อัพเดทการปนเปื้อนอาหารและการตรวจวิเคราะห์

Update food contamination and its detection

Food Science & Technology
AGRO-INDUSTRY
Kasetsart University

by **กฤษกมล ณ จอม**

ภาควิชาวิทยาศาสตร์และเทคโนโลยีการอาหาร
คณะอุตสาหกรรมเกษตร มหาวิทยาลัยเกษตรศาสตร์

หลักสูตรเทคโนโลยีเครื่องดื่มและการจัดการ คณะอุตสาหกรรมเกษตร
มหาวิทยาลัยเกษตรศาสตร์

Food contamination

1. Hydrogenated oils + Trans fat. You know how the FDA is banning trans fats? That's because foods with hydrogenated or partially hydrogenated oils contain trans fat, which are known to cause cancer, heart disease, and other health problems.

2. Nitrites + Nitrosamine. Sodium nitrite, which is in most hot dogs, lunch meat, and other processed meats, is a cancer-causing ingredient that the USDA has been trying to ban since the 1970s. Hence why I don't get the 'new' report. Like, we've known processed meats are bad for almost half a century.

3. Grilled or charcoaled foods. Those char marks on your grilled burger? They are a carcinogen, called **Heterocyclic amines (HCAs) + PAHs.**

4. French fries or potato chips. Acrylamide via Maillard reaction. Glycoalkaloid contamination.

5. Fermented foods. Allergy + Biogenic amines

6. Vegetable and fruit. Pesticides or Herbicides

7. Seafood. Formaline or natural toxin (ç è fl ç ff ç ffi) or heavy metals

8. Nuts. Mycotoxin (Aflatoxin) + **Allergy**

9. Soysauce/ Palm oil. 3-MCPD (3-monochloropropane-1,2diol)

10. Dried food. Food additives, Mycotoxin or Arsenic

11. Rice. Methylbromide or Arsenic or Pesticides

Heterocyclic β-carboline
Lysinoalanine
Surfactant
THC

Contamination during high temperature of heat processing

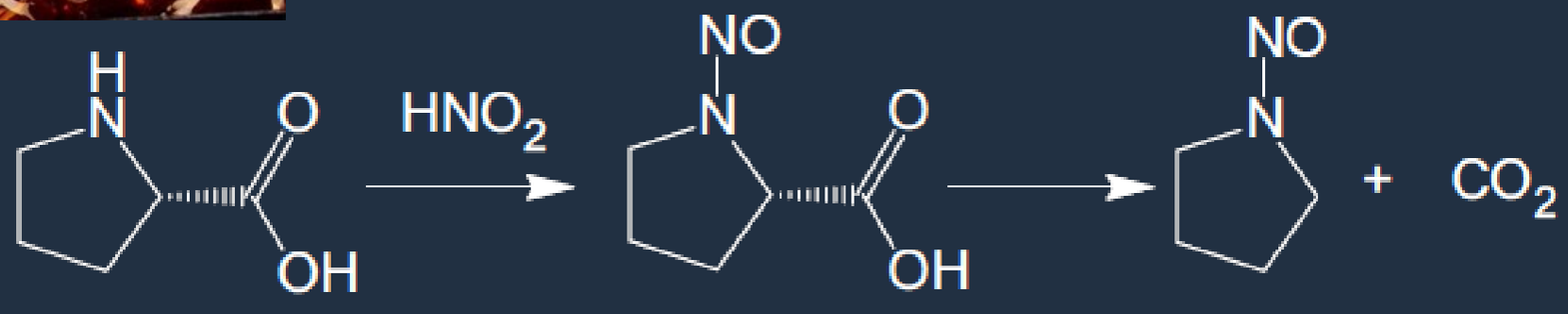
Nitrosamine

$$NO_2 + H^+ \rightleftharpoons HONO \rightleftharpoons NO^+ + H_2O$$

$$\updownarrow R_2NH$$

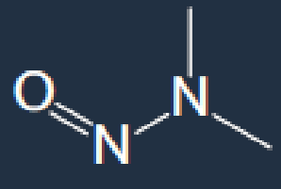
$$H^+ + R_2NNO$$

N-Nitrosamine formation

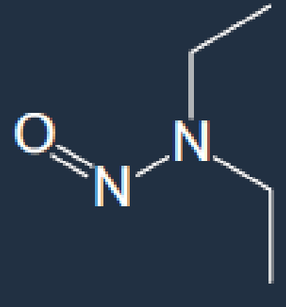


Proline

Nitrosopyrrolidine



Dimethylnitrosamine

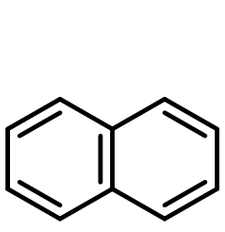


Diethylnitrosamine

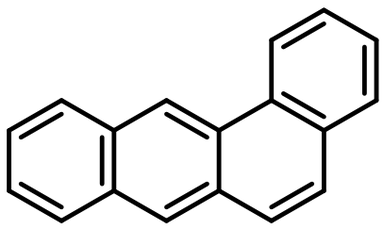
Polycyclic aromatic hydrocarbons (PAHs)

- One of several classes of **carcinogenic chemicals**
- Two or more condensed aromatic carbon rings
- Formed during the **incomplete combustion** of organic material

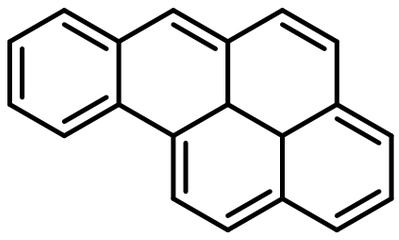
Chemical Structures of PAHs



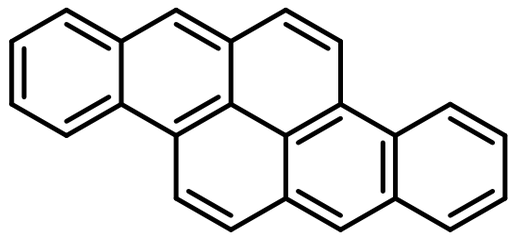
Nap



B*a*A



B*a*P



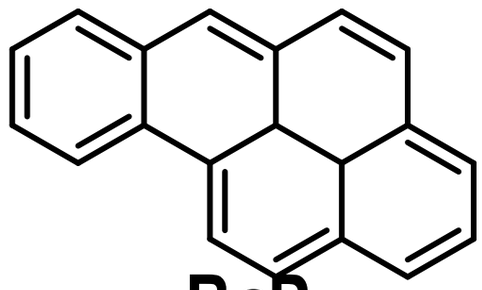
DB*ah*P

Contamination during high temperature of heat processing

European Commission Regulation 835/2011
European Food Safety Authority (EFSA)

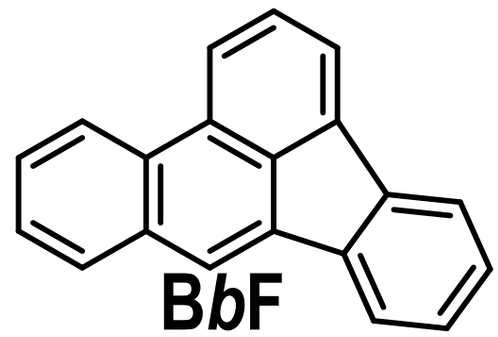
2 µg/kg

Benzo[a]pyrene



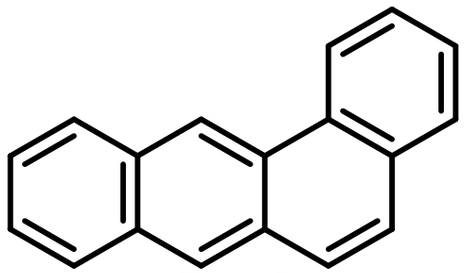
B*a*P

benzo[b]fluoranthene



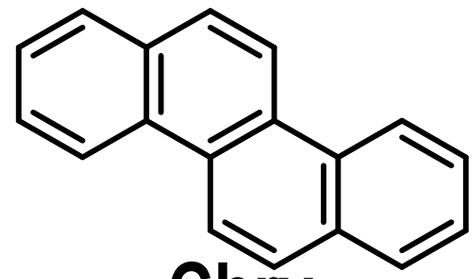
B*b*F

10 mg/kg



B*a*A

benzo[a]anthracene

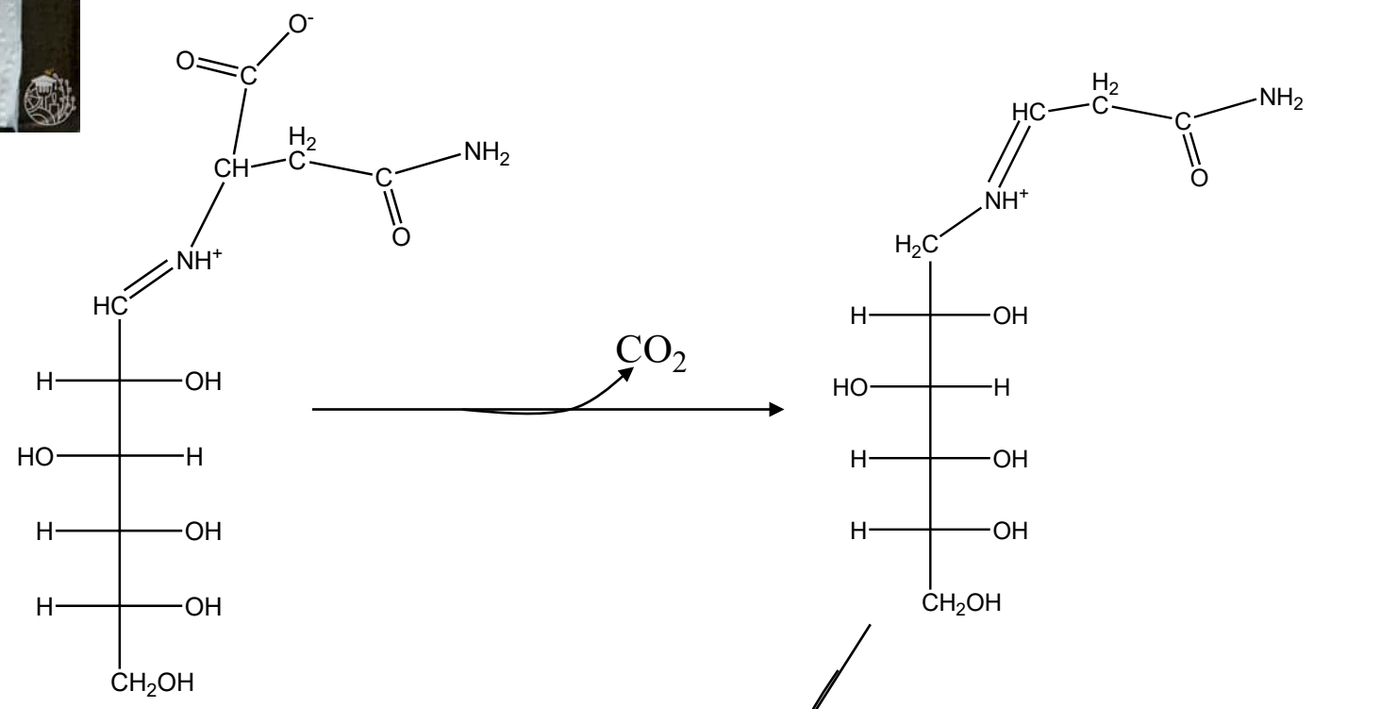


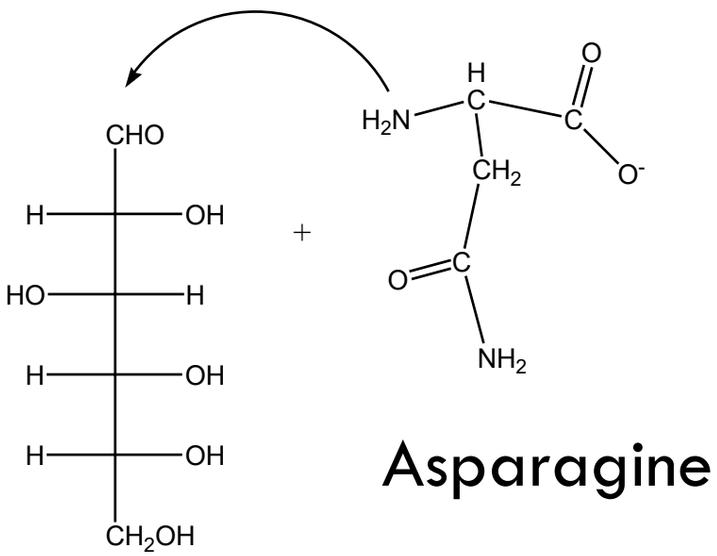
Chry

Chrysene

Dibenzo(ah)anthracene

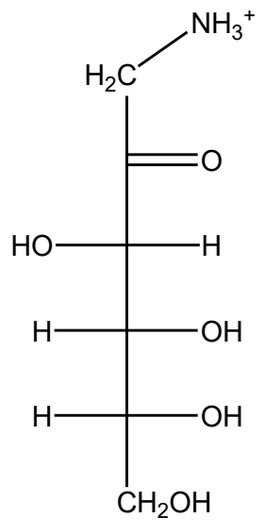
Acrylamide



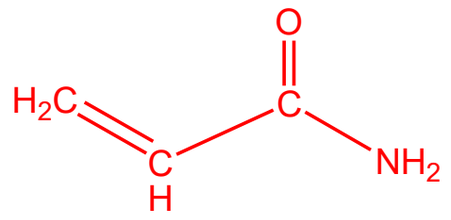


Asparagine

Glucose

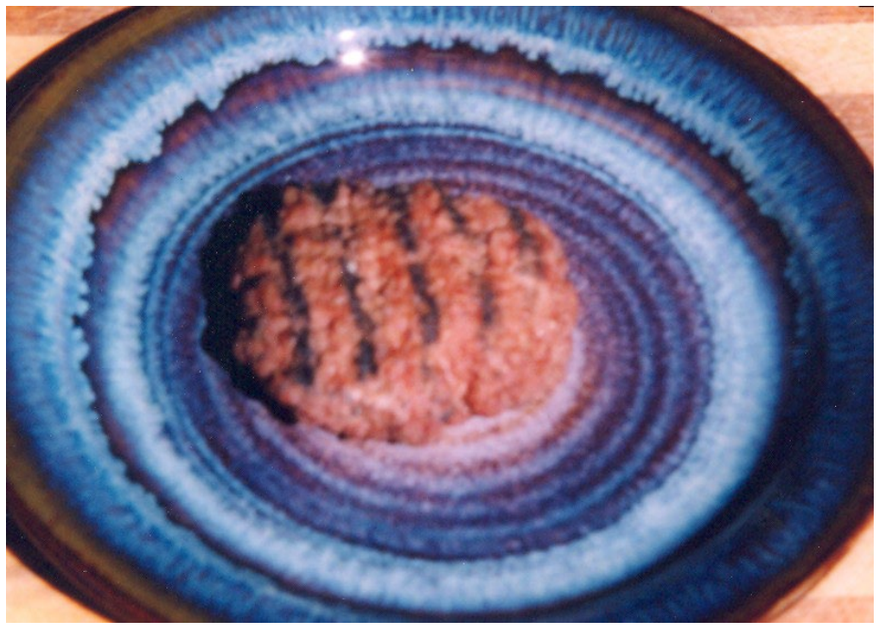


Fructosamine



Acrylamide

Colors



Aromas

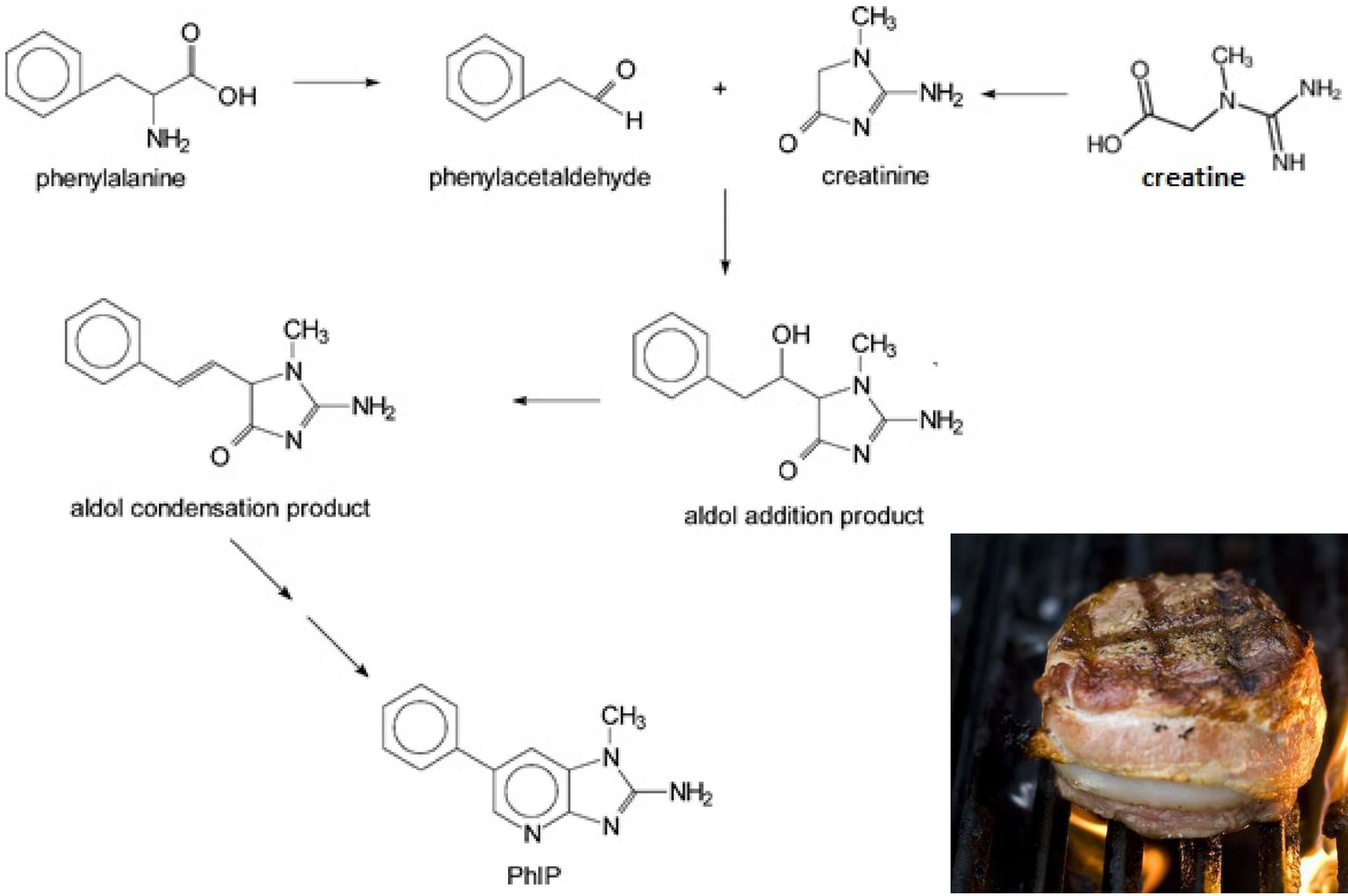
Maillard Reaction

Flavors

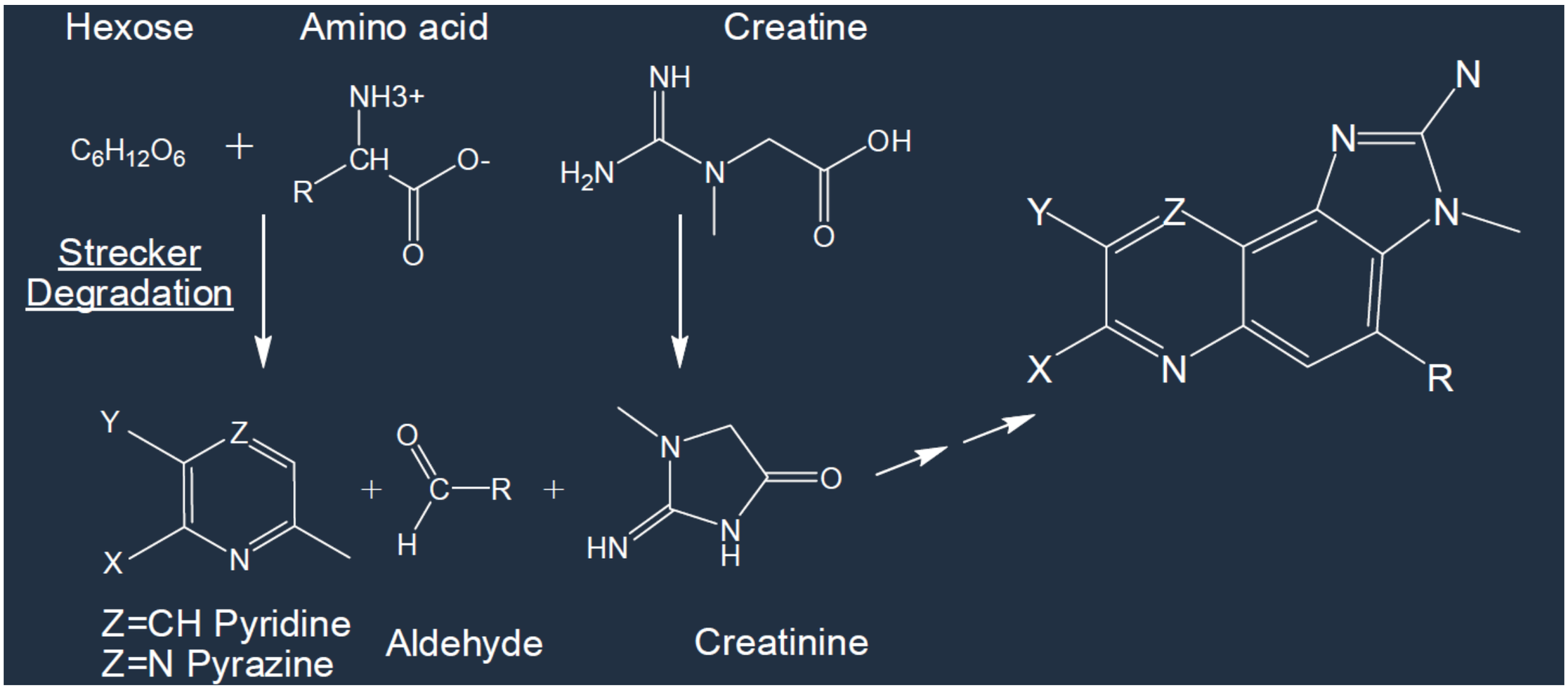
Amino Acid Pyrolysates

- Heterocyclic aromatic amines (HCAs) formed during broiling of meat, fish, or other high protein-rich foods.
- Precursor amino acids: Imidazo-quinoline or imidazo-quinoxalin-2-amine derivatives (IQ compounds) formed from the reaction of Maillard products (pyridines or pyrazines, and aldehydes) with creatinine.
- High temperature thermal degradation products of tryptophan (β-carbolines)
- Lysinoalanine and Lanthionine

Food contamination

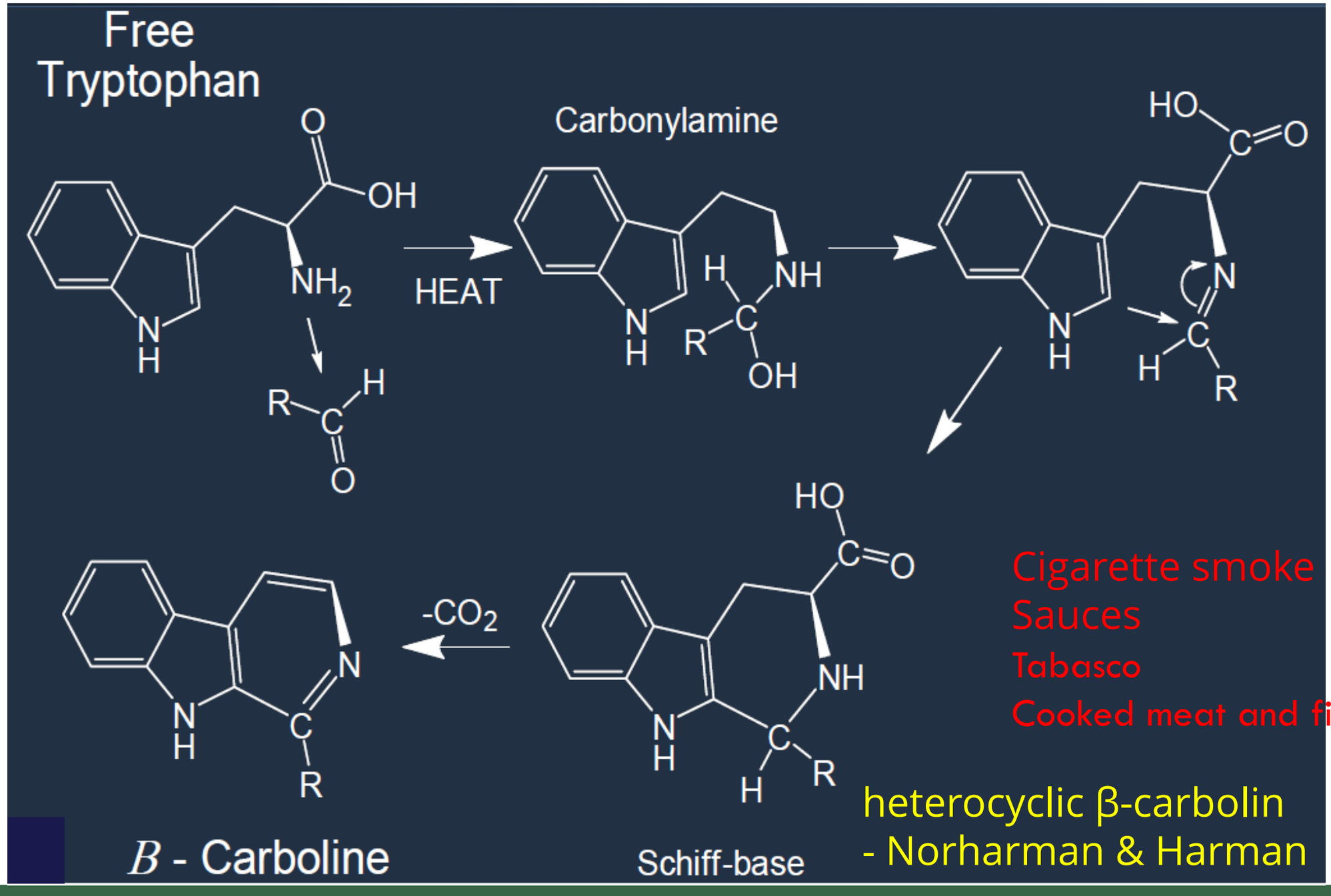


Imidazo-Quinolines & Imidazo-Quinaxolines



Food contamination

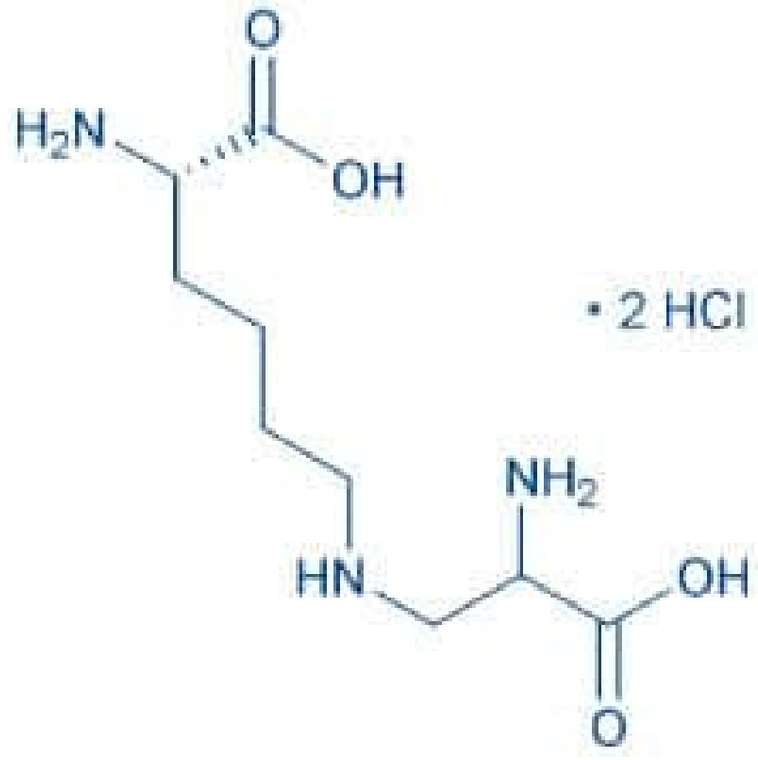
Formation of β-Carbolines



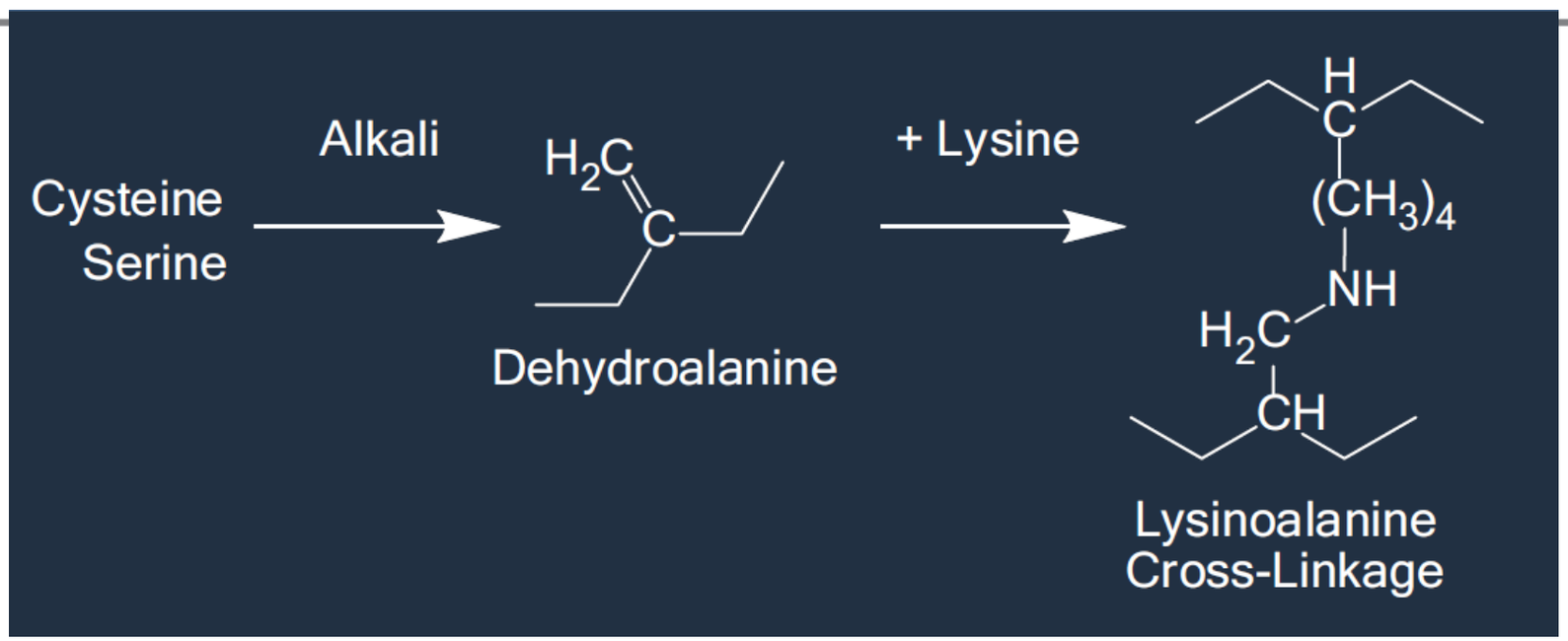
protein concentrates

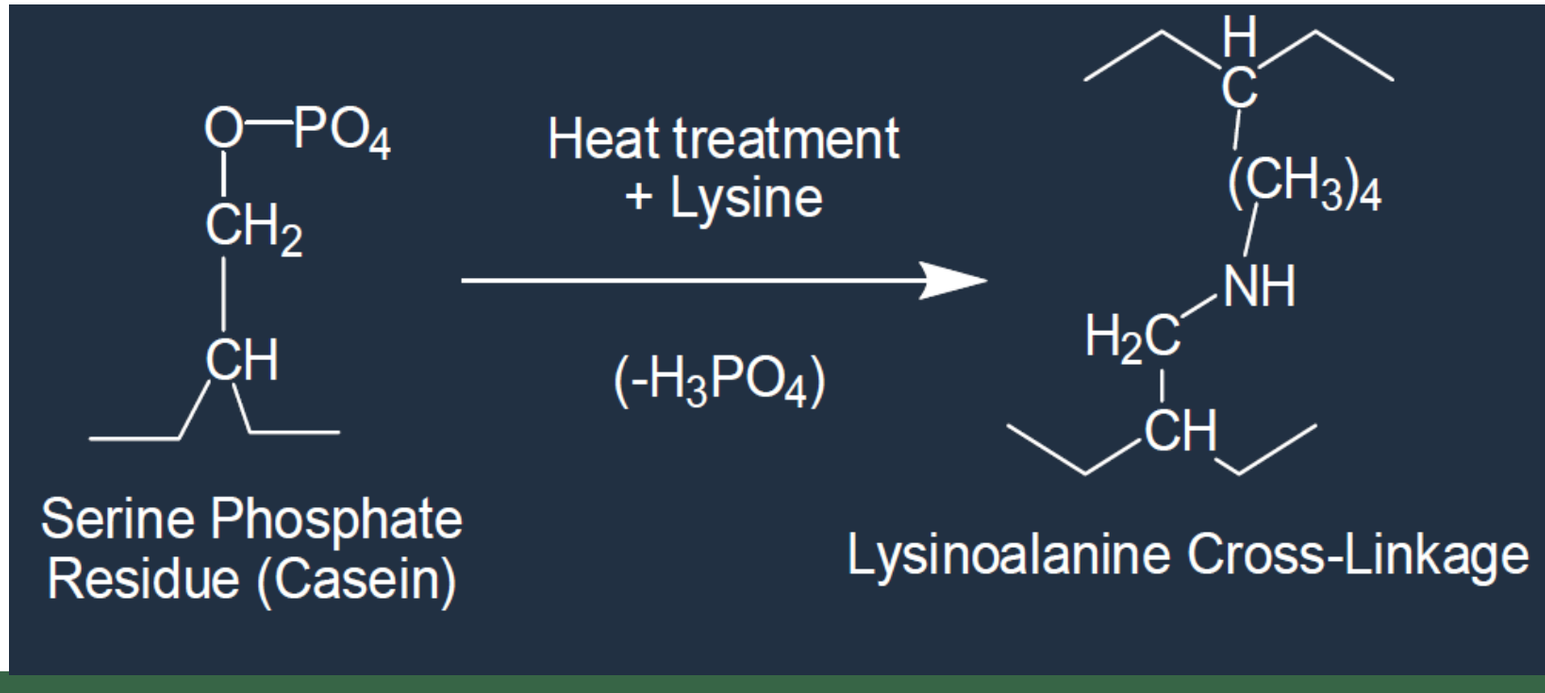
Lysinoalanine in Food

- Cross-linked lysine arising from alkali and heat treatment of proteins.
- Little influence on available lysine.
- Reduced protein digestibility.
- Strong affinity for copper and other metal ions (enzyme inactivation).
- Main concern is toxicological.
- Renal cytomegaly in rats.



Food contamination





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สารลดแรงตึงผิวตกค้างบนผักผลไม้

Method validation

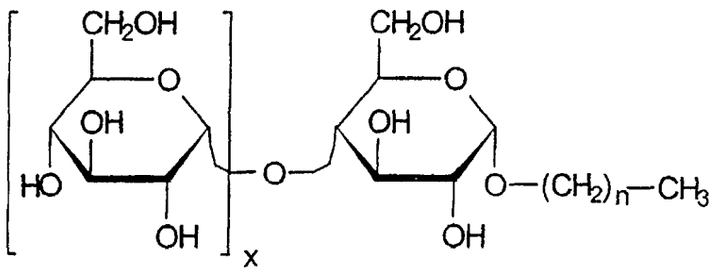
Alkyl poly glycoside

LOD = 450 mg/kg

LOD = 1000 mg/kg

Recovery = 82 – 103%

SD = 7-10%



CAS No 68515-73-1
MW 320.42

Sodium dodecyl sulfate (SDS)

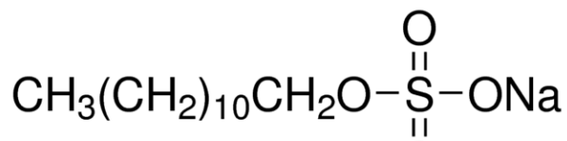
(Sodium lauryl sulfate)

LOD = 500 mg/kg

LOQ = 1500 mg/kg

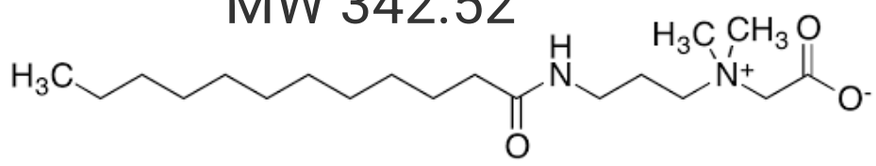
Recovery = 78 – 85%

SD = 10-15%



CAS No 151-21-3 MW 288.38

CAS No 86438-79-1
MW 342.52



Cocamido propyl betaine

LOD = 200 mg/kg

LOQ = 600 mg/kg

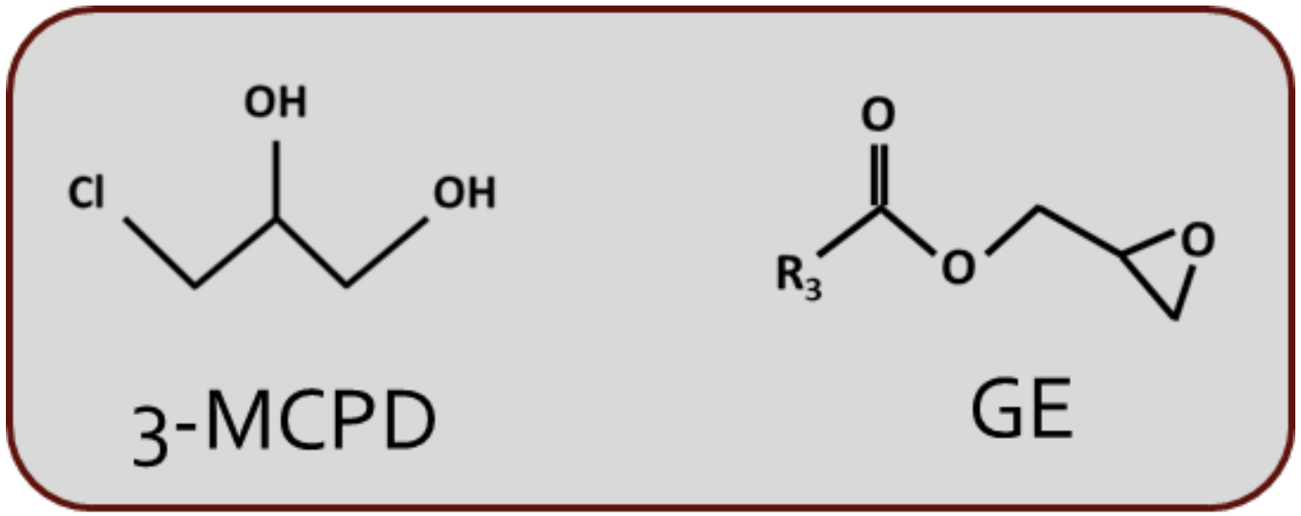
Recovery = 74 – 91%

SD = 7-12%

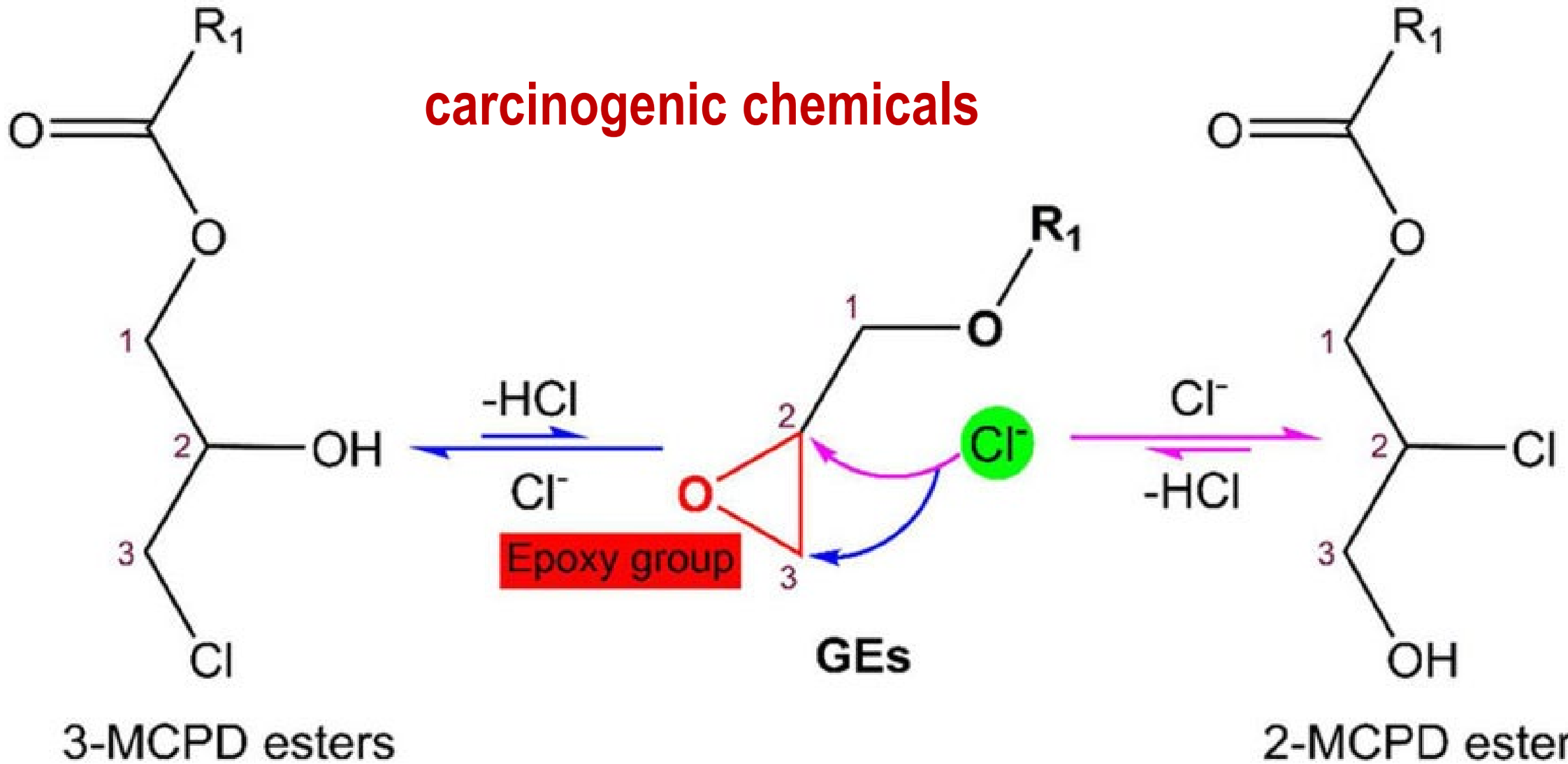
Allergy
Processing

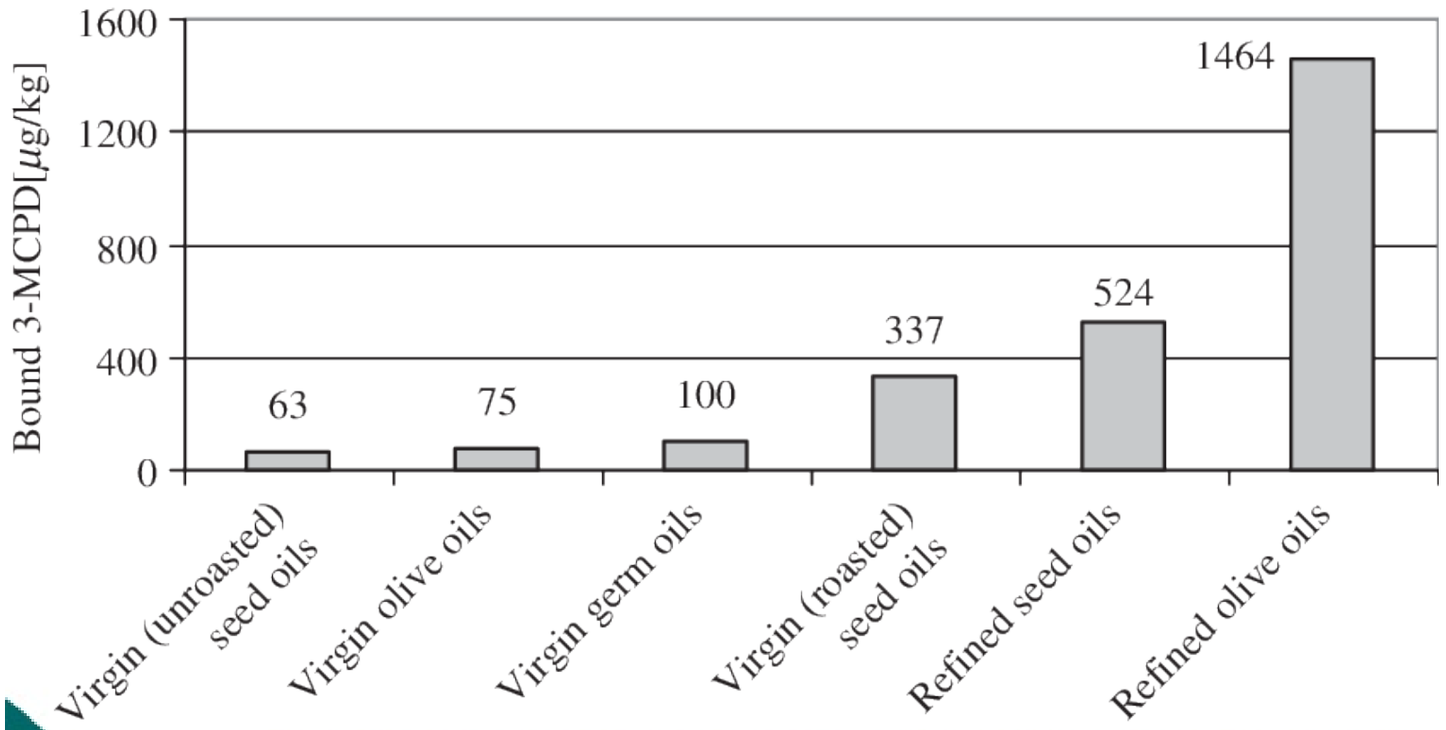
- Allergenic protein content depends on processing and varies by brand
  - Higher allergenic protein content:
    - More mature, larger kernels
    - Drying or curing at higher temperatures
    - Roasting
    - Whipped or emulsified peanut butter
  - Less allergenic protein content:
    - Small kernels
    - Raw peanuts

- Biogenic amines in fishery raw materials and products, fermented food: Inefficient heat treatment/ without optimized storage condition



carcinogenic chemicals



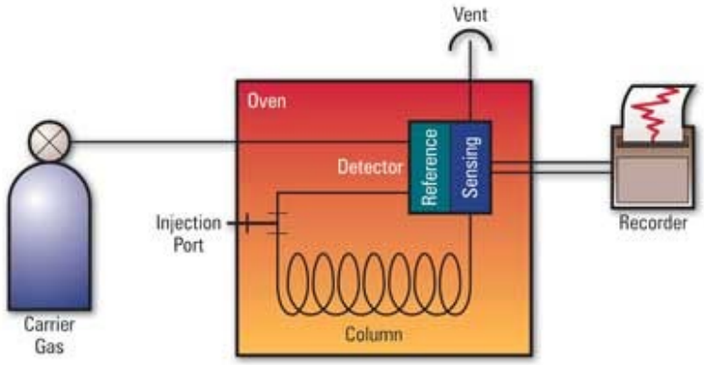


GCMS
FTIR

LCMS
uHPLC
MS

3-MCPD fatty acid esters levels in different vegetable oils

Oils	Number of Samples	3-MCPD fatty acid esters level (μg/kg), expressed as 3-MCPD	
		Mean	Minimum – Maximum
Peanut oil	3	570	500 - 650
Canola oil	3	110	100 - 130
Corn oil	3	280	120 - 470
Olive oil	3	390	250 - 640
Grape seed oil	3	1180	390 - 2500
Extra virgin olive oil	1	10	ND

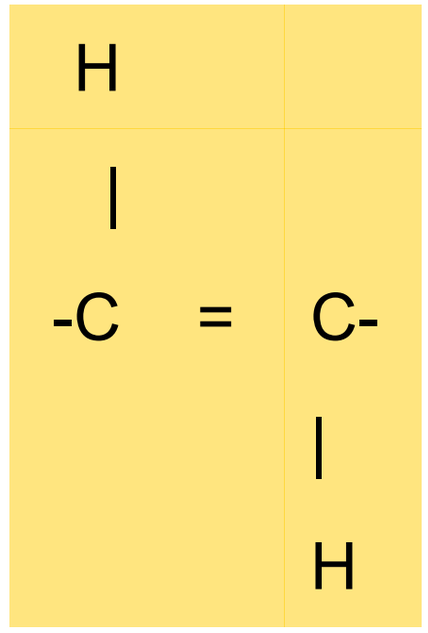


- Local levels ranged 100 - 2500 μg/kg (except extra virgin olive oil)
- Reported levels in other countries <200 – 21500 μg/kg

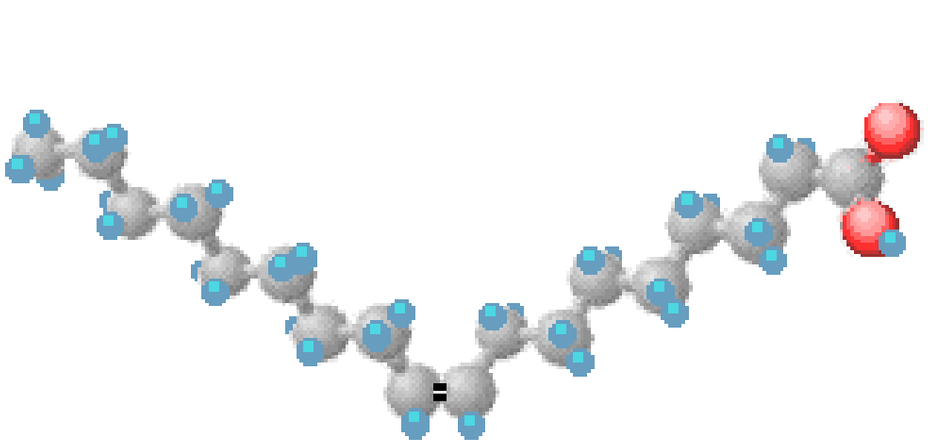
Contamination by process: Trans fat

Hydrogenation

Hydrogen + Vegetable Oil = Hydrogenated Vegetable Oil

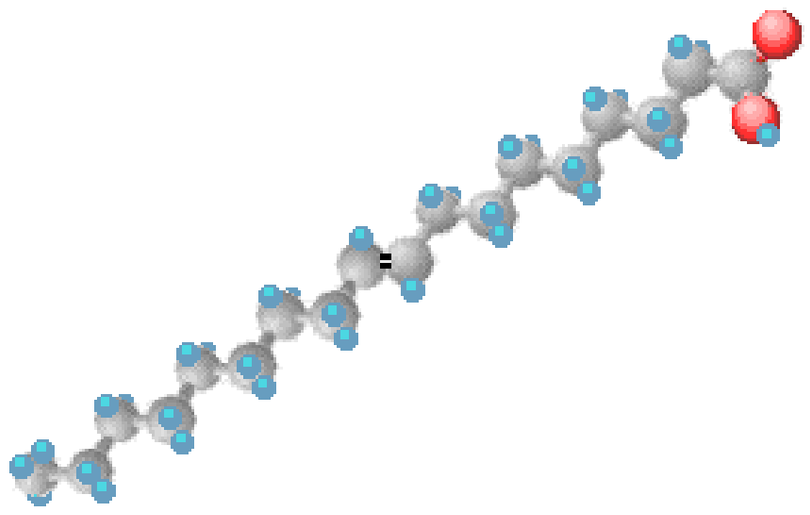


Partially hydrogenated oils contain trans fat



Cis

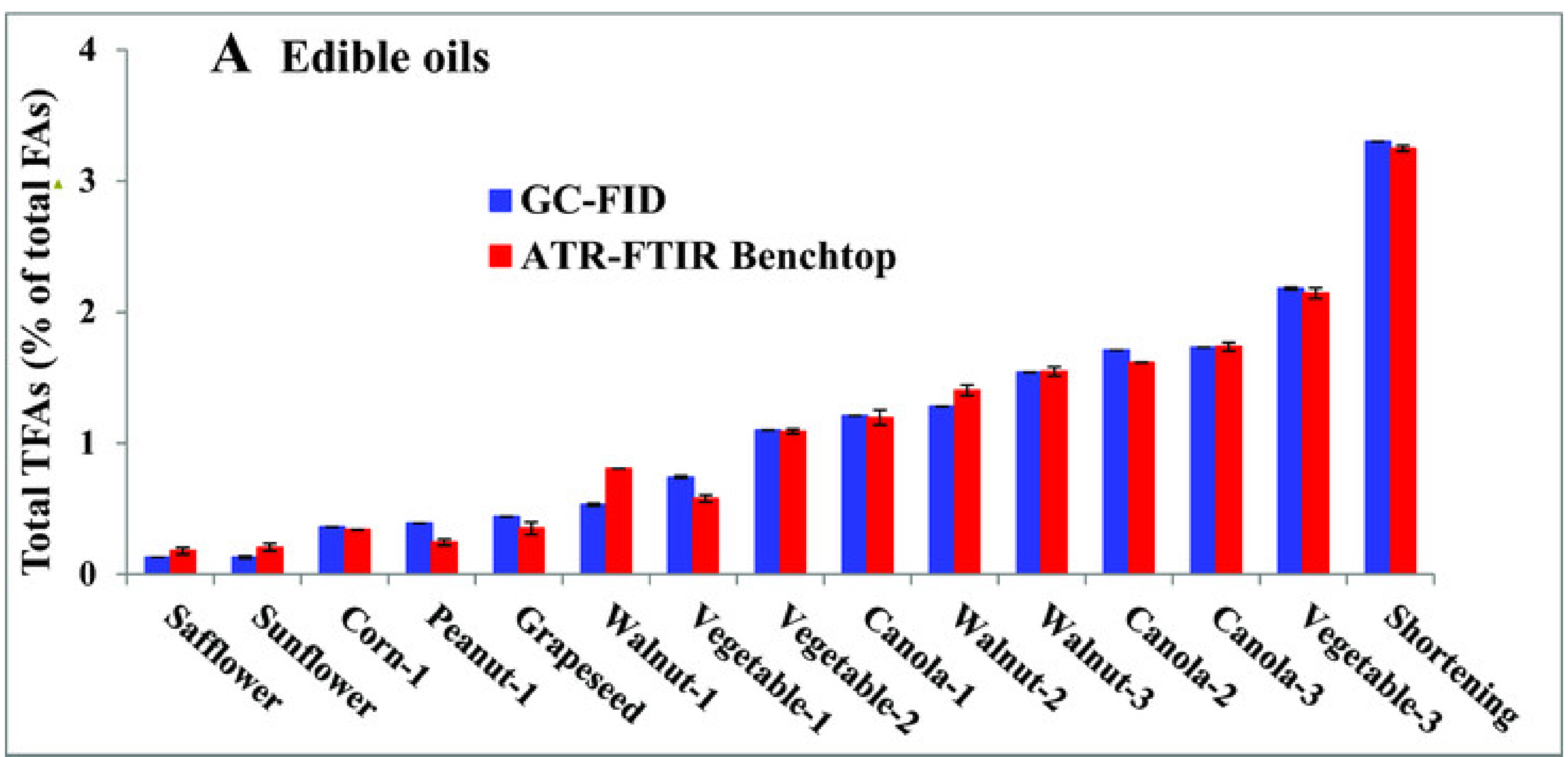
VS.



Trans

H		
|		
-C	=	C-
		|
		H

Contamination by process: Trans fat



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THC

[illegible] 5

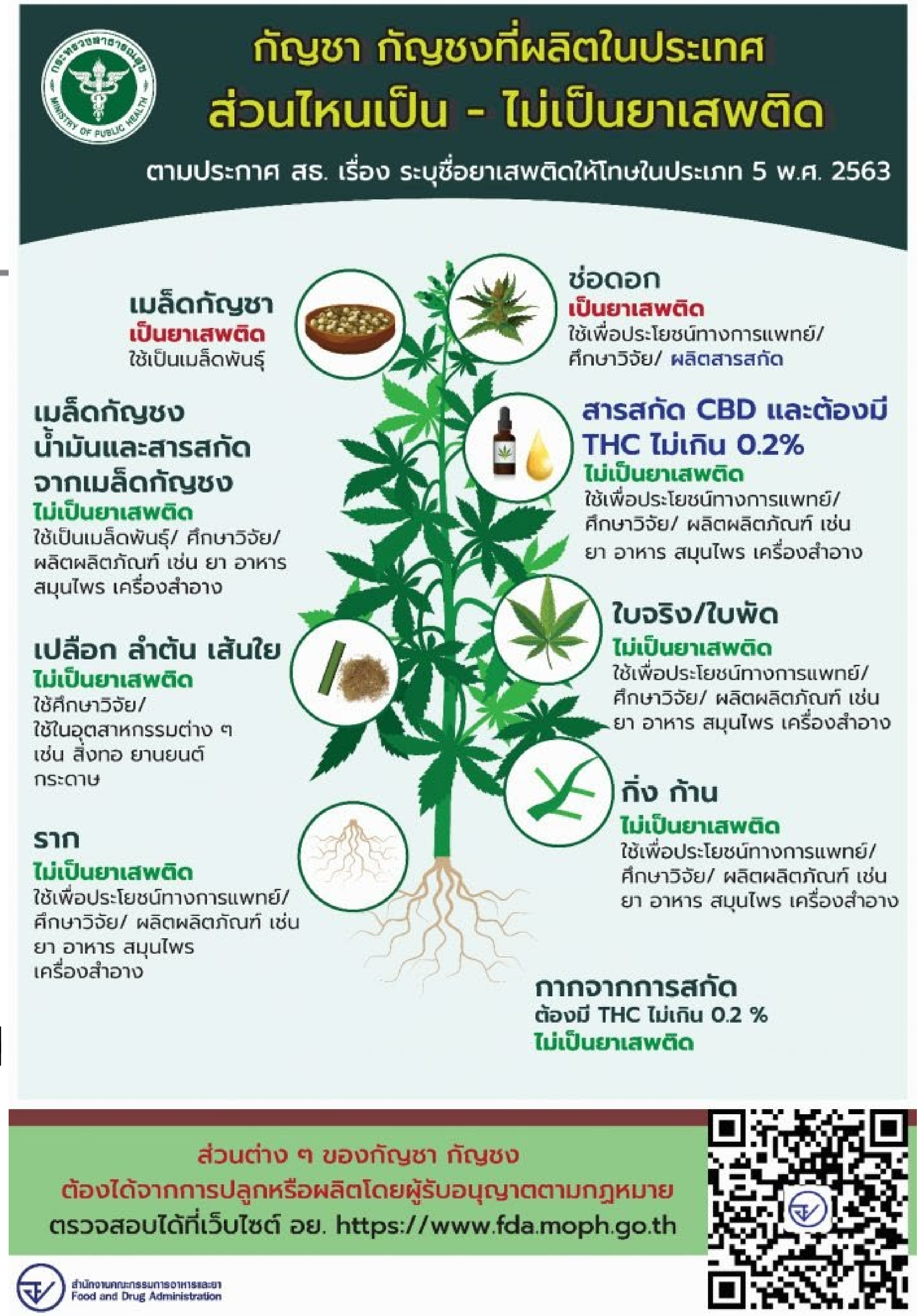
- [illegible]
- [illegible]
- [illegible] CBD [illegible]

[illegible] THC [illegible] 0.2 [illegible]

- [illegible]

[illegible] 5 [illegible] 2563 [illegible] 15 [illegible] 2563

- [illegible]



ข้อมูลจากวิทยากรพิเศษจาก อย. ของหลักสูตรเครื่องดื่มฯ

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8. Nuts. Mycotoxin (Aflatoxin) + **Allergy**

9. Soysauce/ Palm oil. 3-MCPD (3-monochloropropane-1,2diol)

10. Dried food. Food additives, Mycotoxin or Arsenic

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Heterocyclic β-carboline
Lysinoalanine
Surfactant
THC

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Surfactant

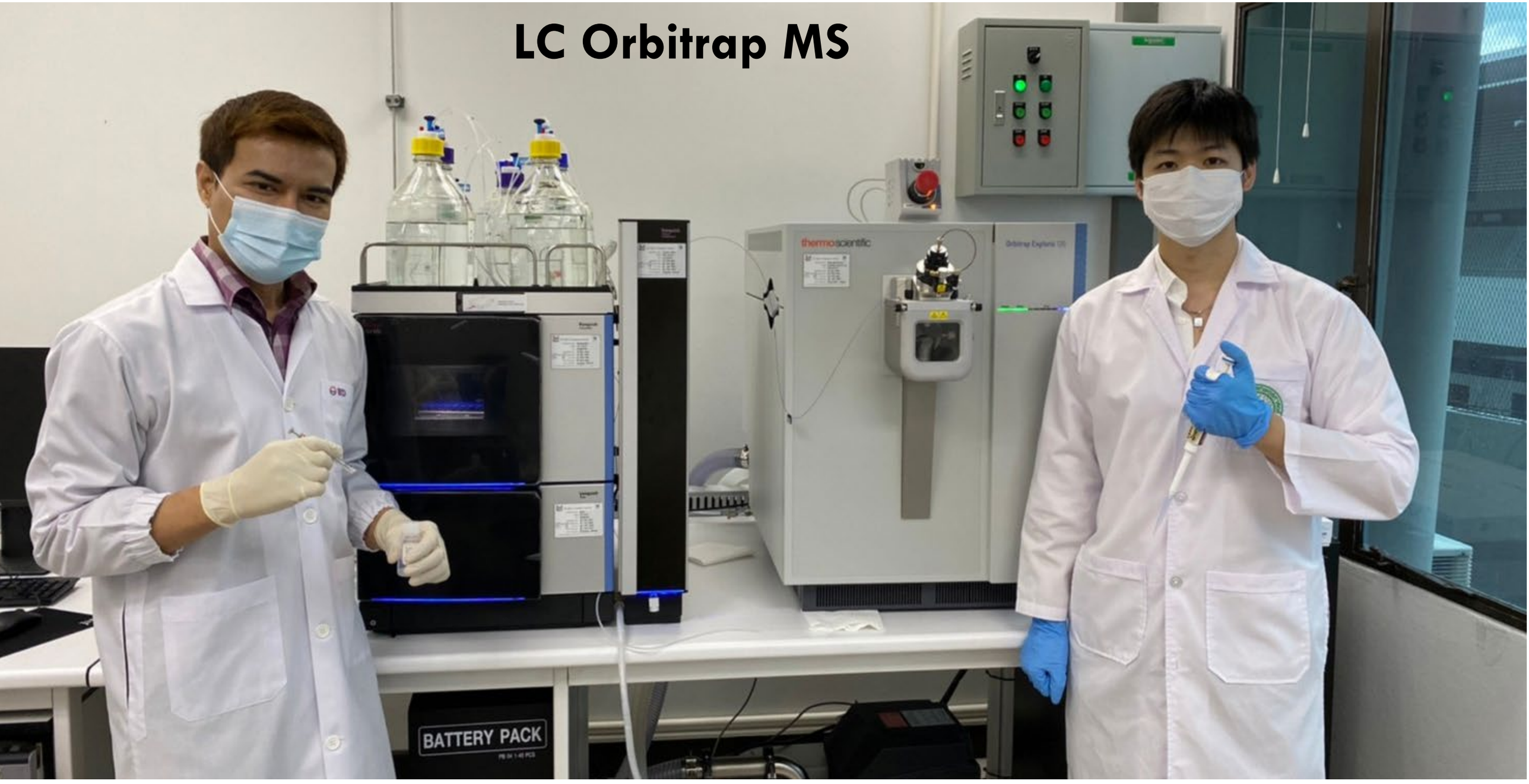
THC

Acrylamide

PAHs

Food contamination

LC Orbitrap MS



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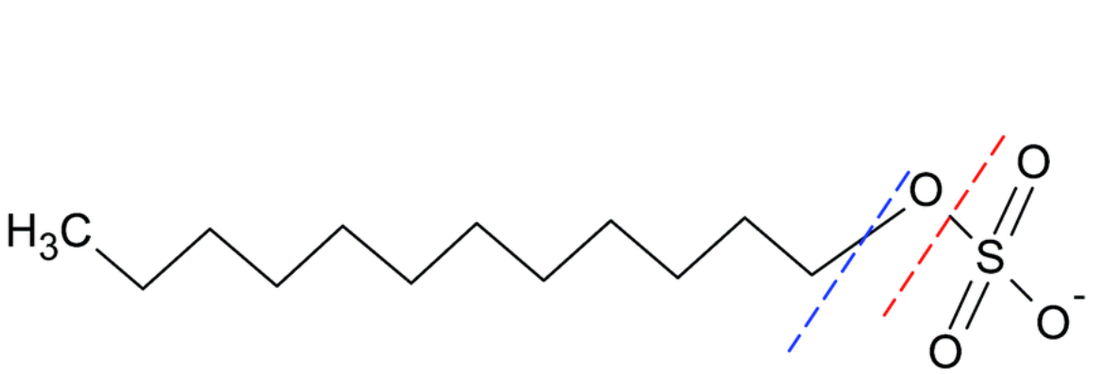
Nitrosamine

3-MCPD

Food contamination

Surfactant

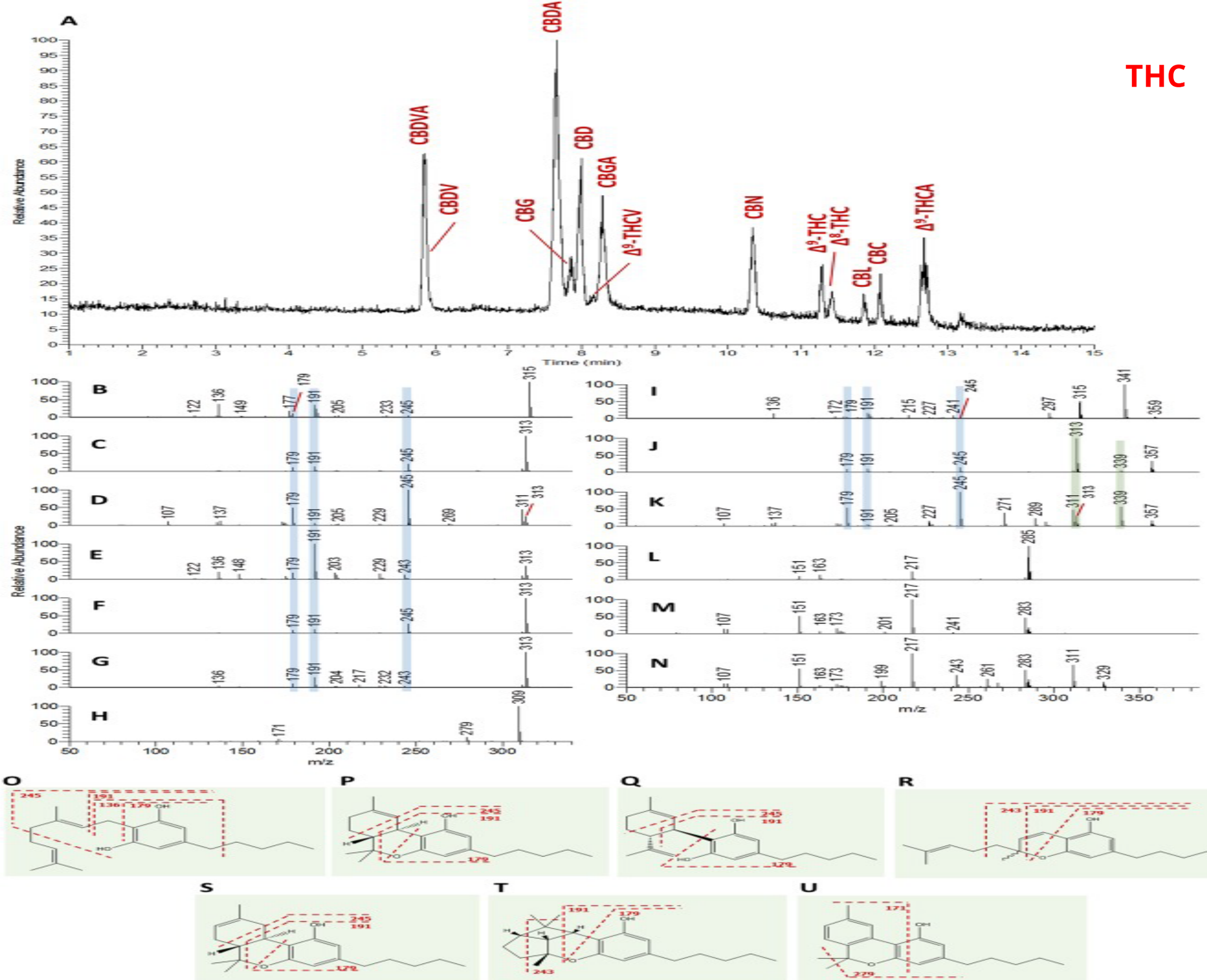


185.3 amu

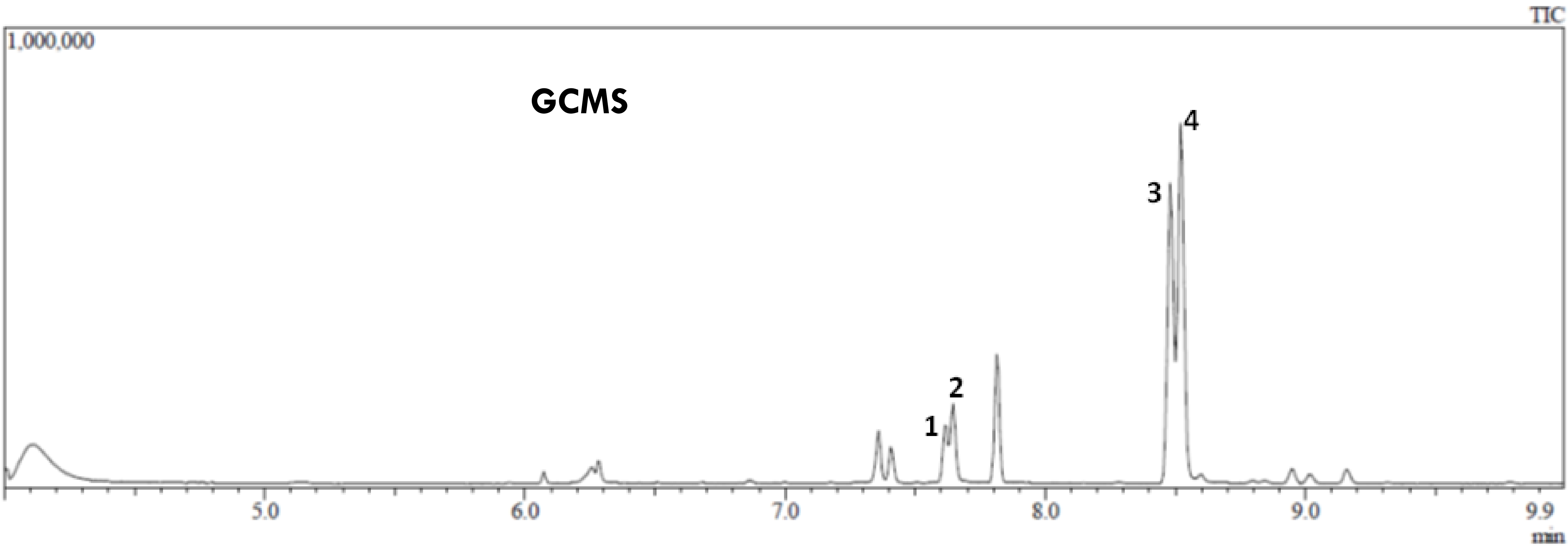
169.3 amu

80.1 amu

96.1 amu
(97.1 with added H)


A
THC
CBDVA
CBDV
CBG
CBDA
CBD
CBGA
Δ9-THCV
CBN
Δ9-THC
Δ8-THC
CBL
CBC
Δ9-THCA
Relative Abundance
Time (min)
B
C
D
E
F
G
H
I
J
K
L
M
N
m/z
O
P
Q
R
S
T
U

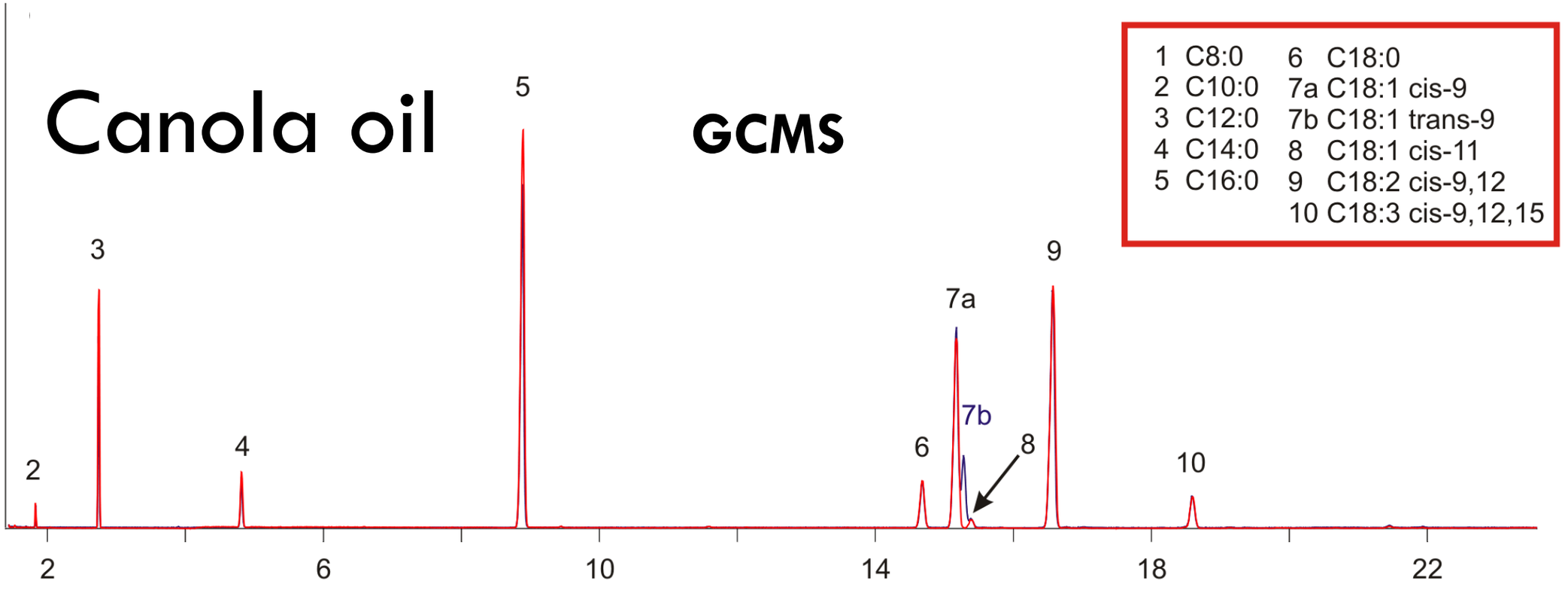
MCPD

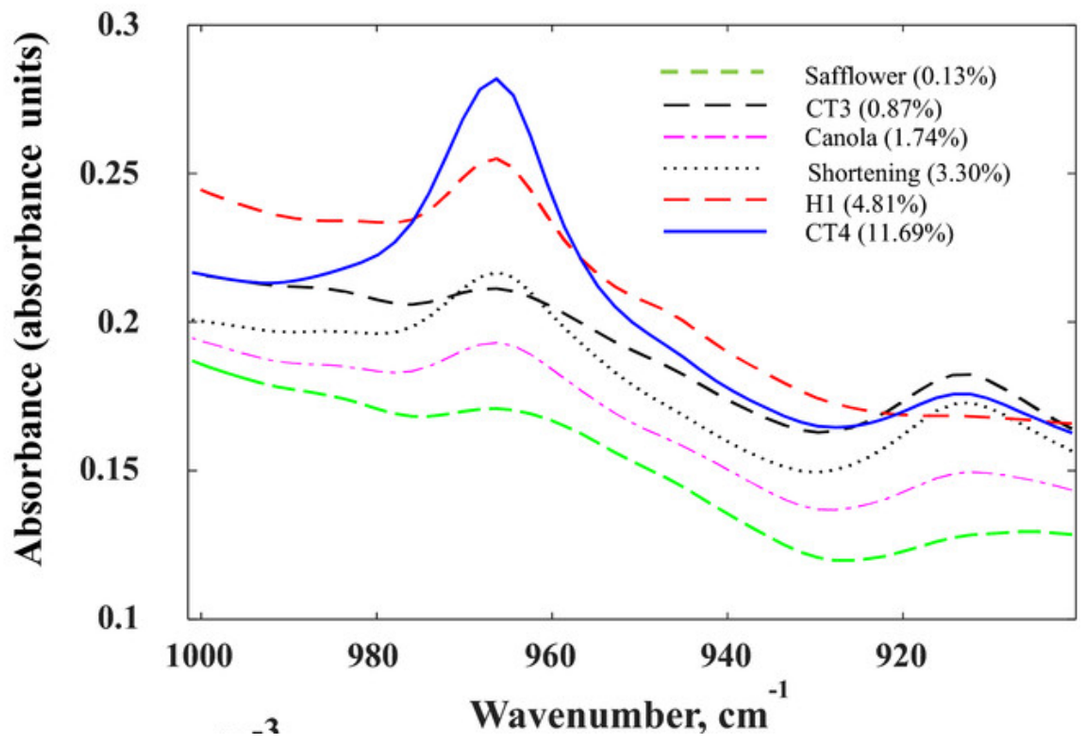


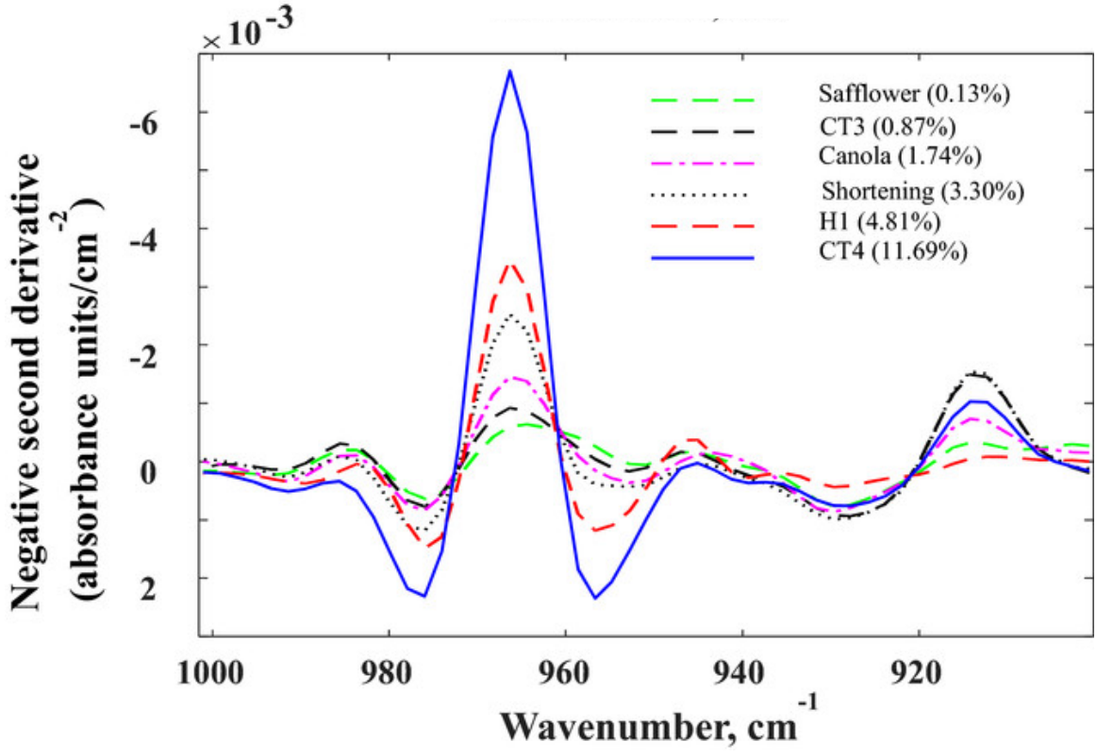
ffi ðďfiffi fiÝ ðďŶ ężēfið 3-MCPD-d5 (1), 3-MCPD (2), MBPD-ester-d5 (3) fièffi MBPD-ester (4)

Canola oil

GCMS

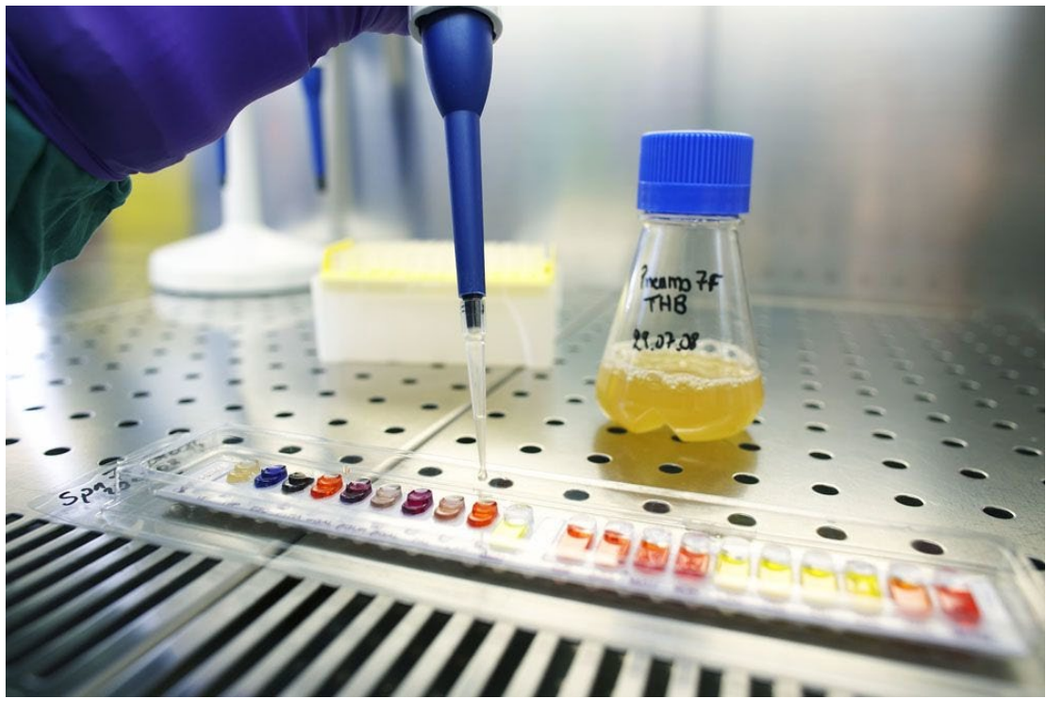


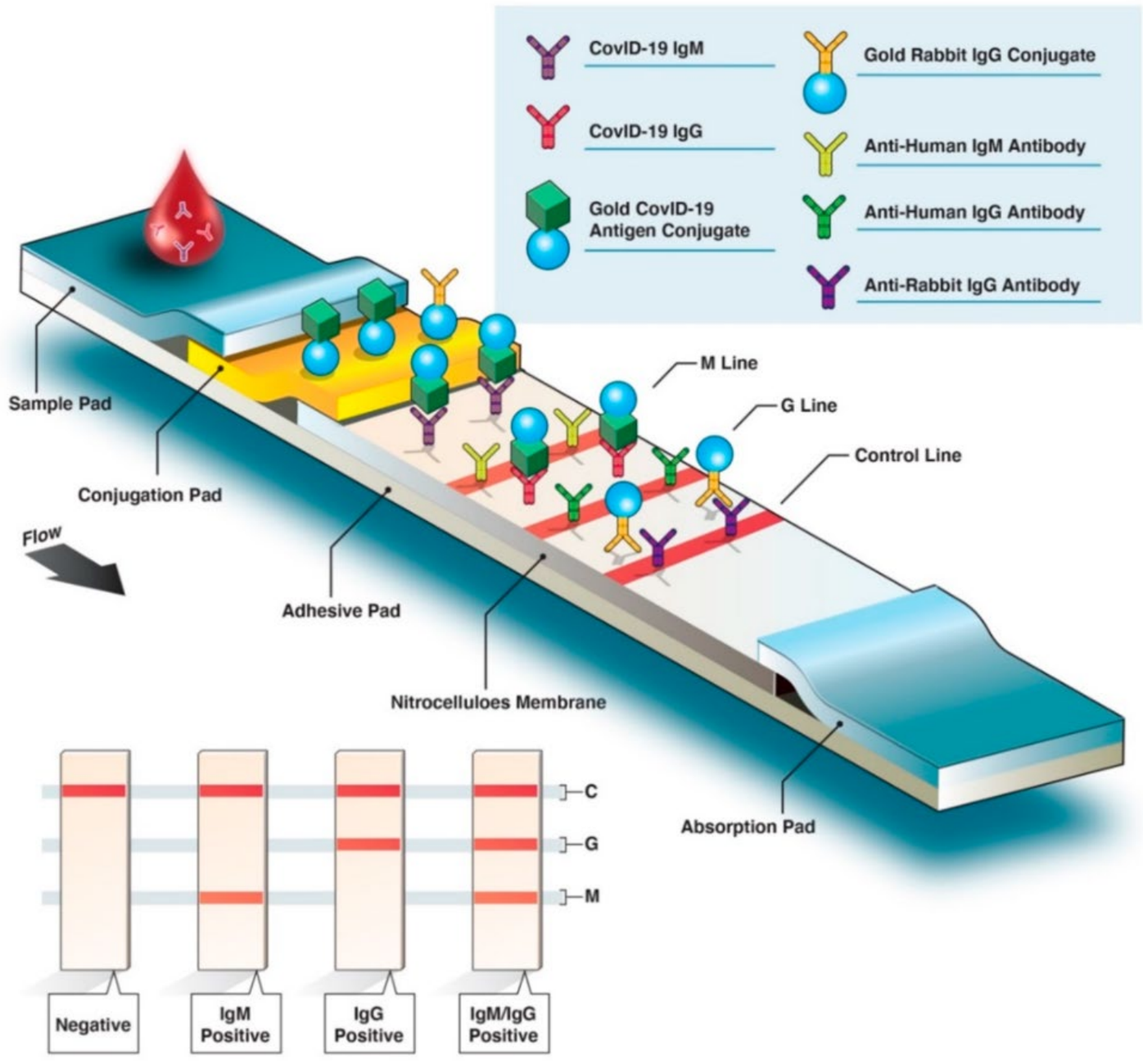




FT-IR

Food contamination





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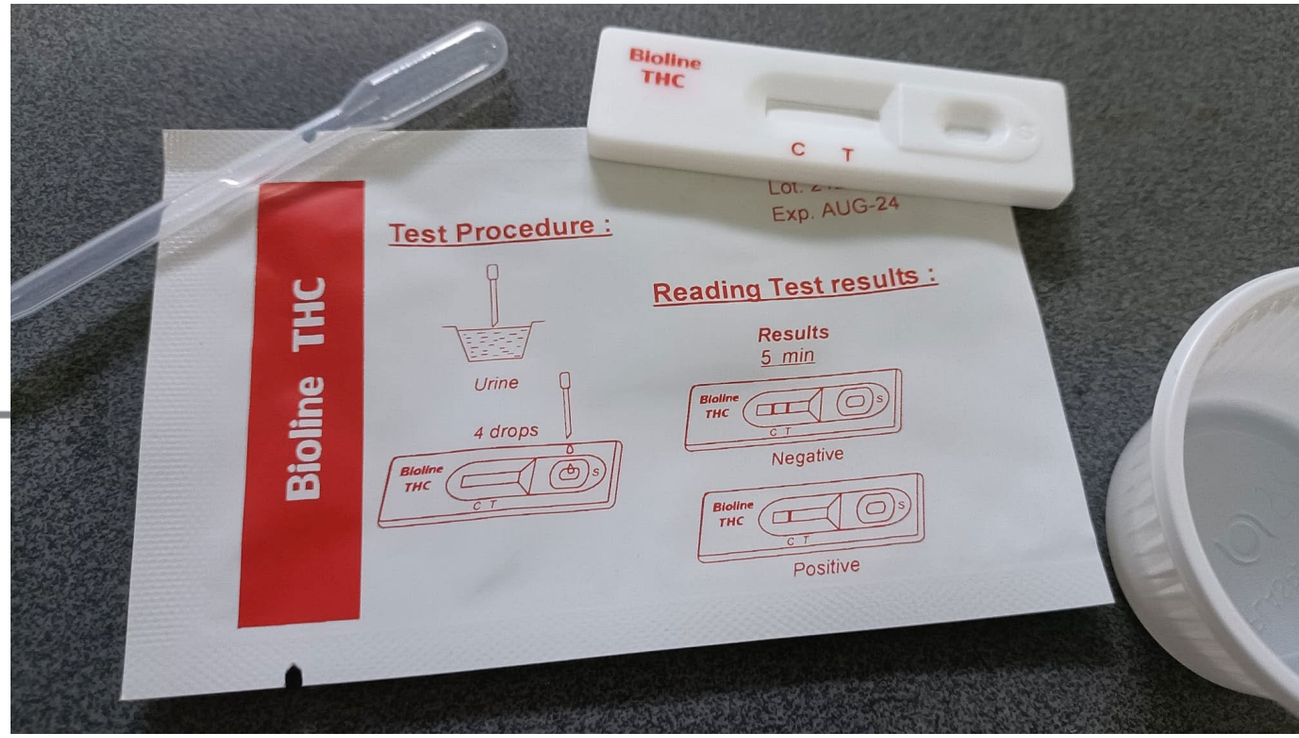
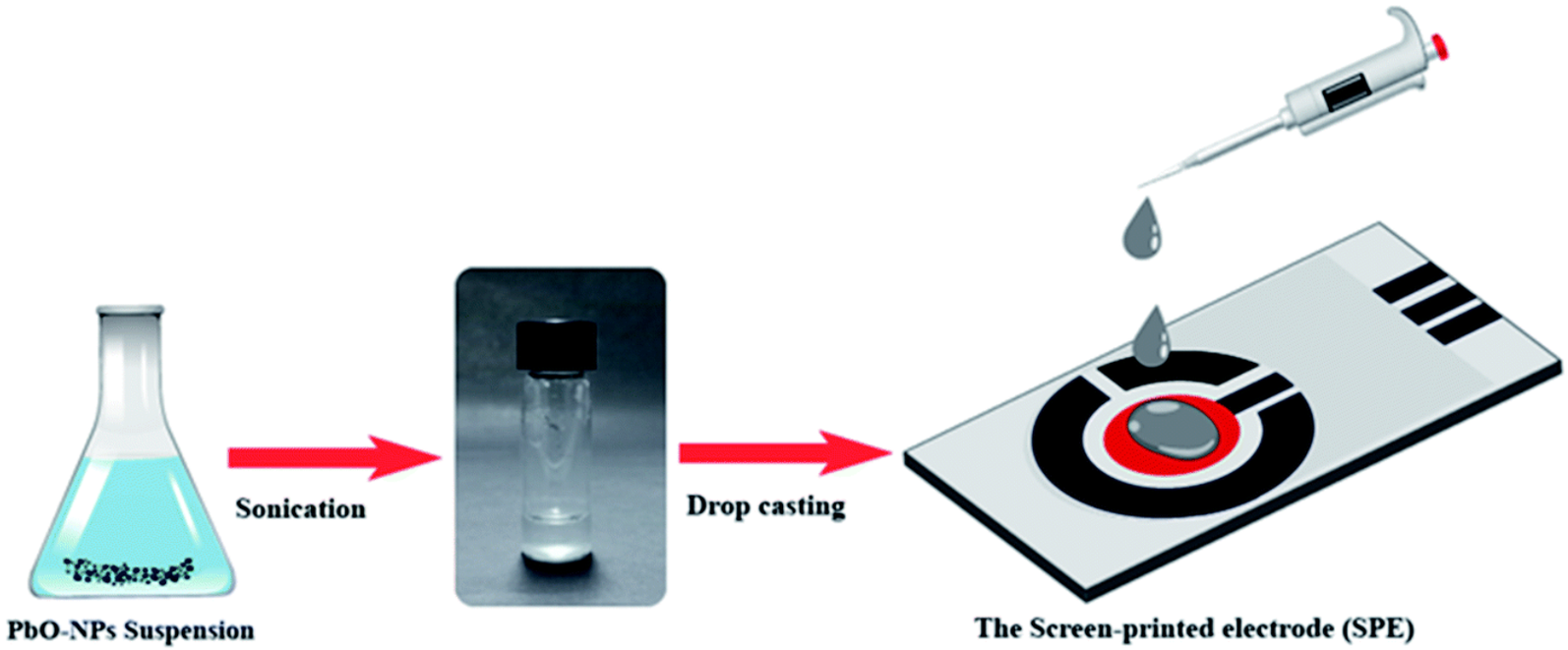
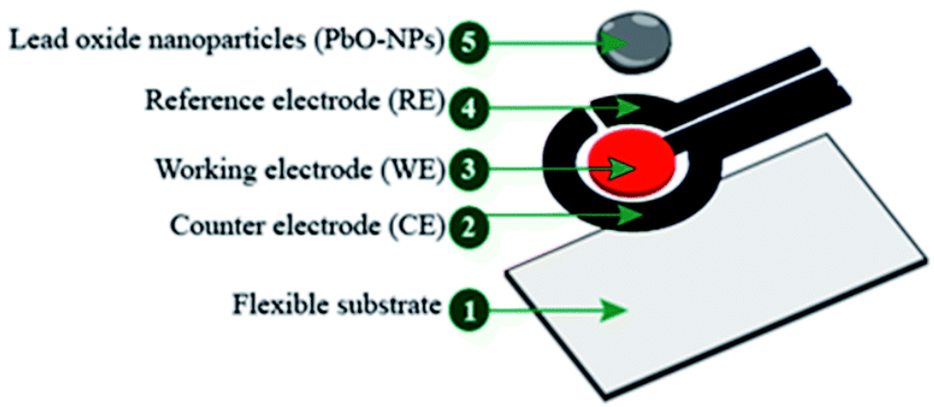
Food contamination





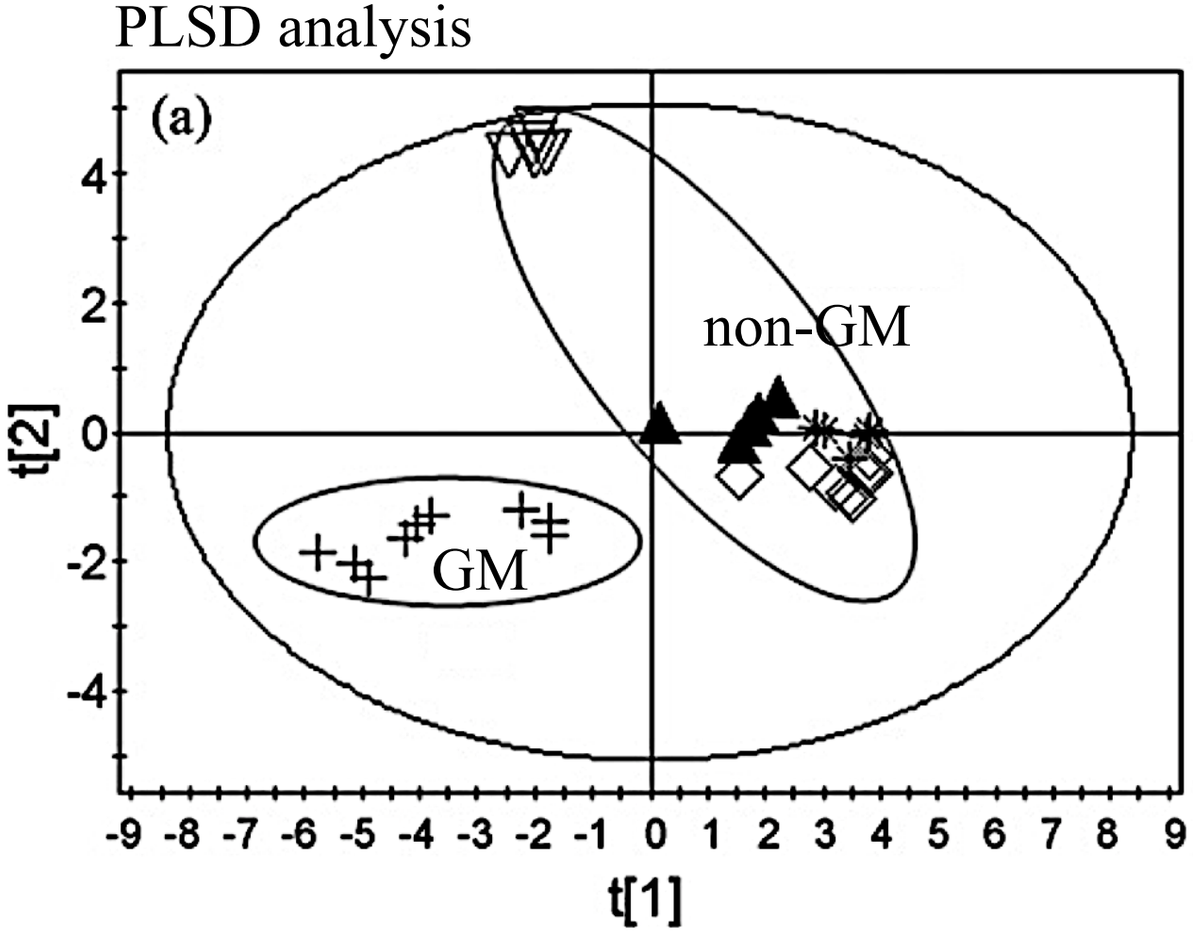


Metabolomics, Lipidomics and Flavoromics

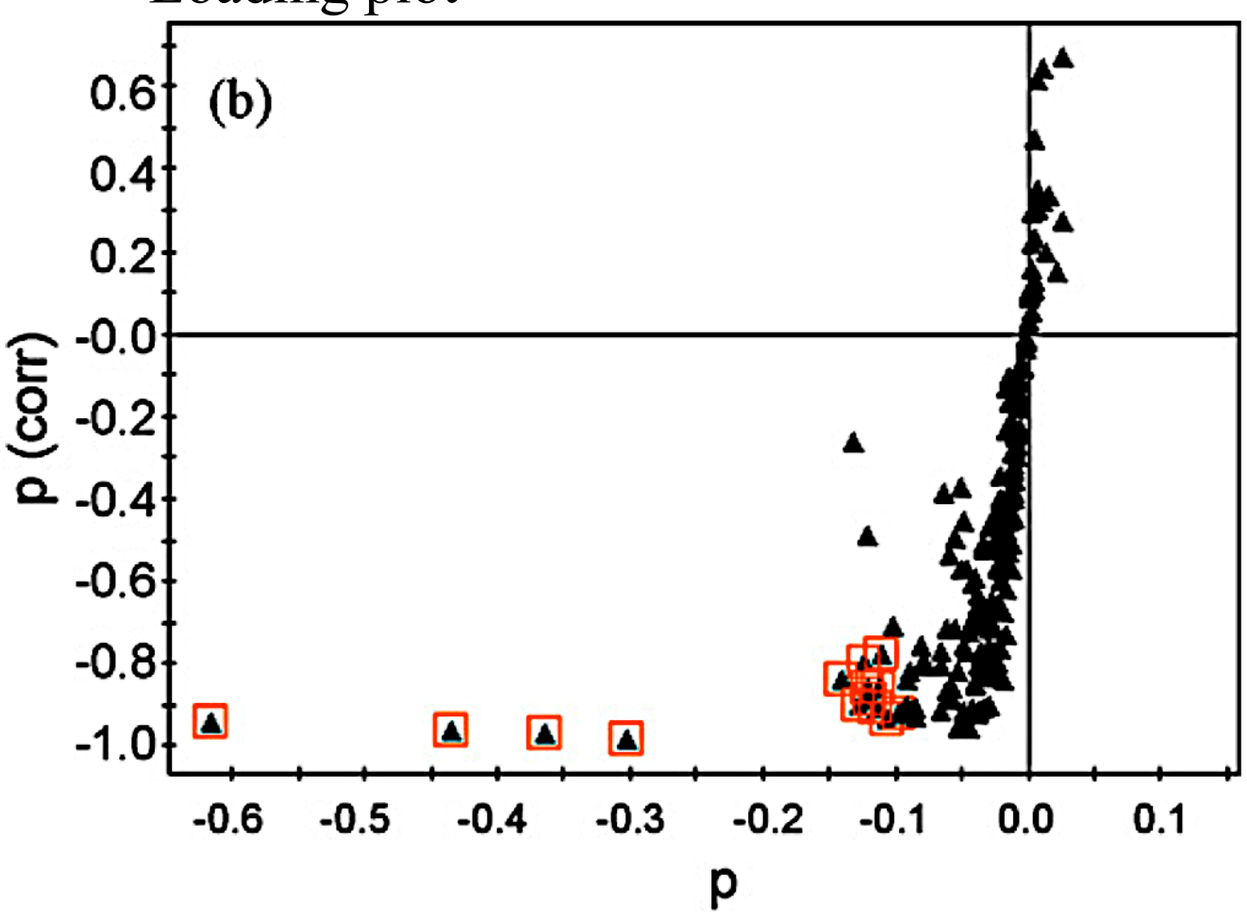
Detecting of transgenic crops

- Sample: rice grains Methodology: LC-MS
- The studying of transgenic rice compared to wild type rice.
- The GM species have insertions of insecticide producing genes (*cryIAc* and *sck*)

PLSD analysis



Loading plot



Source: Zhou *et al.*, (2009)

Detecting of transgenic crops

Metabolites responsible for separation between GM and non-GM groups.

Compound	Variance trend
UN	↑, 2.4
L-Glutamic acid	↑, 2.1
Glycerol-3-phosphate*	↑, 1.4
Citric acid	↑, 1.5
D-Mannitol	↑, 3.0
Linoleic acid	↑, 1.3
Oleic acid	↑, 1.6
Hexadecanoic acid, 2,3-dihydroxypropyl ester*	↑, 1.3
UN	↑, 2.2
Sucrose	↑, 2.4
UN	↑, 1.4
9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester*	↑, 1.2
Trehalose	↓, 0.1
UN	↑, 1.4
UN	↑, 2.0

Source: Zhou *et al.*, (2009)

Detecting of transgenic crops

- Trehalose could be an potent marker.

- At different time of sowing, trehalose content was different in non-GM species.

Metabolites responsible for separation of non-GM rice sown at different time

Classification	Compound	Variance trend	
		M86-D1	M86-D2
M86-D1 and M86-D2 vs. M86-C	Glycerol-3-phosphate*	↑, 1.4	↑, 2.7
	Citric acid	↑, 1.6	↑, 2.5
	Linoleic acid	–	↑, 1.3
	Oleic acid	↑, 1.3	↑, 2.2
	Hexadecanoic acid, 2,3-dihydroxypropyl ester*	↑, 1.2	↑, 1.3
	Sucrose	↑, 1.3	↑, 2.4
	UN	↑, 1.5	↑, 4.0
	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester*	↑, 1.3	↑, 1.8
	Trehalose	↑, 40.7	↑, 392.9
	UN	↑, 4.1	↑, 3.4
	UN	↑, 1.3	↑, 1.4
	UN	↑, 1.6	↑, 3.5

Code: M86-C, M86-D1 and M86-D2 : non-GM rice sown at different time

Source: Zhou *et al.*, (2009)

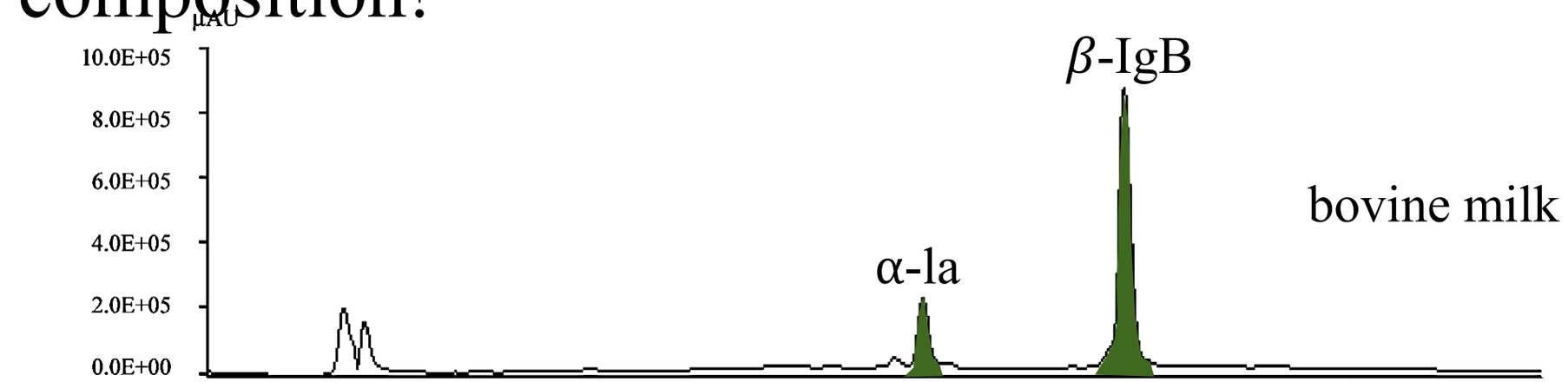
Other study examples

Type	Species	Study synopsis
Cereal	Barley (*Hordeum vuigare*)	Metabolic responses to salt stress in two barley cultivars
	Maize (*Zea mays*)	Metabolite profiling to evaluate the impact of genetic background, growing location and season
Medical plant	Perilla (Shiso) (*Perilla frutescens*)	Functional genomics for accumulation of anthocyanins in red and green perilla
Legume	Pea (*Pisum sativum*)	Metabolite fingerprint of transgenic peas
Flowering plants (*Solanaceae*)	Potato (*Solanum tuberosum*)	Evaluation of genetically modified potatoes
	Tomato (*Solanum lycopersicum*)	Metabolite profiling during fruit development
		Metabolite profiling of genetically modified tomatoes
Fruit	Raspberry (Rubus idaeus)	Metabolite profiling to identify beneficial compound

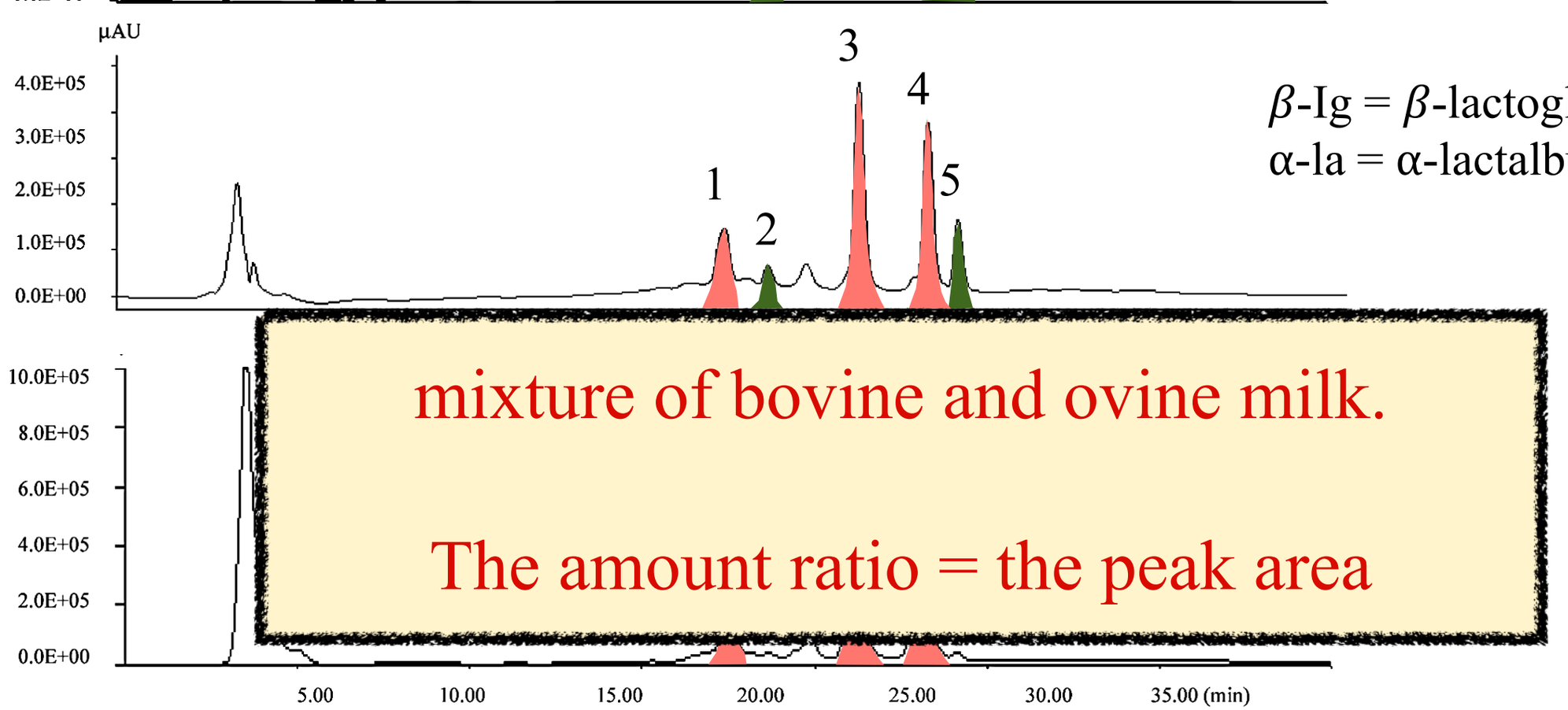
Modified from: Carreno-Quinter *et al.*, (2013)

Detection and quantification of milk composition in protected designation of origin cheeses

- the ratio of β-lactoglobulin in a milk mixture used to produce cheese can tell the difference of cheese's milk composition!



Source: Ferreira and Caçote, (2003)



mixture of bovine and ovine milk.

The amount ratio = the peak area

Detection and quantification of milk composition in protected designation of origin cheeses

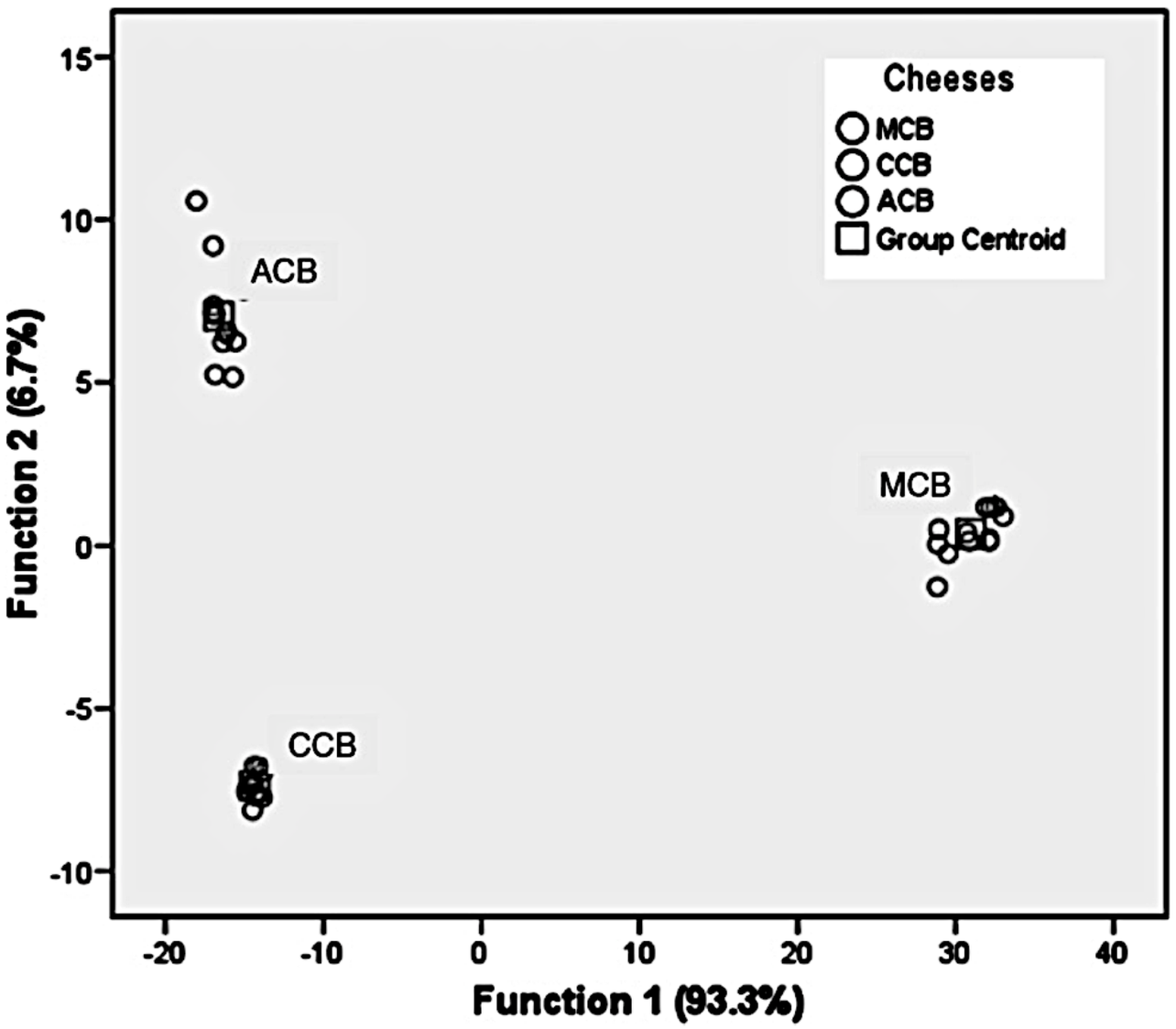
Results of evaluation of commercial PDO cheeses authenticity

Sample no.	PDO cheese	Milk type found
1	"Serra da Estrela"	Ovine milk
2	"Serra da Estrela"	Ovine milk
3	"Terrincho"	Ovine milk
4	"Terrincho"	Ovine milk
5	"Terrincho"	Ovine milk
6	"Terrincho"	Ovine milk
7	"Terrincho"	Ovine milk
8	"Serrano Transmontano"	Caprine milk
9	"Serrano Transmontano"	Caprine milk
10	"Picante da Beira Baixa"	Ovine/caprine milks (40/60%)
11	"Picante da Beira Baixa"	Ovine/caprine milks (49/51%)
12	"Picante da Beira Baixa"	Ovine/caprine milks (46/54%)

Source: Ferreira and Caçote, (2003)

The results are in good agreement with the information obtained from the respective PDO certification organisms.

Volatile fraction of PDO "Castelo Branco cheese" can be used to evaluate breed origin.



Source: Ferreira, Pinho and Sampaio, (2009)

MCB - Merino da Beira Baixa breed
CCB - Crusade of the two races breed
ACB - Assaf breed

Major volatile discriminant

- butan-2-one, ethyl acetate, 3-methylbutanoic acid which is abundant in MCB.

- pentan-2-ol and 3-methylbutyl acetate in ACB cheeses

Discriminant analysis of volatile fraction of the cheeses can tell breed origin of milk used to produce cheeses.

Classification of unifloral honeys with an MS-based electronic nose

- Unifloral honeys are designated by producers as having a main botanical origin.
- Six unifloral honeys were evaluated.

fir

dandelion

lime

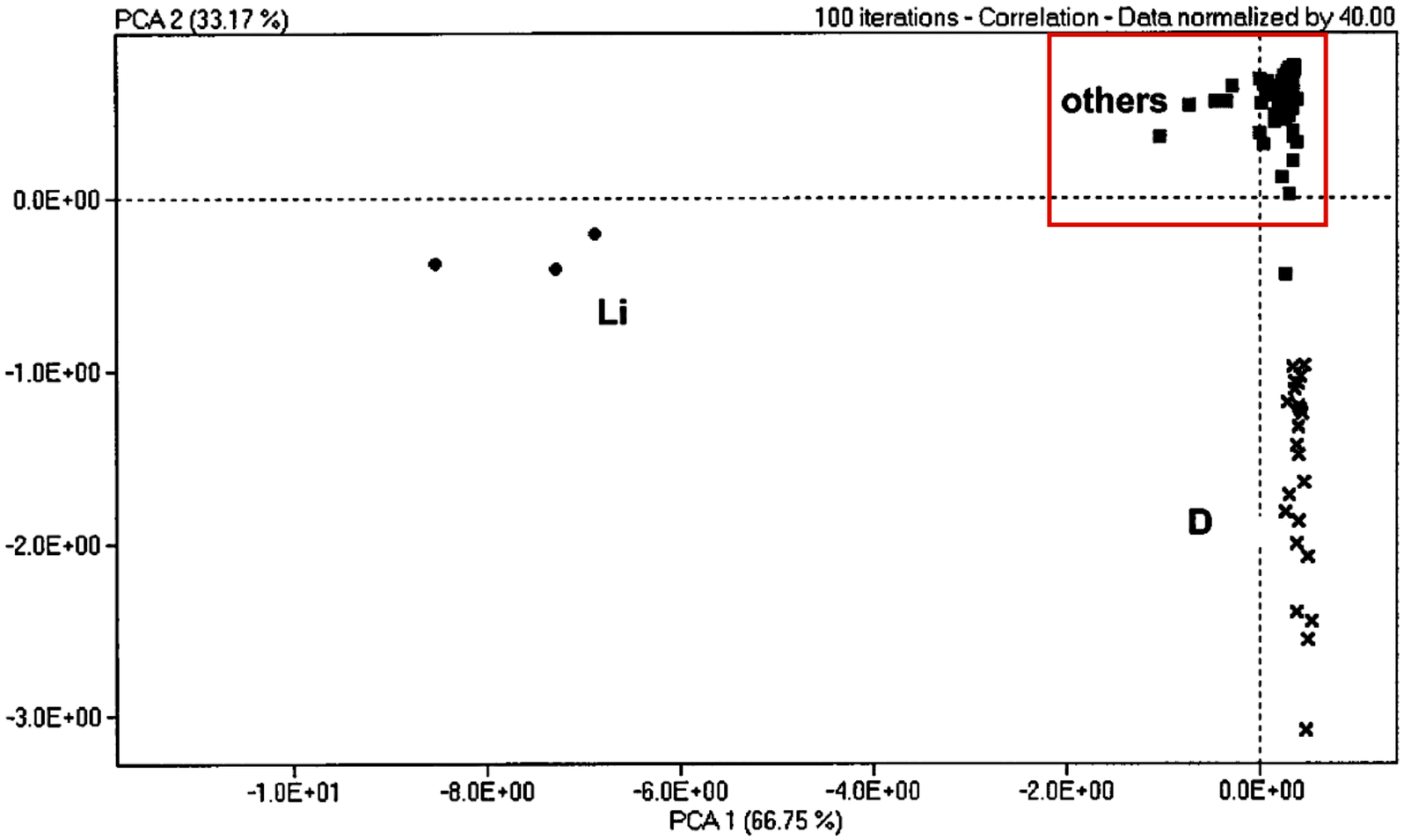
rape

chestnut

acacia

Classification of unifloral honeys with an MS-based electronic nose

- Electronic nose analysis with a static headspace sampling method.



Modified from: Ampuero, Bogdanov and Bosset, (2004)

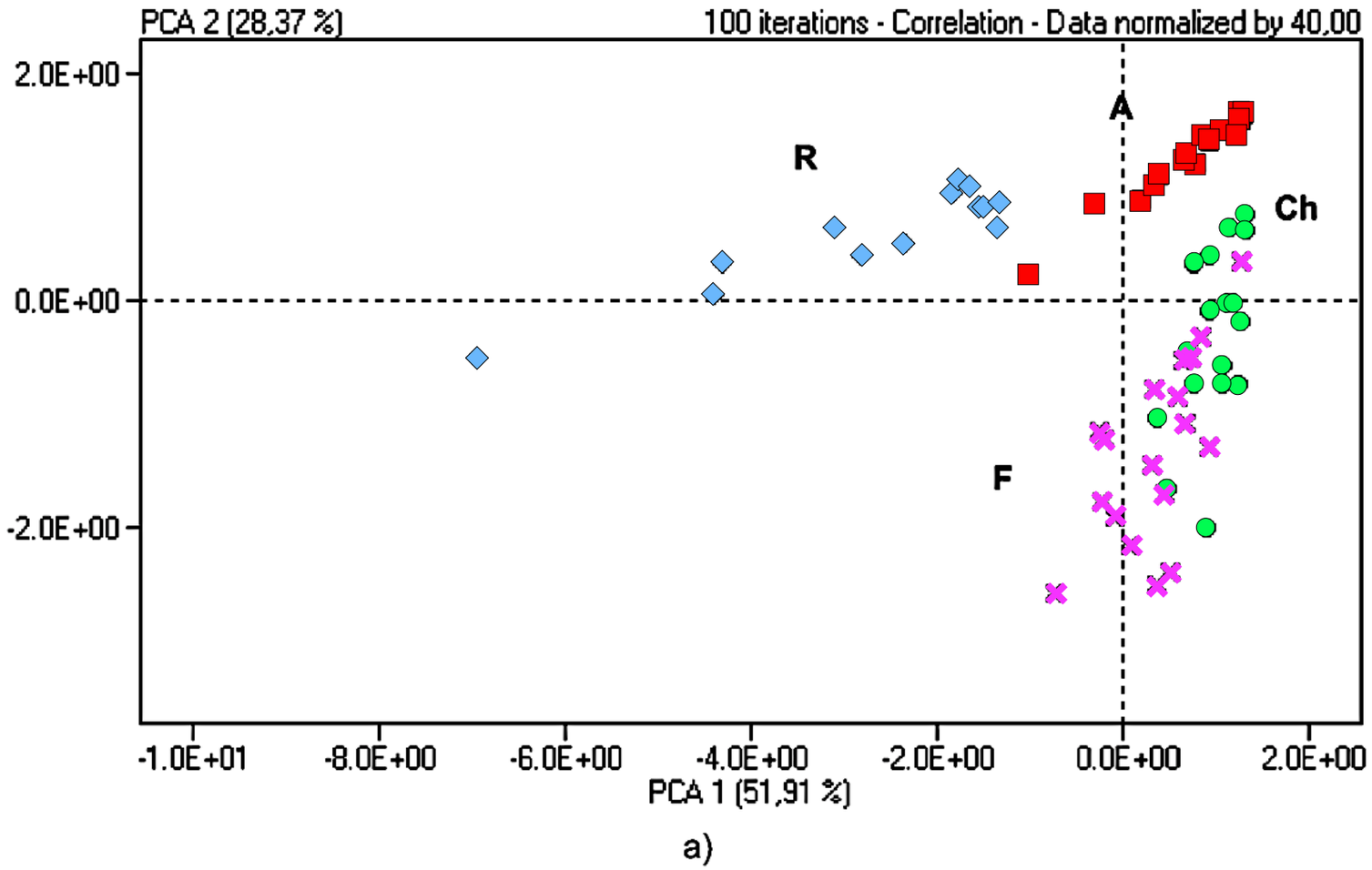
Li = lime
D = dandelion
others = the group formed by acacia, chestnut, rape and fir together

model sample group	correct classification rate (%) by PCA	Discriminant variables (ionic masses)
Dandelion, lime and others (A, Ch, F and R)	100	51, 117, 132

Classification of unifloral honeys with an MS-based electronic nose

- by discriminate out the dandelion and lime, shows the differentiation in others group.

R = rape
A = acacia
Ch = chestnut
F = fir



a)

Modified from: Ampuero, Bogdanov and Bosset, (2004)

model sample group	correct classification rate (%) by PCA	Discriminant variables (ionic masses)
Acacia, chestnut, fir and rape	93.85	44, 47, 54, 58, 94

Food Science & Technology

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LCMS GCMS

ความผิดผลิตภัณฑ์อาหาร

1. อาหารไม่บริสุทธิ์
2. อาหารปลอม
3. อาหารผิดมาตรฐาน
4. อาหารอื่นที่รัฐมนตรีกำหนด

1. ต้องระวางโทษจำคุกไม่เกินสองปีหรือปรับไม่เกินสองหมื่นบาท หรือทั้งจำทั้งปรับ

2. ต้องระวางโทษจำคกตั้งแต่หกเดือนถึงสิบปี และปรับตั้งแต่ห้าพันบาทถึงหนึ่งแสนบาท

3. ต้องระวางโทษปรับไม่เกินห้าหมื่นบาท

4. ต้องระวางโทษจำคุกไม่เกินห้าปี หรือปรับไม่เกินห้าหมื่นบาท หรือทั้งจำทั้งปรับ




ขอบคุณครับ

Email: kriskamol.n@ku.ac.th
Facebook: Kriskamol Na Jom
IG: teacherkriss
Twitter: teacherKriss
Tiktok: teacherkriss
Room: z æ ffeţĩ ē flě Ý ðð ď ffý ë b ð ę flz flð 2
d flz êfi flêfi đ flě flē b ðffję ffţý z ffć ffe đ ffî flðę flě flð
á ď ff 2 ë ęffz 2220
Office: 02 562 5020 bęfĩ 5219
Mobile Phone: 09 7238 29XX