Natural or Synthetic Menthol

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| • Menthol crystals are produced through mint essential oil (mentha arvensis) extraction, the oil is quick frozen and the menthol crystallizes out.  
• The crystals are crystalline in form, more oblong, similar to rock crystals. They are clear to white with a cool minty fresh | General Information |
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Menthol crystals are produced through mint essential oil extraction, the oil is quick frozen and the menthol crystallizes out.
## Synthetic Menthol

*Project, Technology, Patents, Market, Companies*

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### Information at a Glance
- Synthetic menthol has been made according to various processes.
- Synthesize of menthol from thymol, piperitone, pulegone and d-citronellal is well known.
- However, all these synthetic menthols have taste and odor characteristics differ materially from those of the natural product obtained by known means from American, Chinese or Japanese peppermint oils.
- It is noted that de-neomenthol has a

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Production Methods

Today, Synthetic (-)-menthol is provided by three major industrial processes. These are the Haarmann & Reimer (or Symrise) process, the Takasago process and the BASF process.

Overview of the three actual industrial (-)-menthol synthetic routes, the Haarmann & Reimer (or Symrise) process, the Takasago process and the BASF process is explained in the next page/slide.
Haarmann & Reimer process

\[
\begin{align*}
 m\text{-cresol} & \quad \overset{\text{Al(OR)}_3}{\longrightarrow} & \quad \text{thymol} \\
 & \quad 1. \text{hydrogenation} & \quad 2. \text{distillation} \\
 & \quad \text{esterification with MeO}_2\text{Ph} & \quad 1. \text{crystallisation} \\
 & \quad \text{(+/-)-menthol} & \quad \text{(-/-)-menthyl benzoate} \\
\end{align*}
\]

Takasago process

\[
\begin{align*}
 \text{myrcene} & \quad 1. \text{HNE}_2 / \text{BuLi} \\
 & \quad 2. [\text{Rh(S-BINAP)} \text{COD}]\text{ClO}_4 \\
 & \quad \text{H}_2\text{SO}_4(\text{aq.}) \\
 & \quad \text{ZnBr}_2 \\
 & \quad \text{Raney Ni} \\
 & \quad \text{(-)-isopulegol} \\
 & \quad \text{(-)-menthol} \\
\end{align*}
\]

BASF process

\[
\begin{align*}
 \text{E/Z-citral} & \quad \text{distillation} \\
 & \quad \text{Rh-cat.} / \text{H}_2 \\
 & \quad \text{2,6-xylene} \\
 & \quad \text{cat.} / \text{H}_2 \\
\end{align*}
\]

Figure 3: Overview of the three actual industrial (-)-menthol synthetic routes, the Haarmann & Reimer (or Symrise) process, the Takasago process and the BASF process.
Symrise Process (formerly known as Haarmann & Reimer process) (US Patent 3,943,181 (Mar 9 1976)) – In this process (Fig 6.2), thymol is synthesized from m-cresol. Catalytic hydrogenation gave a mixture of Menthols from which menthols were first obtained as a racemic mixture by careful fractional distillation. The residual mixture was epimerised to increase the content of racemic menthol using a patented catalytic process. The breakthrough in the process is the resolution of the benzoate ester of the racemate by recrystallization by a process of seeding the concentrate with one pure epimer. The mother liquor that was now rich in the (+) isomer was recycled by taking it back to the distillation cycle. In this process, overall yield of (-)-menthol is about 90%.
Takasago Process: In this process a (S)-DINAP catalysed isomerization is the key step. Addition of lithium amide to Myrcene gave an addition compound that was isomerised using a chiral ruthenium catalyst. Hydrolysis of the resulting enamine gave an aldehyde citronellal in high enantiomeric purity. This was cyclized by Lewis catalyst. Catalytic reduction of the olefin gave (-)-Menthol1.
CONTINUOUS PROCESS FOR PREPARING MENTHOL IN PURE OR
(03/19/2009).

(-)-Menthol from (+)-Limonene

Limonene is abundantly available from peels of citrus fruits. On selective catalytic reduction with Ra-Ni, it could be reduced to (+)-1-Menthene, which on epoxidation and hydrolysis gave (+)-1-hydroxyneocarvomenthol. Acylation followed by pyrolysis gave (-)-trans-menth-2-ene-1-ol as the major product. The crude product was solvolysed to give a mixture of piperityl actates as the allylic migration products. The crude product was distilled at this stage to separate the cis- and trans piperitols. The minor ring contraction product was useful as perfume intermediate elsewhere. The final reduction was achieved by H2 / Pd-C to give 75% yield of (-)-Menthol after fractional distillation.
Natural vs Synthetic Menthol

There are various routes to synthetic menthol with reagents in plentiful supply, and this makes the synthetic option more financially attractive compared with the natural sources that are sensitive to weather and seasonal fluctuations.
Menthol market Scenario

Decrease in demand for synthetic menthol can happen only if the price difference between natural and synthetic menthol narrows. Since, synthetic menthol is already at lower cost benefit, price gap can be achieved only when natural menthol supply increases / prices decrease, which is unlikely in the short term.
Thanks

Questions?