interesting raw materials for menthol production, not only because of high availability, but also their chirality. The Takasago process can utilize β-pinene as a precursor of myrcene. Other syntheses consisted of many steps with moderate overall menthol yields and could not compete against the established processes. No relevant literature for menthol synthesis from these raw materials has been published in the last 20 years. However, this will probably change in future, as cheap and renewable starting materials will become more and more important.

5 | CONCLUSION

The worldwide usage of (−)-menthol, as one of the most important aroma molecules, is constantly rising. To meet the demand in future, the natural menthol production from mint will not be sufficient. In this context, synthetic menthol production gains in importance. The synthesis routes are starting from *m*-cresol (Symrise) and citral (BASF), both fossil-based, and renewable myrcene (Takasago). In the manufacturing of consumer goods containing menthol, a green image will get more and more important for customers, further driving the industry towards sustainable production. However, the assessment of the sustainability of a process or product is far from easy. Besides the nature of the feedstock, also other aspects like energy consumption, CO_2 emissions and environmental impact have to be taken into account. Some interesting aspects of this problem are discussed by Charles S. Sell in his textbook "Fundamentals of Fragrance Chemistry".[13]

The overall efficiency of the three synthetic routes is high, but realized through different approaches. BASF and Takasago achieve high selectivity through the use of chiral, homogeneous catalysts. The drawback is the difficult recycling of the catalysts. In contrary, Symrise uses heterogeneous catalysts, at the cost of lower selectivity, making a non-trivial racemic resolution step necessary.

For menthol synthesis from *m*-cresol the use of zeolites like ZSM-5 and Y or mesoporous aluminosilicates like Al-MCM-41 has a clear advantage over all other types of acidic catalysts because of their well-defined porous structure, resulting in high selectivity for the formation of the intermediate thymol. The following hydrogenation with common heterogeneous catalysts always results in a mixture of the menthol diastereomers. With platinum group metals under mild reaction conditions, the reaction is kinetically controlled and neoisomenthol is formed as the main product. The formation of the desired and thermodynamically preferred menthol diastereomer is possible through isomerization over nickel and copper chromite catalysts. For the following physical racemic resolution of the menthol enantiomers, alternative enzymatic methods were proposed in the literature.

Most research for the synthesis of menthol has been published for citronellal and citral as starting materials. The cyclization of citronellal to isopulegol has the highest selectivity when catalysed with homogeneous Lewis acids like $ZnBr_2$, AlF_3 or sterically demanding aluminium complexes. Slightly lower selectivity was reported for the use of supported $ZnBr_2$, Sn- and Zr-Beta zeolites, Zr-montmorillonite and Al/Fe-pillared montmorillonite. As the following hydrogenation of isopulegol to menthol presents no difficulties regarding selectivity, the one-pot approach with bifunctional catalysts (acidic and metallic sites) is an interesting possibility. However, unfavourable hydrogenation of citronellal must be prevented, either by careful choice of reaction conditions or by a two-stage approach, with initially inert atmosphere, which is then replaced with hydrogen. For the first option, good results were reported with Pt, Ru and Ir supported on zeolite Beta, Pd and phosphotungstic acid supported on silica or Au on hydroxylated MgF_2. For the second approach, the highest menthol yields were achieved with a combination of Ni/MCM-41 and Zr-Beta zeolite. Remarkably, this catalyst system also enabled a one-pot menthol synthesis starting from citral. Unfortunately, due to the achiral starting material only racemic menthol is formed.

When it comes to menthol synthesis from renewable starting materials (other than myrcene and citronellal), literature in the last 20 years is relatively scarce, concentrating on menthone and pulegone. Both are mainly obtained from mint, e.g. from dementholized cornmint oil, a byproduct of natural menthol production. Hydrogenation over heterogeneous catalysts gives mixtures of menthol diastereomers, while higher selectivity can be obtained with chiral homogeneous catalysts.

Challenges in the transition to renewable feedstocks can be the variable composition of natural raw materials and the dependence of their price and availability on many factors. In this context, there still is a great need for research on sustainable menthol production.

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CONFLICT OF INTEREST

The authors have no conflict of interest in relation to this work.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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REFERENCES

1. Lawrence BM. *Mint: the Genus Mentha*. CRC Press; 2007.
2. Abdelli M, Moghrani H, Aboun A, Maachi R. Algerian *Mentha pulegium* L. leaves essential oil: chemical composition, antimicrobial, insecticidal and antioxidant activities. *Ind crop. Prod*. 2016;94:197-205. doi:10.1016/j.indcrop.2016.08.042
3. Domingues PM, Santos L. Essential oil of pennyroyal (*Mentha pulegium*): composition and applications as alternatives to pesticides—new tendencies. *Ind Crop Prod*. 2019;139:111534. doi:10.1016/j.indcrop.2019.111534
4. Beigi M, Torki-Harchegani M, Ghasemi PA. Quantity and chemical composition of essential oil of peppermint (*Mentha piperita* L.) leaves under different drying methods. *Int J Food Prop*. 2018;21(1):267-276. doi:10.1080/10942912.2018.1453839
5. Taherpour AA, Khaef S, Yari A, Nikeafshar S, Fathi M, Ghambari S. Chemical composition analysis of the essential oil of *Mentha piperita* L. from Kermanshah, Iran by hydrodistillation and HS/SPME methods. *J Anal Sci Technol*. 2017;8:11. doi:10.1186/s40543-017-0122-0
6. Makkar MK, Sharma S, Kaur H. Evaluation of *Mentha arvensis* essential oil and its major constituents for fungitoxicity. *J Food Sci Technol*. 2018;55(9):3840-3844. doi:10.1007/s13197-018-3291-y
7. Ji H, Li YCL, Zy W, Li XH, Zhang HX, Li HT. GC-MS analysis of nematicidal essential oil of Mentha canadensis aerial parts against *Heterodera avenae* and *Meloidogyne incognita*. *J Essent Oil Bear Pl*. 2016;19(8):2056-2064. doi:10.1080/0972060X.2016.1252696
8. Oppenheim A. V.—on the camphor of peppermint. *J Chem Soc* 1862;15(0):24-29. doi:10.1039/JS8621500024
9. Kamatou GPP, Vermaak I, Viljoen AM, Lawrence BM. Menthol: a simple monoterpene with remarkable biological properties. *Phytochemistry*. 2013;96:15-25. doi:10.1016/j.phytochem.2013.08.005
10. Waters KL, Beal GD. Some physical and chemical properties of commercial racemic menthol. *J Am Pharm Assoc*. 1945;34(2):52-56. doi:10.1002/jps.3030340208
11. Clark IV GS. An aroma chemical profile: menthol. *Perfumer & Flavorist* 1998;13(5):37-46.
12. Schaefer B. *Natural Products in the Chemical Industry*. Springer-Verlag; 2014.
13. Sell CS. *Fundamentals of Fragrance Chemistry*. 1st ed. Wiley-VCH; 2019.
14. Schäfer B. Menthol: Minze versus Tagasako-Prozess. *Chem Unserer Zeit*. 2013;47(3):174-182. doi:10.1002/ciuz.201300599
15. Biedermann W, inventor; Bayer AG, assignee. Kontinuierliches Verfahren zur Herstellung von D,L-Menthol. German patent DE2314813 (C3). June 22, 1978.
16. Biedermann W, Koeller H, Wedemeyer K, inventors; Bayer AG, assignee. Verfahren zur Herstellung von Thymol. German patent DE2528303 (C3). February 16, 1978.
17. Wimmer P, Buysch HJ, Puppe L, inventors; Bayer AG, assignee. Verfahren zur Herstellung von Thymol. German patent application DE3824284 (A1). January 18, 1990.
18. Dudas J, Hanika J. Design, scale up and safe piloting of thymol hydrogenation and menthol racemisation. *Chem Eng Red des*. 2009;87(1):83-90. doi:10.1016/j.cherd.2008.07.005
19. Fleischer J, Bauer K, Hopp R, inventors; Haarmann & Reimer GmbH, assignee. Verfahren zur Abtrennung von optisch reinem D- und L-Menthol. German patent DE2109456 (C3). March 10, 1977.
20. Etzold B, Jess A, Nobis M. Epimerisation of menthol stereoisomers: kinetic studies of the heterogeneously catalysed menthol production. *Catal Today*. 2009;140(1):30-36. doi:10.1016/j.cattod.2008.07.009
21. Etzold B, Jess A. Heterogeneously catalyzed epimerization of menthol stereoisomers – an instructive example to account for diffusion limitations in complex reaction networks. *Chem Eng Technol*. 2008;31(9):1282-1289. doi:10.1002/ceat.200700486
22. Naghdi Badi H, Abdollahi M, Mehrafarin A, et al. An overview on two valuable natural and bioactive compounds, thymol and carvacrol, in medicinal plants. *J Medicinal Plants* 2017;16(63):1-32.
23. O'Connor CT, Moon G, Böhringer W, Fletcher JCQ. Alkylation of phenol and m-cresol over zeolites. *Collect Czech Chem Commun*. 2003;68(10):1949-1968. doi:10.1135/cccc20031949
24. Selvaraj M, Kawi S. Comparison of mesoporous and microporous solid acid catalysts for highly selective synthesis of thymol by vapor phase isopropylation of m-cresol. *Micropor Mesopor Mat*. 2008;109(1–3):458-469. doi:10.1016/j.micromeso.2007.05.053
25. Shanmugapriya K, Palanichamy M, Arabindoo B, Murugesan V. A novel route to produce thymol by vapor phase reaction of m-cresol with isopropyl acetate over Al-MCM-41 molecular sieves. *J Catal*. 2004;224(2):347-357. doi:10.1016/j.jcat.2004.03.019
26. Umamaheswari V. Isopropylation of m-cresol over mesoporous Al–MCM-41 molecular sieves. *J Catal*. 2002;210(2):367-374. doi:10.1006/jcat.2002.3709
27. Afreen G, Patra T, Upadhyayula S. Zn-loaded HY zeolite as active catalyst for iso-propylation of biomass-derived phenolic compounds: a comparative study on the effect of acidity and porosity of zeolites. *Mol Catal*. 2017;441:122-133. doi:10.1016/j.mcat.2017.08.010
28. Afreen G, Pathak S, Upadhyayula S. Gas phase alkylation of biomass-derived m-cresol with iso-propanol over zinc modified HY zeolite: elucidating reaction mechanism and kinetics including deactivation. *Chem Eng J*. 2020;400:125824. doi:10.1016/j.cej.2020.125824
29. Afreen G, Upadhyayula S. Disruption of the Faujasite framework by incorporation of zinc and their effect on thymol formation. *Mater Lett*. 2019;254:320-323. doi:10.1016/j.matlet.2019.07.104
30. Afreen G, Patra T, Upadhyayula S. Thermodynamic insights into valorization of biomass-derived oxygenates and reconciliation with experimental study. *J Chem Eng Data*. 2018;63(6):2197-2210. doi:10.1021/acs.jced.8b00171
31. Nie L, Resasco DE. Improving carbon retention in biomass conversion by alkylation of phenolics with small oxygenates. *Appl Catal A-Gen*. 2012;447-448:14-21. doi:10.1016/j.apcata.2012.08.041
32. Grabowska H, Miśta W, Trawczyński J, Wrzyszcz J, Zawadzki M. A method for obtaining thymol by gas phase catalytic alkylation of m-cresol over zinc aluminate spinel. *Appl Catal A-Gen*. 2001;220(1-2):207-213. doi:10.1016/S0926-860X(01)00722-0
33. Patra T, Afreen G, Parveen F, Kumar K, Bahri S, Upadhyayula S. Synergistic Brønsted-Lewis acidity effect on upgrading biomass-derived phenolic compounds: statistical optimization of process parameters, Kinetic Investigations and DFT Study. *ChemistrySelect*. 2018;3(2):634-647. doi:10.1002/slct.201702848
34. Liu S, Liu X, Wang C. Isopropylation of m-cresol catalyzed by recoverable acidic ionic liquids. *Ind Eng Chem Res*. 2013;52(47):16719-16723. doi:10.1021/ie402394p
35. Malkar RS, Yadav GD. Selectivity engineering in synthesis of thymol using sulfated ZrO_2–TiO_2. *Ind Eng Chem Res*. 2017;56(30):8437-8447. doi:10.1021/acs.iecr.7b01454
36. Grabowska H, Syper L, Zawadzki M. Vapour phase alkylation of ortho-, meta- and Para-cresols with isopropyl alcohol in the presence of sol–gel prepared alumina catalyst. *Appl Catal A-Gen*. 2004;277(1–2):91-97. doi:10.1016/j.apcata.2004.08.034
37. Sreevardhan Reddy S, Siva Kumar V, Padmasri AH, Satyanarayana CVV, David Raju B, Rama Rao KS. Beneficial role of SiO_2 plugging in $AlCl_3$ heterogenized plugged hexagonal templated silica (PHTS) for the isopropylation of m-cresol. *Catal Commun*. 2007;8(7):1080-1087. doi:10.1016/j.catcom.2006.10.024
38. Grabowska H, Wrzyszcz J. C-alkylation of m-cresol with n- and iso-propanol over iron catalyst. *Res Chem Intermed*. 2001;27(3):281-285. doi:10.1163/156856701300356491
39. Velu S, Sivasanker S. Alkylation of m-cresol with methanol and 2-propanol over calcined magnesium-aluminium hydrotalcites. *Res Chem Intermed*. 1998;24(6):657-666. doi:10.1163/156856798X00555

40. Besson M, Bullivant L, Nicolaus N, Gallezot P. Stereoselective thymol hydrogenation. *J Catal*. 1993;140(1):30-40. doi:10.1006/jcat.1993.1066
41. Besson M, Bullivant L, Nicolaus-Dechamp N, Gallezot P. Stereoselective thymol hydrogenation: comparative study of charcoal-supported, platinum, rhodium and iridium catalysts. *Stud Surf Sci Catal*. 1993;78:115-122. doi:10.1016/S0167-2991(08)63310-8
42. Cardenas G, Oliva R, Reyes P. Catalytic hydrogenation of thymol over pd/MgO prepared by SMAD method. *J Chil Chem Soc*. 2006;51(4):1053-1056. doi:10.4067/S0717-97072006000400013
43. Solladié-Cavallo A, Baram A, Choucair E, Norouzi-Arasi H, Schmitt M, Garin F. Heterogeneous hydrogenation of substituted phenols over Al_2O_3 supported ruthenium. *J Mol Catal A-Chem*. 2007;273(1–2):92-98. doi:10.1016/j.molcata.2007.03.001
44. Tungler A, Mathe T, Petro J, Tarnai T. Role of catalyst preparation and pretreatment in the stereoselective hydrogenation of thymol. *Appl Catal A-Gen*. 1991;79(2):161-165. doi:10.1016/0926-860X(91)80002-G
45. Barney AL, Hass HB. Racemic menthol. New synthesis from thymol. *Ind Eng Chem*. 1944;36(1):85-87. doi:10.1021/ie50409a018
46. Brode WR, van Dolah RW. Synthesis of racemic menthol. *Ind Eng Chem*. 1947;39(9):1157-1160. doi:10.1021/ie50453a021
47. Allakhverdiev AI, Kulkova NV, Murzin DY. Liquid-phase stereoselective thymol hydrogenation over supported nickel catalysts. *Catal Lett*. 1994;29(1-2):57-67. doi:10.1007/BF00814252
48. Allakhverdiev AI, Kul'kova NV, Murzin DY. Kinetics of thymol hydrogenation over a Ni-Cr_2O_3 catalyst. *Ind Eng Chem Res*. 1995;34(5):1539-1547. doi:10.1021/ie00044a005
49. Kumar A, Goyal V, Sarki N, et al. Biocarbon supported nanoscale ruthenium oxide-based catalyst for clean hydrogenation of arenes and heteroarenes. *ACS Sustainable Chem Eng*. 2020;8(41):15740-15754. doi:10.1021/acssuschemeng.0c05773
50. Murugesan K, Senthamarai T, Alshammari AS, et al. Cobalt-nanoparticles catalyzed efficient and selective hydrogenation of aromatic hydrocarbons. *ACS Catal*. 2019;9(9):8581-8591. doi:10.1021/acscatal.9b02193
51. Ravi P, Divakar S. Stereoselective hydrogenation of thymol over rh/alumina in the presence of β-cyclodextrin and its derivatives. *J Inclusion Phenom*. 2001;39(1/2):27-33. doi:10.1023/A:1008166428342
52. Yoshida T, Komatsu A, Indo M. Isomerization and racemization of menthols. *Agr Biol Chem Tokyo*. 1965;29(9):824-831. doi:10.1080/00021369.1965.10858468
53. Vorlová S, Bornscheuer UT, Gatfield I, Hilmer J-M, Bertram H-J, Schmid RD. Enantioselective hydrolysis of D,L-menthyl benzoate to L-(−)-menthol by recombinant *Candida rugosa* lipase LIP1. *Adv Synth Catal*. 2002;344(10):1152-1155. doi:10.1002/1615-4169(200212)344:10<1152:AID-ADSC1152>3.0.CO;2-N
54. Gatfield IL, Hilmer JM, Bornscheuer U, Schmidt R, Vorlova S, inventors; Symrise AG, assignee. Process for the preparation of L-menthol. US patent 6,706,500 (B2). March 16, 2004.
55. Zheng G-W, Yu H-L, Zhang J-D, Xu J-H. Enzymatic production of L-menthol by a high substrate concentration tolerable esterase from newly isolated *Bacillus subtilis* ECU0554. *Adv Synth Catal*. 2009;351(3):405-414. doi:10.1002/adsc.200800412
56. Brady D, Reddy S, Mboniswa B, et al. Biocatalytic enantiomeric resolution of L-menthol from an eight isomeric menthol mixture through transesterification. *J Mol Catal B-Enzym*. 2012;75:1-10. doi:10.1016/j.molcatb.2011.10.011
57. Li M, Yang L-R, Xu G, Wu J-P. Highly diastereoselective acylation of L-menthol by a lipase from *Stenotrophomonas maltophilia* CGMCC 4254. *Biochem Eng J*. 2016;109:81-87. doi:10.1016/j.bej.2016.01.005
58. Serra S, Brenna E, Fuganti C, Maggioni F. Lipase-catalyzed resolution of p-menthan-3-ols monoterpenes: preparation of the enantiomer-enriched forms of menthol, isopulegol, trans- and cis-piperitol, and cis-isopiperitenol. *Tetrahedron-Asymmetr*. 2003;14(21):3313-3319. doi:10.1016/j.tetasy.2003.08.010
59. Sun J, Ding C, Zheng J-Y, Yu X-J, Zhao M, Wang Z. Improved enantioselective esterification of DL-menthol catalyzed by immobilized TL 100L lipase. *J Mol Catal B-Enzym*. 2016;133:S271-S276. doi:10.1016/j.molcatb.2017.01.013
60. Craveiro R, Meneses L, Durazzo L, et al. Deep eutectic solvents for enzymatic esterification of racemic menthol. *ACS Sustainable Chem Eng*. 2019;7(24):19943-19950. doi:10.1021/acssuschemeng.9b05434
61. Wang D-L, Nag A, Lee G-C, Shaw J-F. Factors affecting the resolution of DL-menthol by immobilized lipase-catalyzed esterification in organic solvent. *J Agric Food Chem*. 2002;50(2):262-265. doi:10.1021/jf010657j
62. Emura M, Matsuda H. A green and sustainable approach: celebrating the 30th anniversary of the asymmetric L-menthol process. *Chem Biodivers*. 2014;11(11):1688-1699. doi:10.1002/cbdv.201400063
63. AkutagawaS.AsymmetricsynthesisbymetalBINAPcatalysts.*ApplCatal A-Gen*. 1995;128(2):171-207. doi:10.1016/0926-860X(95)00097-6
64. Akutagawa S. Enantioselective isomerization of allylamine to enamine: practical asymmetric synthesis of (−)-menthol by rh–BINAP catalysts. *Top Catal*. 1997;4(3/4):271-274. doi:10.1023/A:1019112911246
65. Noyori R. Asymmetric catalysis: science and opportunities (Nobel lecture 2001). *Adv Synth Catal*. 2003;345(12):15-32. doi:10.1002/adsc.200390002
66. Behr A, Johnen L. Myrcene as a natural base chemical in sustainable chemistry: a critical review. *ChemSusChem*. 2009;2(12):1072-1095. doi:10.1002/cssc.200900186
67. Takabe K, Katagiri T, Tanaka J, Fujita T, Watanabe S, Suga K. Addition of dialkylamines to myrcene: N,N-Diethylgeranylamine. *Org Synth*. 1989;67:44. doi:10.15227/orgsyn.067.0044
68. Miyashita A, Yasuda A, Takaya H, et al. Synthesis of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), an atropisomeric chiral bis(triaryl)phosphine, and its use in the rhodium(I)-catalyzed asymmetric hydrogenation of α-(acylamino)acrylic acids. *J Am Chem Soc*. 1980;102(27):7932-7934. doi:10.1021/ja00547a020
69. Takaya H, Akutagawa S, Noyori R. R-(+)- and (S)-(−)-2,2'-bis(diphenylphosphino)-1,1′-binaphtyl (BINAP). *Organic Synth*. 1989;67:20. doi:10.15227/orgsyn.067.0020
70. Kumobayashi H, Akutagawa S, inventors; Takasago Perfumery Co. Ltd., assignee. Rhodium-phosphine complex. US patent 4,605,750. August 12, 1986.
71. Tani K, Yamagata T, Otsuka S, Kumobayashi H, Akutagawa S. R-(−)-N,N-diethyl-(E)-citronellalenamine and R-(+)-citronellal via isomerization of N,N-diethylgeranylamine or N,N-diethylnerylamine. *Organic Synth*. 1989;67:33. doi:10.15227/orgsyn.067.0033
72. Inoue S, Takaya H, Tani K, Otsuka S, Sato T, Noyori R. Mechanism of the asymmetric isomerization of allylamines to enamines catalyzed by 2,2′-bis(diphenylphosphino)-1,1′binaphthyl-rhodium complexes. *J Am Chem Soc*. 1990;112(12):4897-4905. doi:10.1021/ja00168a040
73. Tani K, Yamagata T, Akutagawa S, et al. Highly enantioselective isomerization of prochiral allylamines catalyzed by chiral diphosphine rhodium(I) complexes. Preparation of optically active enamines. *J Am Chem Soc*. 1984;106(18):5208-5217. doi:10.1021/ja00330a029
74. Wegner G, Kaibel G, Therre J, Aquila W, Fuchs H, inventors; BASF AG, assignee. Continuous method for producing citral. WIPO patent application WO2008037693 (A1). April 3, 2008.
75. Hoelderich WF. Environmentally benign manufacturing of fine and intermediate chemicals. *Catal Today*. 2000;62(1):115-130. doi:10.1016/S0920-5861(00)00413-2
76. Ager DJ, de Vries JG. Industrial applications of asymmetric reduction of C=C bonds. In: Carreira EM, Yamamoto H, eds. *Comprehensive Chirality*. Elsevier Science; 2012:73-82.
77. Jäkel C, Paciello R. The asymmetric hydrogenation of enones – access to a new L-menthol synthesis. In: Blaser H-U, Federsel H-J, eds. *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches, and Solutions*. 2nd ed. Wiley-VCH; 2010:187-205.

78. Stolle A, Gallert T, Schmöger C, Ondruschka B. Hydrogenation of citral: a wide-spread model reaction for selective reduction of α,β-unsaturated aldehydes. *RSC Adv*. 2013;3(7):2112-2153. doi:10.1039/C2RA21498A
79. Friedrich M, Ebel K, Goetz N, Krause W, Zahm C, inventors; BASF AG, assignee. Diarylphenoxy aluminum compounds. WIPO patent application WO2006092433 (A1). September 8, 2006.
80. Friedrich M, Ebel K, Goetz N, inventors; BASF AG, assignee. Method for the production of isopulegol. US patent 7,550,633 (B2). June 23. 2009.
81. Heydrich G, Gralla G, Rauls M, et al., inventors; BASF SE, assignee. Method for producing optically active, racemic menthol. WIPO patent application WO2009068444 (A2). June 4, 2009.
82. Gralla G, Heydrich G, Bergner EJ, Ebel K, inventors; BASF SE, assignee. Process for preparation of menthol by hydrogenation of isopulegol. WIPO patent application WO2009013192 (A1). January 29, 2007.
83. Bergner EJ, Ebel K, Johann T, Lober O, Loeber O, inventors; BASF AG, assignee. Method for the production of menthol. US patent 7,709,688 (B2). May 4, 2010.
84. Nakatani Y, Kawashima K. A highly stereoselective preparation of L-isopulegol. *Synthesis*. 1978;1978(02):147-148. doi:10.1055/s-1978-24696
85. Imachi S, Owada K, Onaka M. Intramolecular carbonyl-ene reaction of citronellal to isopulegol over $ZnBr_2$-loading mesoporous silica catalysts. *J Mol Catal A-Chem*. 2007;272(1–2):174-181. doi:10.1016/j.molcata.2007.03.032
86. Corma A, Renz M. Sn-Beta zeolite as diastereoselective water-resistant heterogeneous Lewis-acid catalyst for carbon-carbon bond formation in the intramolecular carbonyl-ene reaction. *Chem Commun*. 2004;5:550-551. doi:10.1039/b313738d
87. J-i T, Kimura A, Takasuka M, Uemura S. Metal cation-exchanged montmorillonite(M^{n+}-Mont)-catalysed carbonyl-ene reactions. *J Chem Soc, Perkin Trans 1*. 1997;(15):2169-2174. doi:10.1039/a702906c
88. Yongzhong Z, Yuntong N, Jaenicke S, Chuah G. Cyclisation of citronellal over zirconium zeolite beta – a highly diastereoselective catalyst to (±)-isopulegol. *J Catal*. 2005;229(2):404-413. doi:10.1016/j.jcat.2004.11.015
89. Cramarossa MR, Forti L, Pagnoni UM, Vidali M. Cyclization of citronellal to menthone and isomenthone catalyzed by Al/Fe-pillared clays. *Synthesis*. 2001;2001(01):52-54. doi:10.1055/s-2001-9762
90. Coman SM, Patil P, Wuttke S, Kemnitz E. Cyclisation of citronellal over heterogeneous inorganic fluorides – highly chemo- and diastereoselective catalysts for (±)-isopulegol. *Chem Commun*. 2009;4:460-462. doi:10.1039/b817572a
91. Itoh H, Maeda H, Yamada S, Hori Y, Mino T, Sakamoto M. Highly selective aluminium-catalysed intramolecular Prins reaction for L-menthol synthesis. *RSC Adv*. 2014;4(106):61619-61623. doi:10.1039/C4RA12470G
92. Itoh H, Maeda H, Yamada S, Hori Y, Mino T, Sakamoto M. Kinetic resolution of citronellal by chiral aluminum catalysts: L-menthol synthesis from citral. *Org Chem Front*. 2014;1(9):1107-1115. doi:10.1039/C4QO00222A
93. Aggarwal VK, Vennall GP, Davey PN, Newman C. Scandium trifluoromethaneslfonate, an efficient catalyst for the intermolecular carbonyl-ene reaction and the intramolecular cyclisation of citronellal. *Tetrahedron Lett*. 1998;39(14):1997-2000. doi:10.1016/S0040-4039(98)00115-4
94. Anikeev VI, Il'ina IV, Volcho KP, Salakhutdinov NF. Cyclization of citronellal in a supercritical solvent in a flow reactor in the presence of Al_2O_3. *Russ J Phys Chem*. 2012;86(12):1917-1919. doi:10.1134/S0036024412120035
95. Arata K, Matsuura C. Isomerizations of citronellal to isopulegol and geraniol to linalool catalyzed by solid acids and bases. *Chem Lett*. 1989;18(10):1797-1798. doi:10.1246/cl.1989.1797
96. Jimeno C, Miras J, Esquena J. $TiO_2(SiO_2)_x$ and $ZrO_2(SiO_2)_x$ cryogels as catalysts for the citronellal cyclization to isopulegol. *Catal Lett*. 2013;143(6):616-623. doi:10.1007/s10562-013-1007-5
97. Jimeno C, Miras J, Esquena J. Hafnia-silica cryogels: solvent-assisted textural and catalytic control in the citronellal cyclization. *ChemCatChem*. 2014;6(9):2626-2633. doi:10.1002/cctc.201402189
98. Telalović S, Ramanathan A, Ng JF, et al. On the synergistic catalytic properties of bimetallic mesoporous materials containing aluminum and zirconium: the Prins cyclisation of citronellal. *Chem-Eur J*. 2011;17(7):2077-2088. doi:10.1002/chem.201002909
99. Vrbková E, Šteflová B, Zapletal M, Vyskočilová E, Červený L. Tungsten oxide-based materials as effective catalysts in isopulegol formation by intramolecular Prins reaction of citronellal. *Res Chem Intermed*. 2020;46(9):4047-4059. doi:10.1007/s11164-020-04190-z
100. Bertero NM, Trasarti AF, Acevedo MC, Marchi AJ, Apesteguía CR. Solvent effects in solid acid-catalyzed reactions: the case of the liquid-phase isomerization/cyclization of citronellal over SiO_2-Al_2O_3. *Mol Catal*. 2020;481:110192. doi:10.1016/j.mcat.2018.09.009
101. Braga PRS, Costa AA, de Freitas EF, et al. Intramolecular cyclization of (+)-citronellal using supported 12-tungstophosphoric acid on MCM-41. *J Mol Catal A-Chem*. 2012;358:99-105. doi:10.1016/j.molcata.2012.03.002
102. da Silva KA, Robles-Dutenhefner PA, Sousa EMB, Kozhevnikova EF, Kozhevnikov IV, Gusevskaya EV. Cyclization of (+)-citronellal to (−)-isopulegol catalyzed by $H_3PW_{12}O_{40}/SiO_2$. *Catal Commun*. 2004;5(8):425-429. doi:10.1016/j.catcom.2004.05.001
103. Shah AK, Park S, Khan HA, et al. Citronellal cyclisation over heteropoly acid supported on modified montmorillonite catalyst: effects of acidity and pore structure on catalytic activity. *Res Chem Intermed*. 2018;44(4):2405-2423. doi:10.1007/s11164-017-3237-4
104. Chen H, Zou H, Hao Y, Yang H. Flow Pickering emulsion interfaces enhance catalysis efficiency and selectivity for cyclization of citronellal. *ChemSusChem*. 2017;10(9):1989-1995. doi:10.1002/cssc.201700318
105. Andrade CKZ, Vercillo OE, Rodrigues JP, Silveira DP. Intramolecular ene reactions catalyzed by $NbCl_5$, $TaCl_5$ and $InCl_3$. *J Braz Chem Soc*. 2004;15(6):813-817. doi:10.1590/S0103-50532004000600005
106. Jacob RG, Perin G, Loi LN, Pinno CS, Lenardão EJ. Green synthesis of (−)-isopulegol from (+)-citronellal: application to essential oil of citronella. *Tetrahedron Lett*. 2003;44(18):3605-3608. doi:10.1016/S0040-4039(03)00714-7
107. Makiarvela P. Cyclization of citronellal over zeolites and mesoporous materials for production of isopulegol. *J Catal*. 2004;225(1):155-169. doi:10.1016/j.jcat.2004.03.043
108. Shieh D-L, Tsai C-C, Ko A-N. Liquid-phase synthesis of isopulegol from citronellal using mesoporous molecular sieves MCM-41 and zeolites. *React Kinet Catal L*. 2003;79(2):381-389. doi:10.1023/A:1024510907799
109. Vajglová Z, Kumar N, Mäki-Arvela P, et al. Synthesis and physicochemical characterization of shaped catalysts of β and Y zeolites for cyclization of citronellal. *Ind Eng Chem Res*. 2019;58(39):18084-18096. doi:10.1021/acs.iecr.9b02829
110. Shah AK, Maitlo G, Korai RM, et al. Citronellal cyclisation to isopulegol over micro-mesoporous ZSM-5 zeolite: effects of desilication temperature on textural and catalytic properties. *Reac Kinet Mech Cat*. 2019;128(1):507-522. doi:10.1007/s11144-019-01617-6
111. Shieh D-L, Tsai C-C, Chen C-W, Ko A-N. Vapor-phase reaction of citronellal over mesoporous molecular sieves MCM-41 and zeolites. *Jnl Chinese Chemical Soc*. 2003;50(4):853-860. doi:10.1002/jccs.200300119
112. Vrbková E, Prejza T, Lhotka M, Vyskočilová E, Červený L. Fe-modified zeolite BETA as an active catalyst for intramolecular

Prins cyclization of citronellal. *Catal Lett*. 2020;151(7):1993-2003. doi:10.1007/s10562-020-03456-w
113. Rubiyanto D, Prakoso NI, Sahroni I, Nurillahi R, Fatimah I. ZnO-porous clay heterostructure from saponite as green catalyst for citronellal cyclization. *Bull Chem React Eng Catal*. 2020;15(1):137-145. doi:10.9767/bcrec.15.1.5800.137-145
114. Yadav GD, Nair JJ. Novelties of eclectically engineered sulfated zirconia and carbon molecular sieve catalysts in cyclisation of citronellal to isopulegol. *Chem Commun*. 1998;21:2369-2370. doi:10.1039/a806815a
115. Chuah GK, Liu SH, Jaenicke S, Harrison LJ. Cyclisation of citronellal to isopulegol catalysed by hydrous zirconia and other solid acids. *J Catal*. 2001;200(2):352-359. doi:10.1006/jcat.2001.3208
116. Kikukawa Y, Yamaguchi S, Nakagawa Y, et al. Synthesis of a dialuminum-substituted silicotungstate and the diastereoselective cyclization of citronellal derivatives. *J Am Chem Soc*. 2008;130(47):15872-15878. doi:10.1021/ja8014154
117. Ribeiro MSP, Pinto RRS, da Silva Rocha KA, Vieira CG. Sulfonated expanded polystyrene waste promotes the (+)-citronellal cyclization reaction: a sustainable alternative process for biomass valorization. *Waste Biomass Valor*. 2021;12(8):4695-4702. doi:10.1007/s12649-020-01319-4
118. Nomoto Y, Horinouchi R, Nishiyama N, Nakano K, Ichikawa Y, Kotsuki H. Trityl cation catalyzed intramolecular carbonyl-ene cyclization and [2+2] cycloaddition. *Synlett*. 2017;28(02):265-269. doi:10.1055/s-0036-1588618
119. Dongil AB, Pastor-Pérez L, Fierro JLG, Escalona N, Sepúlveda-Escribano A. Effect of the surface oxidation of carbon nanotubes on the selective cyclization of citronellal. *Appl Catal A-Gen*. 2016;524:25-31. doi:10.1016/j.apcata.2016.05.021
120. Azkaar M, Mäki-Arvela P, Vajglová Z, et al. Synthesis of menthol from citronellal over supported Ru- and Pt-catalysts in continuous flow. *React Chem Eng*. 2019;4(12):2156-2169. doi:10.1039/C9RE00346K
121. Mertens P, Verpoort F, Parvulescu A, Devos D. Pt/H-beta zeolites as productive bifunctional catalysts for the one-step citronellal-to-menthol conversion. *J Catal*. 2006;243(1):7-13. doi:10.1016/j.jcat.2006.06.017
122. Plößer J, Lucas M, Claus P. Highly selective menthol synthesis by one-pot transformation of citronellal using Ru/H-BEA catalysts. *J Catal*. 2014;320:189-197. doi:10.1016/j.jcat.2014.10.007
123. Plößer J, Dedeaga F, Lucas M, Claus P. The effect of catalyst preparation conditions on the synthesis of menthol from citronellal on Ru/H-BEA. *Appl Catal A-Gen*. 2016;516:100-108. doi:10.1016/j.apcata.2016.02.014
124. Neaţu F, Coman S, Pârvulescu VI, Poncelet G, de Vos D, Jacobs P. Heterogeneous catalytic transformation of citronellal to menthol in a single step on Ir-Beta zeolite catalysts. *Top Catal*. 2009;52(9):1292-1300. doi:10.1007/s11244-009-9270-9
125. Iosif F, Coman S, Pârvulescu V, et al. Ir-Beta zeolite as a heterogeneous catalyst for the one-pot transformation of citronellal to menthol. *Chem Commun*. 2004;11:1292-1293. doi:10.1039/B403692A
126. da Silva Rocha KA, Robles-Dutenhefner PA, Sousa EMB, Kozhevnikova EF, Kozhevnikov IV, Gusevskaya EV. Pd–heteropoly acid as a bifunctional heterogeneous catalyst for one-pot conversion of citronellal to menthol. *Appl Catal A-Gen*. 2007;317(2):171-174. doi:10.1016/j.apcata.2006.10.019
127. Negoi A, Wuttke S, Kemnitz E, et al. One-pot synthesis of menthol catalyzed by a highly diastereoselective au/MgF_2 catalyst. *Angew Chem Int ed Engl*. 2010;49(44):8134-8138. doi:10.1002/anie.201002090
128. Nie Y, Chuah G-K, Jaenicke S. Domino-cyclisation and hydrogenation of citronellal to menthol over bifunctional Ni/Zr-Beta and Zr-beta/Ni-MCM-41 catalysts. *Chem Commun*. 2006;7:790-792. doi:10.1039/b513430g
129. Nie Y, Niah W, Jaenicke S, Chuah G. A tandem cyclization and hydrogenation of (±)-citronellal to menthol over bifunctional Ni/Zr-beta and mixed Zr-beta and Ni/MCM-41. *J Catal*. 2007;248(1):1-10. doi:10.1016/j.jcat.2007.02.018
130. ten Dam J, Ramanathan A, Djanashvili K, Kapteijn F, Hanefeld U. Synthesis, characterization and performance of bifunctional catalysts for the synthesis of menthol from citronellal. *RSC Adv*. 2017;7(20):12041-12053. doi:10.1039/C6RA25931F
131. Cirujano FG, Llabrés i Xamena FX, Corma A. MOFs as multifunctional catalysts: one-pot synthesis of menthol from citronellal over a bifunctional MIL-101 catalyst. *Dalton Trans*. 2012;41(14):4249-4254. doi:10.1039/c2dt12480g
132. Cortés CB, Galván VT, Pedro SS, García TV. One pot synthesis of menthol from (±)-citronellal on nickel sulfated zirconia catalysts. *Catal Today*. 2011;172(1):21-26. doi:10.1016/j.cattod.2011.05.005
133. Milone C, Gangemi C, Neri G, Pistone A, Galvagno S. Selective one step synthesis of (−)-menthol from (+)-citronellal on Ru supported on modified SiO_2. *Appl Catal A-Gen*. 2000;199(2):239-244. doi:10.1016/S0926-860X(99)00560-8
134. Vajglová Z, Kumar N, Peurla M, Eränen K, Mäki-Arvela P, Murzin DY. Cascade transformations of (±)-citronellal to menthol over extruded Ru-MCM-41 catalysts in a continuous reactor. *Cat Sci Technol*. 2020;10(23):8108-8119. doi:10.1039/D0CY01251C
135. Moreno-Marrodan C, Liguori F, Barbaro P, Caporali S, Merlo L, Oldani C. Metal nanoparticles supported on perfluorinated superacid polymers: a family of bifunctional catalysts for the selective, one-pot conversion of vegetable substrates in water. *ChemCatChem*. 2017;9(22):4256-4267. doi:10.1002/cctc.201700945
136. Ravasio N, Poli N, Psaro R, Saba M, Zaccheria F. Bifunctional copper catalysts. Part II. Stereoselective synthesis of (−)-menthol starting from (+)-citronellal. *Top Catal*. 2000;13(3):195-199. doi:10.1023/A:1009086317432
137. Zuliani A, Cova CM, Manno R, Sebastian V, Romero AA, Luque R. Continuous flow synthesis of menthol via tandem cyclisation–hydrogenation of citronellal catalysed by scrap catalytic converters. *Green Chem*. 2020;22(2):379-387. doi:10.1039/C9GC03299A
138. Trasarti AF, Marchi AJ, Apesteguia CR. Design of catalyst systems for the one-pot synthesis of menthols from citral. *J Catal*. 2007;247(2):155-165. doi:10.1016/j.jcat.2007.01.016
139. Trasarti AF, Marchi AJ, Apesteguía CR. Highly selective synthesis of menthols from citral in a one-step process. *J Catal*. 2004;224(2):484-488. doi:10.1016/j.jcat.2004.03.016
140. Nie Y, Jaenicke S, Chuah G-K. Zr-zeolite beta: a new heterogeneous catalyst system for the highly selective cascade transformation of citral to (±)-menthol. *Chem-Eur J*. 2009;15(8):1991-1999. doi:10.1002/chem.200801776
141. Makiarvela P, Kumar N, Kubicka D, et al. One-pot citral transformation to menthol over bifunctional micro- and mesoporous metal modified catalysts: effect of catalyst support and metal. *J Mol Catal A-Chem*. 2005;240(1):72-81. doi:10.1016/j.molcata.2005.06.023
142. Negoi A, Teinz K, Kemnitz E, Wuttke S, Parvulescu VI, Coman SM. Bifunctional nanoscopic catalysts for the one-pot synthesis of (±)-menthol from citral. *Top Catal*. 2012;55(7–10):680-687. doi:10.1007/s11244-012-9850-y
143. Virtanen P, Karhu H, Toth G, Kordas K, Mikkola J-P. Towards one-pot synthesis of menthols from citral: modifying supported ionic liquid catalysts (SILCAs) with Lewis and Brønsted acids. *J Catal*. 2009;263(2):209-219. doi:10.1016/j.jcat.2009.02.005
144. Leffingwell JC, Shackleford RE. Laevo-menthol: syntheses and organoleptic properties. *Cosmet Perfum*. 1974;89:69-78.
145. Philippov AA, Chibiryaev AM, Martyanov ON. Base-free transfer hydrogenation of menthone by sub- and supercritical alcohols. *J Supercrit Fluids*. 2019;145:162-168. doi:10.1016/j.supflu.2018.12.011
146. Philippov AA, Chibiryaev AM, Martyanov ON. Simple H_2-free hydrogenation of unsaturated monoterpenoids catalyzed by Raney

nickel. *Mendeleev Commun*. 2019;29(4):380-381. doi:10.1016/j.mencom.2019.07.006
147. Vetere V, Santori GF, Moglioni A, Moltrasio Iglesias GY, Casella ML, Ferretti OA. Hydrogenation of (−)-menthone, (+)-isomenthone, and (+)-pulegone with platinum/tin catalysts. *Catal Lett*. 2002;84(3/4):251-257. doi:10.1023/A:1021444407222
148. Ravasio N, Zaccheria F, Fusi A, Psaro R. One pot selective hydrogenation and dynamic kinetic resolution over cu/Al_2O_3: a way to (−)-menthol starting from low value mint oils. *Appl Catal A-Gen*. 2006;315:114-119. doi:10.1016/j.apcata.2006.09.010
149. Ravasio N, Psaro R, Zaccheria F. Cu/SiO_2-catalyzed hydrogenation of cyclohexanones under very mild conditions. *Tetrahedron Lett*. 2002;43(21):3943-3945. doi:10.1016/S0040-4039(02)00671-8
150. Baratta W, Ballico M, Del Zotto A, Siega K, Magnolia S, Rigo P. Osmium pyme complexes for fast hydrogenation and asymmetric transfer hydrogenation of ketones. *Chemistry*. 2008;14(8):2557-2563. doi:10.1002/chem.200701719
151. Mahdi T, Stephan DW. Facile protocol for catalytic frustrated Lewis pair hydrogenation and reductive deoxygenation of ketones and aldehydes. *Angew Chem Int Edit*. 2015;54(29):8511-8514. doi:10.1002/anie.201503087
152. Kukula P, Červený L. Stereoselective hydrogenation of (−)-menthone and (+)-isomenthone mixture using nickel catalysts. *Res Chem Intermed*. 2000;26(9):913-922. doi:10.1163/156856700X00390
153. Kukula P. Červený L. the kinetics of stereoselective hydrogenation of (−)-menthone and (+)-isomenthone mixture using nickel catalysts. *Appl Catal A-Gen*. 2000;193(1–2):285-290. doi:10.1016/S0926-860X(99)00443-3
154. Manuale DL, Betti C, Marchi AJ, Yori JC, Romeo E. Synthesis of liquid menthol by hydrogenation of dementholized peppermint oil over Ni catalysts. *Quím Nova*. 2010;33(6):1231-1234. doi:10.1590/S0100-40422010000600002
155. Ravi P, Ravichandran R, Divakar S. Stereoselective hydrogenation of R-(+)-pulegone and (2S,5R)-(−)-menthone in presence of β-cyclodextrin and its derivatives. *J Mol Catal A-Chem*. 1999;148(1–2):145-155. doi:10.1016/S1381-1169(99)00036-9
156. Ravichandran R. Stereoselective hydrogenation of (2S,5R)-(−)-menthone in presence of β-cyclodextrin. *J Mol Catal A-Chem*. 2006;256(1–2):216-218. doi:10.1016/j.molcata.2006.04.066
157. Mummadi S, Brar A, Wang G, et al. "Inverse" frustrated Lewis pairs: an inverse FLP approach to the catalytic metal free hydrogenation of ketones. *Chem-Eur J*. 2018;24(62):16526-16531. doi:10.1002/chem.201804370
158. Yori JC, Manuale DL, Marchi AJ, Grau JM. Liquid-phase hydrogenation of dementholized peppermint oil on Pt/Al_2O_3 catalysts. *Appl Catal A-Gen*. 2004;275(1–2):221-226. doi:10.1016/j.apcata.2004.07.041
159. Ohshima T, Tadaoka H, Hori K, Sayo N, Mashima K. Highly enantio- and s-trans C=C bond selective catalytic hydrogenation of cyclic enones: alternative synthesis of (−)-menthol. *Chemistry*. 2008;14(7):2060-2066. doi:10.1002/chem.200701505
160. Bogel-Łukasik E. Selective catalytic conversion of pulegone in supercritical carbon dioxide towards natural compounds: carvone, thymol or menthone. *J Supercrit Fluids*. 2015;99:121-128. doi:10.1016/j.supflu.2015.02.004
161. Alonso F, Riente P, Yus M. Hydrogen-transfer reduction of carbonyl compounds promoted by nickel nanoparticles. *Tetrahedron*. 2008;64(8):1847-1852. doi:10.1016/j.tet.2007.11.093
162. Song T, Duan Y, Yang Y. Chemoselective transfer hydrogenation of α,β-unsaturated carbonyls catalyzed by a reusable supported pd nanoparticles on biomass-derived carbon. *Catal Commun*. 2019;120:80-85. doi:10.1016/j.catcom.2018.11.017
163. Song T, Ma Z, Yang Y. Chemoselective hydrogenation of α,β-unsaturated carbonyls catalyzed by biomass-derived cobalt nanoparticles in water. *ChemCatChem*. 2019;11(4):1313-1319. doi:10.1002/cctc.201801987
164. Lima MVF, Menezes FD, de Barros Neto B, Navarro M. A factorial design analysis of (+)-pulegone electrocatalytic hydrogenation. *J Electroanal Chem*. 2008;613(1):58-66. doi:10.1016/j.jelechem.2007.10.010

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