Aromachemicals Found in The Brewing Process & Finished Beer – Part 2

26th April 2025

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(vi) Hops

Background

Headspace Analysis of Hops by GCMS

Sulphur compounds in Hops

(iv) Hops

Background

A dried hop cone consists of

8 to 10% moisture,

40 to 50%cellulose,

up to 15% protein,

8 to 10% ash,

2% pectins

up to 5% lipids and waxes

2 to 5% polyphenols,

0 to 10% beta acids

0 to 22 % alpha acids,

0.5 to 4% essential oils

(iv) Hops

Background

Along with alpha and beta acids hops contain other acids: short chain organic acids such as

- **2 methyl butyric**
- **3 methyl butyric (isovaleric) acids**

28, 29

These are responsible for the sweaty cheesy aromas found particularly in aged or aging hops

(iv) Hops

Background

Hop oils, also known as essential oils include:

- 50 to 80% hydrocarbons,
- 20 to 50% oxygenated hydrocarbons,
- <1% Sulphur compounds.

The Hydrocarbons are volatile, not very soluble, and are perceptible in finished beer only when added very late in the boil or post-fermentation.

The oxygenated compounds are more soluble and aromatic.

Their aromas, or new ones resulting from the fermentation process, are more likely to show up in finished beer.

Although sulphur compounds are a small portion of the oils, they have very low odour threshold and can positively and negatively influence the aroma in finished beer.

(iv) Hops

Background

Hop catalogues routinely provide information about the four most prominent compounds in their variety profiles: **Myrcene, Caryophyllene**, Humulene, and Farnesene. 30, 31

The first is a monoterpene, meaning it consists of 10 carbon units

The latter are sesquiterpenes (15 carbon units).

Myrcene has a green, herbaceous, resinous aroma associated with fresh hops and not always considered desirable.

It is volatile, and most of its aroma is lost during boiling.

The sesquiterpenes are more likely to survive into finished beer

Their resulting aromas often described as “fine” or “noble.”

Caryophyllene and humulene are traditionally evaluated in tandem. Nowadays Humulene is more commonly referred to as α caryophyllene and caryophyllene as β caryophyllene

(iv) Hops

Background

As a hop ripens, many other monoterpenes form along with myrcene, their presence often measured in tenths of a percent.

J. L. Hanin first used steam distillation to isolate hop oils in 1819, but it was not until the end of the nineteenth century that Alfred Chapman identified the key compounds Myrcene, Humulene**, Linalool, Geraniol,** Nerol**, Citronellol, Isobutyl Isobutyrate, And Limonene**

32-37

He knew there were still more constituents to be discovered. He wrote “No one, for example, relying on the sense of smell alone could mistake Californian for Bavarian hops, or the latter for the produce of Kent,”

Since the composition of the compounds he identified did not explain those differences, he hypothesised that small quantities of other fragrant substances must be present. They simply could not be separated using technology available at the time.

(iv) Hops

Background

The invention of gas chromatography (GC) in 1955 allowed scientists to take a complex smell and pull it apart over time, creating a visual record of its volatile components.
it revolutionized the analysis of hop oils and aroma. Researchers soon identified more than 400 compounds.

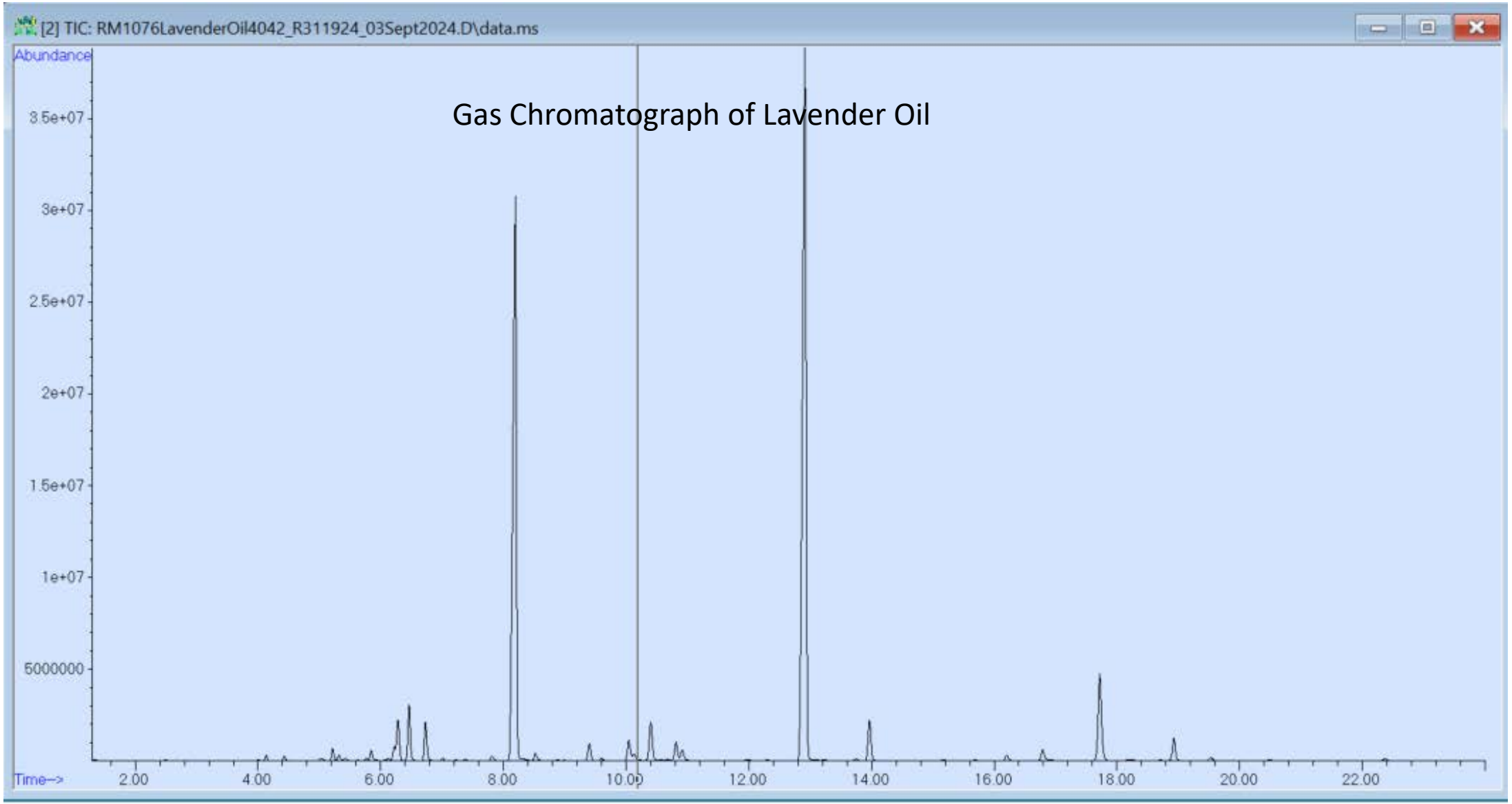
Individual components that emerge from the GC are fed into a mass spectrometer, (MS) which came into use in the 1970s, to provide a definitive identification of the molecule.

Headspace Analysis of Hops by GCMS

Gas Chromatography

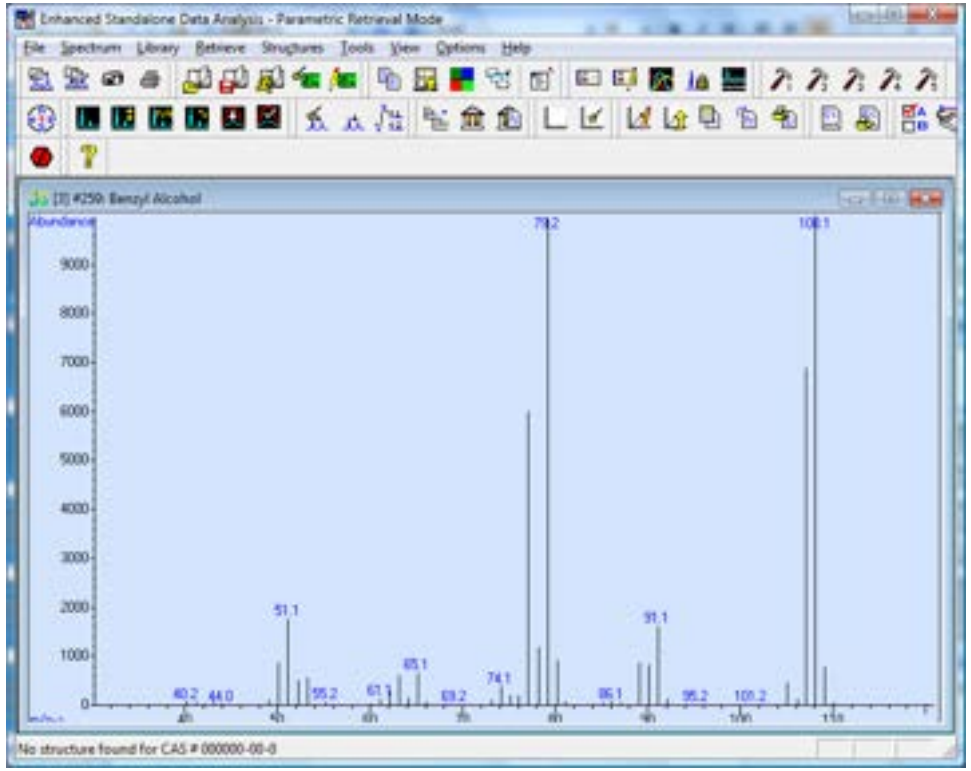
Gas Chromatography

Gas Chromatography

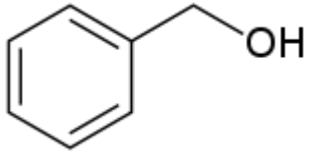


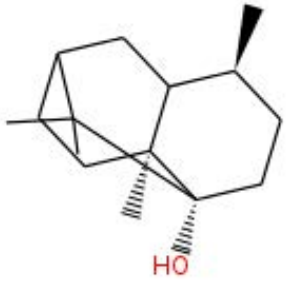
Gas Chromatograph of Lavender Oil

CPL AROMAS

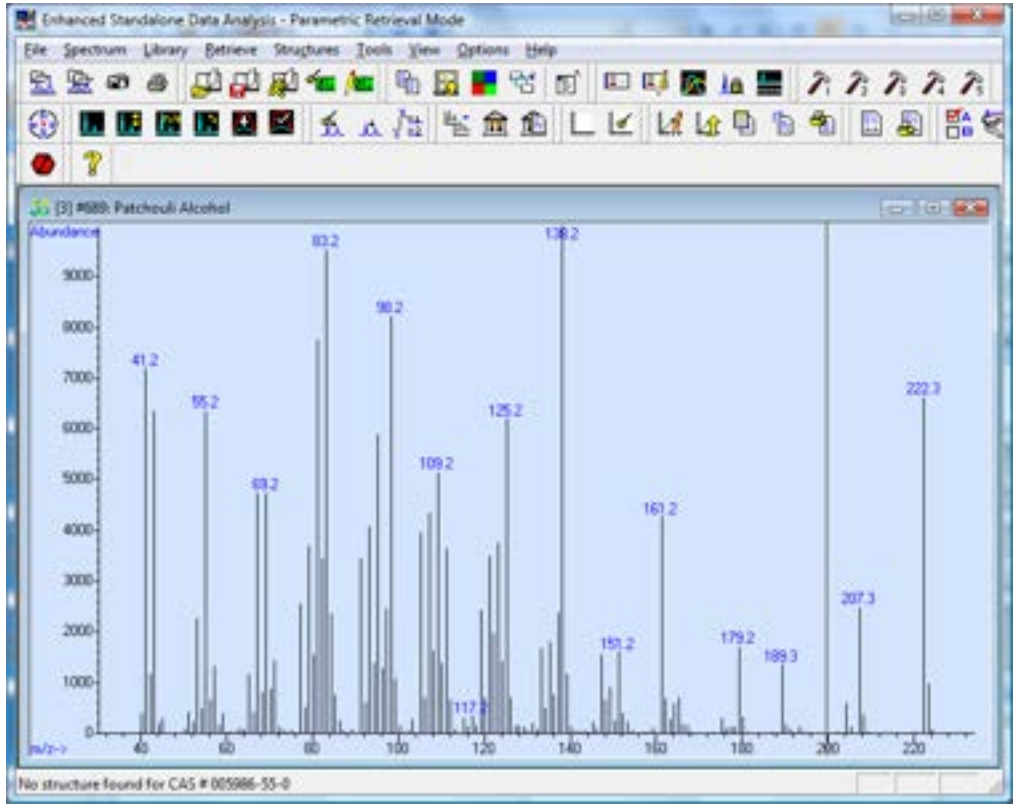


benzyl alcohol





patchouli alcohol



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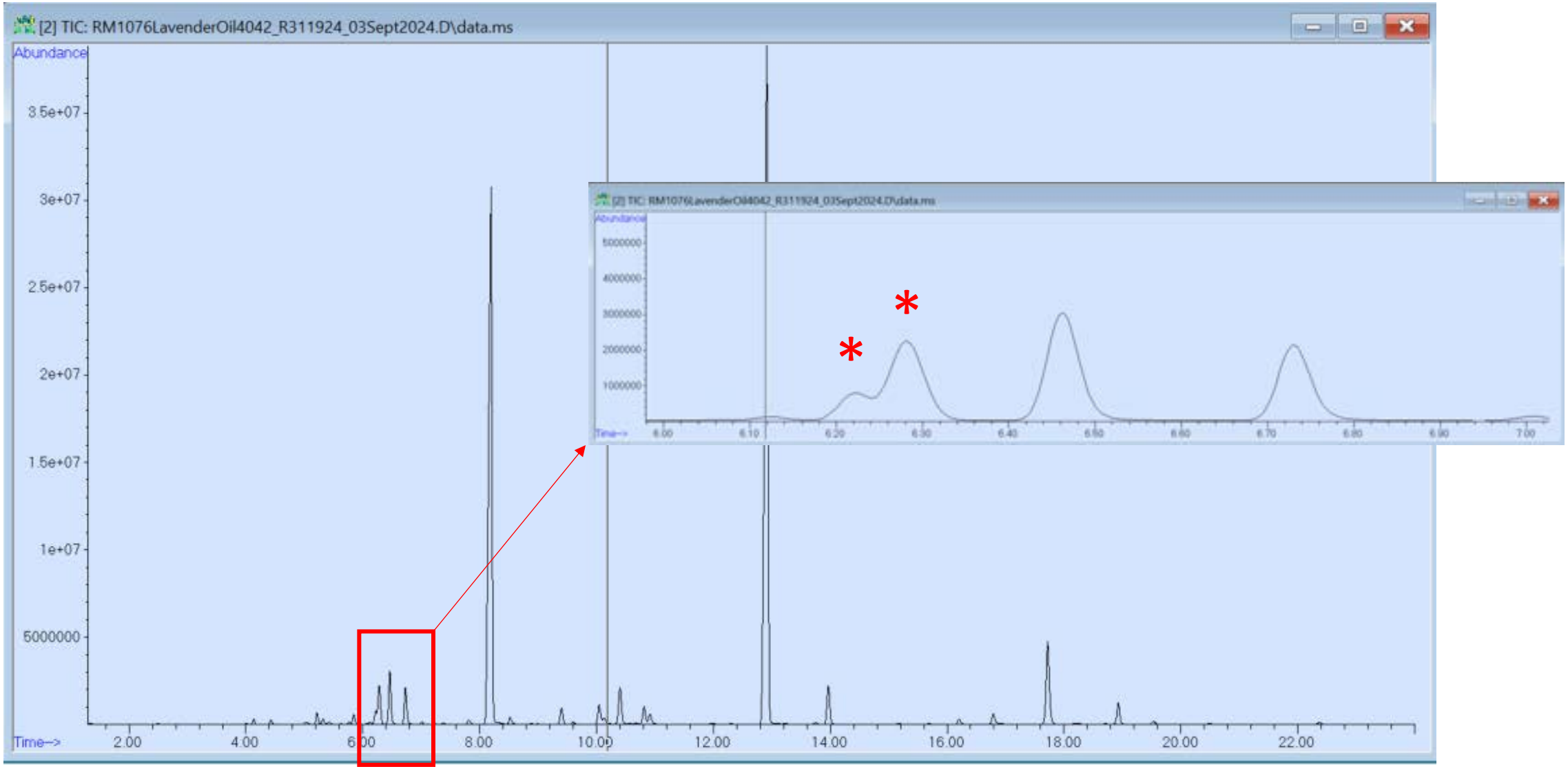
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3e+07
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1.5e+07
1e+07
5000000
Time-->
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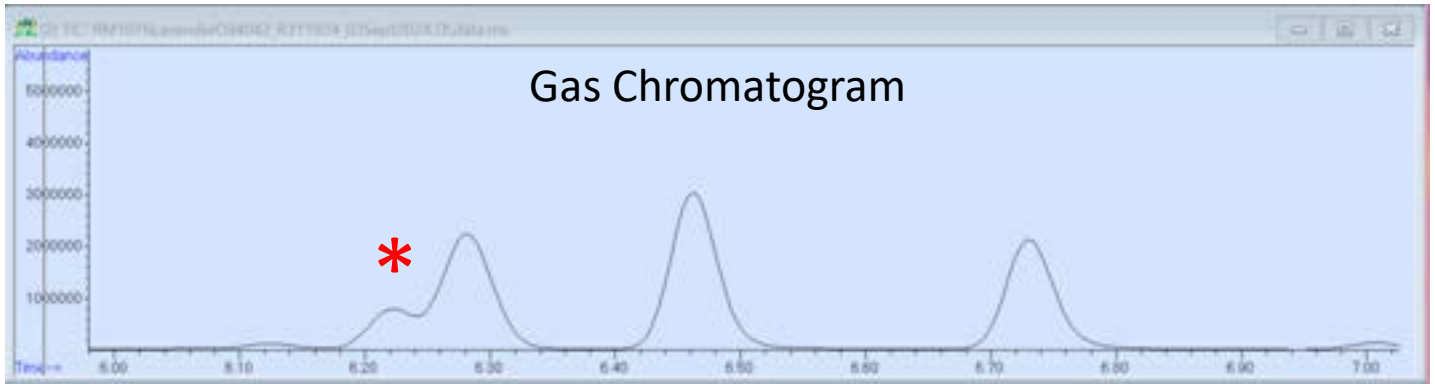
Gas Chromatogram
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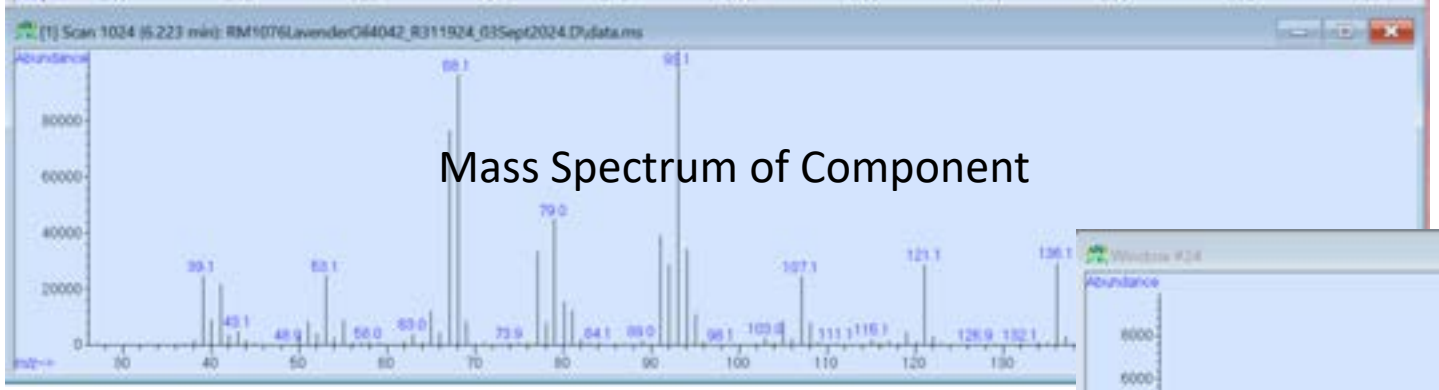
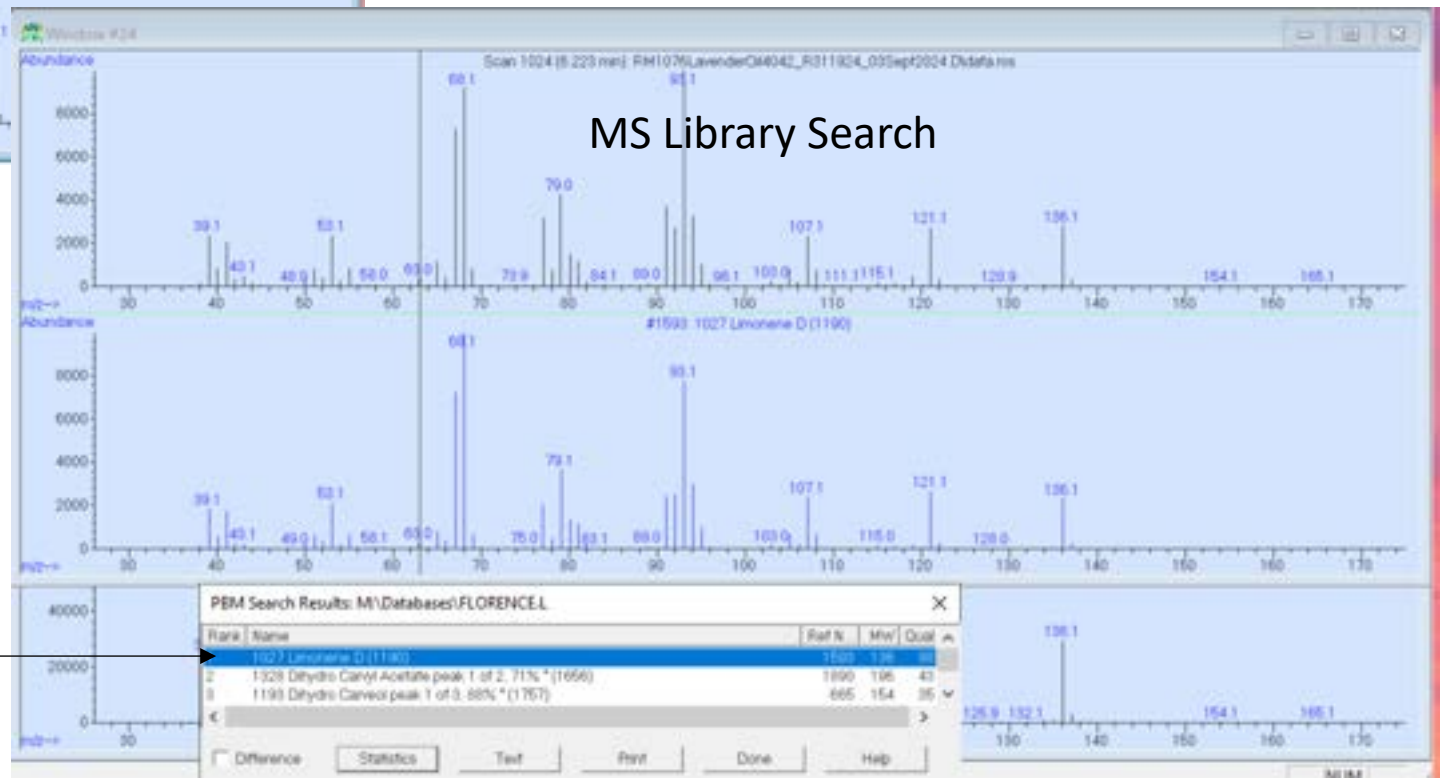

Mass Spectrum of Component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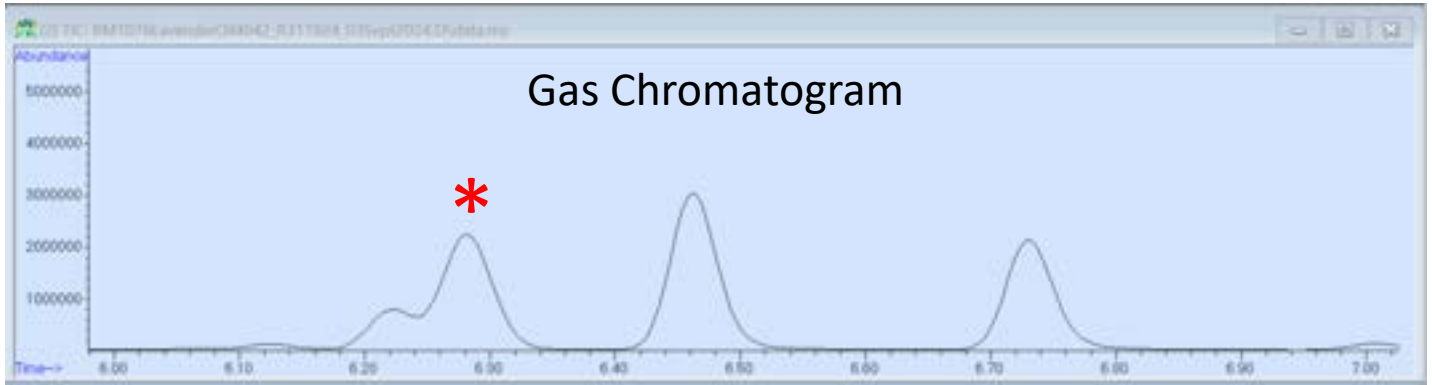
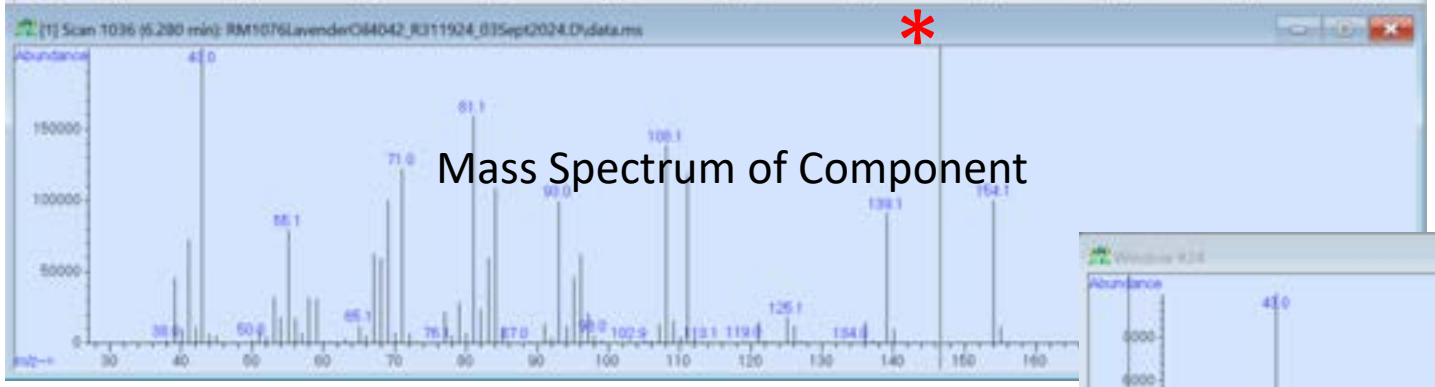
PBM Search Results: M:\Databases\FLORENCE.L
1027 Limonene D (1190)
1328 Dihydro Carvyl Acetate peak 1 of 2, 71% * (1656)
1193 Dihydro Carveol peak 1 of 3, 88% * (1767)
Difference
Statistics
Text
Print
Done
Help

D-Limonene


Gas Chromatogram
*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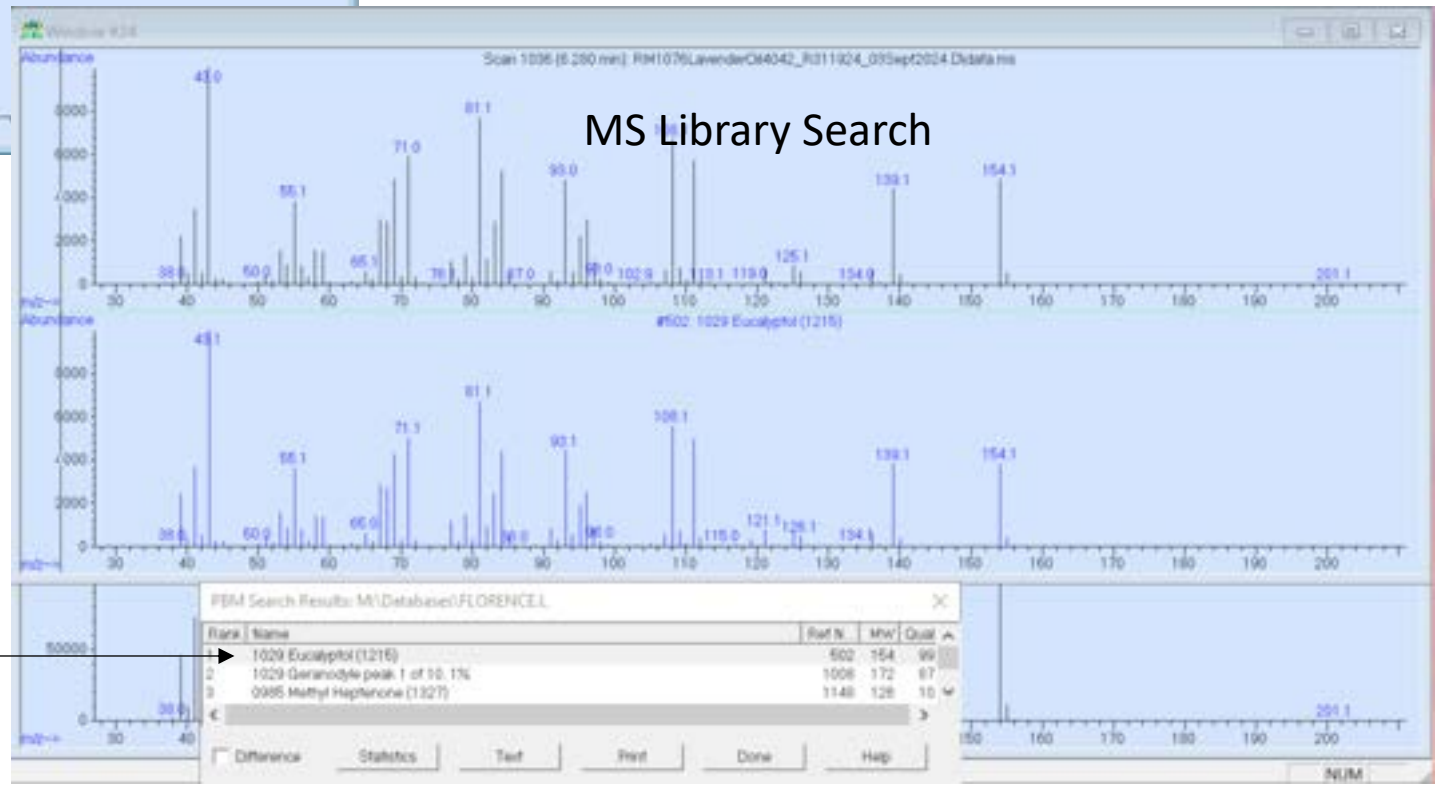
Mass Spectrum of Component


MS Library Search
PBM Search Results: M:\Database\FLORENCE.L
Rank
Name
Ref N.
MW
Qual
1 1029 Eucalyptol (1215) 602 154 99
2 1029 Geranodyle peak 1 of 10, 1% 1008 172 87
3 0985 Methyl Heptenone (1327) 1148 126 10
Difference
Statistics
Text
Print
Done
Help

Eucalyptol

Headspace Analysis

Headspace Sampling

Headspace work was traditionally performed using handheld vacuum pumps to create an airflow through the tube.

These are simple, effective, affordable and portable. However, they have several drawbacks;

- Contamination; they draw their air from the surrounding environment. It is practically impossible to eliminate contamination from outside
- The pumps are difficult to keep calibrated, and minor fluctuations in gas flows can have a major effect
- Cannot control the surrounding environment (temperature, air flow, light)

Micro Extraction Chamber

- This chamber allows us to extract headspace in a controlled way.
- Sample is placed inside chamber
- Inert nitrogen gas is used to pump through the chamber
- Temperature can be set and controlled
- Environment is carefully controlled and contamination eliminated
- Not portable!

Hop Headspace Results

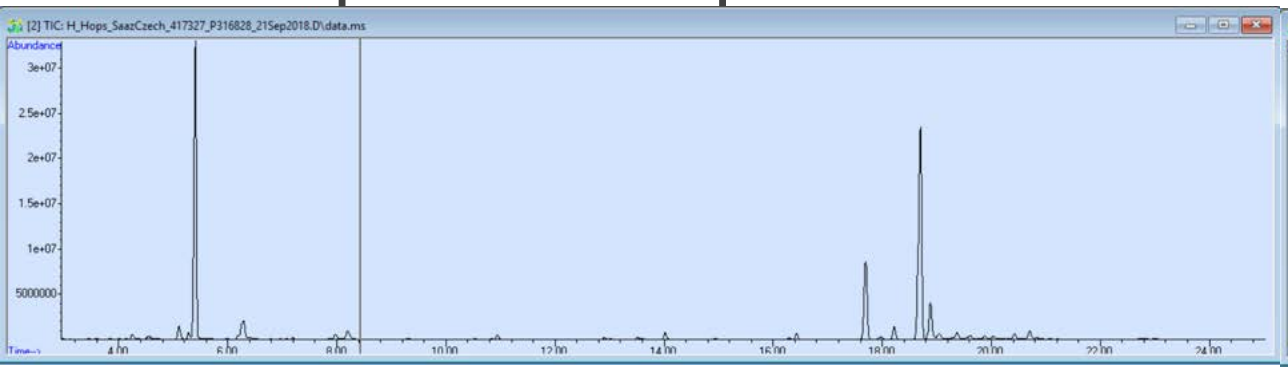
- Saaz

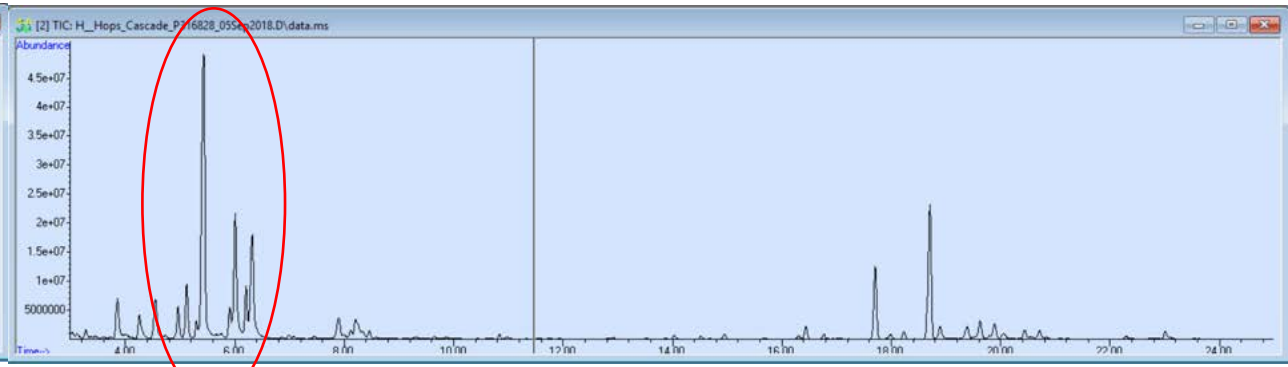
- Fuggles
- East Kent Golding

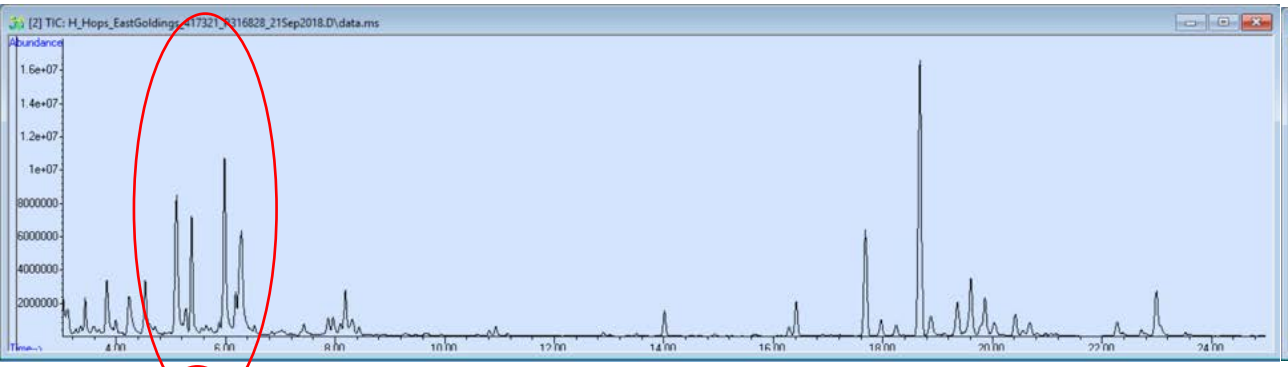
- Cascade
- Citra

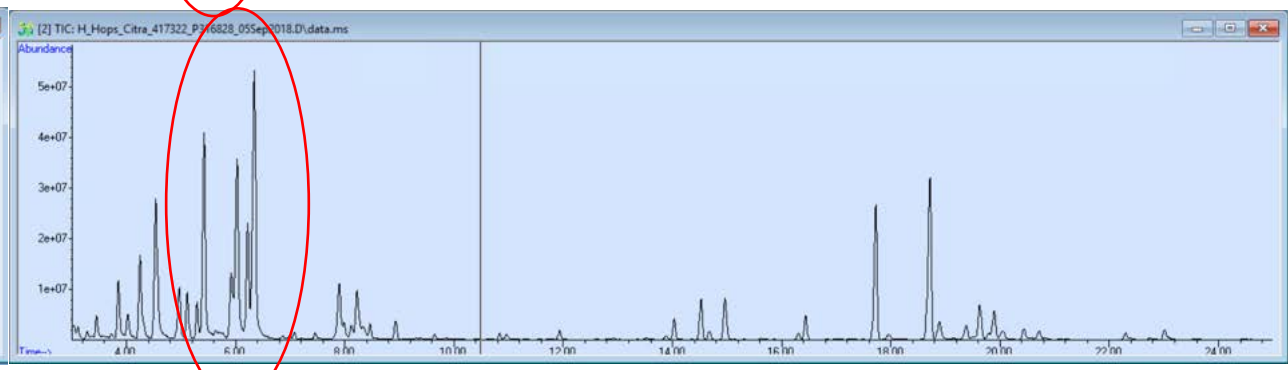
- Tettnang

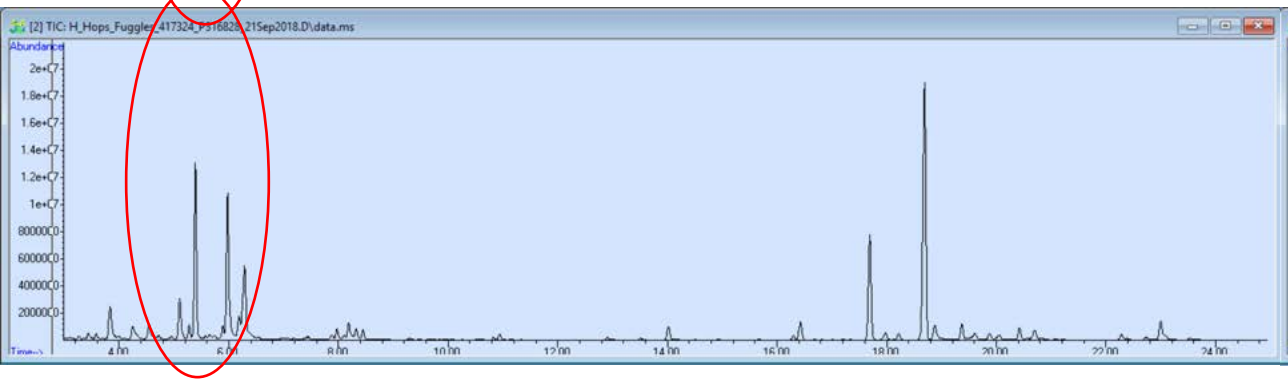
Hop Headspace Results

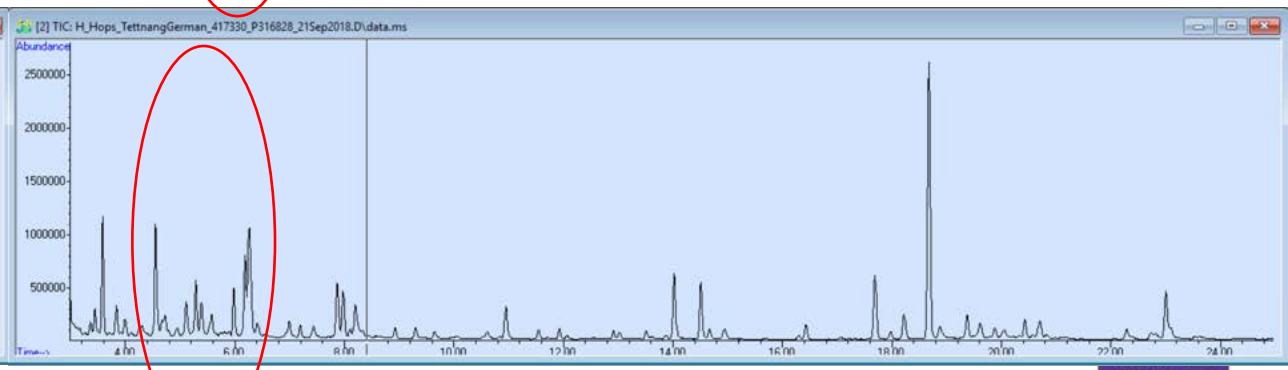






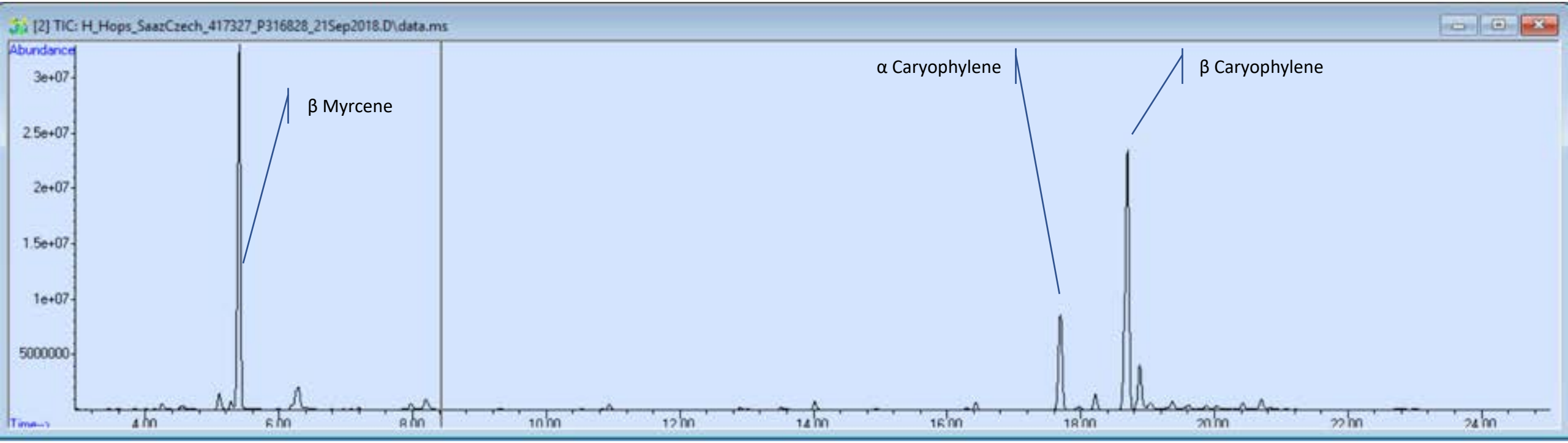






AROMAS

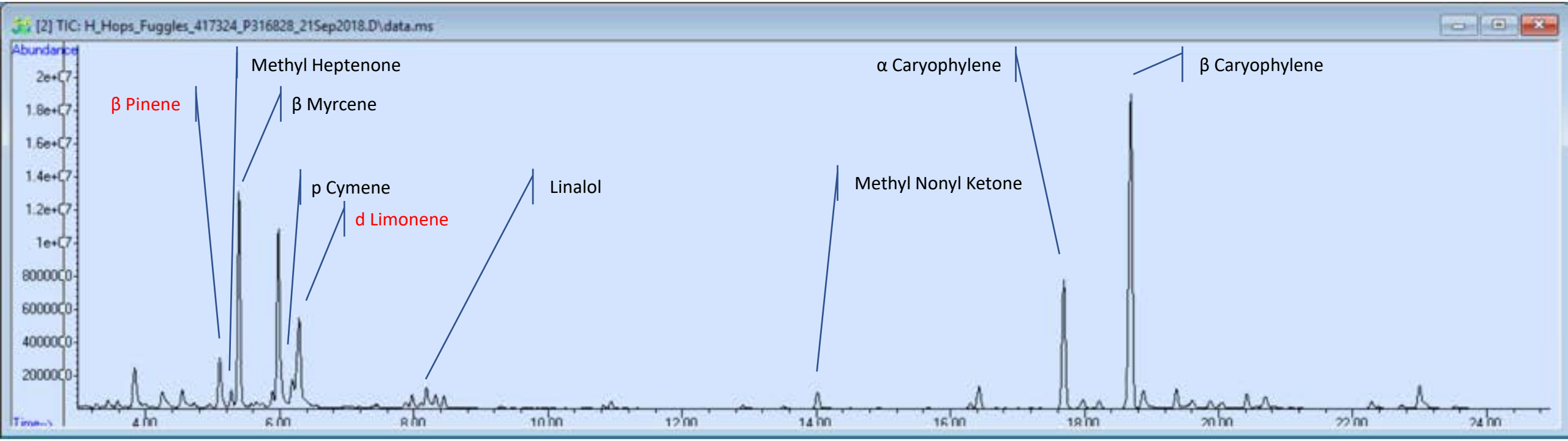
Hop Headspace - Saaz



30,31

Earthy, Herbal, Floral

Hop Headspace - Fuggles



Grassy, Minty, Earthy

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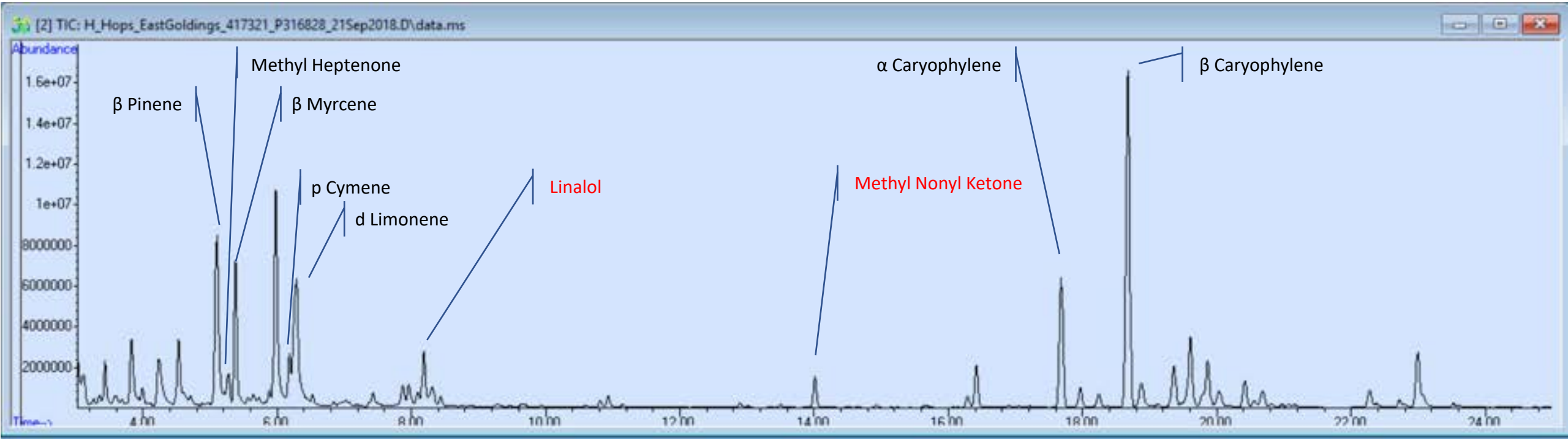
Hop Headspace - EKG



32,39

Spicy, Honey, Earthy

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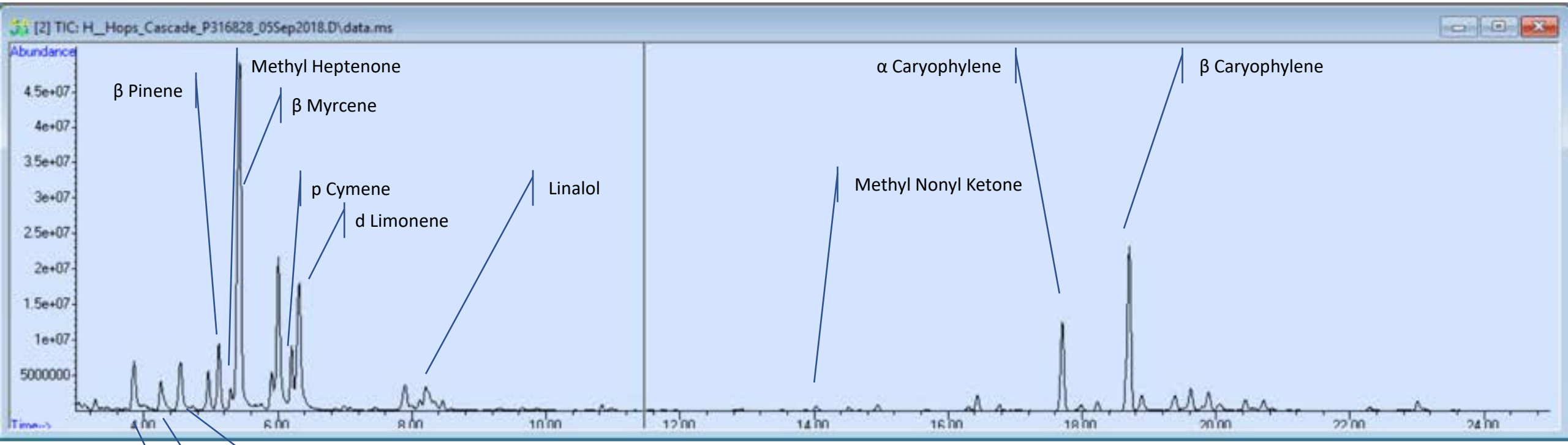
Hop Headspace - Cascade



35, 40

Lychee, Floral, Grapefruit

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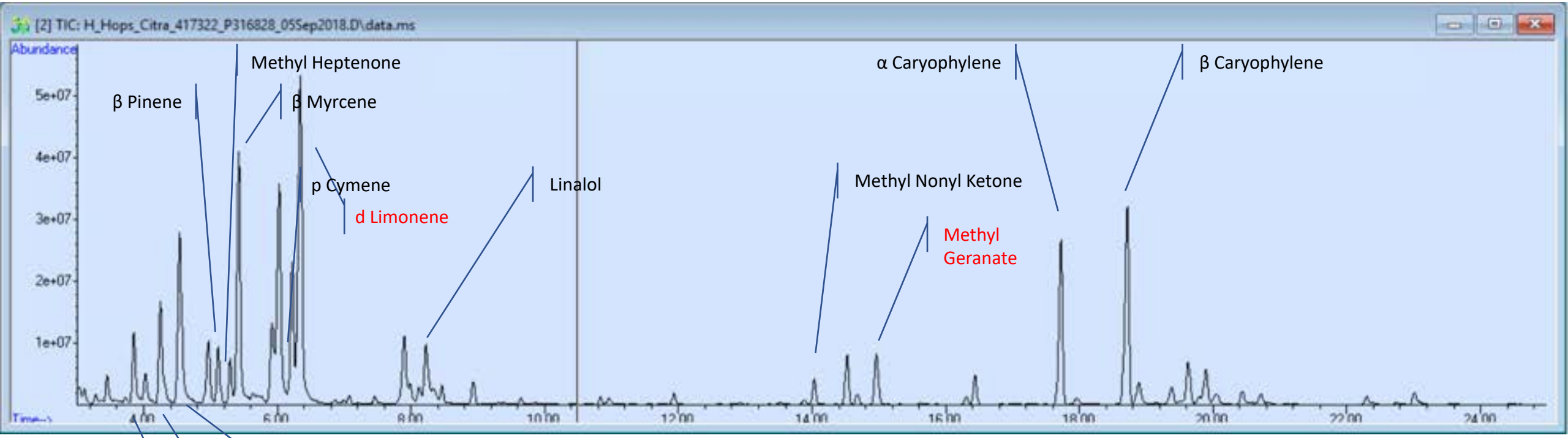
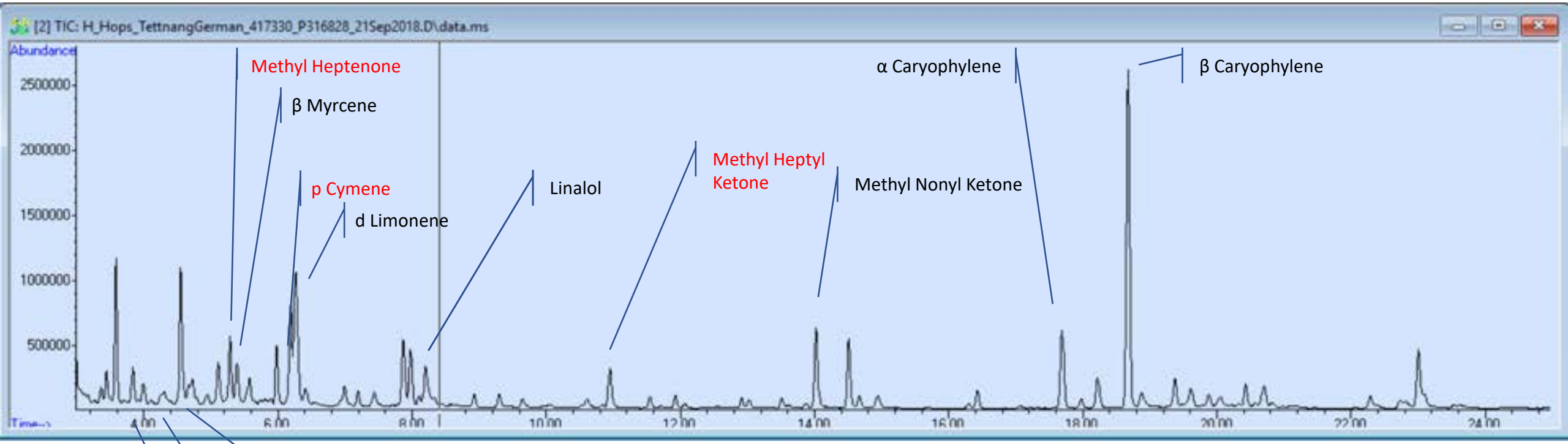
Hop Headspace - Citra



34, 41

Mango, Tropical Fruit, Lime

Hop Headspace - Tettnang



42,43, 44

Earthy, Herbal, Floral

(iv) Hops

Sulphur compounds in Hops

45

In the early days of US hop cultivation, the traditionalist complained about “catty” and “blackcurrant” flavours.

It would be decades before scientists would discover using gas chromatography/olfactometry analysis that **4-mercapto-4-methylpentan-2-one** (otherwise referred to as 4MMP) is a main contributor to muscat grape/black currant character associated with American-bred hops such as Cascade and Simcoe.

It has a low odour threshold and occurs naturally in grapes, wine, green tea, and grapefruit juice.

(iv) Hops

Sulphur compounds in Hops

Hops grown in New Zealand and Australia as well as the United States, contain 4MMP and other compounds found only at trace levels in hops grown in England and on the European continent.

Grown in the United States, cultivars such as Perle or Nugget contained 4MMP, but grown in Germany those same varieties had none.

Nelson Sauvin, from New Zealand with notable exotic fruit and white wine character, contains both 3-mercapto-4-methylpentan-1-ol (3M4MP), and **3-mercapto-4-methylpentyl acetate** (3M4MPA).

They are also present in passion fruit and Sauvignon Blanc wines and are described as smelling grapefruit, gooseberry, and rhubarb like.

(iv) Hops

Other Aromachemicals Reported in Hops

cis-rose oxide	prominent in Centennial hops
β Ionone	

(iv) Hops

Other Aromachemicals Reported in Hops

Desirable fruity esters that are not present in unhopped wort or hops themselves but result from fermentation and aging of beer arise from the breakdown of alpha and beta acid side chains and the subsequent cheesy-smelling, short-chain acids mentioned previously.

The flavour implications are significant but complicated, because a larger concentration of those short-chain fatty acids creates a greater potential for pleasant, fruity odours, **Ethyl isovalerate??**

Aromachemicals Found in The Brewing Process & Finished Beer – Part 2

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