Natural or Synthetic Menthol

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Menthol-Crystal Project, Production, Machinery, Process, Patent, Consultants, Company Profiles, Suppliers, Plant

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Natural Menthol

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Synthetic Menthol Project, Technology, Patents, Market, Companies

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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



Symrise Process (formerly know 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 ENRICHED FORM, WIPO Patent Application WO/2009/033870 (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 (+)-1hydroxyneocarvomenthol. 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.



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.

ESTIMATED PRODUCTION AND CONSUMPTION OF MENTHA OIL



Menthol market Scenario

Natural & Synthetic

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

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Thanks

Questions?