

分析化学会 GC研究懇談会 2017.12.1

におい受容機構を考慮した GC-MSデータの見方

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Saitama University
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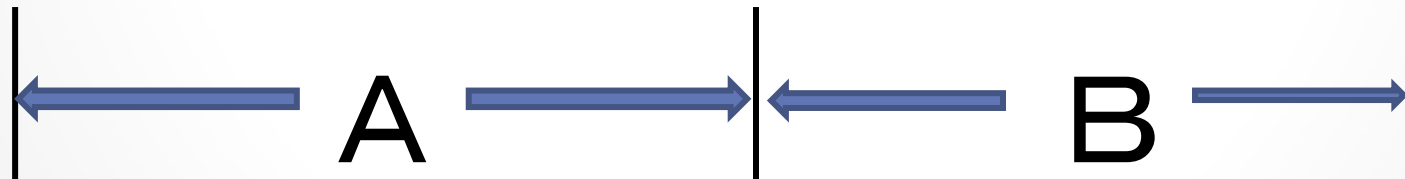
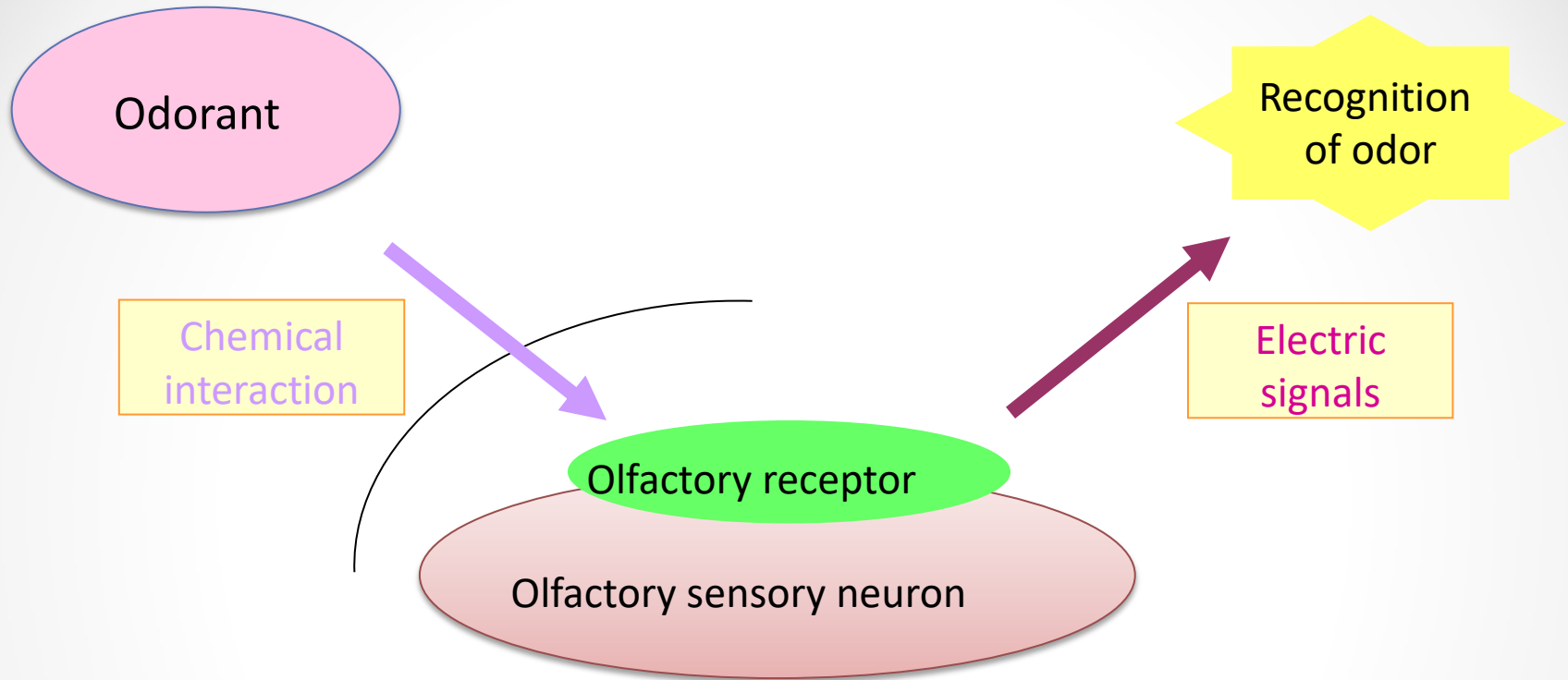
題 目

1. におい受容機構を考慮した複合臭の取り扱いとは？

2. 白檀などの香気素材の香気特性をどう扱うか？

3. 実際のGCデータをどのように解釈したらいいのか？

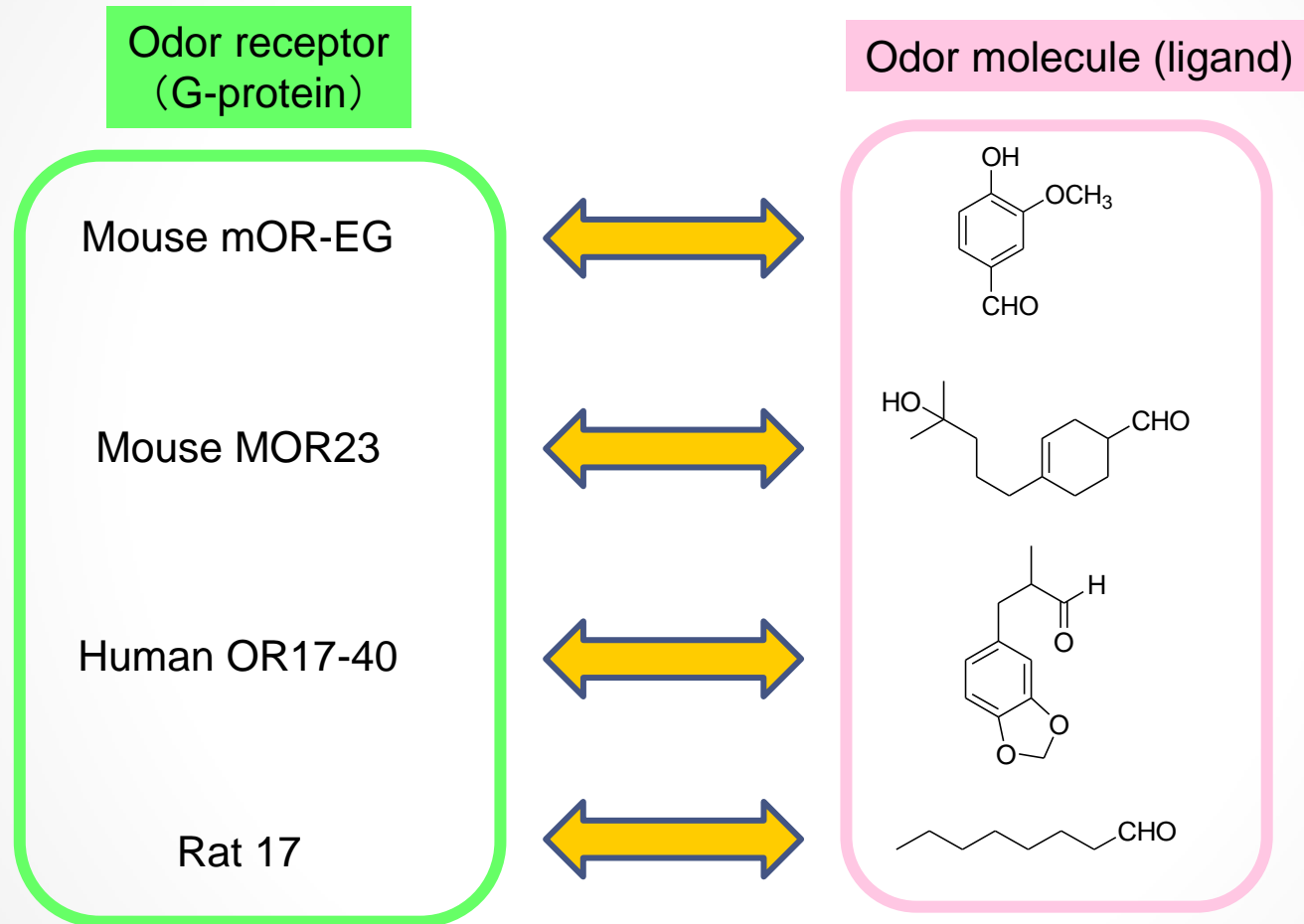
におい受容機構



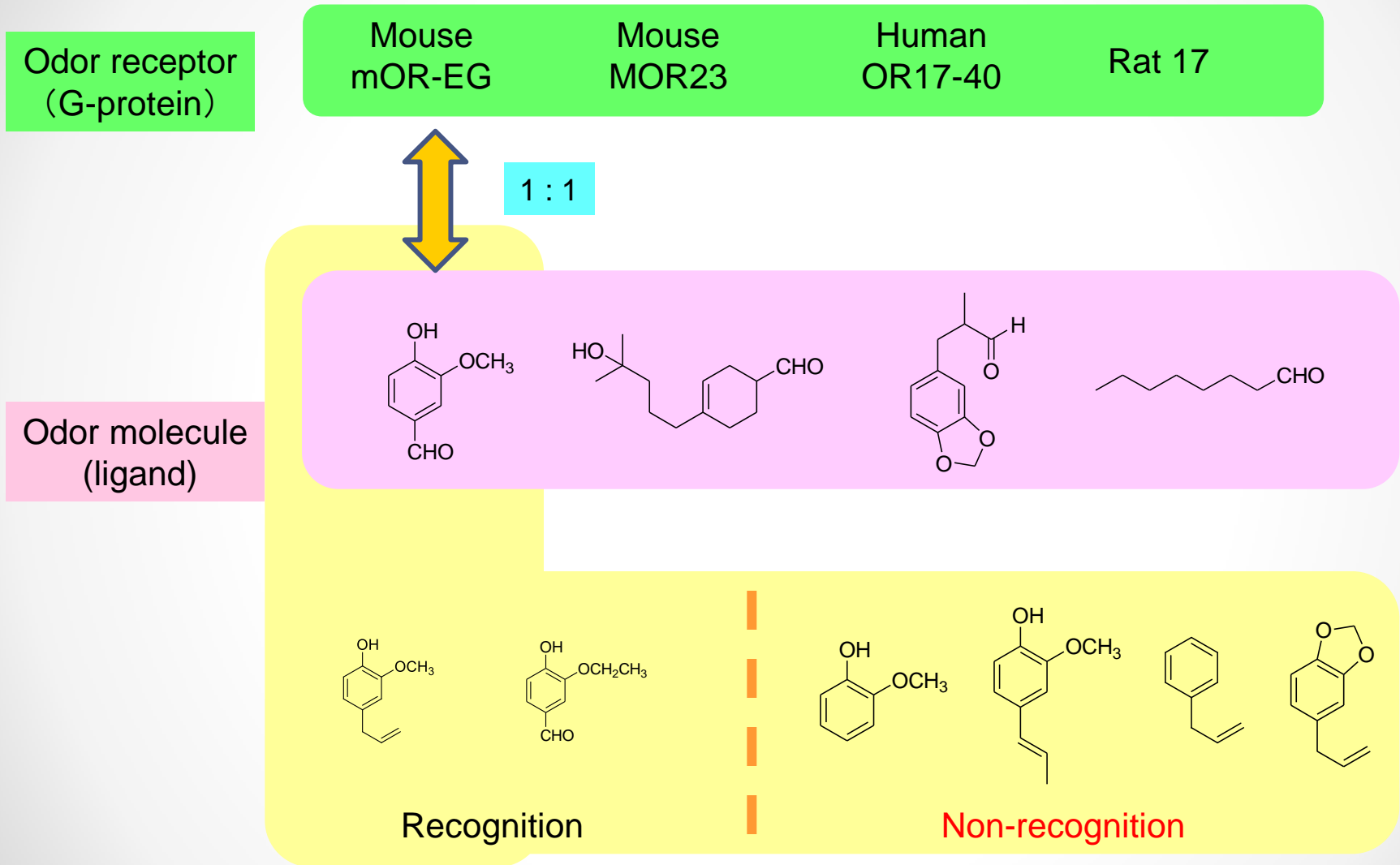
におい分子をにおい分子受容体
でとらえる

におい分子とにおい分子受容体
相互作用の情報を脳で判断

Odor Receptors and Odor Molecules



Odor Receptors and Odor Molecules



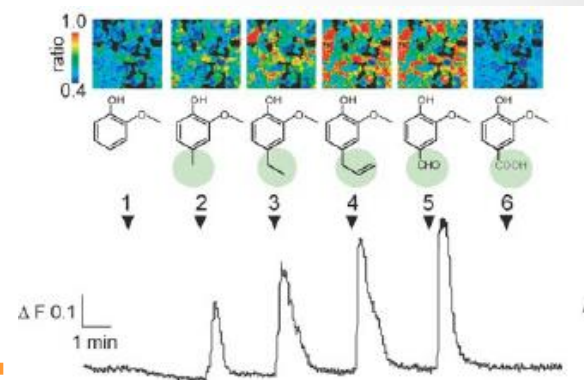
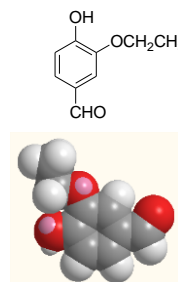
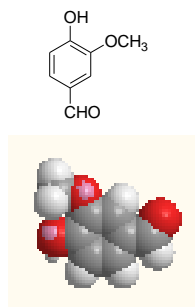
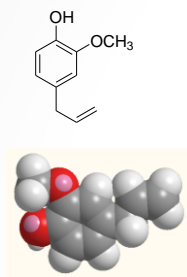
Touhara K. et al., *J. Neuroscience*. 2005, 25, 1806–1815.

Odor Receptors and Odor Molecules

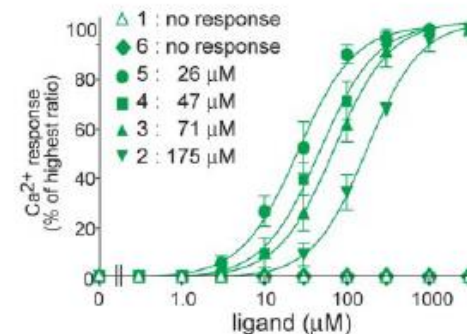
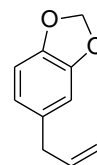
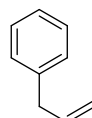
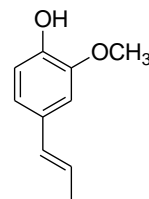
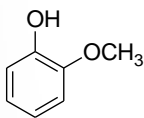
Mouse mOR-EG受容体

Vanilin

Recognition



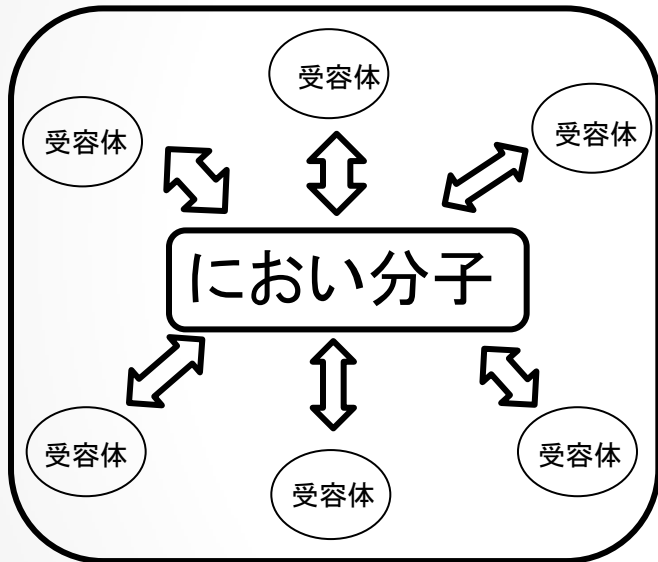
Non-recognition



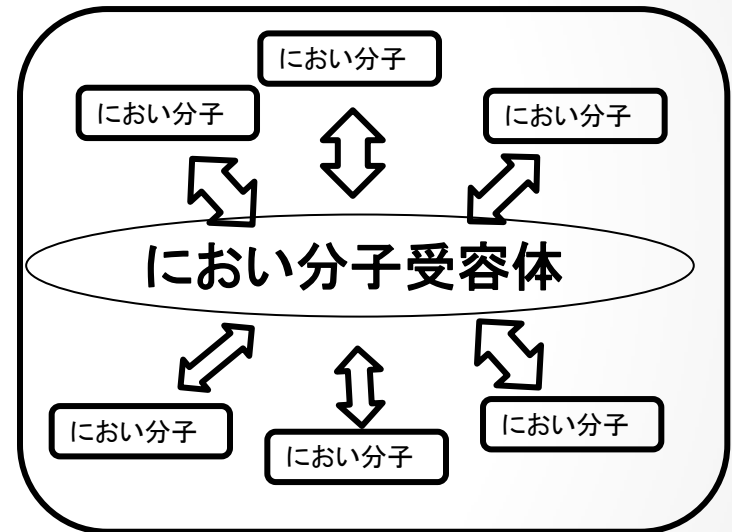
Touhara K. et al., *J. Neuroscience*. 2005, 25, 1806–1815.

Relationship Between Odorant and Receptor

におい分子とにおい受容体とは複雑な関係で相互作用している

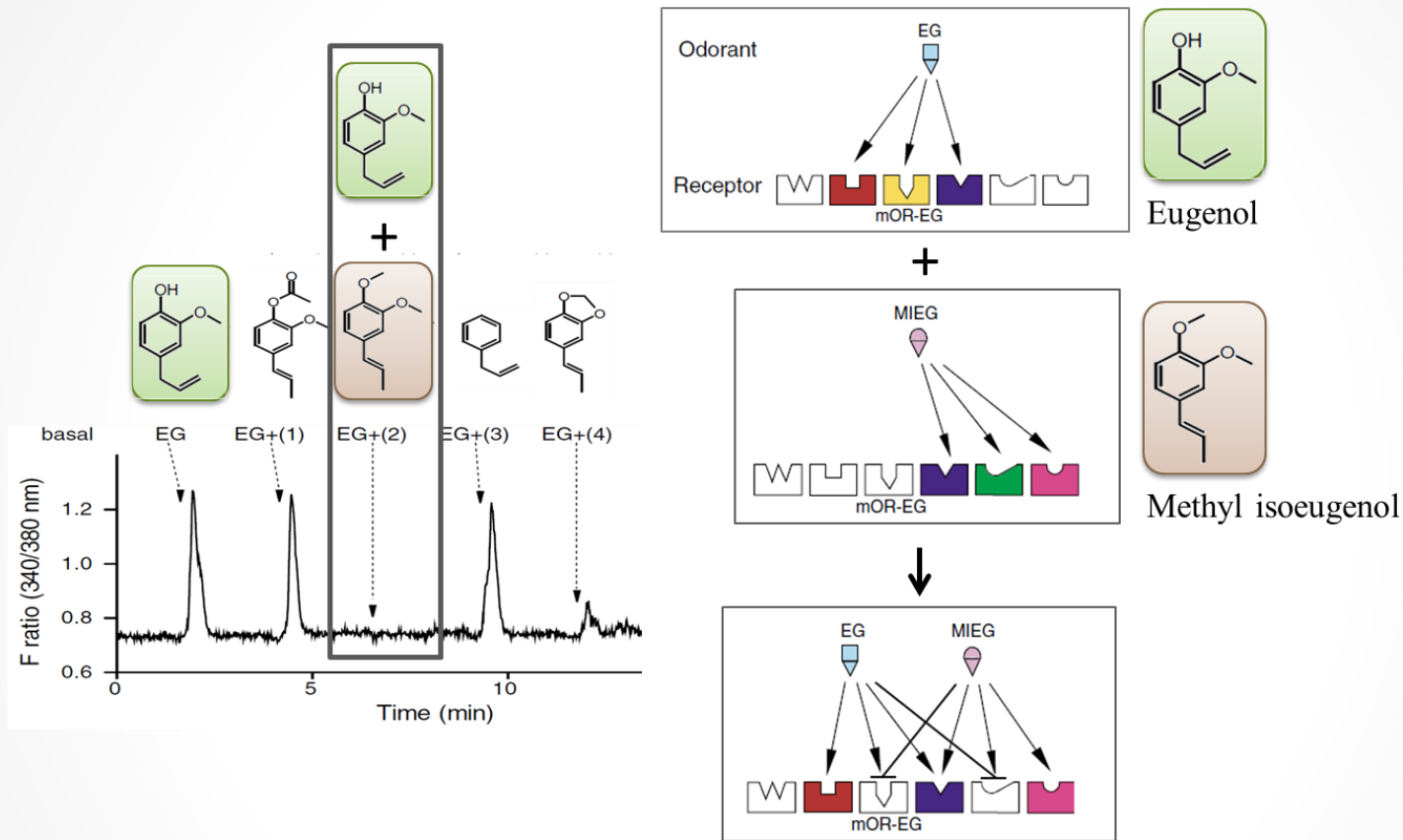


1つのにおい分子は、異なった強度で複数のにおい分子受容体と相互作用する



1つのにおい分子受容体は、異なった強度で複数のにおい分子と相互作用する

Effect on Receptor when Odor Compounds with Similar Structure are Mixed



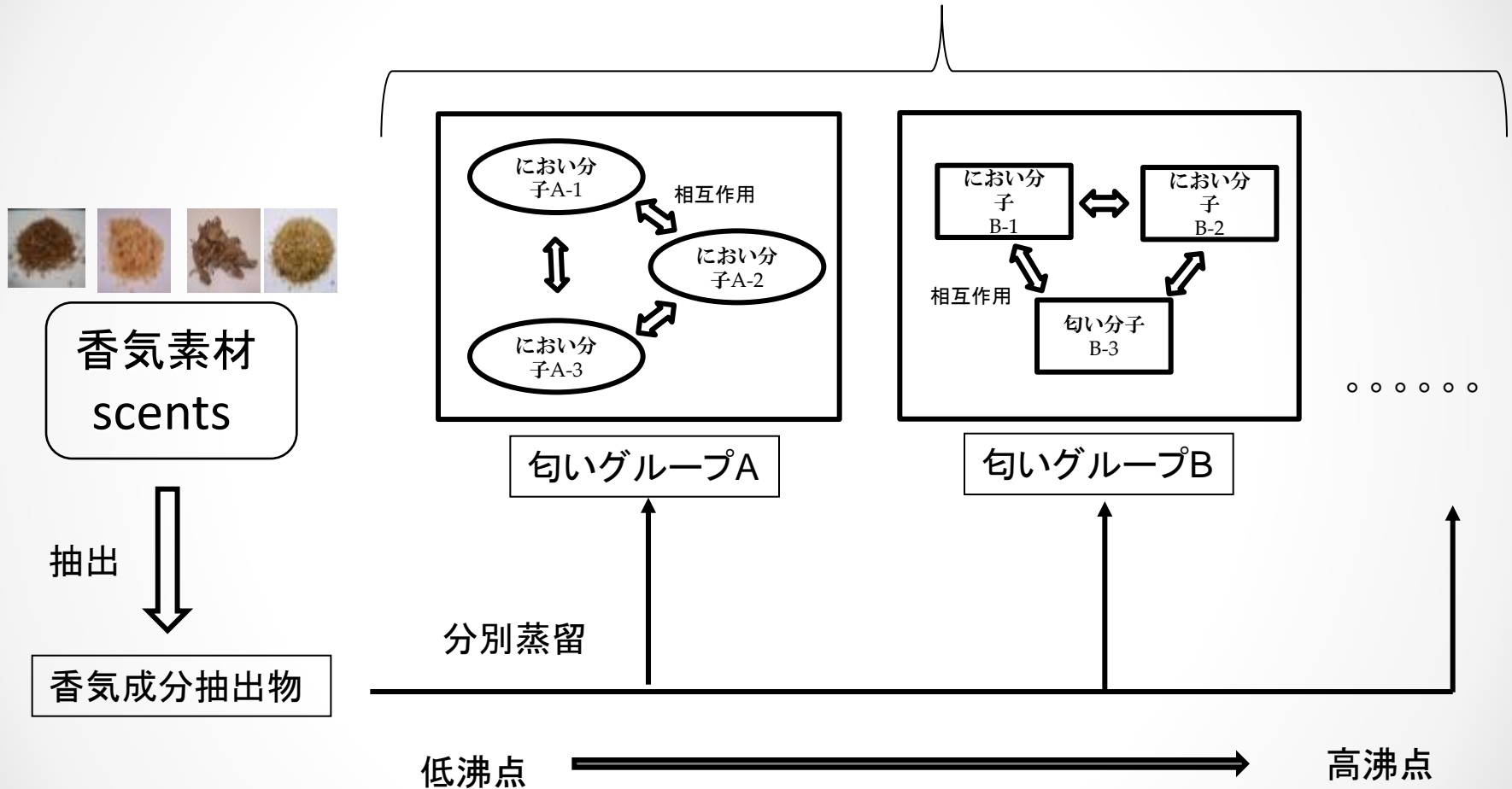
The above literature indicates that the odor of a given material is not the simple sum of the odors of each constituent.

And, the interactions of several constituents with similar structure are important for the aroma profile.

Oka, Y.; Omura, M.; Kataoka, H.; Touhara, K. *The EMBO J.* **2004**, 23, 120-126.

Proposed Method: Aroma Profile Analysis

いくつかの匂いグループが合わさって香気素材香気を形成



<抽出方法の違い>

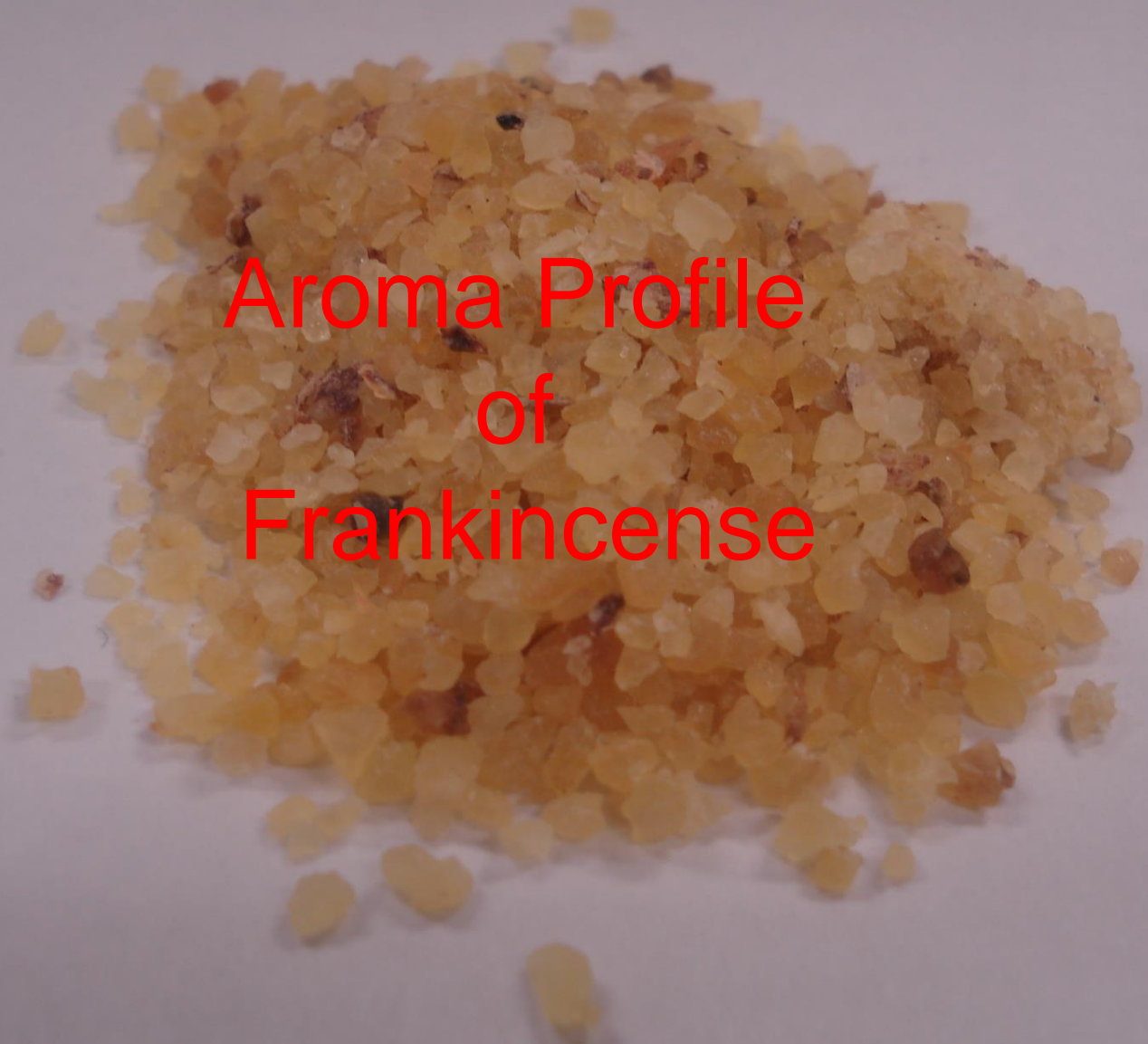
<沸点の違い>

題 目

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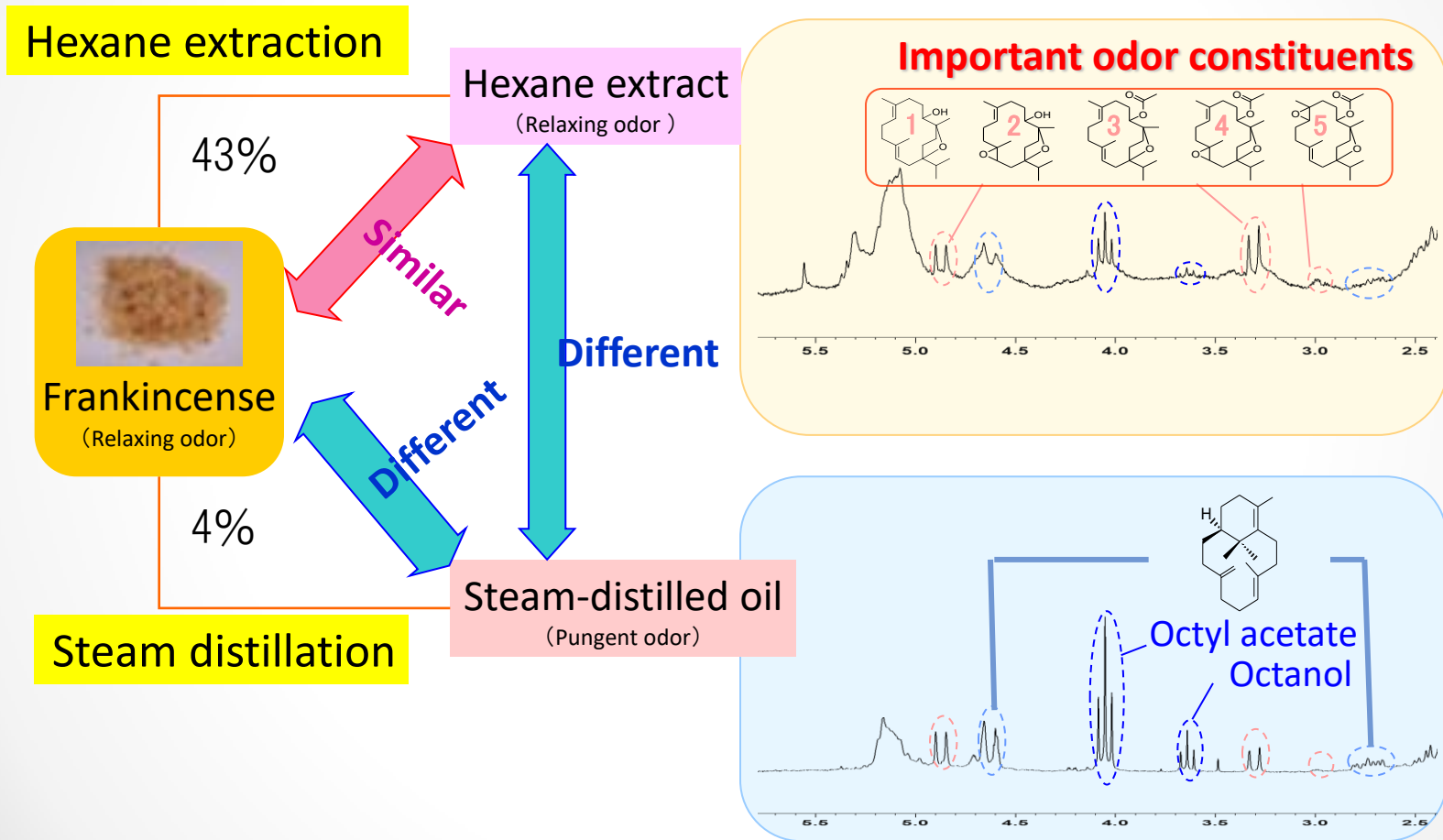
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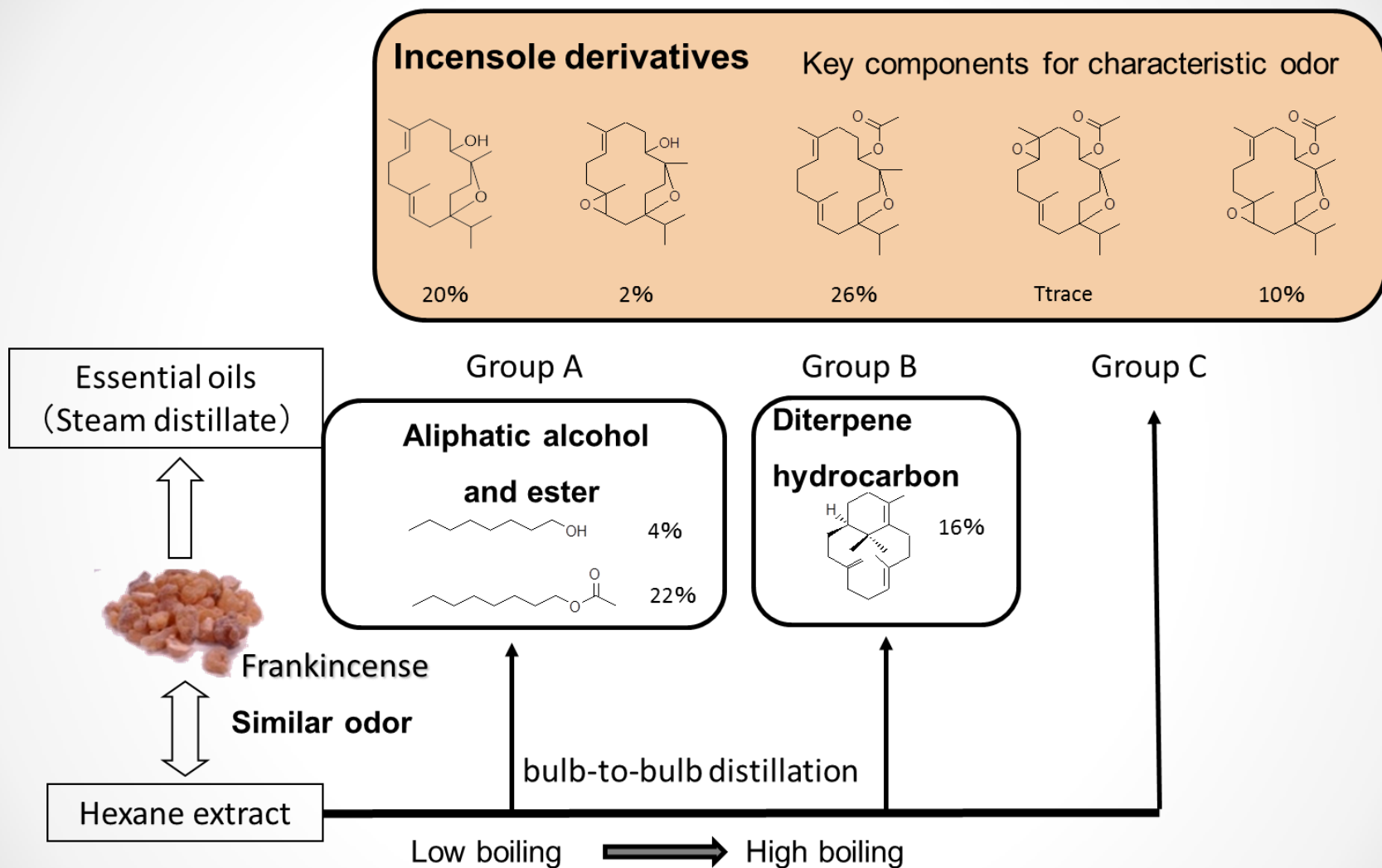
Aroma Profile
of
Frankincense

Comparison of Constituents of Hexane Extract and Steam-Distilled Oil



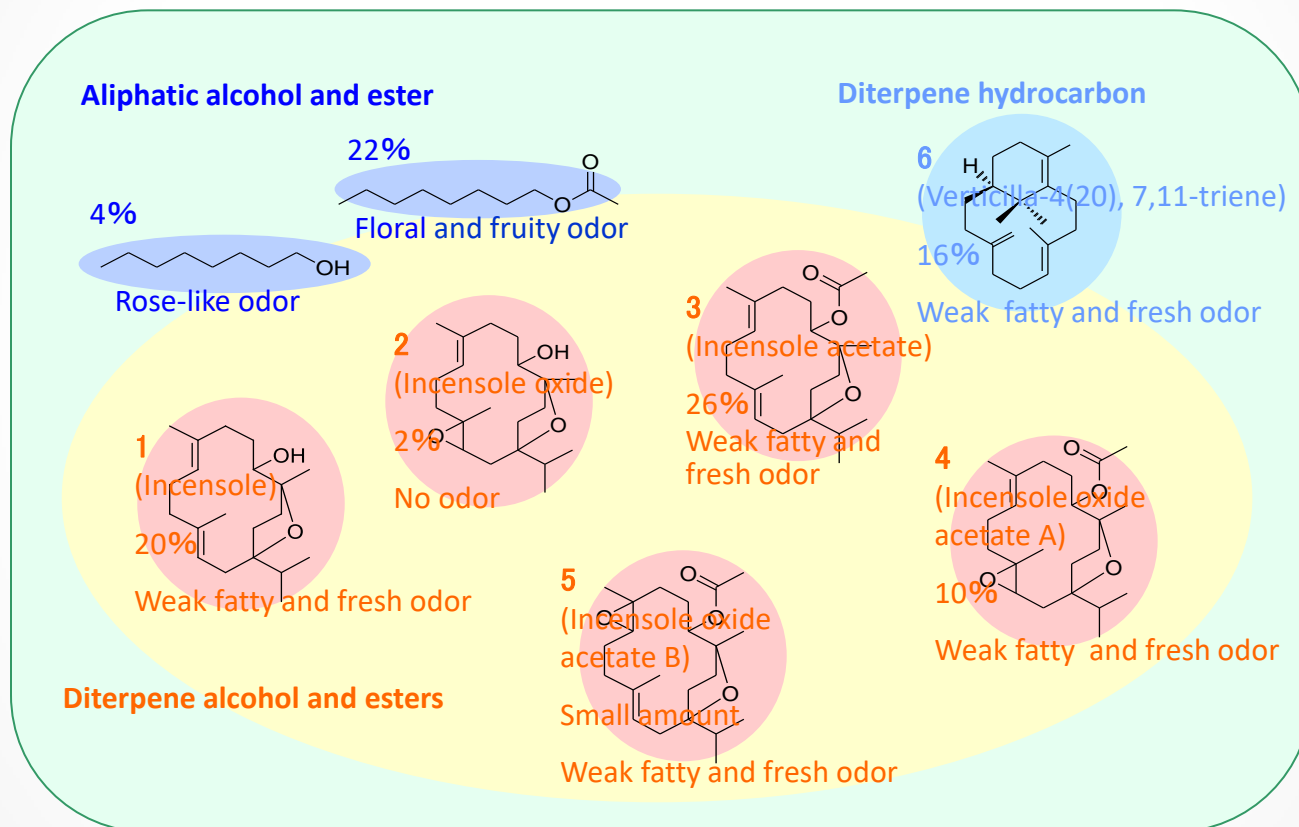
^1H NMR (200 MHz, CDCl_3)

Investigation of Aroma Components of Frankincense



Hasegawa, T et al., . *Natural Product Communications*, **2012**, 24, 593-598.

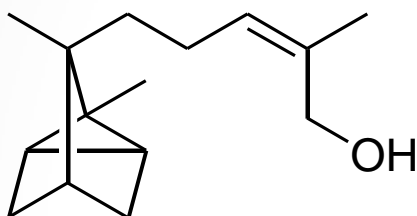
Main Constituents in Hexane Extract of Frankincense



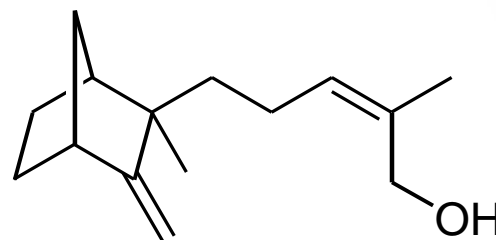


Aroma Profile
of
Sandalwood

Main Constituents of Sandalwood



α -Santalol



β -Santalol

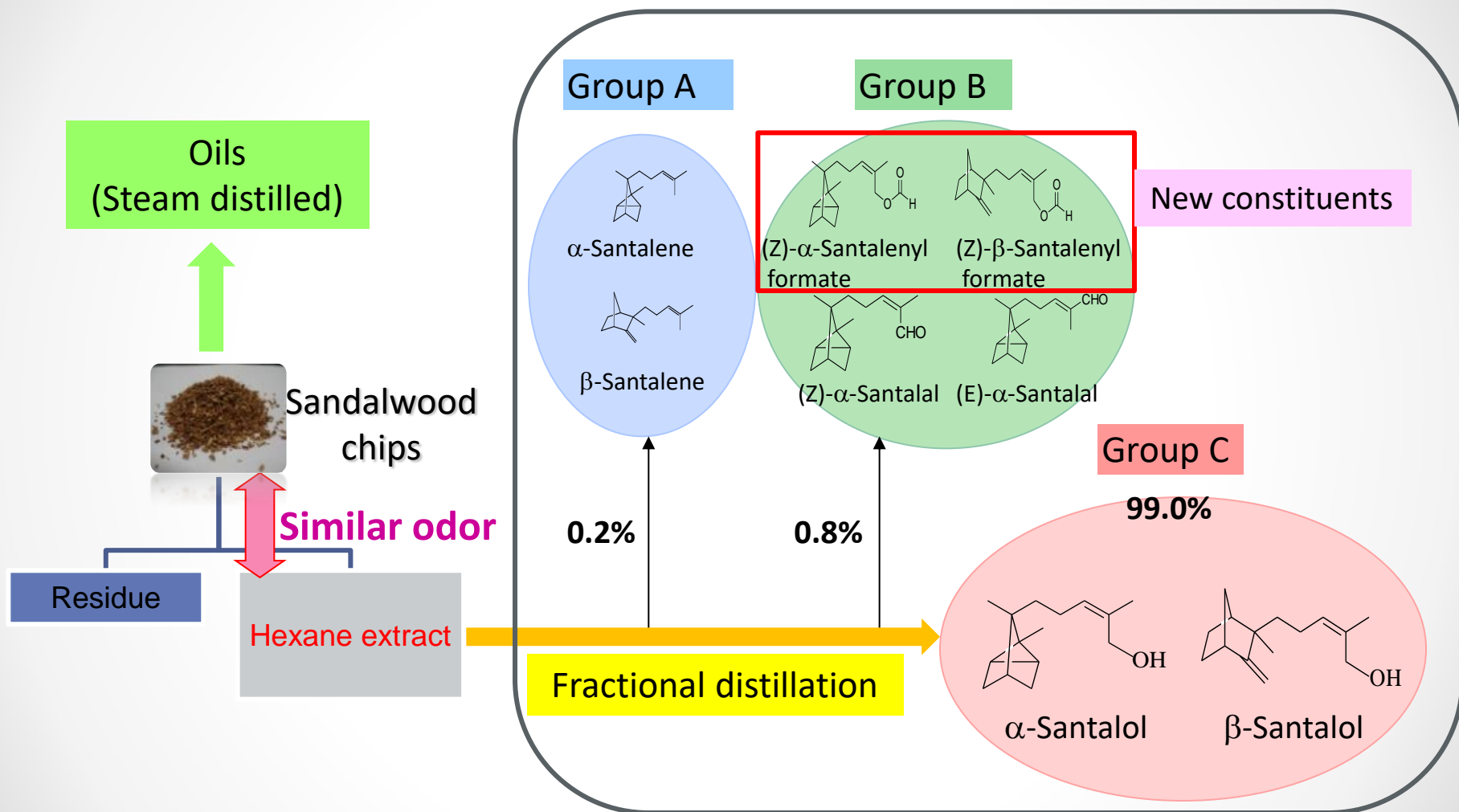
Many studies have been reported on sandalwood, and the structure–odor relationships of β -santalol and its related compounds have been investigated in detail .

[1] Stappen, I.; Hoefinghoff, J.; Friedl, S.; Pammer, C.; Wolschann, P.; Buchbauer, G., *Eur. J. Med. Chem.*, **2008**, 43, 1525–1529.

[2] Brocke, C.; Eh, M.; Finke, A. *Chem. & Bio.*, **2008**, 5, 1000–1010.

[3] Buchbauer, G.; Stappen, I.; Pretterklieber, C.; Wolschann, P., *Eur. J. Med. Chem.*, **2004**, 39, 1039–1046.

Investigation of Aroma Components of Sandalwood

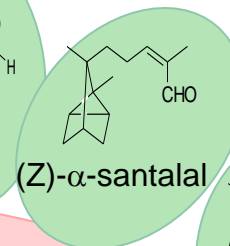
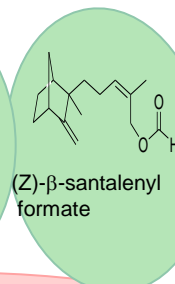
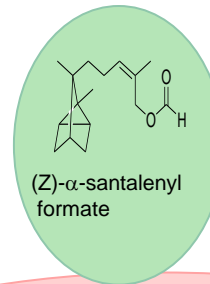
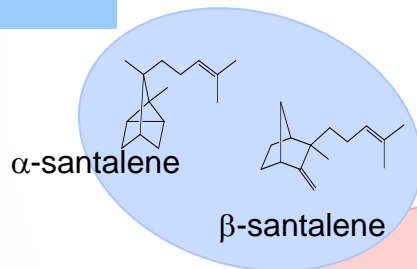


Hasegawa, T.; Toriyama, T.; Ohshima, N.; Tajima, Y.; Mimura, I.; Hirota, K.; Nagasaki, Y., and Yamada, H. *Flavour and Fragrance Journal*, **2011**, 26, 98–100.

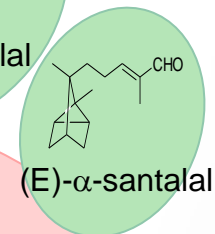
Aroma Profile of Sandalwood

白檀の香気プロフィール

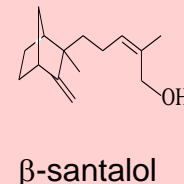
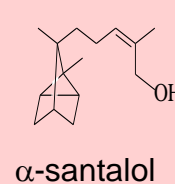
Group A



Group B



Group C

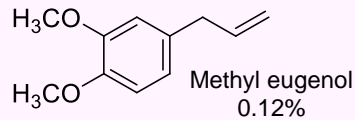
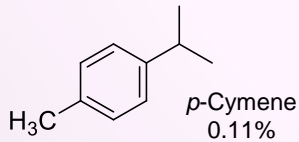
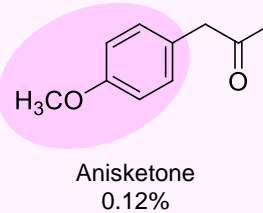
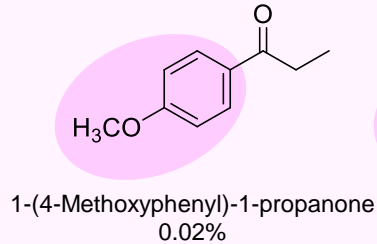
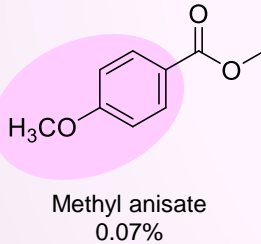
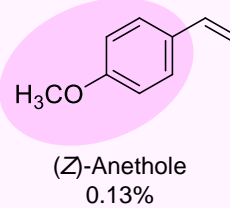
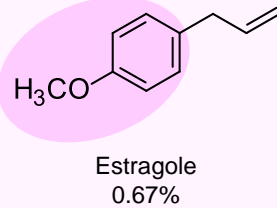
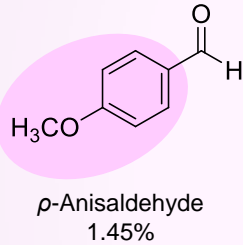
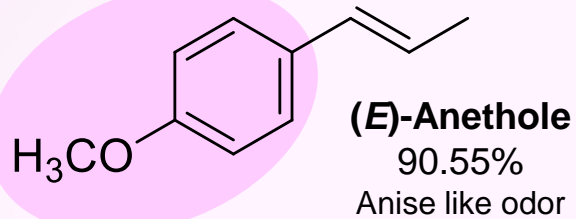




Aroma Profile
of
Star Anise

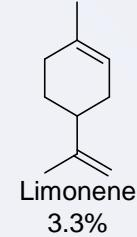
Constituents of Star Anise

Benzene derivatives



9 compounds, 93.2%

Terpenoid compounds

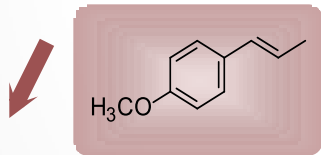
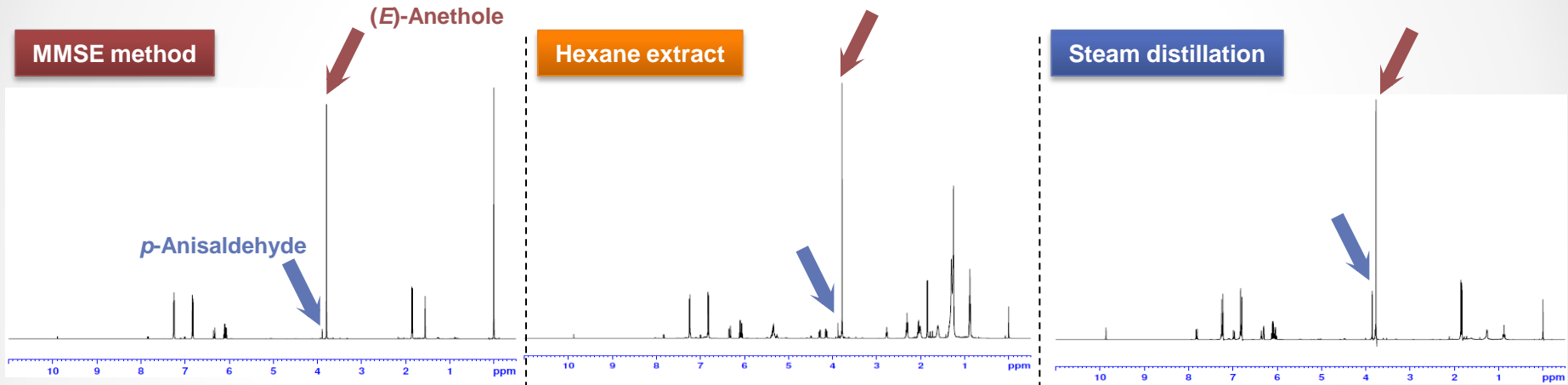


18 compounds, 6.8%

Benzene derivatives
93.2%

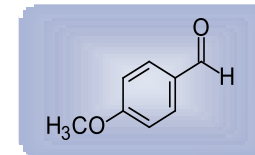
^1H NMR Comparison of Components of Extracts Obtained by Three Different Methods

^1H NMR (CDCl_3 , 500 MHz)



21:1

(E) -Anethole (1): p -Anisaldehyde (2)



6:1

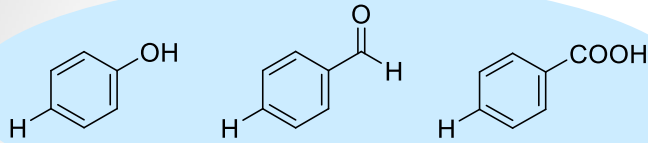
High

Low

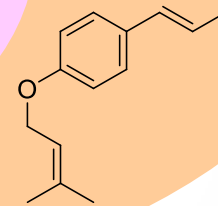
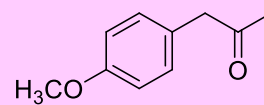
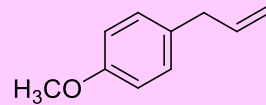
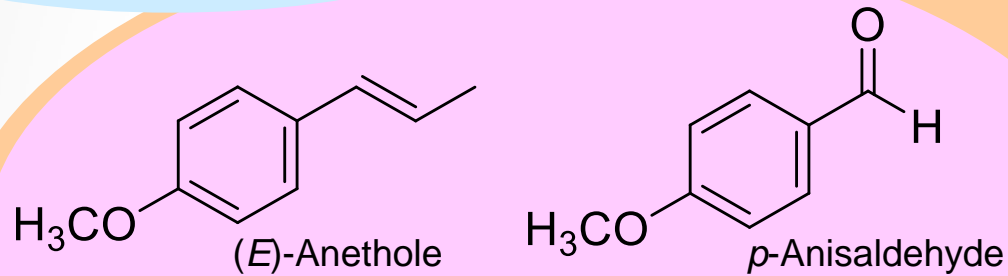
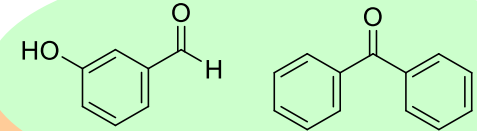
Similarity of odor to star anise

Aroma Profile of Star Anise

Monosubstituted benzene



Others



Para-disubstituted benzene

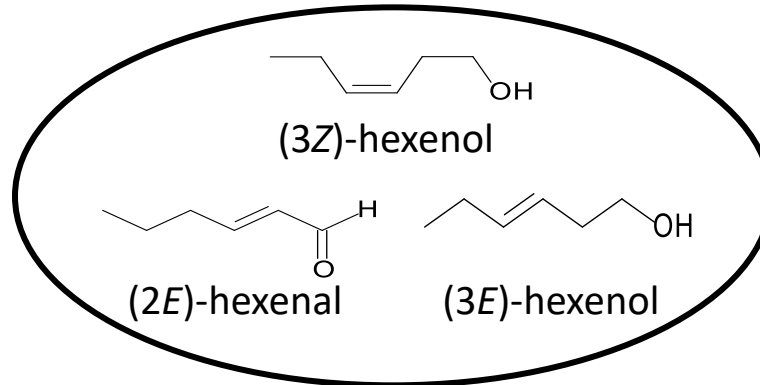
The odor of star anise consisted of the combination of three groups of compounds.

A close-up photograph of tea leaves on a branch. The leaves are vibrant green with serrated edges and prominent veins. The background is a soft-focus green, suggesting a tea plantation. The text 'Aroma Profile of Green Tea Leaves' is overlaid in red.

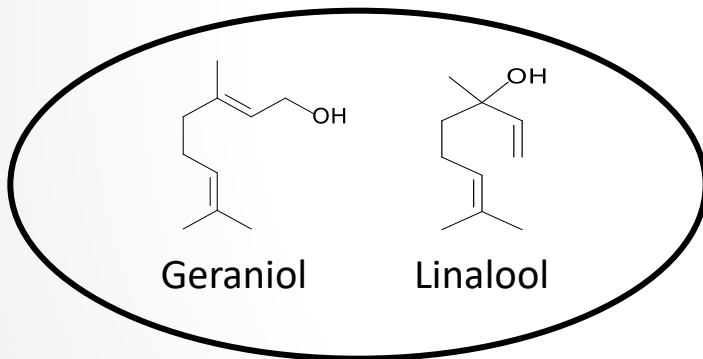
Aroma Profile of Green Tea Leaves

Aroma Compounds in Green Tea Leaves

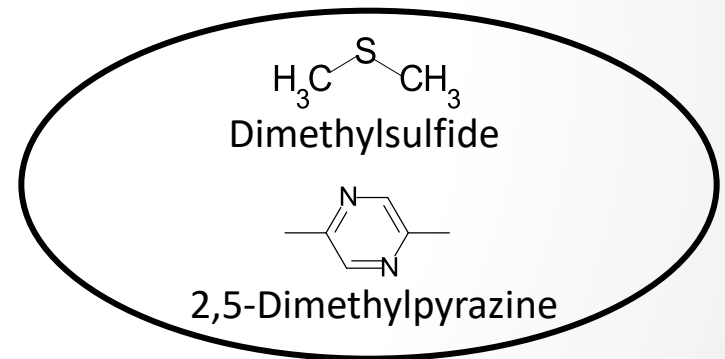
Greenish



Floral



Roast



Green tea-like odor



Reduction of Compounds with a Formyl group in the Residue

The residue



Alcohols

Odor

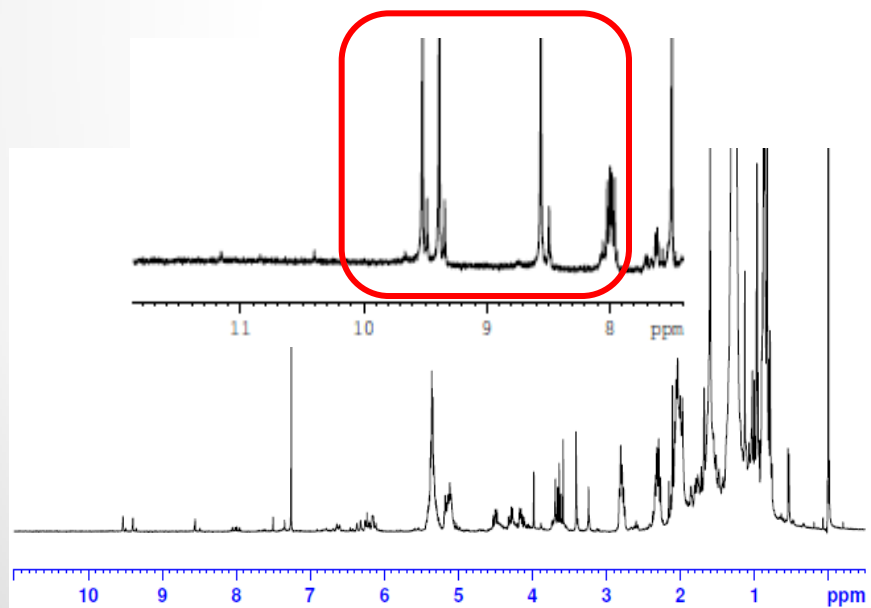
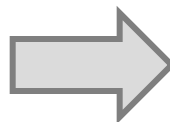
Matcha-like

~~*Matcha-like*~~

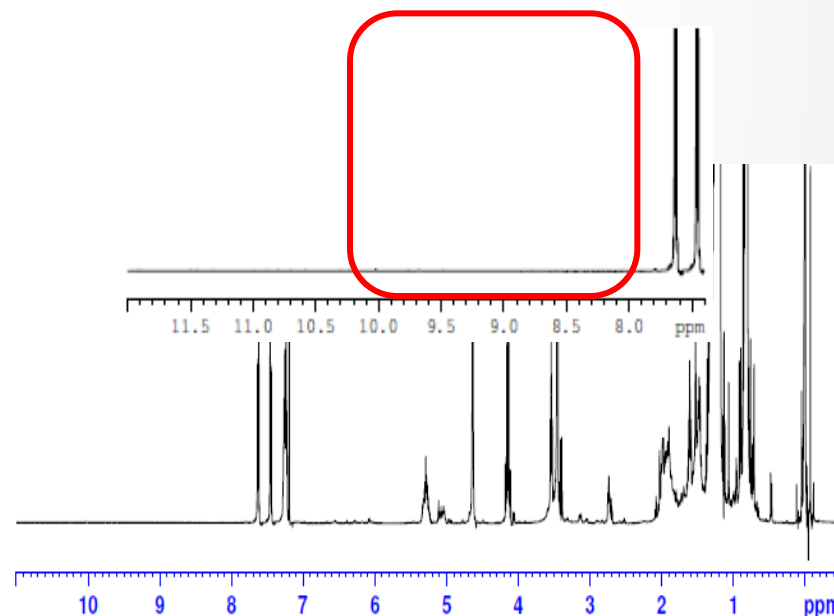
Components

Derived from
Formyl group

~~Derived from
Formyl group~~



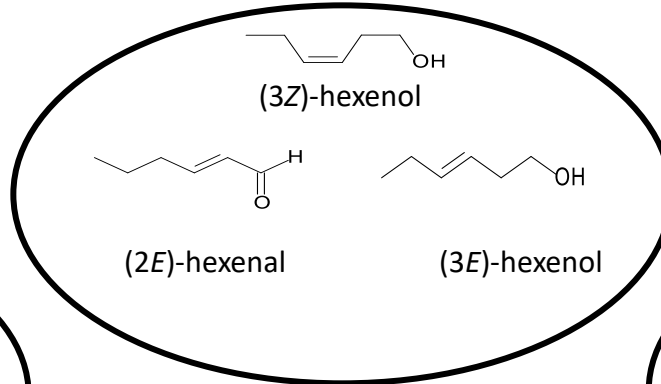
^1H NMR (500 MHz, CDCl_3)



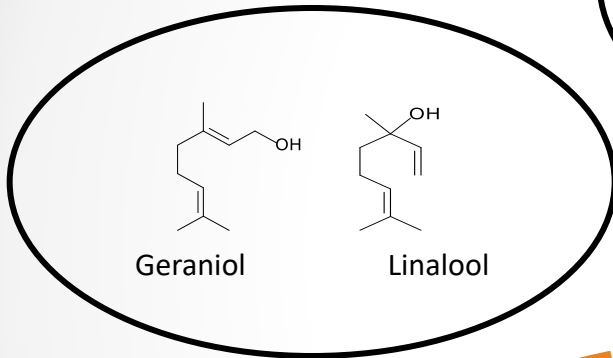
^1H NMR (500 MHz, CDCl_3)

Aroma Profile of Green Tea

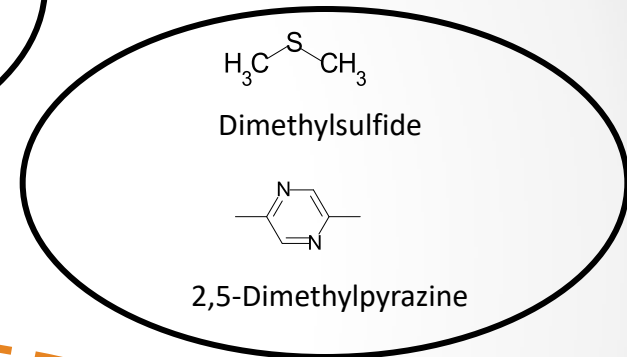
Greenish



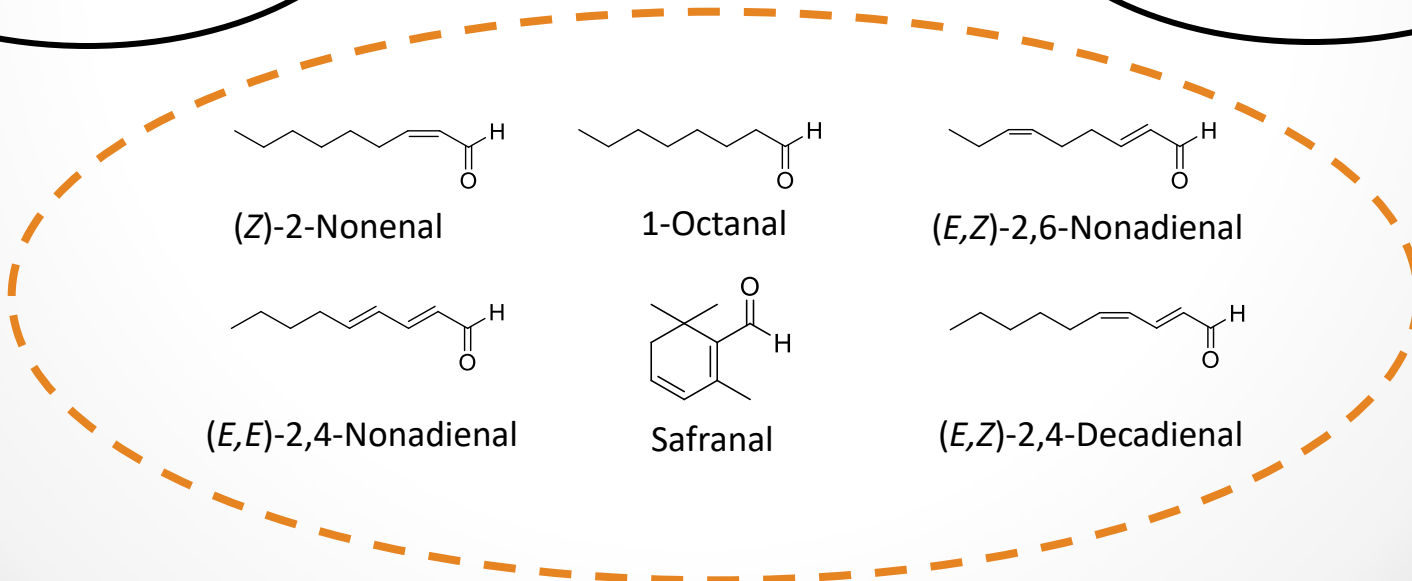
Floral



Roast



Matcha-like



におい分子の構造の類似性とは？

種々の
におい分子

構造変換

におい分子同士が類似のにおいを示す

におい分子同士が異なったにおいを示す

におい受容体は類似の構造として認識している

におい受容体は異なった構造として認識している

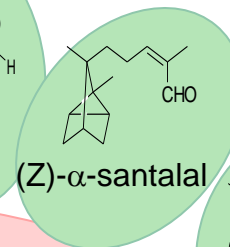
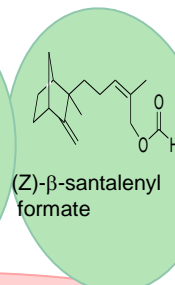
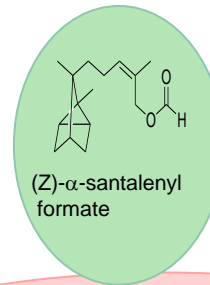
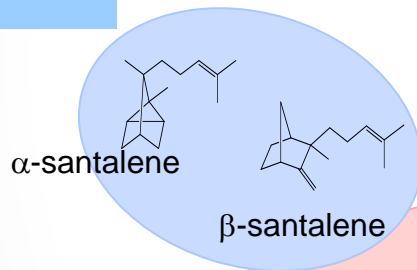
類似のにおい受容体グループ

異なったにおい受容体グループ

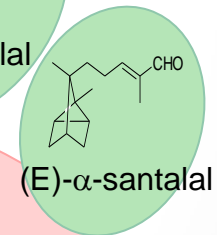
Aroma Profile of Sandalwood

白檀の香気プロフィール

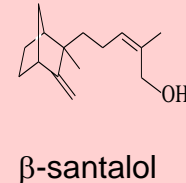
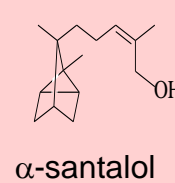
Group A



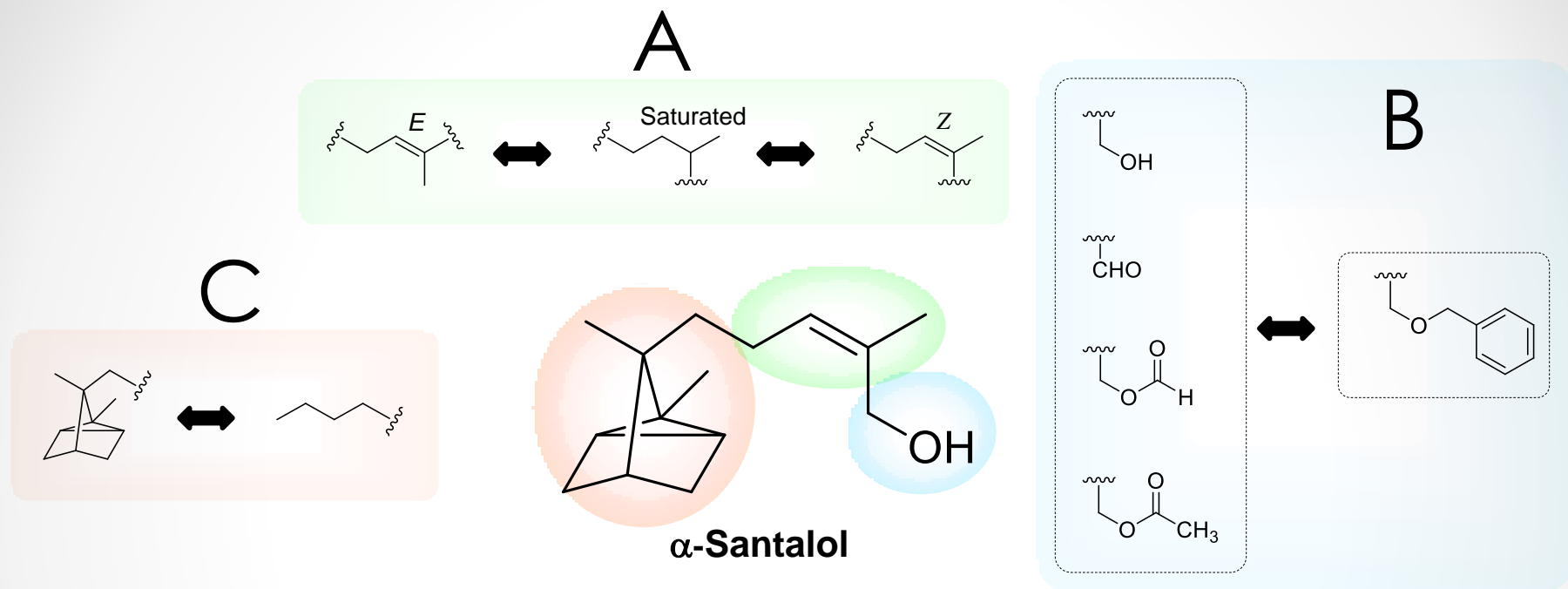
Group B



Group C



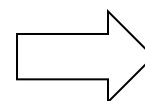
Structure-odor Relationship of α -Santalol



Part A: Geometric isomers

Part B: Replacement of functional groups

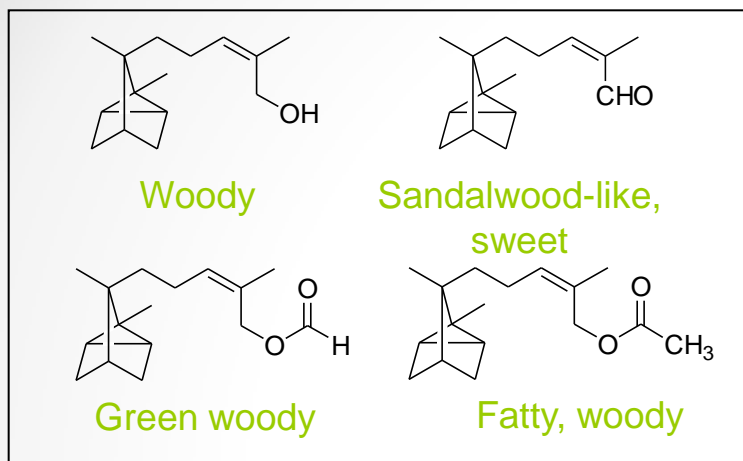
Part C: Loss of bulky polycyclic moiety



**Dramatic
odor change**

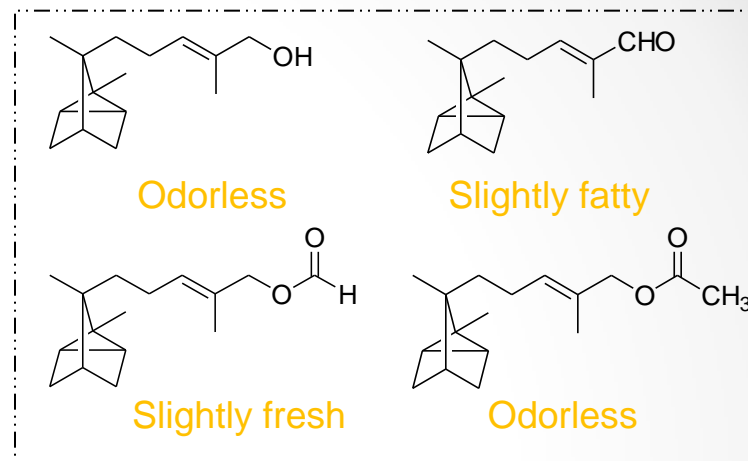
Effect of changing part A on odor

Z-Isomer



Characteristic woody odor

E-Isomer

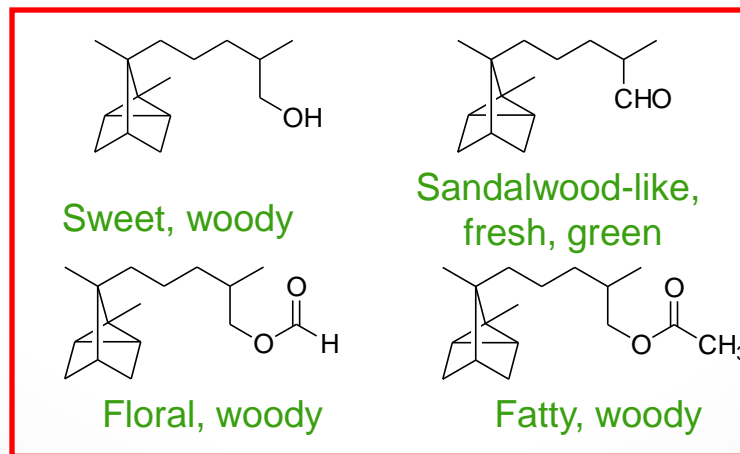


Very weak odor

Different odor



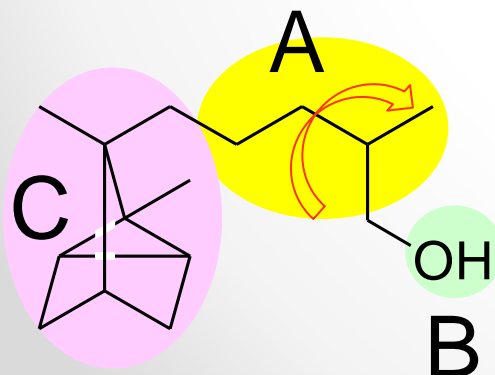
Saturated compound



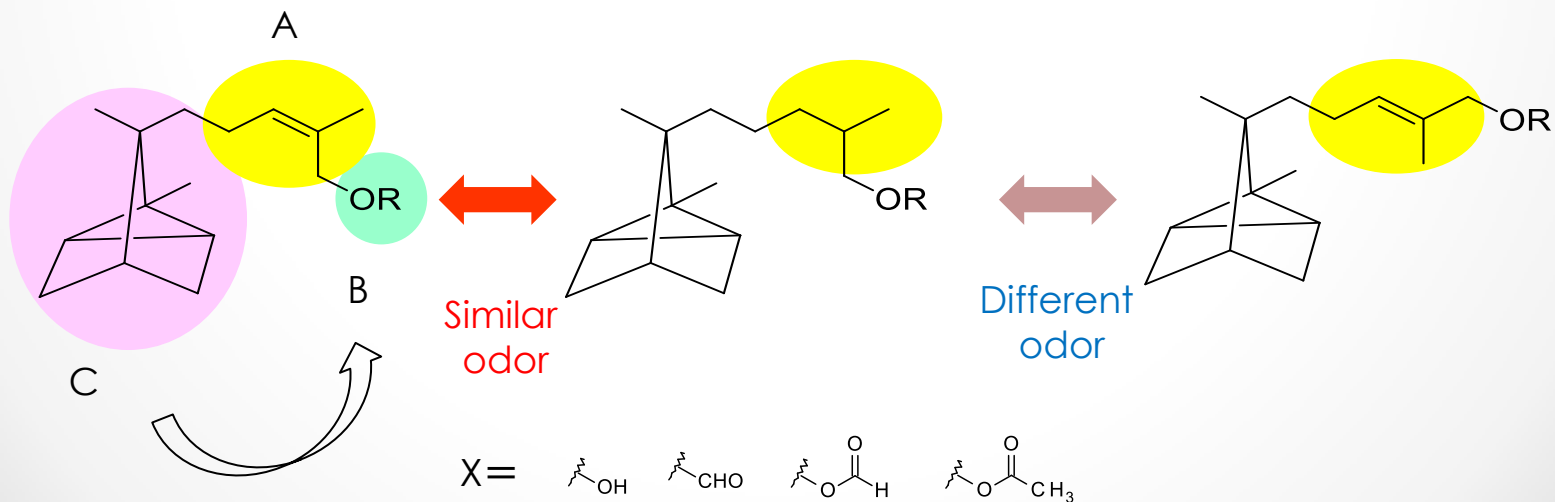
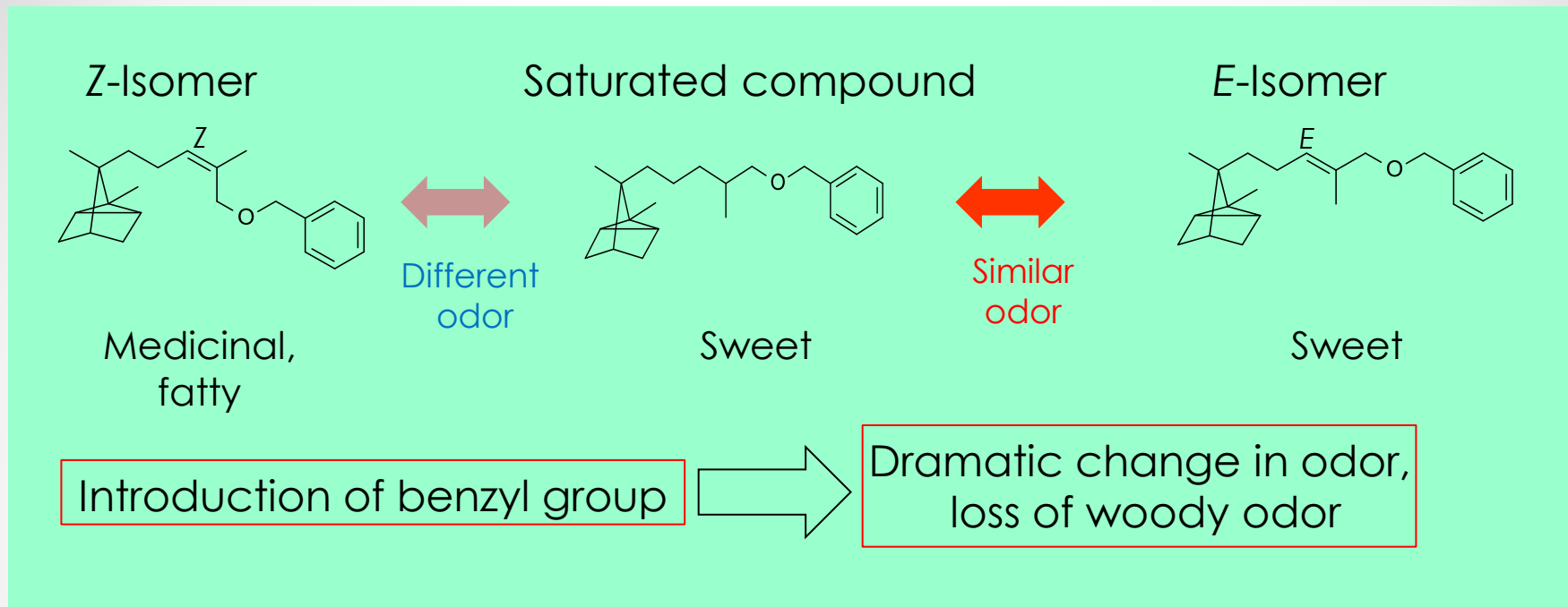
Different odor

Woody odors

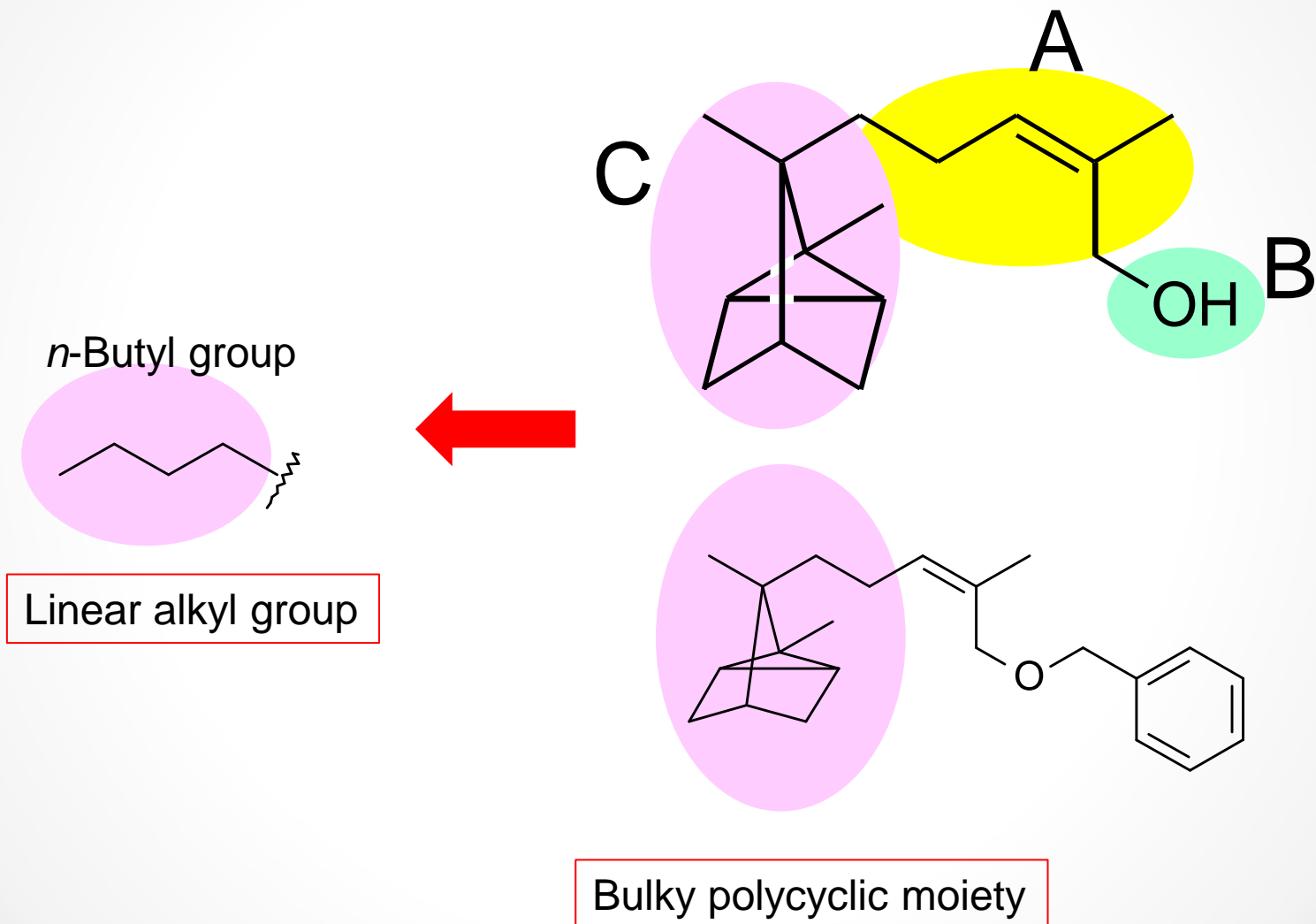
Similar odor



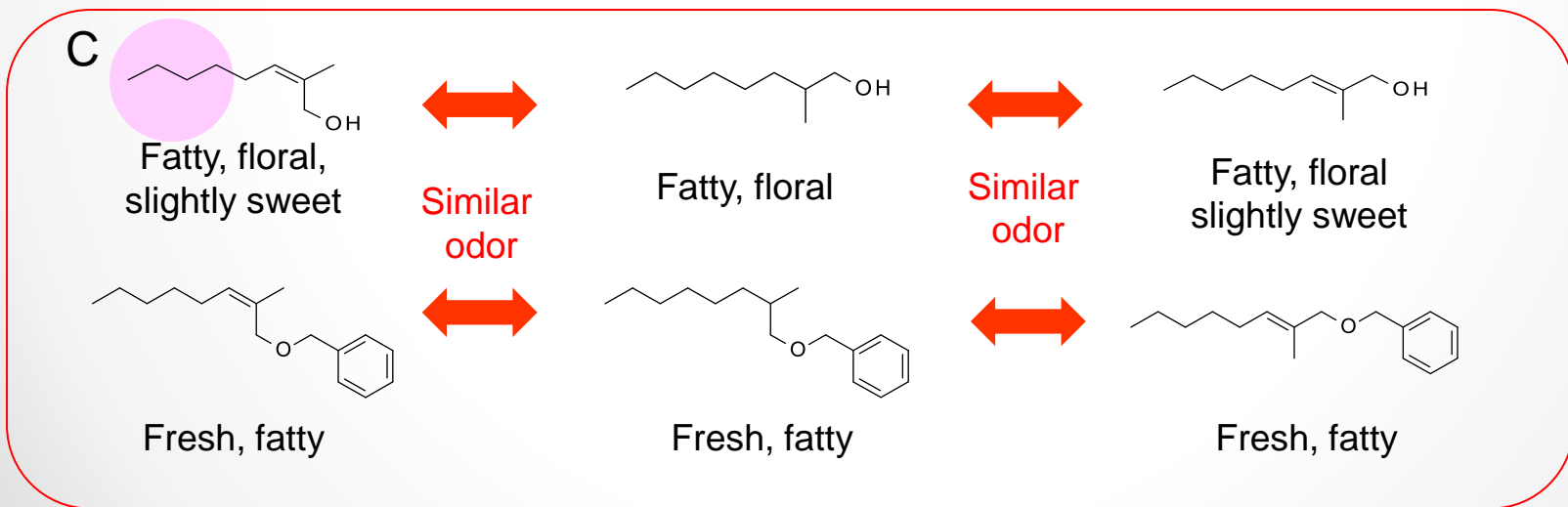
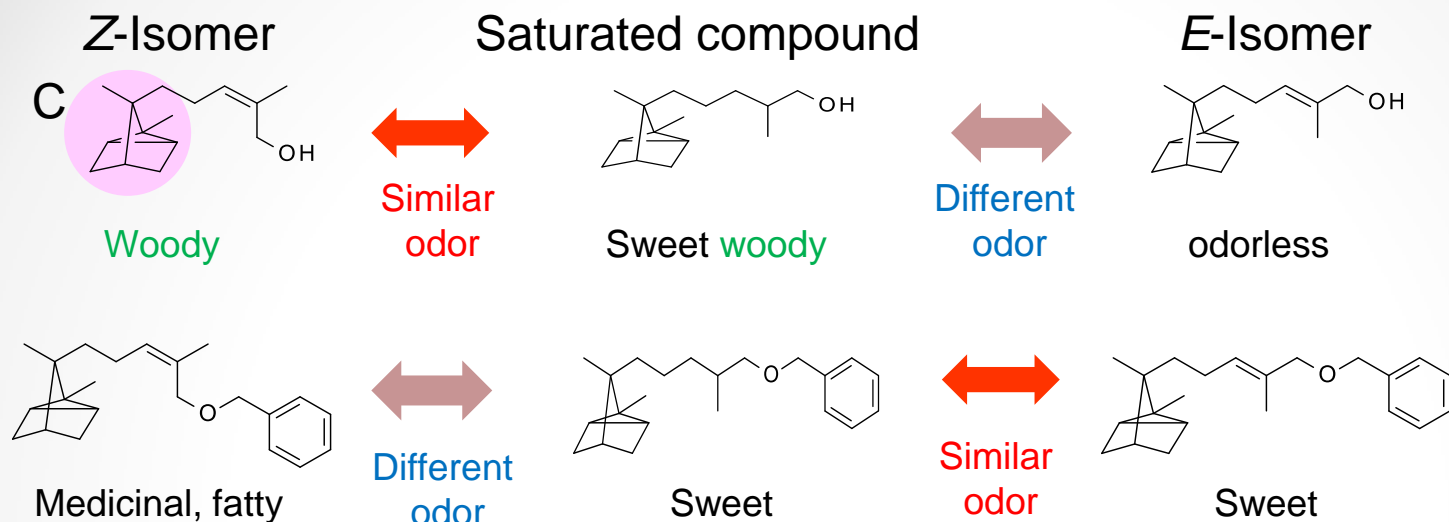
Effect of changing part B on odor



Effect of part C on odor



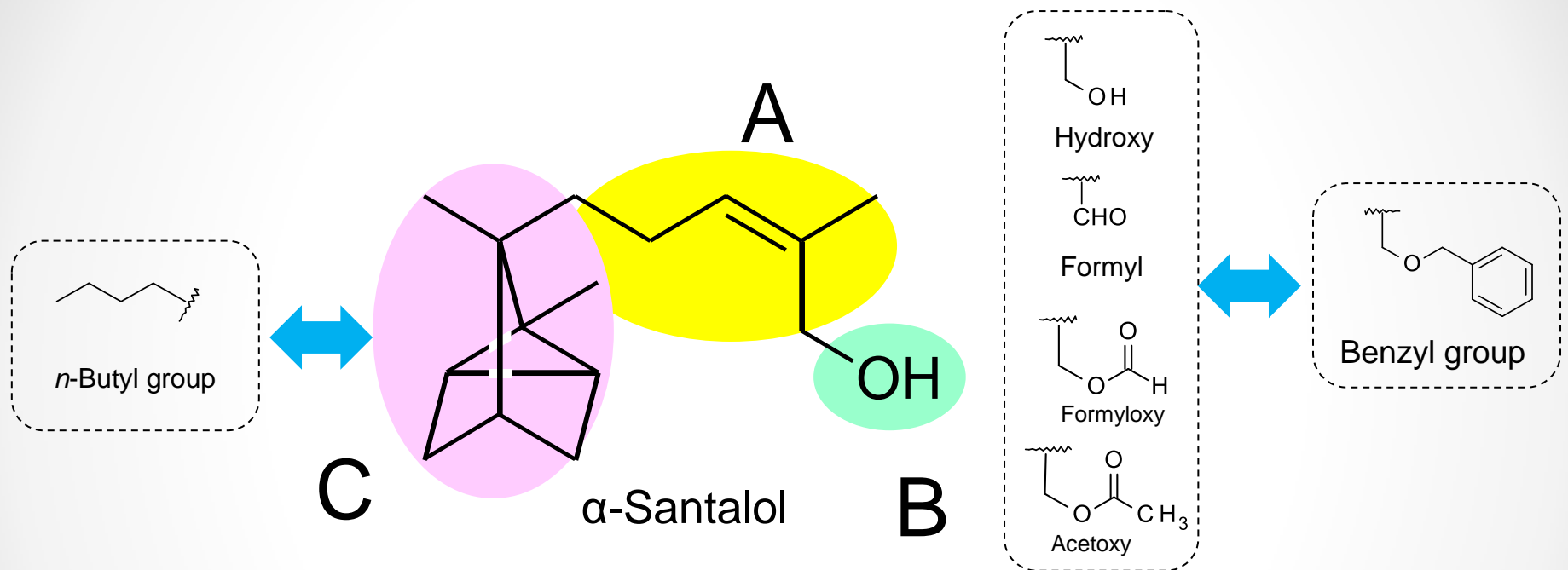
Effect of changing part C on odor



Loss of woody note and difference in odors between geometric isomers

α -サンタロールの構造と匂いの関係

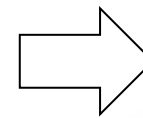
Structure-Odor Relationship of α -Santalol



Part A: Geometric isomers

Part B: Replacement of functional groups

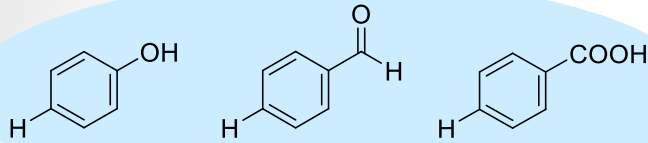
Part C: Loss of bulky polycyclic moiety



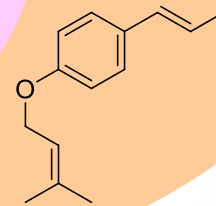
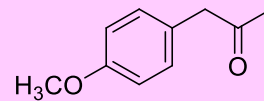
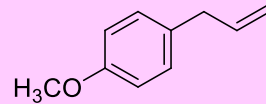
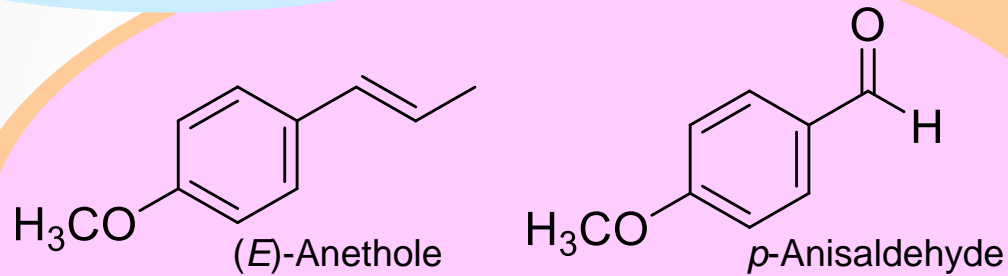
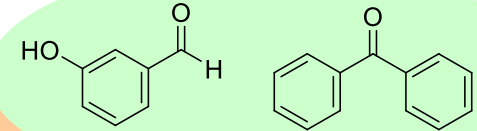
**Dramatic
odor change**

Aroma Profile of Star Anise

Monosubstituted benzene



Others



Para-disubstituted benzene

The odor of star anise consisted of the combination of three groups of compounds.

Structural Features That Affect the Odor of Anethole

Anethole	B Double bond In the side chain		C Polar group			Santalol ¹⁾	
<u>System 1</u> 	Sour fresh fruity	Anise-like	fresh Fatty	Unpleasant	Slightly Sweet		Woody
<u>System 2</u> 	Fatty fruity	Anise-like	Fatty fresh floral	Fatty fruity	Slightly sweet fatty		Woody
<u>System 3</u> 	Fatty floral	Fatty sweet	Fatty	Fatty fresh sweet	Slightly fatty fresh		Fatty floral
	A		Methoxy group				

Removing the *p*-substituted benzene moiety caused the loss of characteristic odors.

複合臭の香気特性の解明

Comprehend the Odor Character
of Complex Odor Materials



Approach Based on Odor Recognition Mechanism



臭い受容機構に基づいたアプローチ

有機化学的観点による
受容機構の解明

Evaluation of the Mechanism
from the Viewpoint of Organic Chemistry

Aroma Profile
Analysis

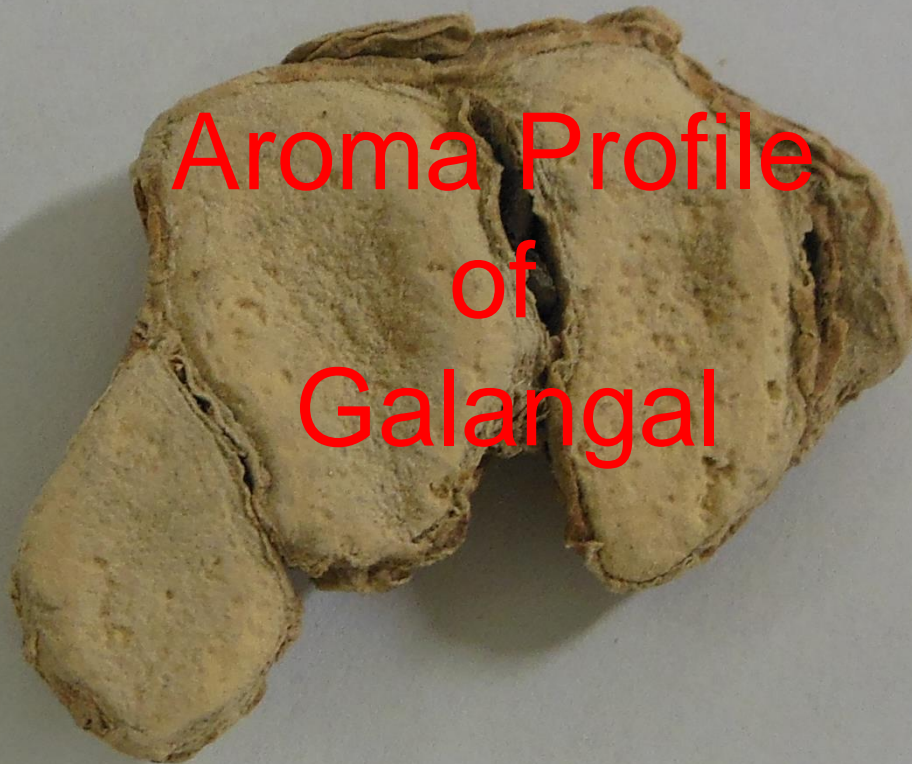
香気プロフィール解析

Structure-Odor
Relationship

構造と香りの関係

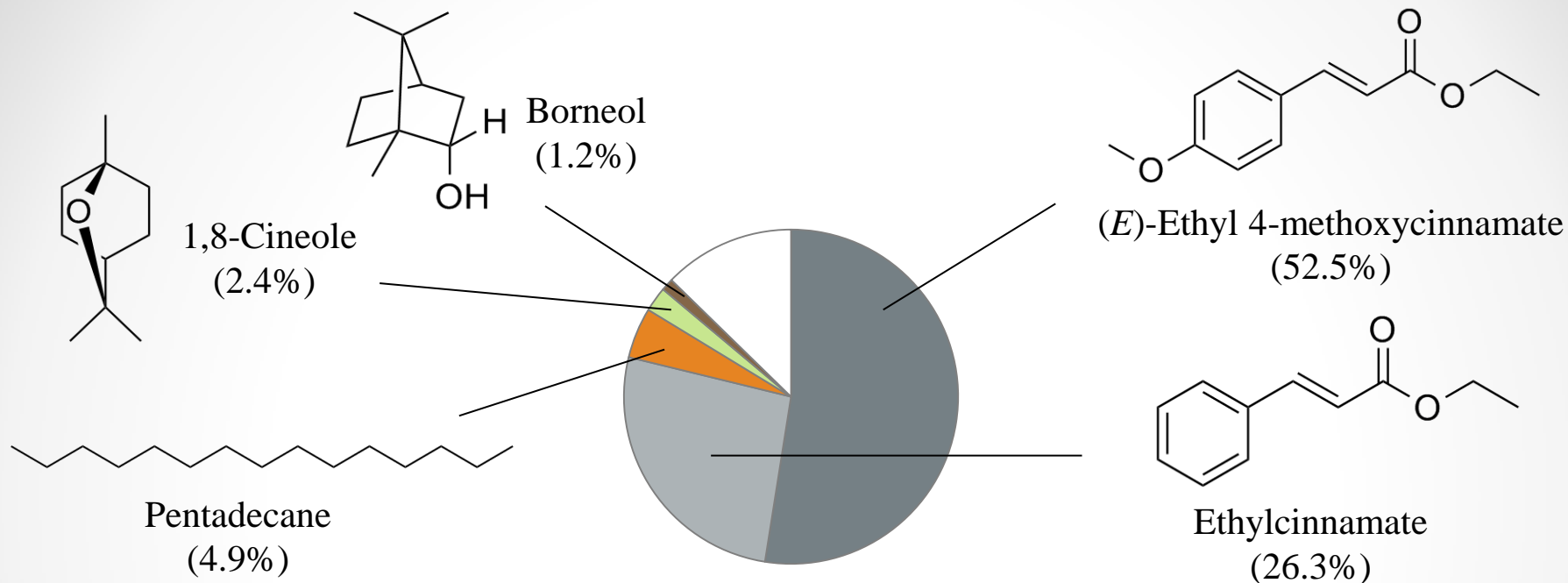
題 目

1. におい受容機構を考慮した複合臭の取り扱いとは？
2. 白檀などの香気素材の香気特性をどう扱うか？
3. 実際のGCデータをどのように解釈したらいいのか？



Aroma Profile
of
Galangal

Studies of the Components and Aroma of Galangal



“The cinnamate derivatives are responsible for the aromatic-spicy odor impression, whereas especially the monoterpenes, like 1,8-cineole, borneol, δ -3-carene, carvone and carvone oxide generally possess pleasant-fresh odor notes.”

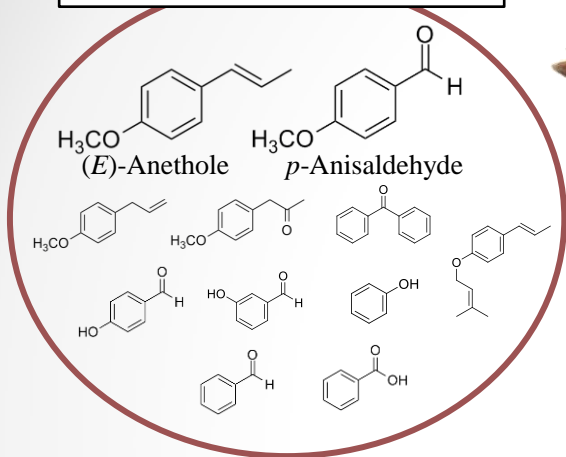
Leopold Jirovetz *et al.* *Acta Pharmaceutica Turcica*, 2001, 43, 107–110.

Galangal contains various aroma components.

However, it is not clear which compounds contribute to its aroma.

Aroma Profile of Star Anise

Aroma profile of star anise



The ratio of the two main components

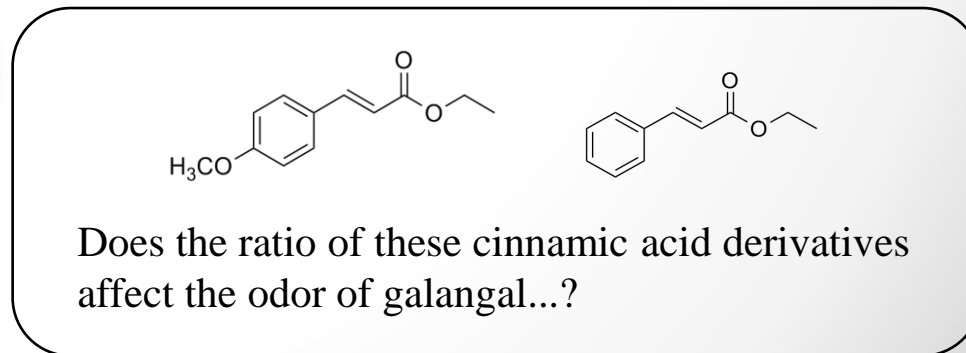
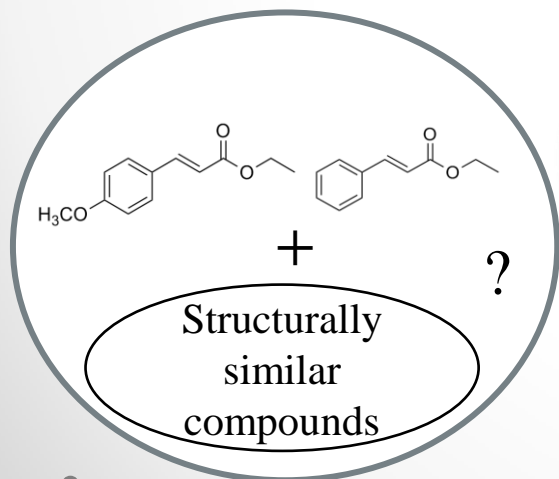
	<chem>CC=CC1=CC=C(OC)C=C1</chem> <chem>O=Cc1ccc(OC)cc1</chem> (<i>E</i>)-Anethole: <i>p</i> -anisaldehyde ^{a)}	Odor similarity to the material
MMSE *	21 : 1	high
Hexane extract	11 : 1	
Steam distillate	6 : 1	

*Monolithic Material Sorptive Extraction

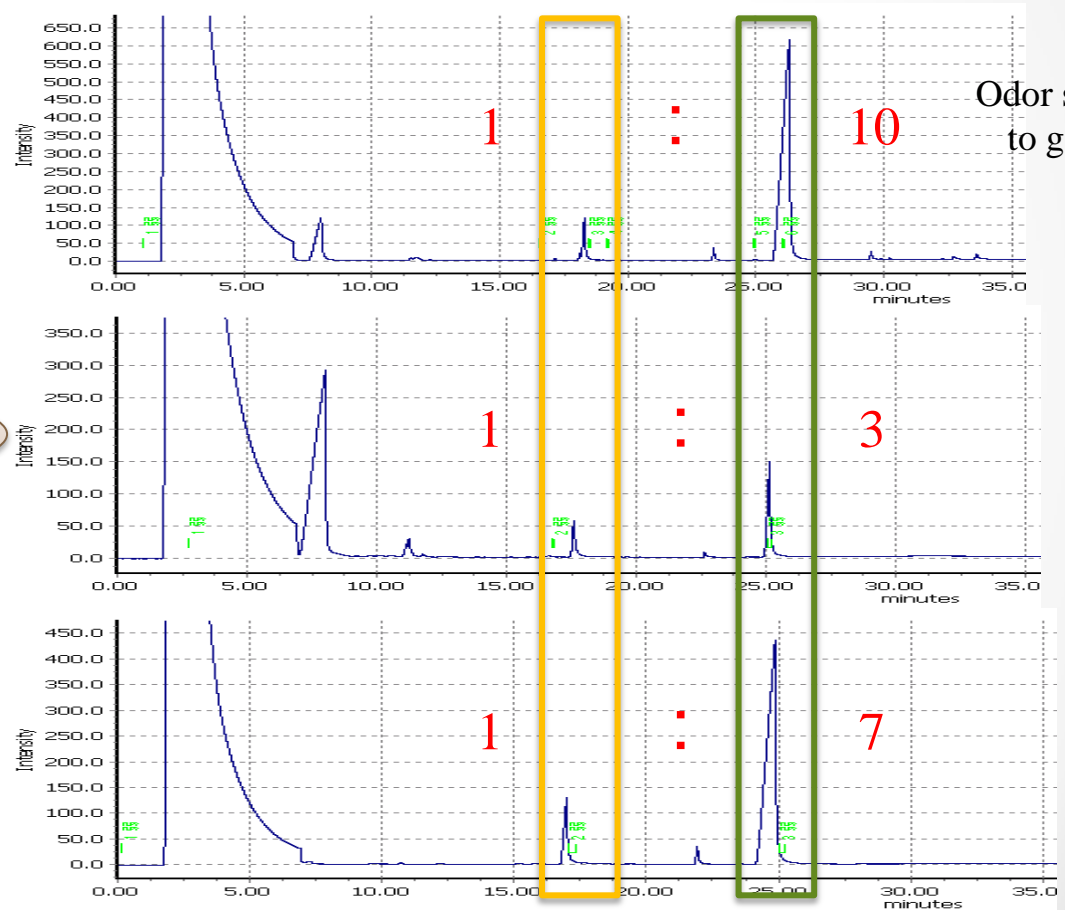
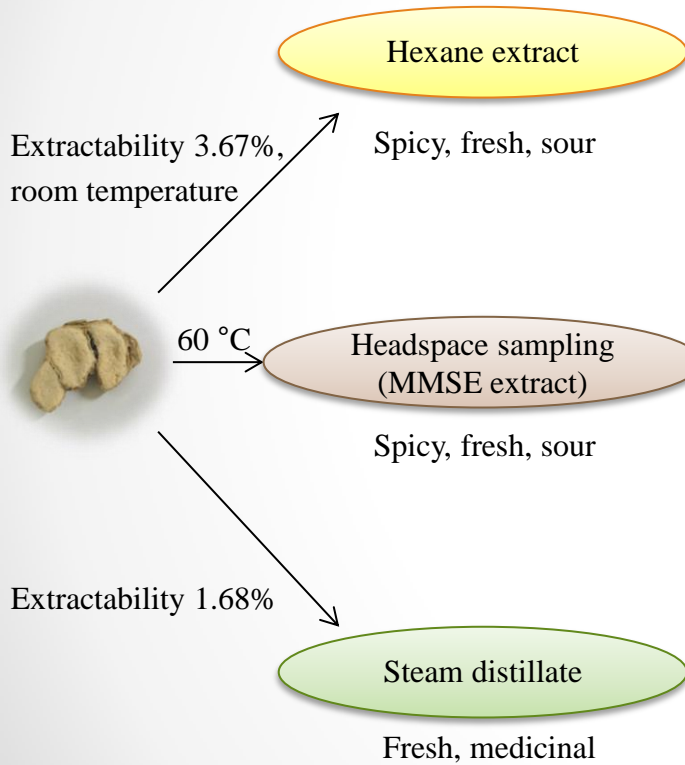
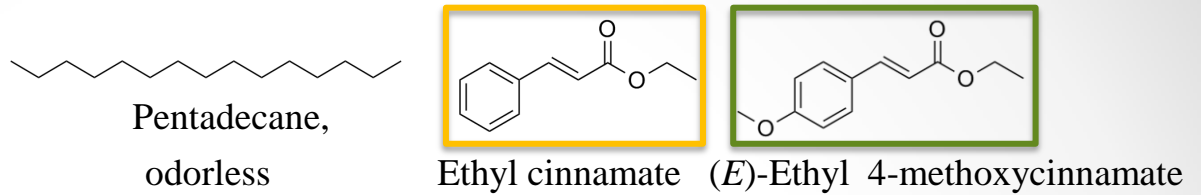
^{a)} Calculated by ¹H NMR

The ratio of (*E*)-anethole to *p*-anisaldehyde was associated with the level of odor similarity to star anise.

Hasegawa, T. ; Seimiya, H. ; Fujihara, T. ; Fujiwara, N. ; Yamada, H. *Natural Product Communications*, **2014**, 9, 251–256.



Investigation of Galangal Odor by Approach I



Odor similarity to galangal

High

Low

The aroma didn't depend on the ratio of the cinnamic acid derivatives.

Searching for Key Odor Compounds by Approach II

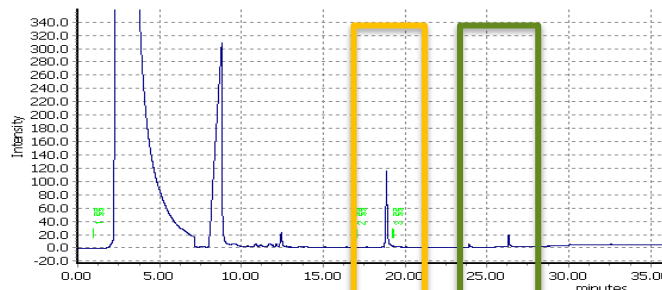
Hexane extract

Low bp

Fraction 1

20–62 °C
0.20–0.60 Torr

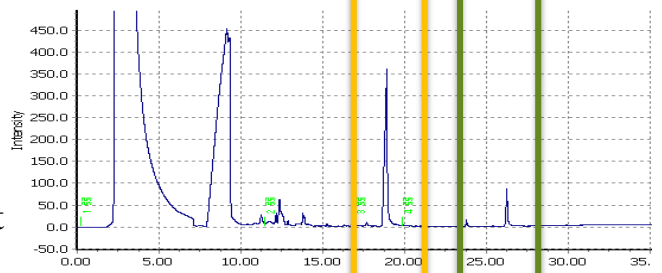
Spicy, sour



Fraction 2

62–84 °C
0.20–0.80 Torr

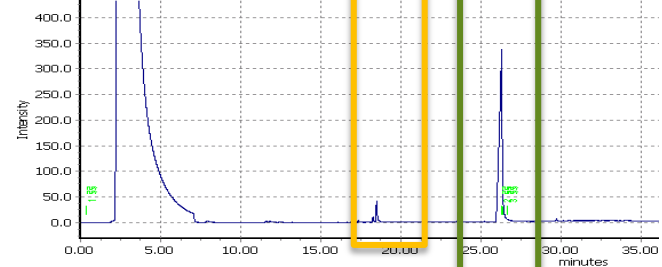
Spicy, sour, sweet



Fraction 3

84–175 °C
0.20–0.70 Torr

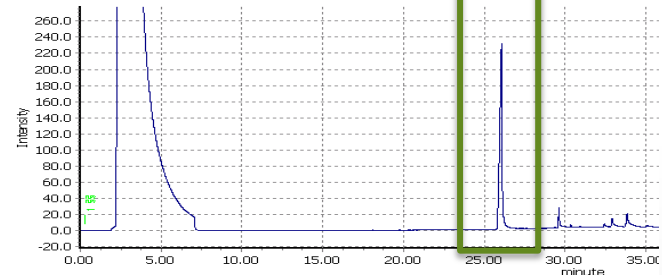
Sour, medicinal



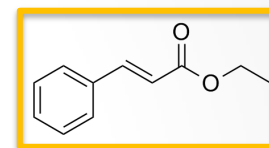
High bp

Residue

Slightly sour

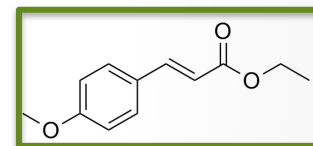


Galangal-like odor



12%*

Ethylcinnamate



77%*

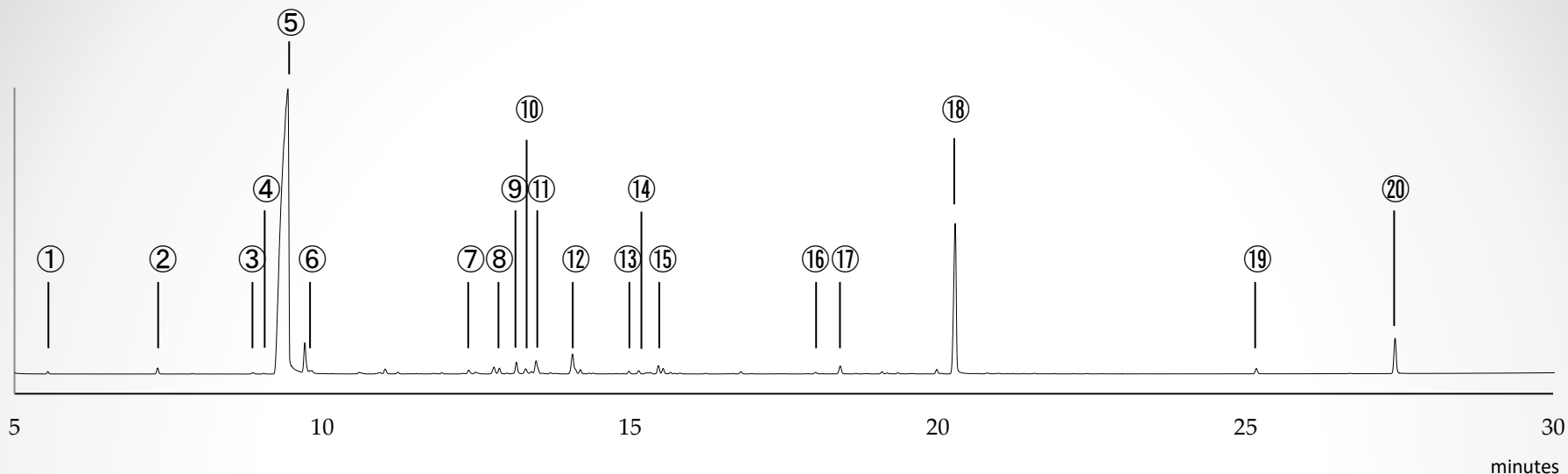
Ethyl 4-methoxycinnamate

* Percentage in the hexane extract

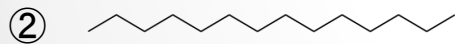
Ethyl cinnamate made a larger contribution to the aroma of galangal than (*E*)-ethyl 4-methoxycinnamate.

Bulb-to-bulb distillation

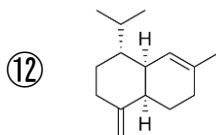
GC-MS Analysis of the Components in Fraction 2



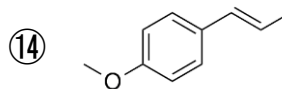
- | | | | | |
|----------------------|-----------------------|------------------------|--------------------------------|---|
| ① Tridecane | ⑤ Pentadecane | ⑨ Heptadecane | ⑬ 2-Tridecanone | ⑰ Anisaldehyde |
| ② Tetradecane | ⑥ α -Gurjunene | ⑩ α -Selinene | ⑭ Anethole | ⑱ (<i>Z</i>)-Ethyl 4-methoxycinnamate |
| ③ α -Ylangene | ⑦ Humulene | ⑪ 8-Heptadecene | ⑮ <i>p</i> -Cymen-8-ol | ⑳ (<i>E</i>)-Ethyl 4-methoxycinnamate |
| ④ α -Copaene | ⑧ endo-Borneol | ⑫ γ -Muuroleone | ⑯ (<i>Z</i>)-Ethyl cinnamate | |



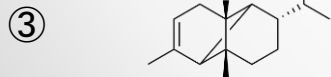
Linear chain compounds



Cyclic terpenes



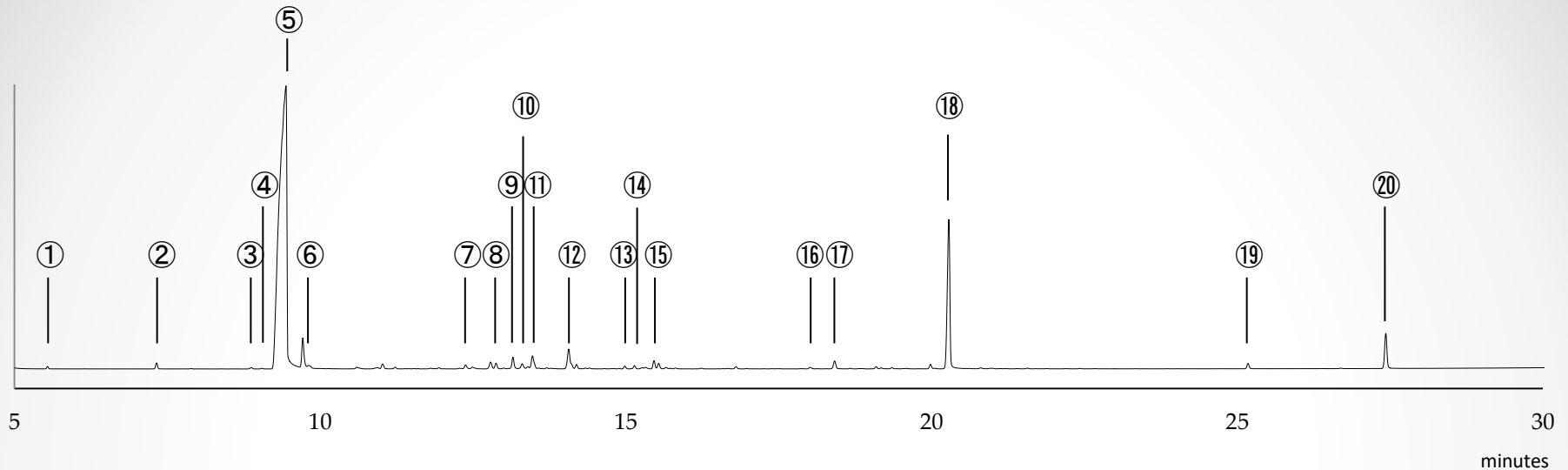
Aromatic compounds



Cyclic terpenes

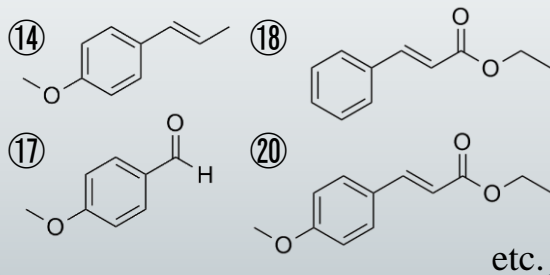
etc.

含有成分の構造類似性を考慮したGC-MSデータ解析

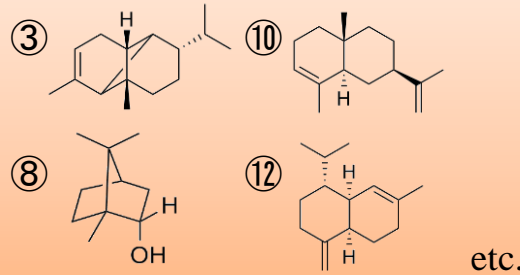


- | | | | | |
|----------------------|-----------------------|-----------------------|--------------------------------|---|
| ① Tridecane | ⑤ Pentadecane | ⑨ Heptadecane | ⑬ 2-Tridecanone | ⑰ Anisaldehyde |
| ② Tetradecane | ⑥ α -Gurjunene | ⑩ α -Selinene | ⑭ Anethole | ⑱ (<i>E</i>)-Ethyl cinnamate |
| ③ α -Ylangene | ⑦ Humulene | ⑪ 8-Heptadecene | ⑮ <i>p</i> -Cymen-8-ol | ⑲ (<i>Z</i>)-Ethyl 4-methoxycinnamate |
| ④ α -Copaene | ⑧ endo-Borneol | ⑫ γ -Muurolene | ⑯ (<i>Z</i>)-Ethyl cinnamate | ⑳ (<i>E</i>)-Ethyl 4-methoxycinnamate |

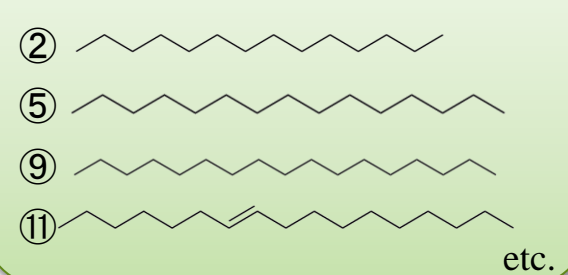
Aromatic compounds



Cyclic terpenes



Linear chain compounds



These compounds were classified as aromatic compounds, cyclic terpenes, and linear chain compounds, according to their characteristic structures.