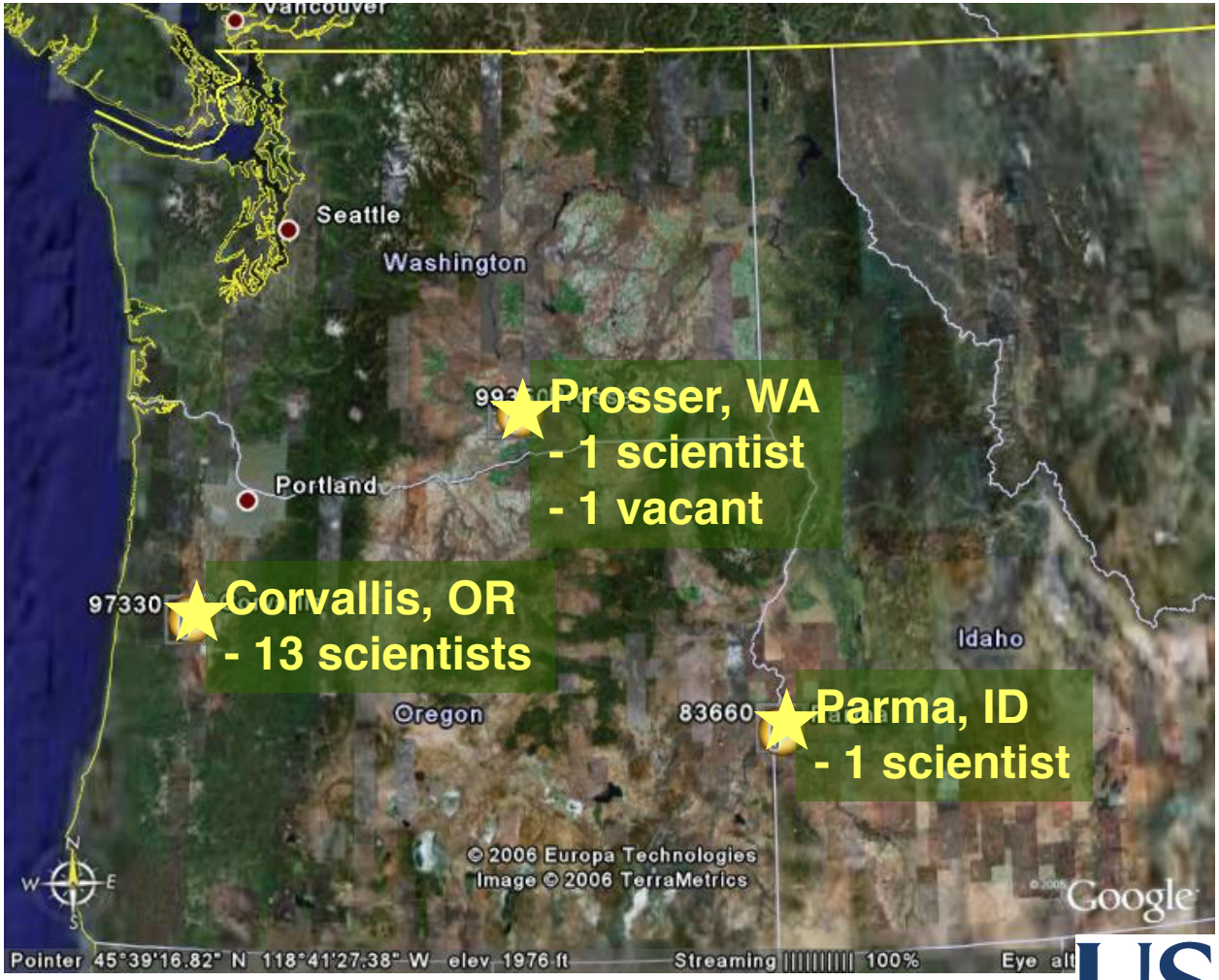
Cranberry phenolics: a crash course

Jungmin Lee



Horticultural Crops Research Unit
Food Chemistry Laboratory

USDA

Over
100 MILLION
Americans have **DIABETES** or **PREDIABETES**

Diabetes can lead to **heart disease, stroke, nerve and kidney diseases,** and **vision loss**

- Centers for Disease Control and Prevention, 2017

Study of
DRIED CRANBERRIES
after a high fat/high sugar meal **improved glucose response, inflammation and oxidation** for people with type 2 diabetes

- Food & Function, DOI:10.1039/C7FO00900C

Some studies show that
POLYPHENOLS
may help reduce diabetes risk

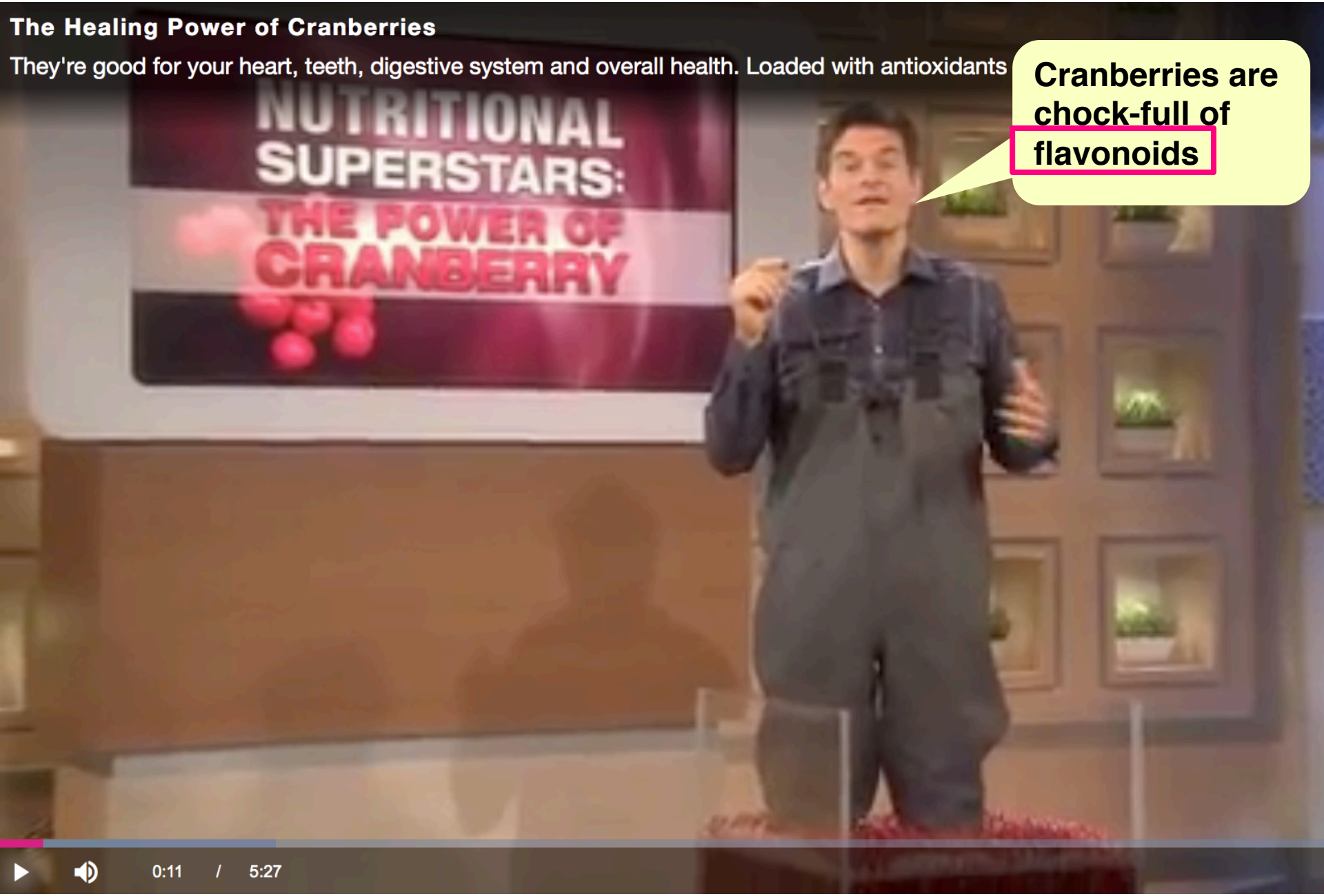
- Nutrients. 2016 Jan; 8(1): 17

GLUCOSE REGULATION and INSULIN SENSITIVITY — key for **prevention**

A trial found that the **polyphenols** in STRAWBERRIES and **CRANBERRIES improved insulin sensitivity** in non-diabetic, overweight people

- Br J Nutr.117(4):519-531

The CRANBERRY INSTITUTE™

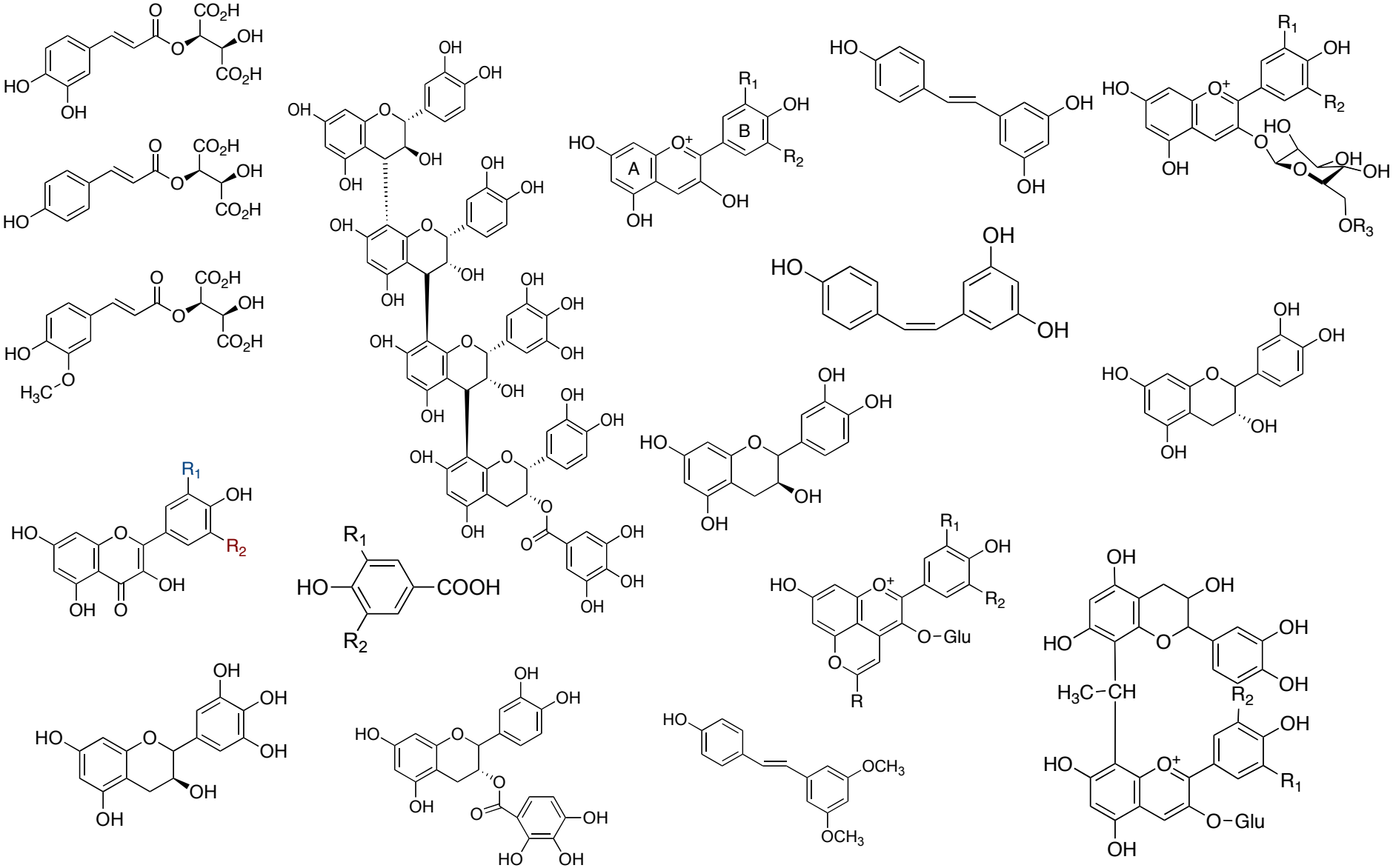

The Healing Power of Cranberries
They're good for your heart, teeth, digestive system and overall health. Loaded with antioxidants
NUTRITIONAL SUPERSTARS:
THE POWER OF CRANBERRY
Cranberries are chock-full of flavonoids
0:11 / 5:27

Phenolics

Cranberry Phytochemicals = Phytonutrients

- **Phenolics**
  - **Proanthocyanidins**
  - **Anthocyanin**
  - **Flavonol-glycosides**
  - **Phenolic acids**
- **Carbohydrates**
  - **Dietary fibers**
- **Organic acids**
- **Triterpenoids**
- **Vitamins**
- **Minerals**

Phenolics = Polyphenolics



> 6,000 identified

Petunia integerifolia

Petunia axillaris

Why do plants produce phenolics?

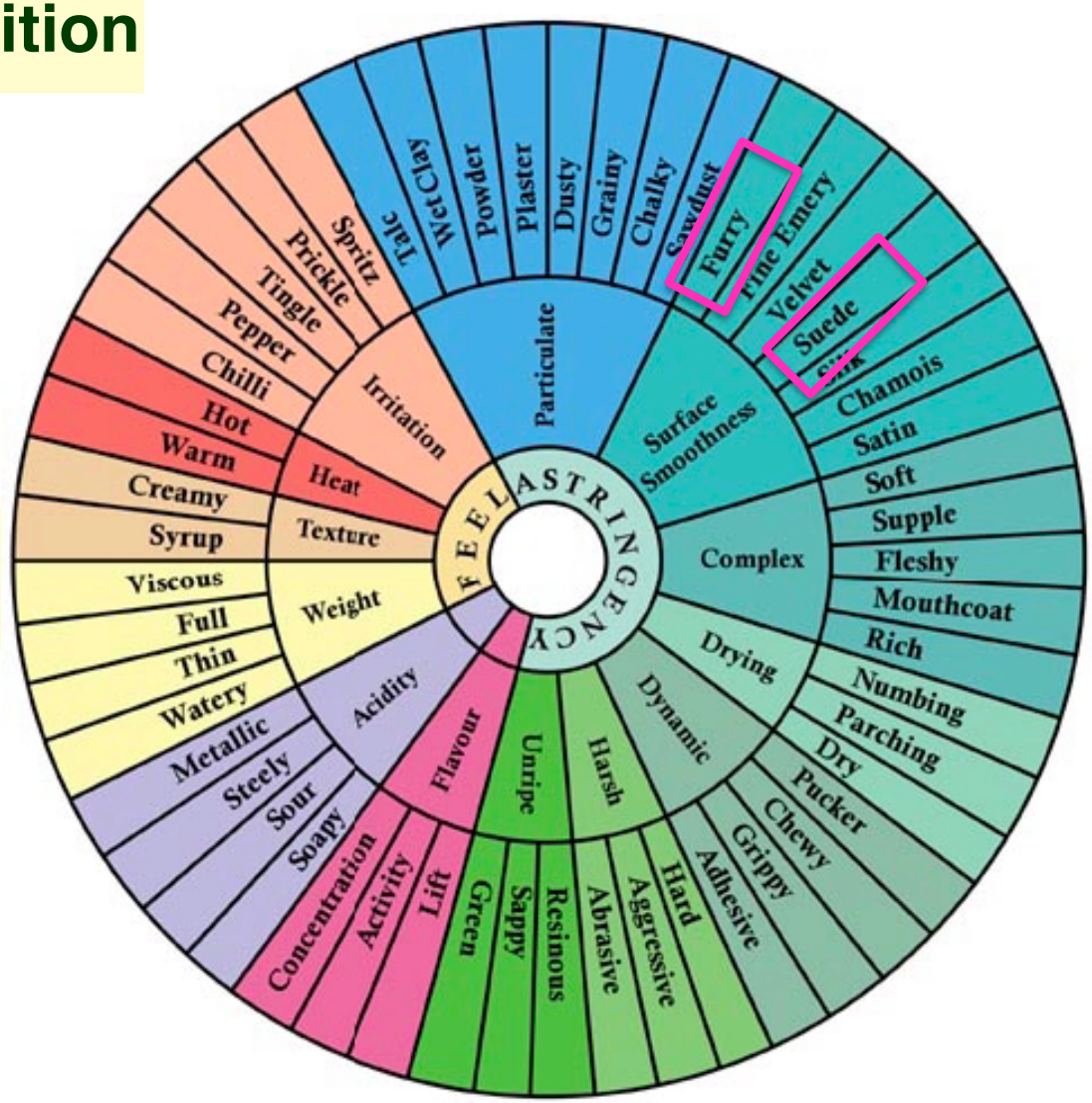
- Protection against UV
- Signaling
- Antifungal properties - phytoalexin
- Attraction / repulsion for pollinators and seed dispersers
- Possible role in plant growth and fruit ripening
- Wound healing

Cranberry juice composition

- Water ~87%
- Other compounds ~12%
- Phenolics ~1%

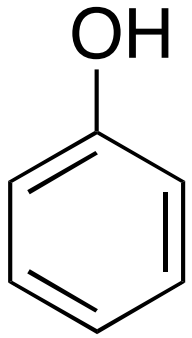
Importance of phenolics

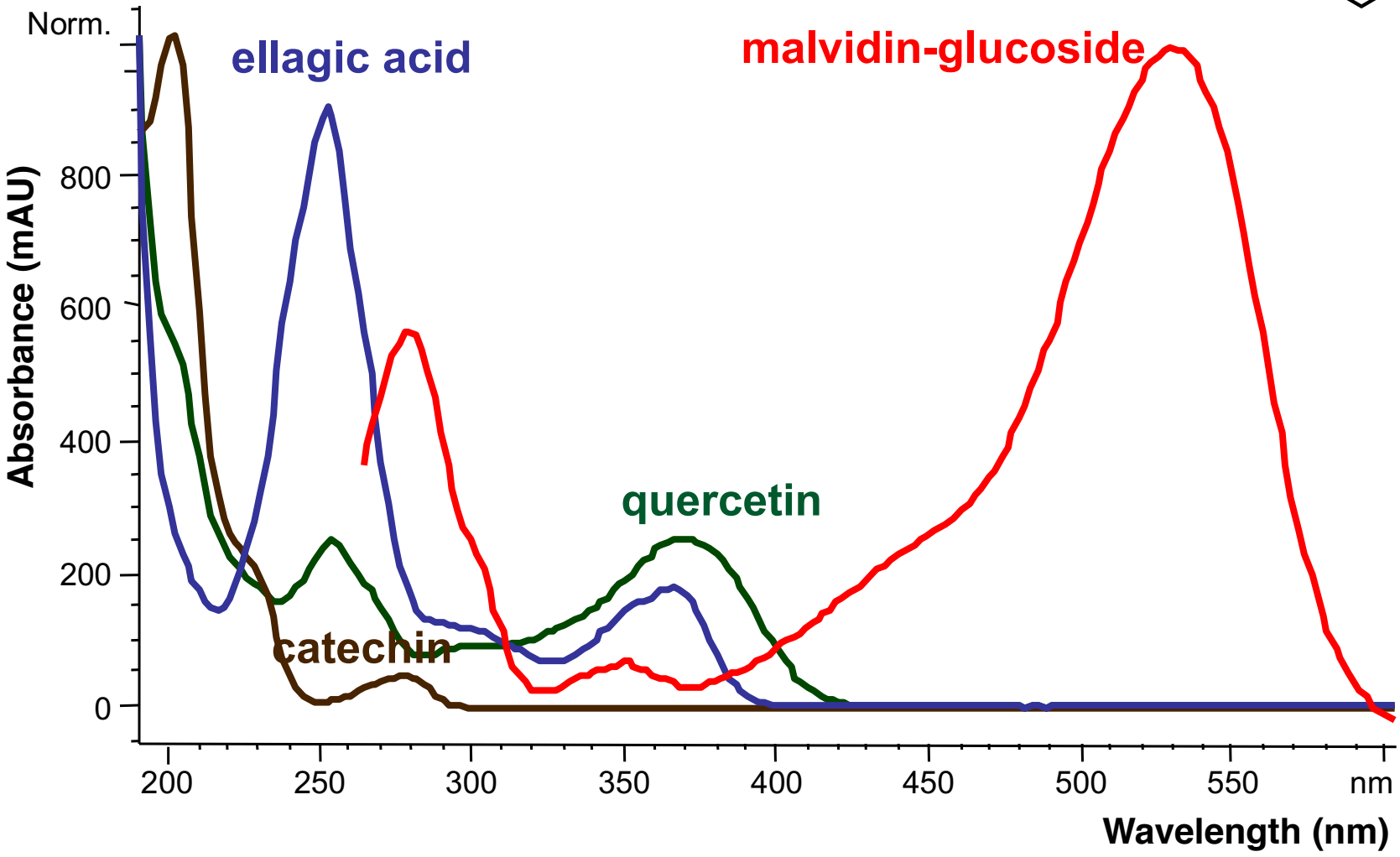
- Taste and mouthfeel (bitterness and astringency)
- Color (appearance)
- Preservative
- Health benefits

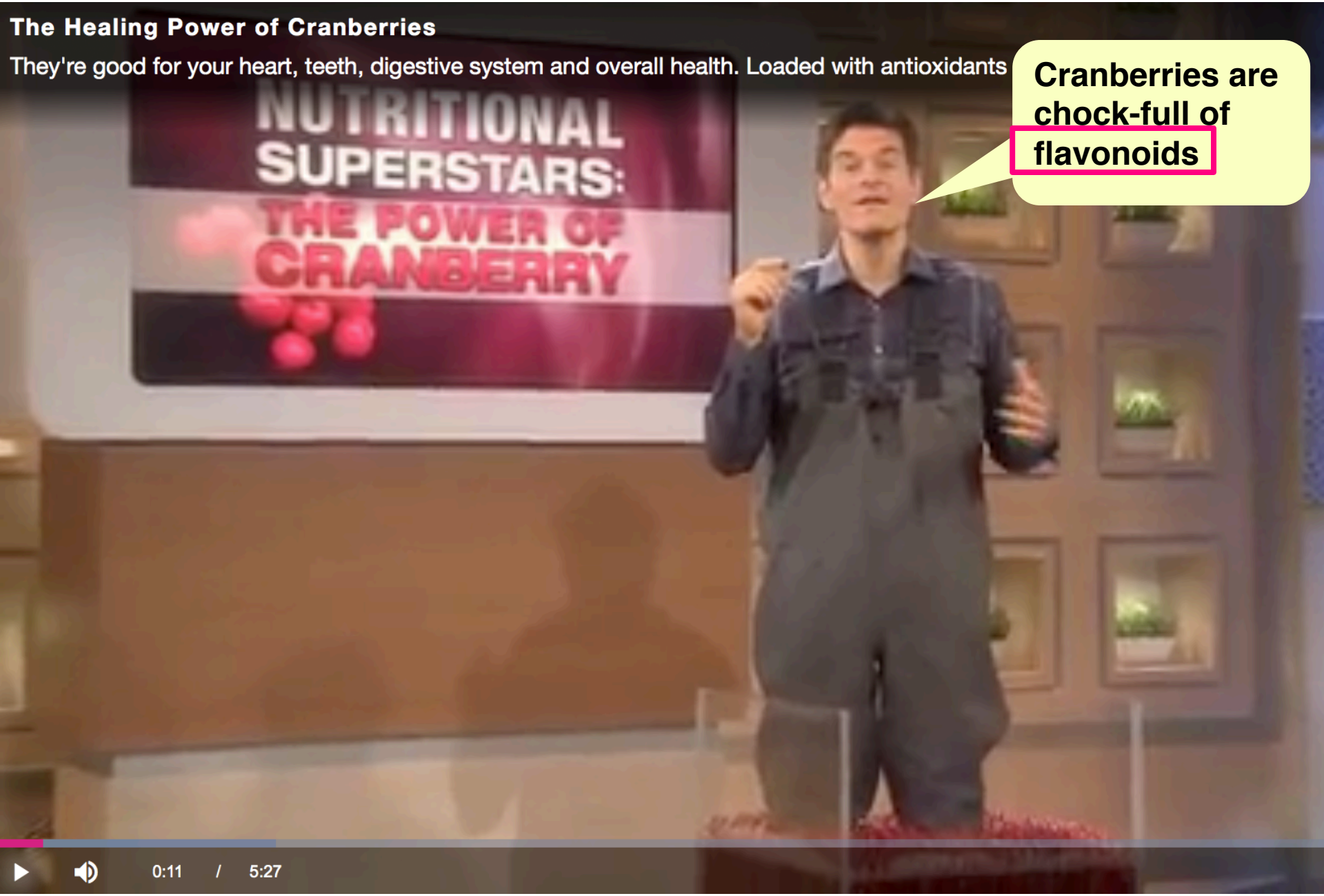


(Gawel, Oberholster, & Francis, 2000)

Phenolics = polyphenolics



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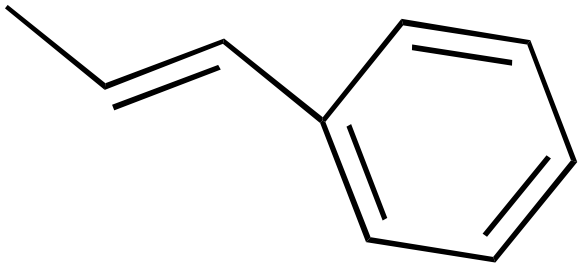
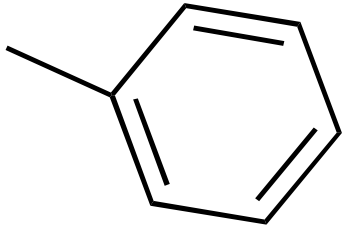
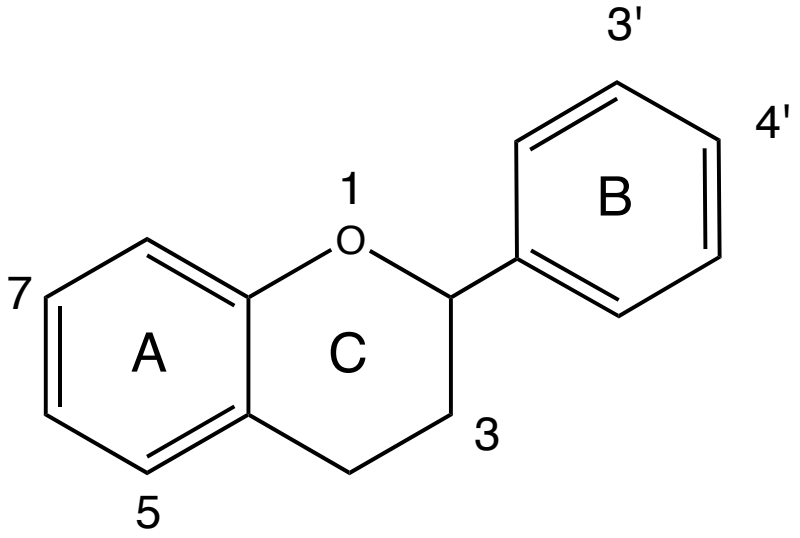
Non-flavonoid (C_3C_6 or C_1C_6)





Flavonoid ($C_6C_3C_6$)



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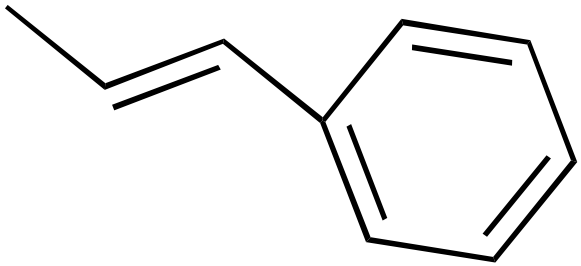

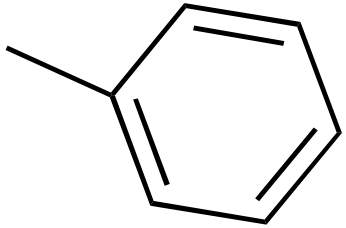

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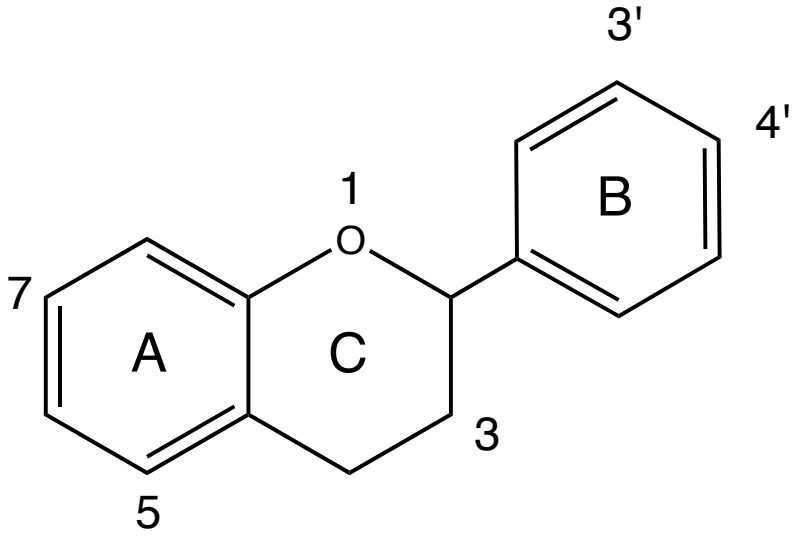
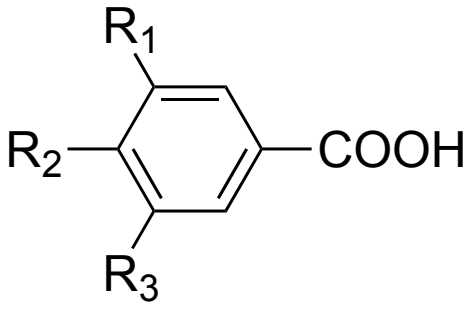


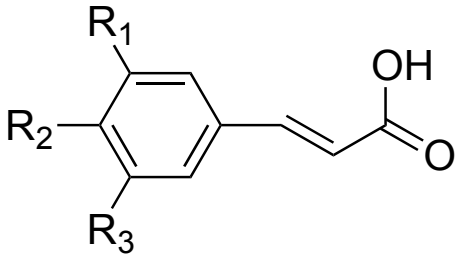
Non-flavonoids (mostly phenolic acids)

Benzoic acids



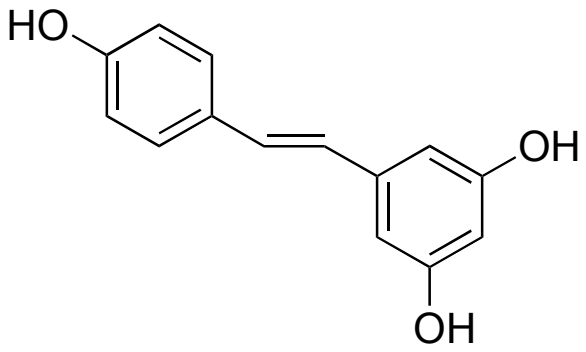
Benzoic acid
Hydroxybenzoic acid
Dihydroxybenzoic acid

Cinnamic acids



p-coumaric acid
Caffeic acid
Ferulic acid
Sinapic acid

Stilbenes



Resveratrol

Non-flavonoids (mostly phenolic acids)

J. Amer. Soc. Hort. Sci. 135(6):494–500. 2010.

Variation in Concentration of Phenolic Acid Derivatives and Quercetin Glycosides in Foliage of Cranberry that May Play a Role in Pest Deterrence

Catherine C. Neto and Christine A. Dao
Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, 285 Old Westport Road, N. Dartmouth, MA 02747

Michelle R. Salvas
University of Massachusetts Amherst, Cranberry Experiment Station, 1 State Bog Road, P.O. Box 569, E. Wareham, MA 02538

Wesley R. Autio
Department of Plant, Soil, and Insect Sciences, University of Massachusetts Amherst, Amherst, MA 01003

Justine E. Vanden Heuvel[1,2]
University of Massachusetts Amherst, Cranberry Experiment Station, 1 State Bog Road, P.O. Box 569, E. Wareham, MA 02538

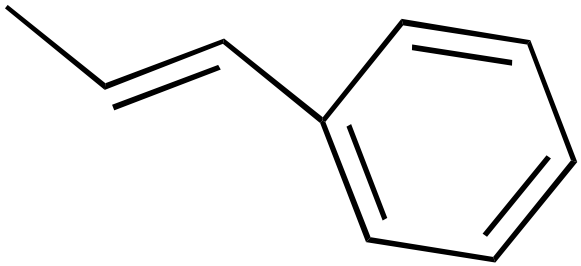
Additional index words. *Vaccinium macrocarpon*, gypsy moth, cranberry weevil, red-headed flea beetle

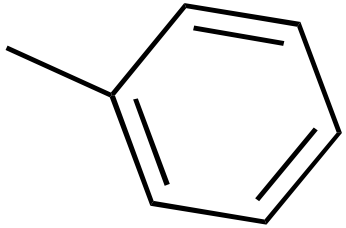
Abstract. **Several insect herbivores have been anecdotally reported to prefer 'Howes' cranberry leaves (*Vaccinium macrocarpon*) over those of 'Early Black'. A series of studies were undertaken to determine whether these anecdotal reports are accurate and to compare phenolic profiles in the foliage of 'Early Black' and 'Howes' for compounds that differ in concentration and could be further investigated as possible feeding deterrents. Gypsy moth larvae (*Lymantria dispar*) demonstrated a significant feeding preference for 'Howes' over 'Early Black'. Red-headed flea beetle adults (*Systena frontalis*) demonstrated a similar but not statistically significant trend, whereas cranberry weevil (*Anthonomus musculus*) did not prefer either cultivar. Compounds giving rise to six peaks in the phenolic profile were significantly greater in concentration in 'Early Black' than 'Howes' on at least one of three sampling dates during the growing season. Five of these compounds were isolated from leaves harvested at the June time point coinciding with gypsy moth infestation and identified as: 5-O-caffeoylquinic acid, 3-O-p-coumaroylquinic acid, 5-O-p-coumaroylquinic acid, quercetin-3-O-galactoside, and quercetin-3-O-rhamnoside.**

Non-flavonoids

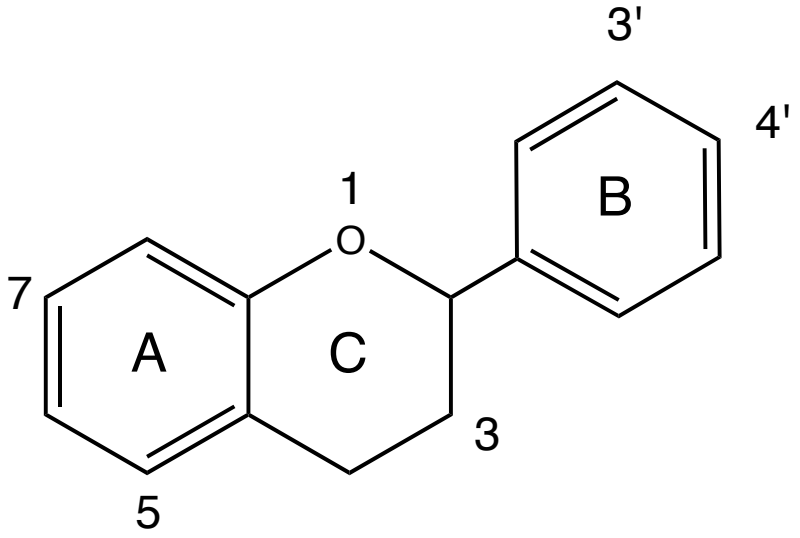
- **Benzoic acids**
  - Benzoic acid
  - Hydroxybenzoic acid
- **Cinnamic acids**
  - *p*-Coumaric acid
  - Caffeic acid
  - Ferulic acid
  - Sinapic acid
- **Stilbenes**
  - Resveratrol

Non-flavonoid (C_3C_6 or C_1C_6)

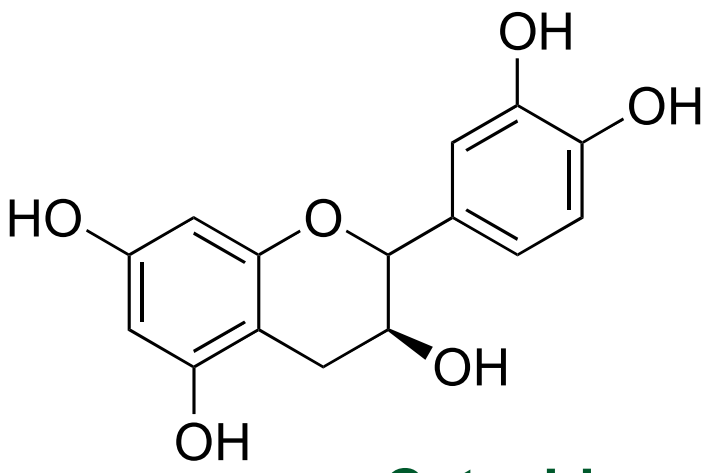




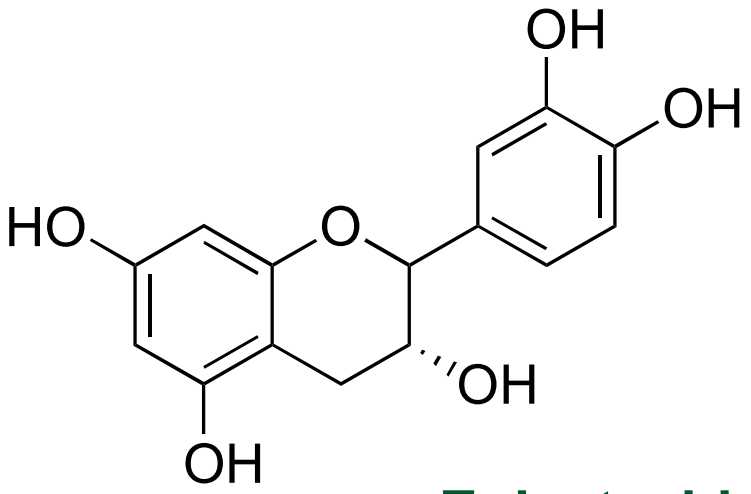
Flavonoid ($C_6C_3C_6$)



Flavanol = Flavan-3-ol

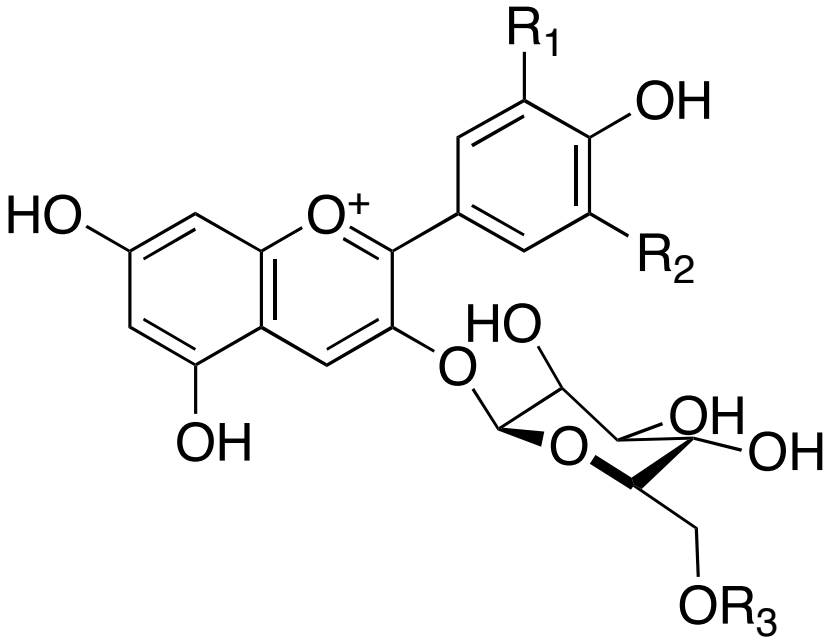


Catechin

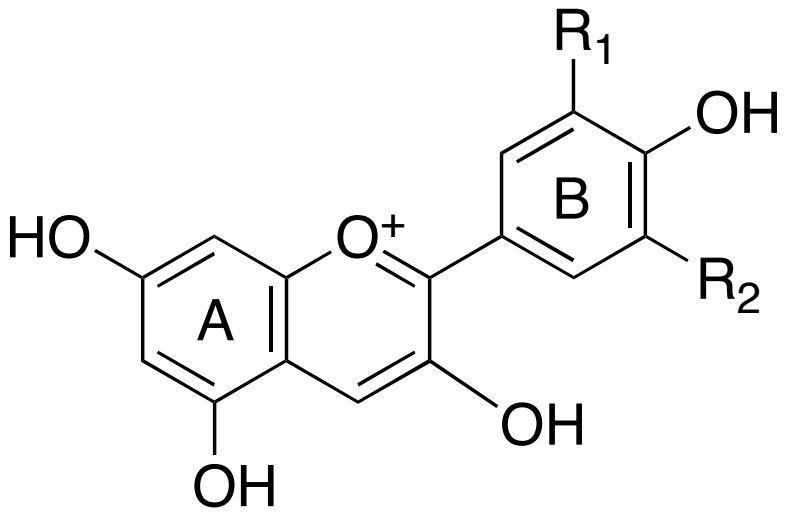


Epicatechin

Anthocyanin

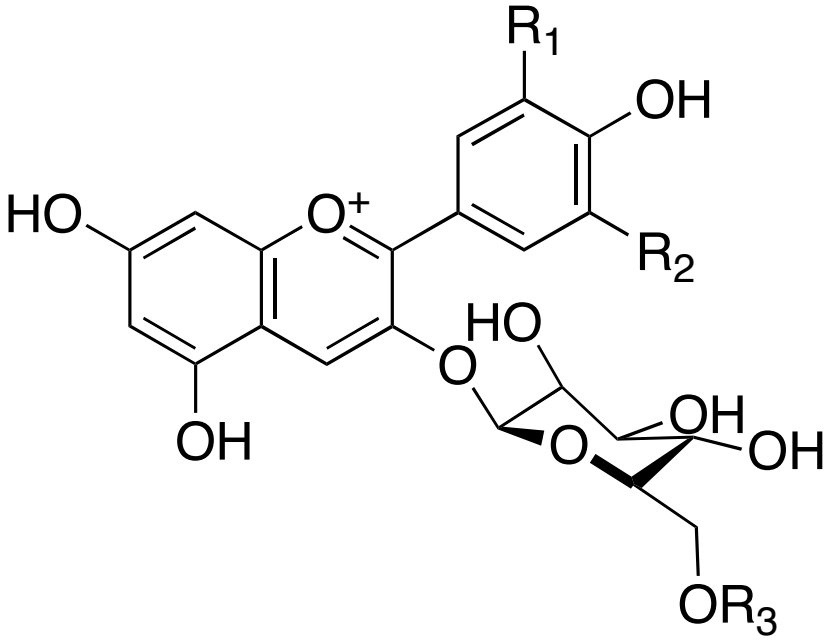


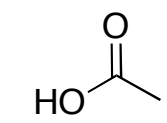
Anthocyanidin = Aglycone



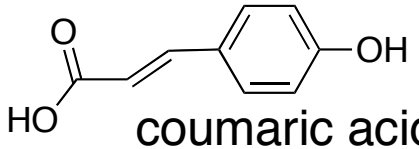
$R_1=R_2=H$	Pelargonidin
$R_1=OH$ $R_2=H$	Cyanidin*
$R_1=OCH_3$ $R_2=H$	Peonidin*
$R_1=R_2=OH$	Delphinidin
$R_1=OCH_3$ $R_2=OH$	Petunidin
$R_1=R_2=OCH_3$	Malvidin

Anthocyanin

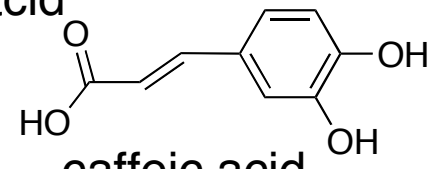




acetic acid

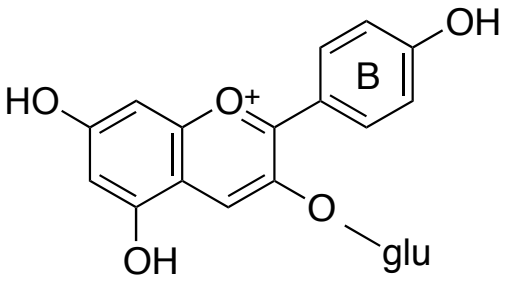


coumaric acid

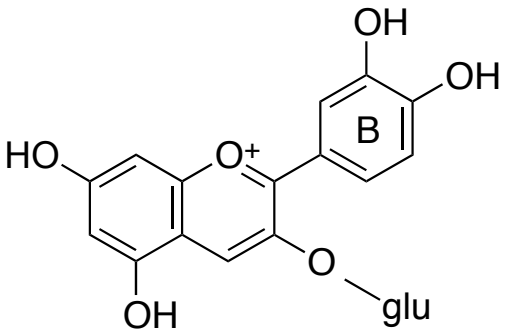


caffeic acid

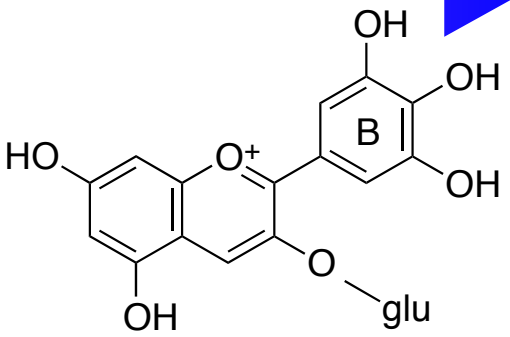
Anthocyanin color



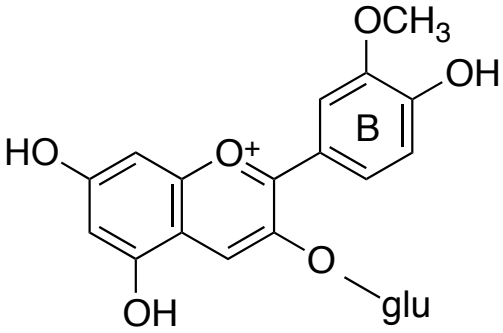
Pelargonidin



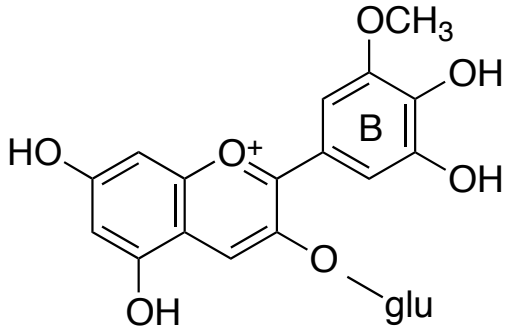
Cyanidin



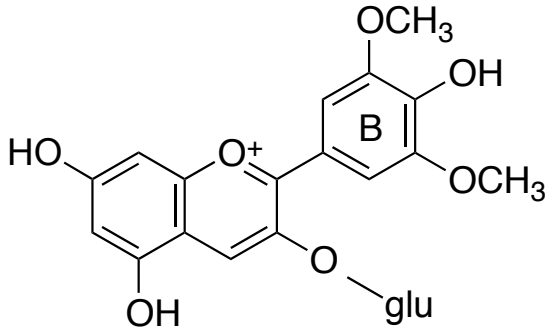
Delphinidin



Peonidin

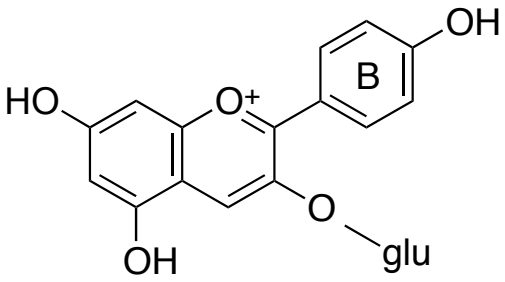


Petunidin

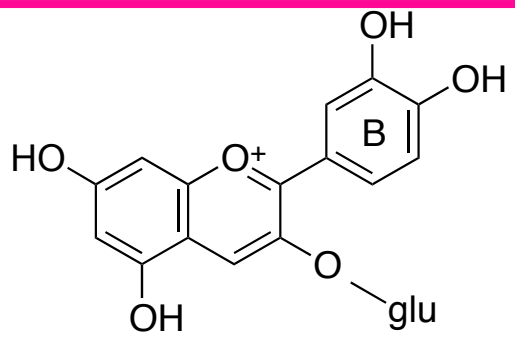


Malvidin

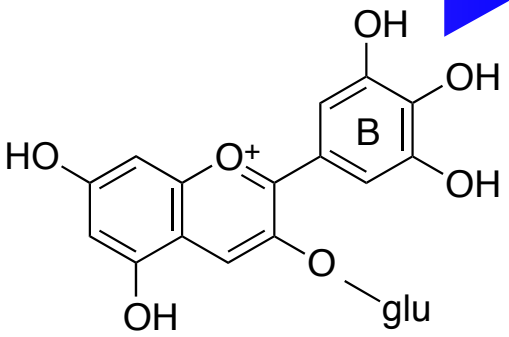
Anthocyanin color



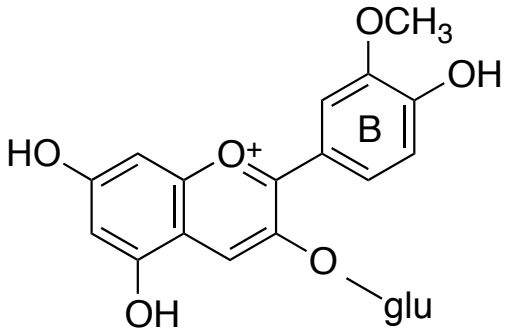
Pelargonidin



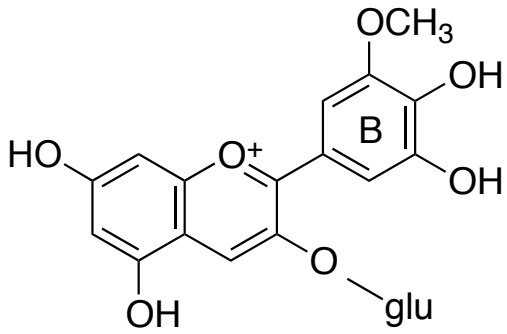
Cyanidin



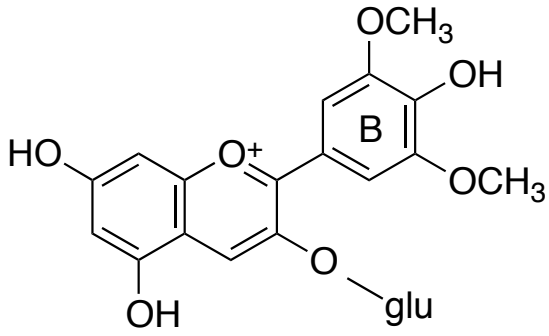
Delphinidin



Peonidin

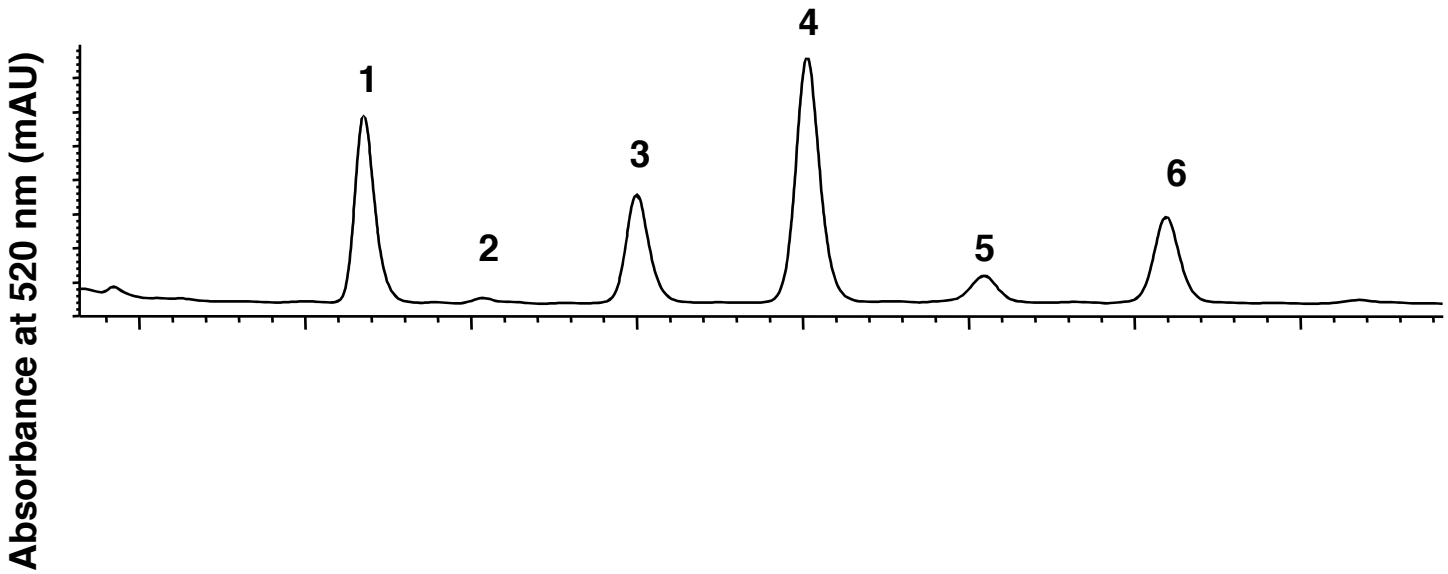


Petunidin



Malvidin

American cranberry product authenticity



1= cyd-gal

2= cyd-glu

3= cyd-arab

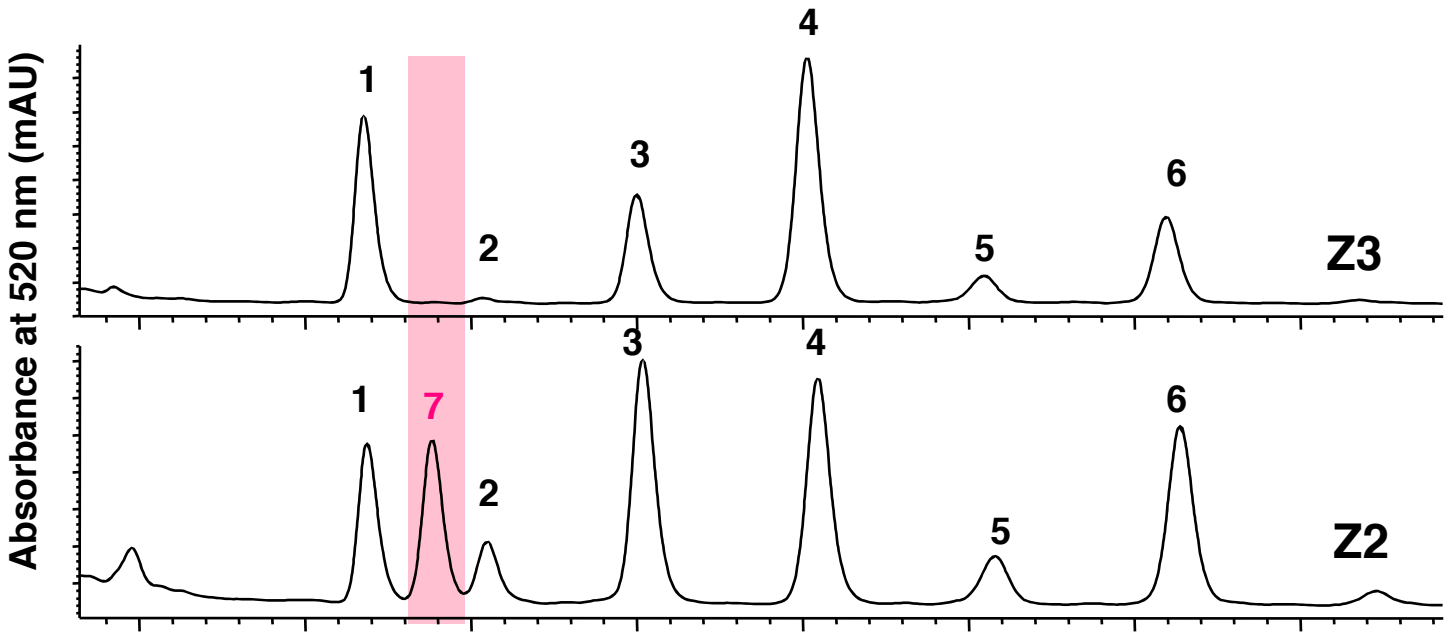
4= ped-gal

5= ped-glu

6= ped-arab

Lee (2013)

American cranberry product authenticity



1= cyd-gal

2= cyd-glu

3= cyd-arab

4= ped-gal

5= ped-glu

6= ped-arab

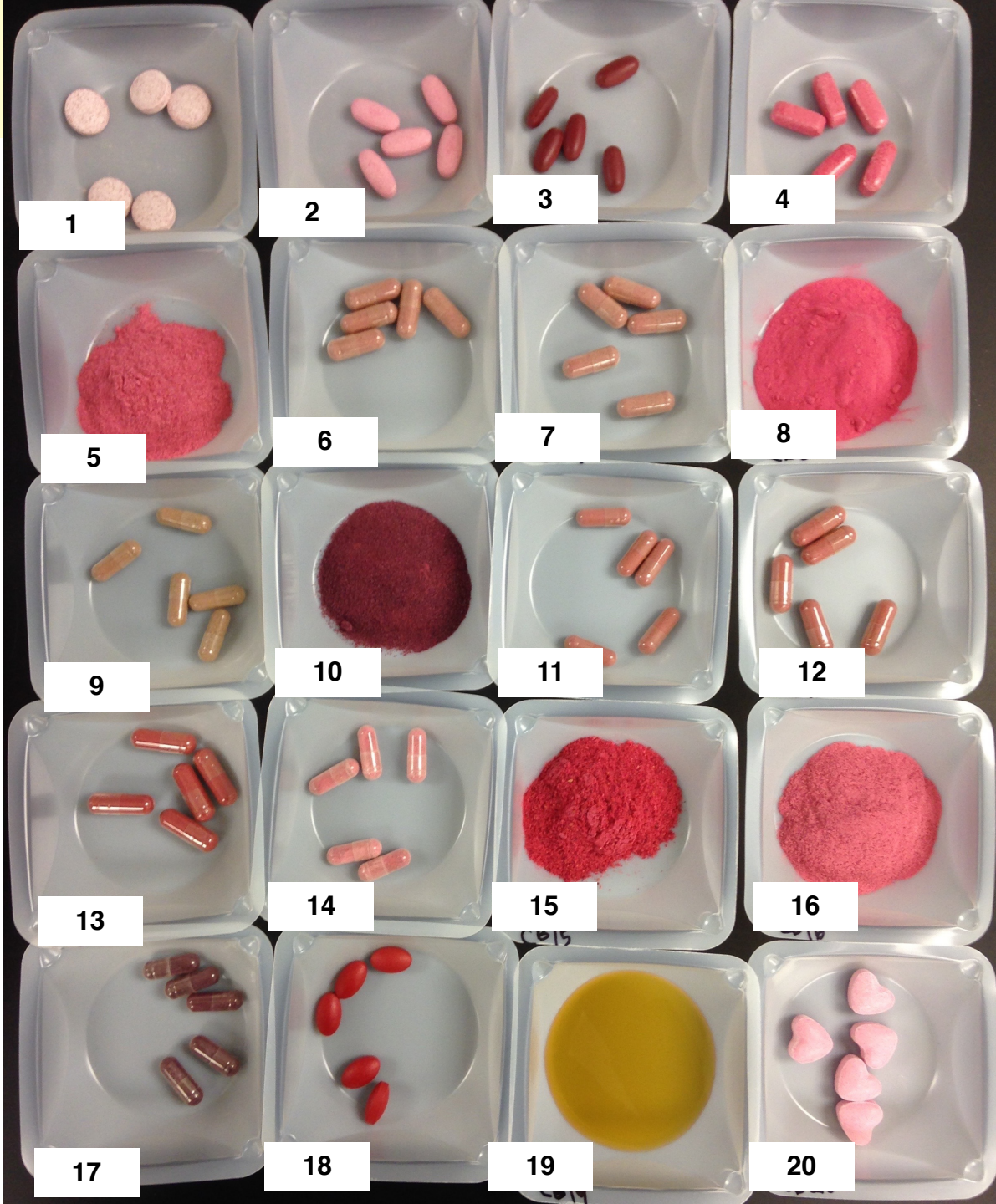
7= ??

Sample "Z3" typical cranberry fruit / juice anthocyanin profile

Peak 7 = peak not found in American cranberry fruit

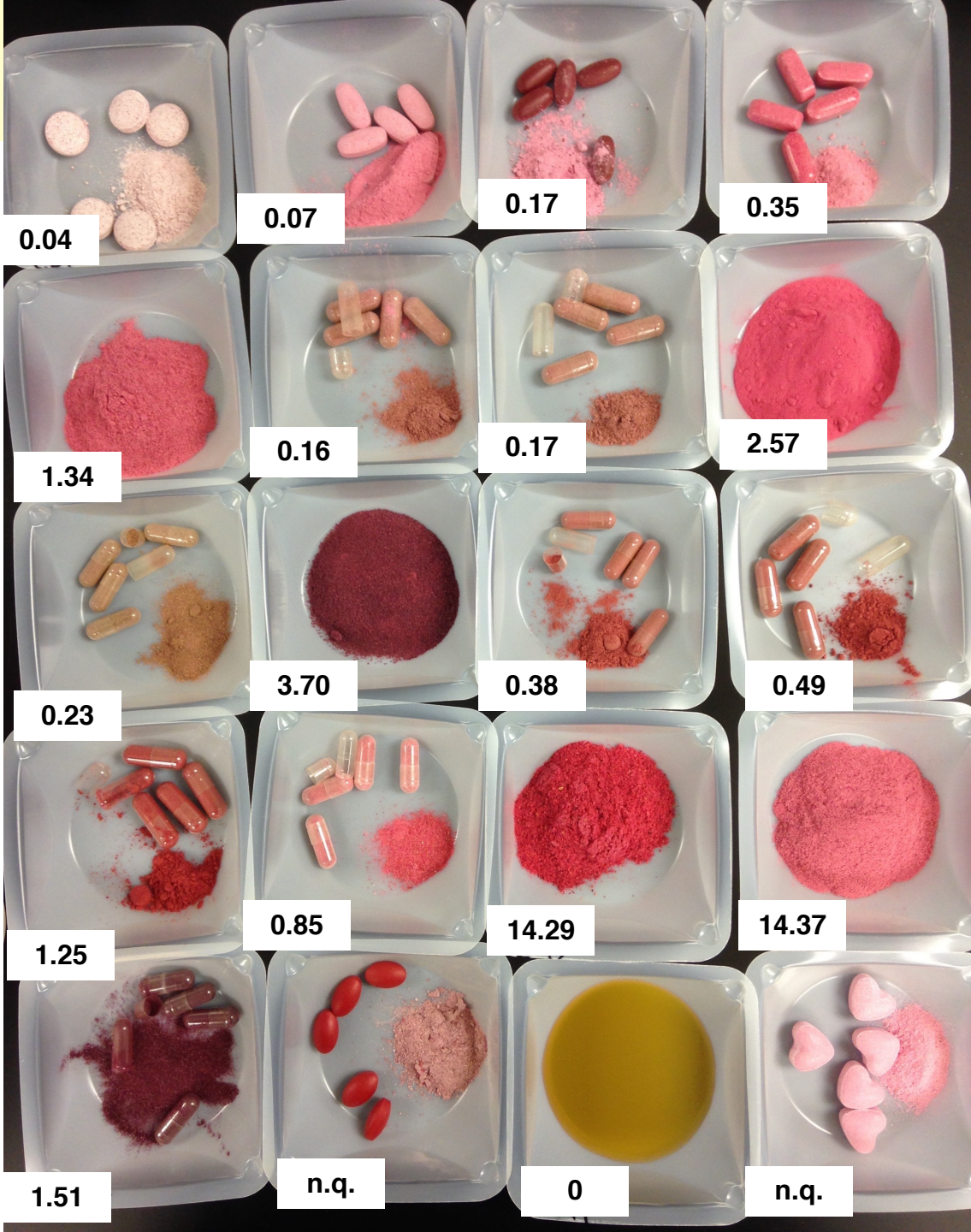
Lee (2013)

Cranberry dietary supplements



(Lee, 2016)

Cranberry dietary supplements (in mg / capsule, tablet, or tsp)



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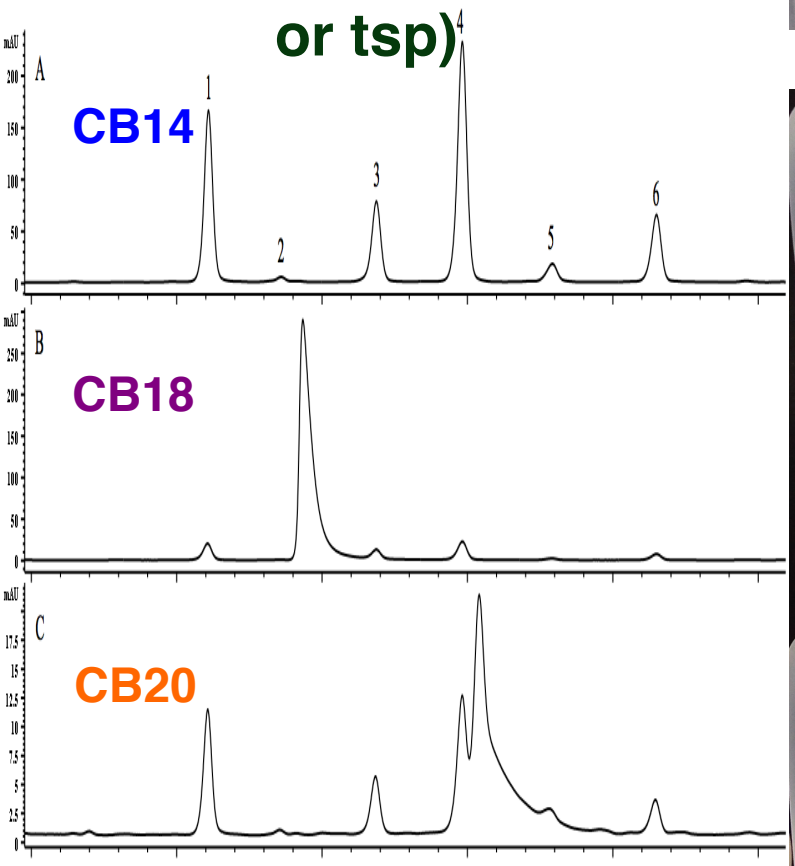

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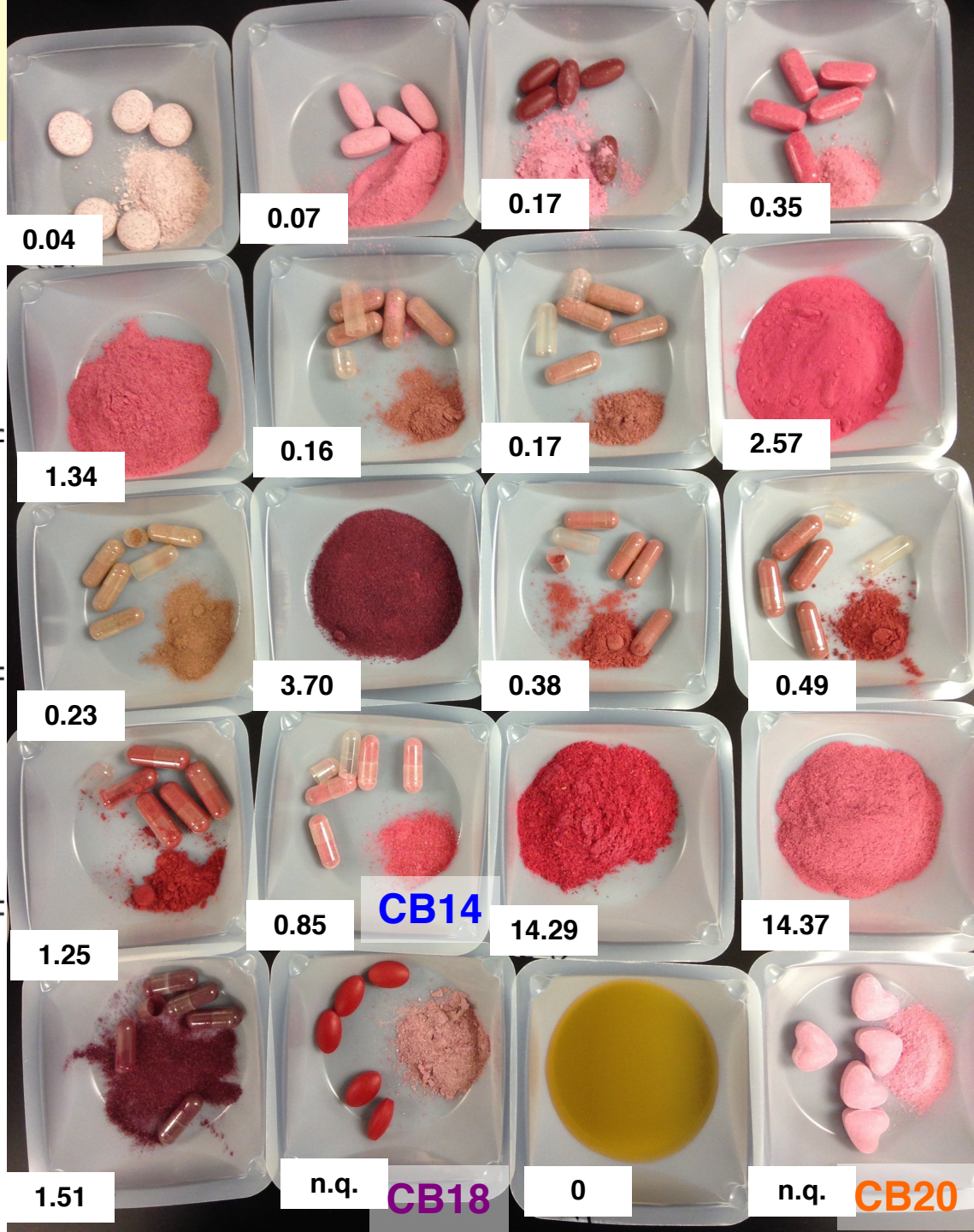
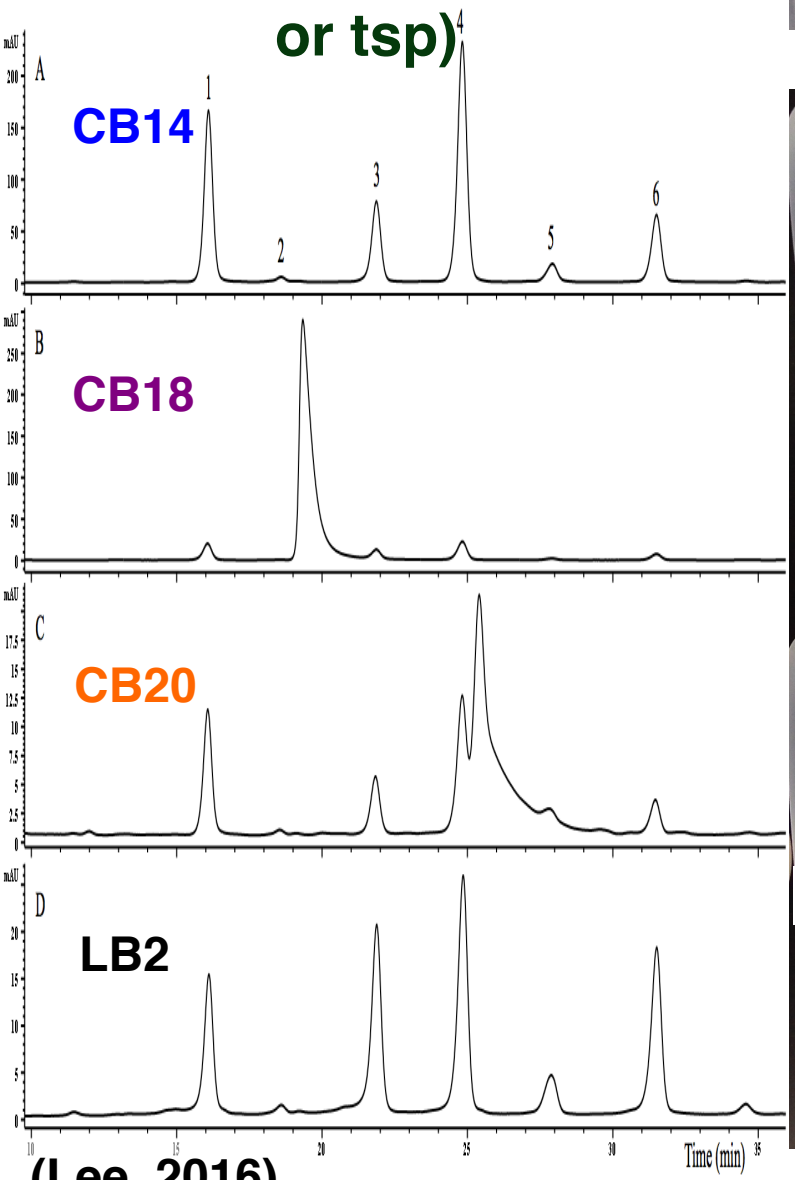
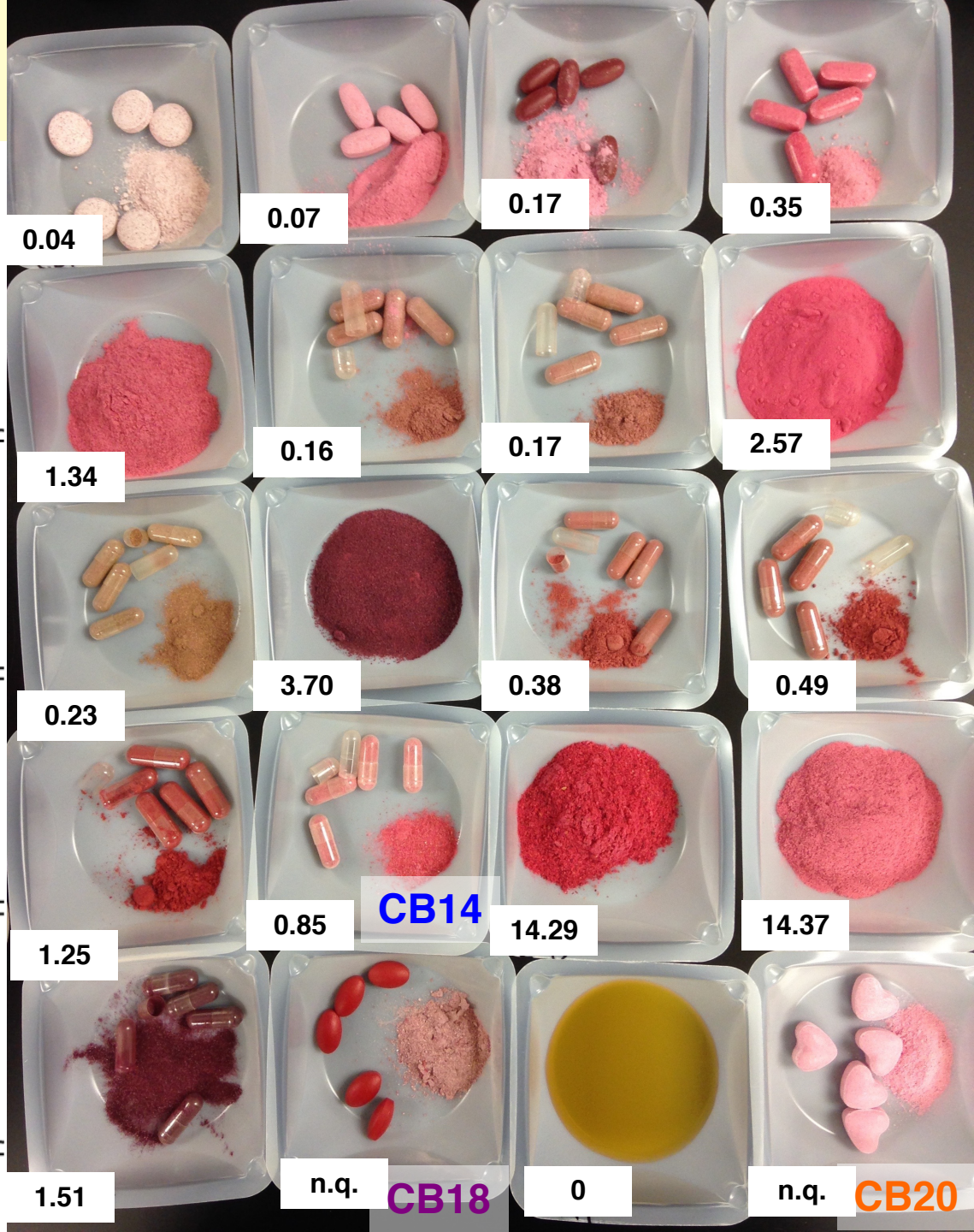


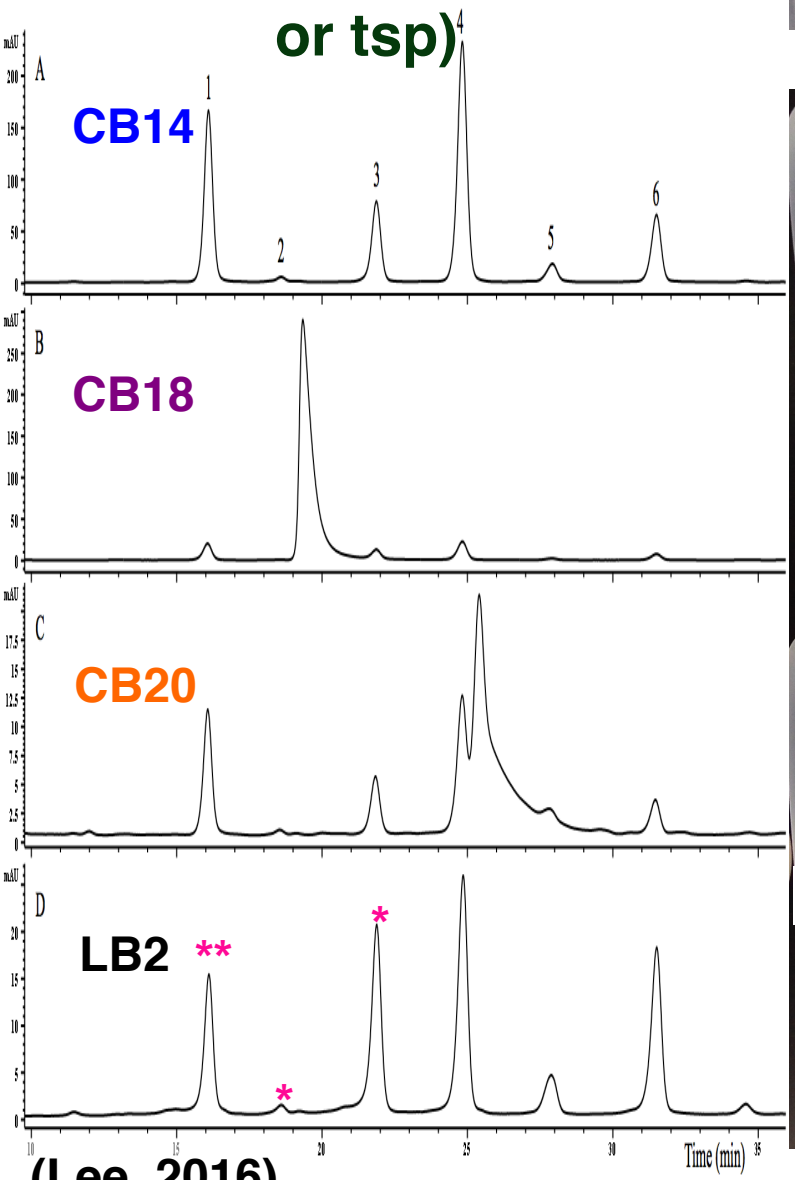
Cranberry dietary supplements (in mg / capsule, tablet, or tsp)



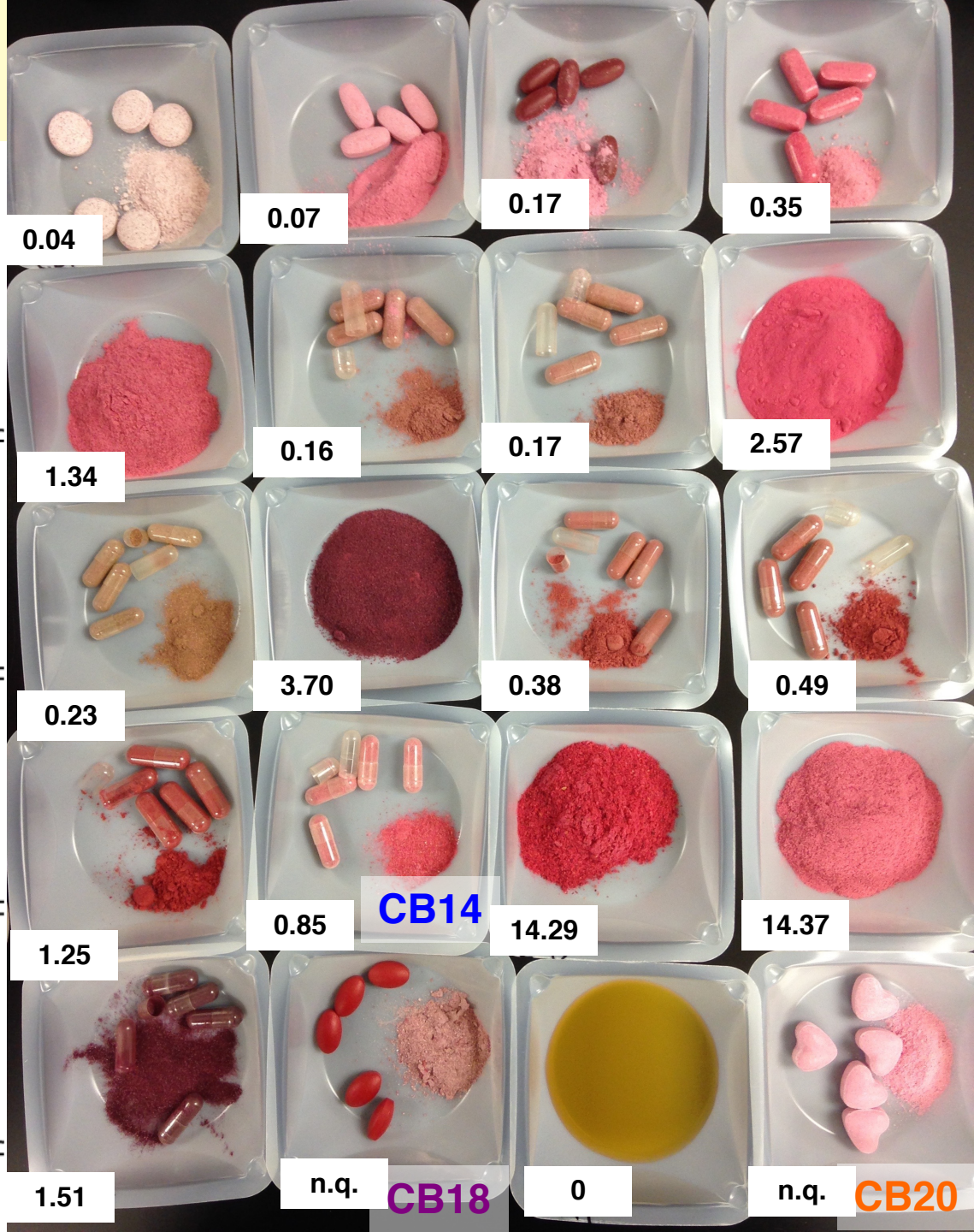
(Lee, 2016)



Cranberry dietary supplements (in mg / capsule, tablet, or tsp)



(Lee, 2016)

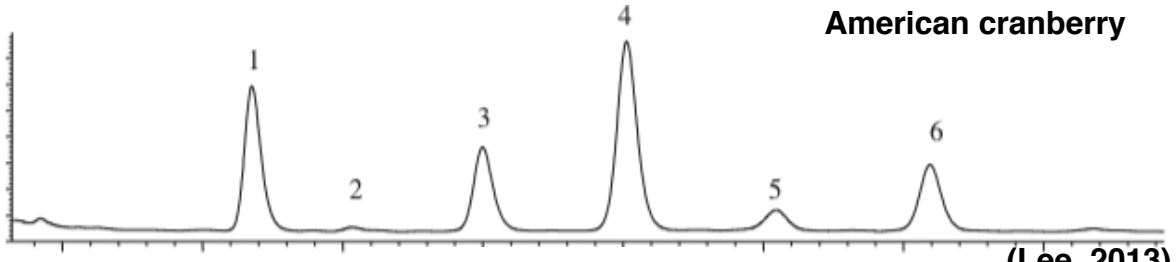


Anthocyanins in cranberry

	V. macrocarpon	*V. oxycoccus*
dpd	-	+
cyd	+	+
ped	+	-

Anthocyanins in cranberry

	V. macrocarpon	*V. oxycoccus*
dpd	-	+
cyd	+	+
ped	+	-



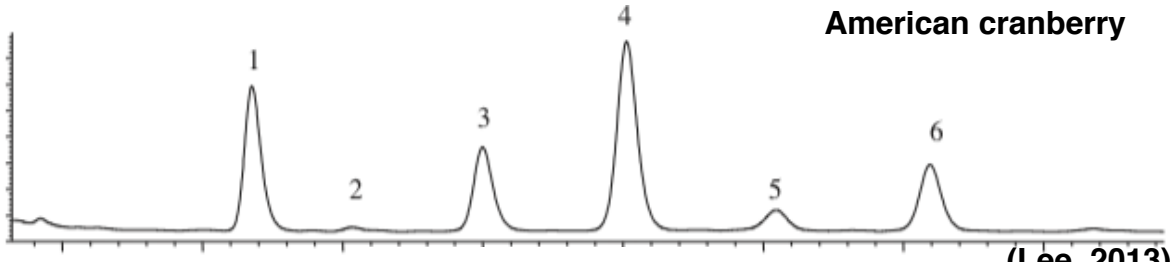
American cranberry

(Lee, 2013)

1= cyd-gal, 2= cyd-glu, 3= cyd-arab, 4= ped-gal, 5= ped-glu, and 6= ped-arab

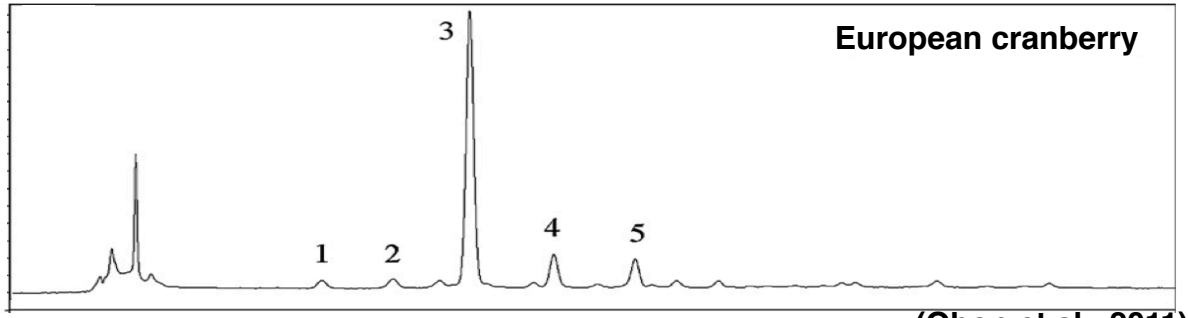
Anthocyanins in cranberry

	V. macrocarpon	*V. oxycoccus*
dpd	-	+
cyd	+	+
ped	+	-



(Lee, 2013)

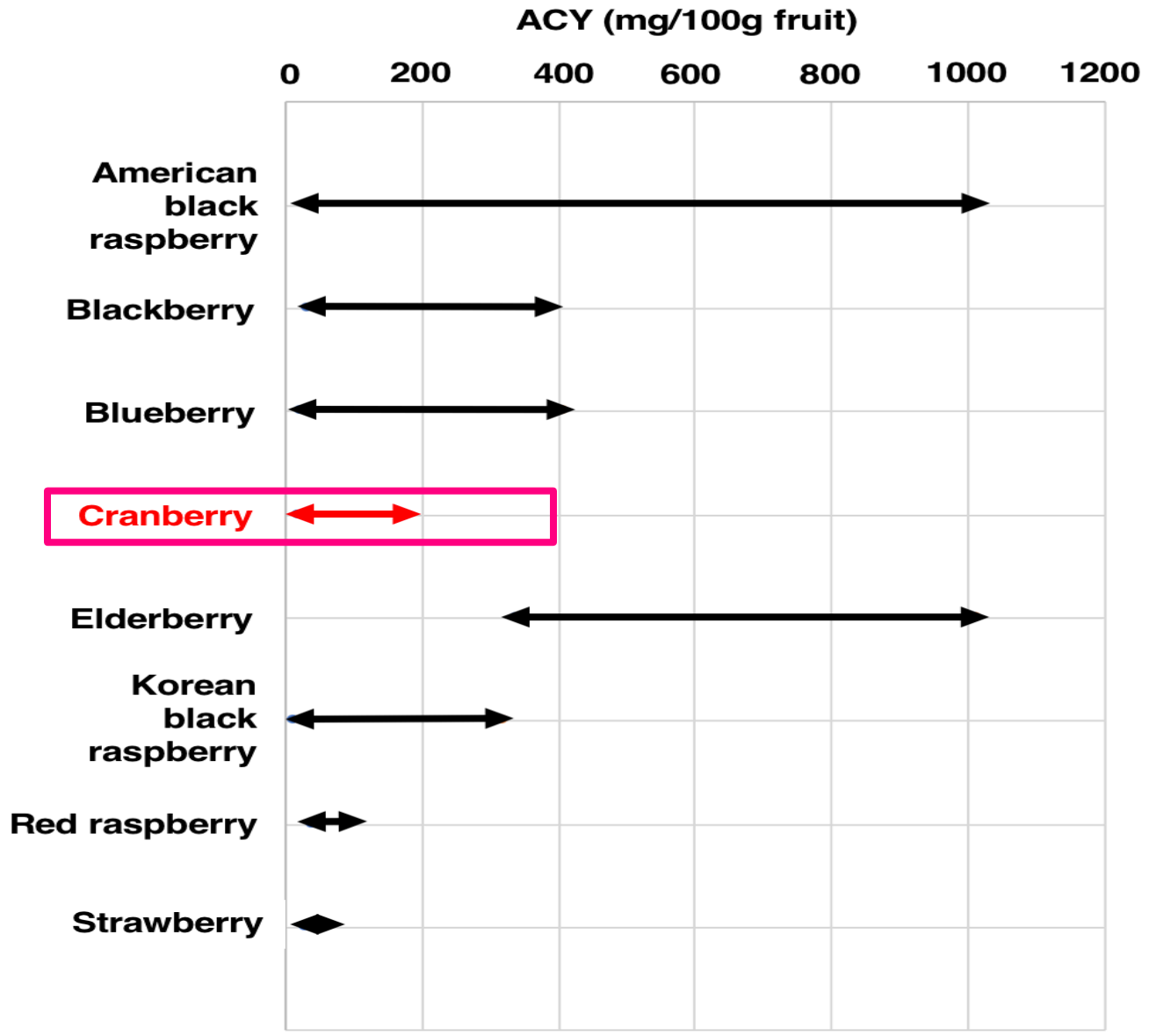
1= cyd-gal, 2= cyd-glu, 3= cyd-arab, 4= ped-gal, 5= ped-glu, and 6= ped-arab



(Obon et al., 2011)

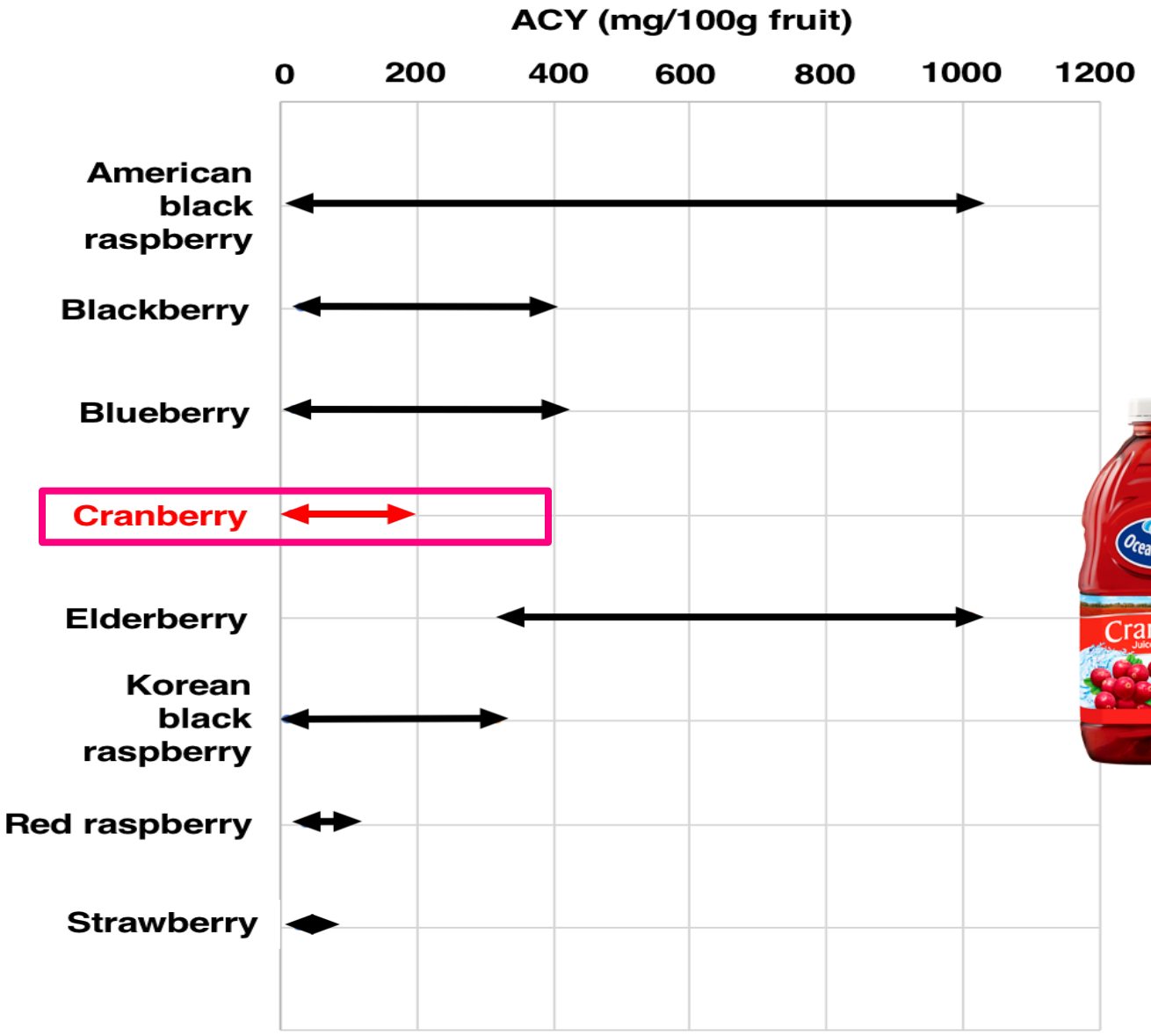
1= dpd-gal, 2= dpd-glu, 3= cyd-gal, 4= cyd-glu, and 5= cyd-arab

Anthocyanin ranges

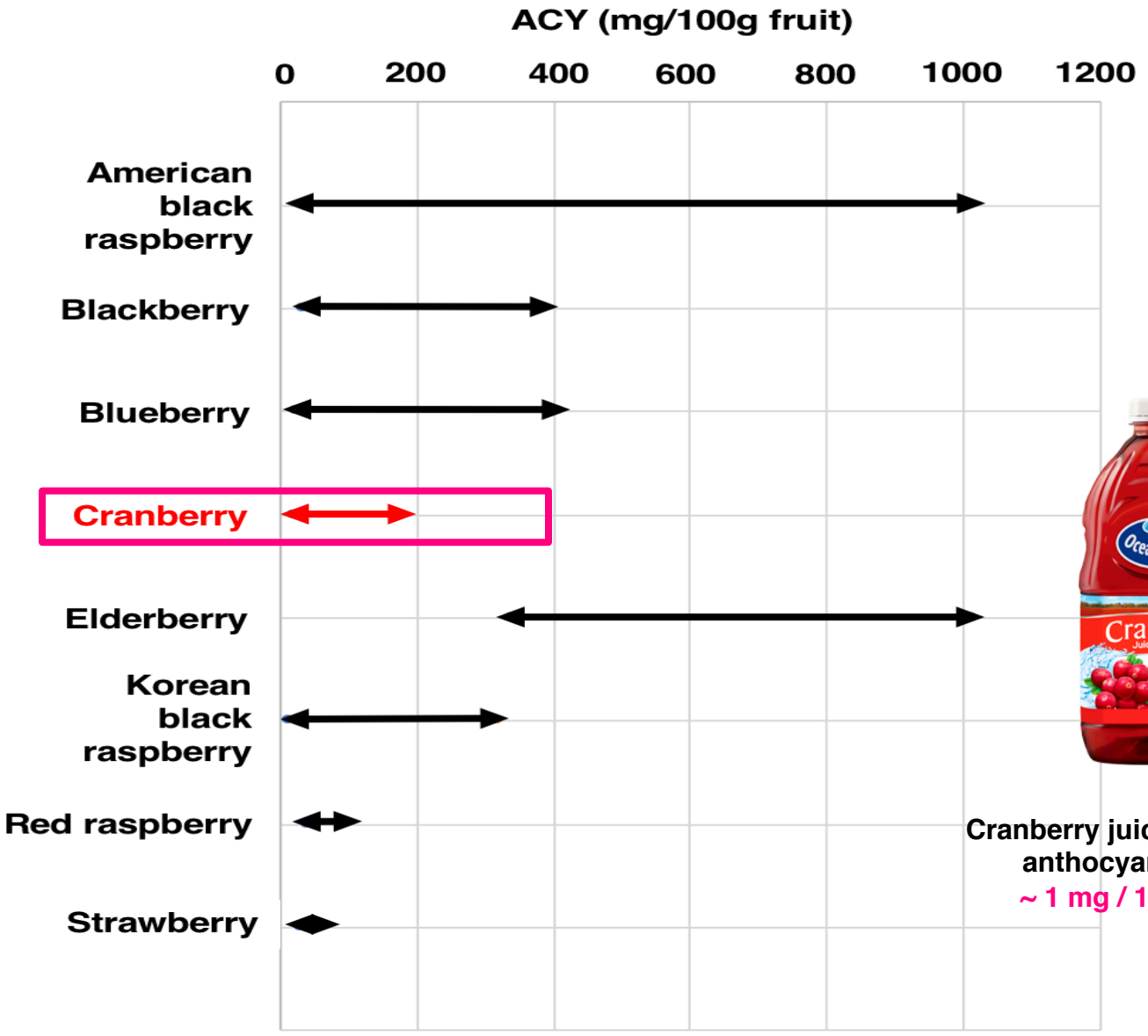


(Lee, 2013, 2016, 2017; Lee & Finn, 2007; Lee et al., 2004, 2012, 2013)

Anthocyanin ranges

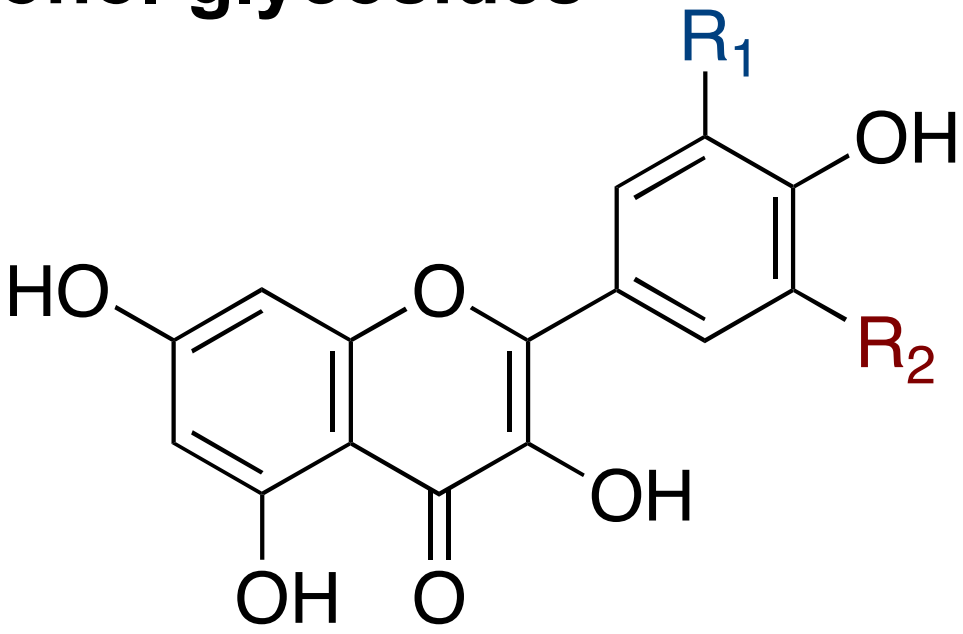


Anthocyanin ranges

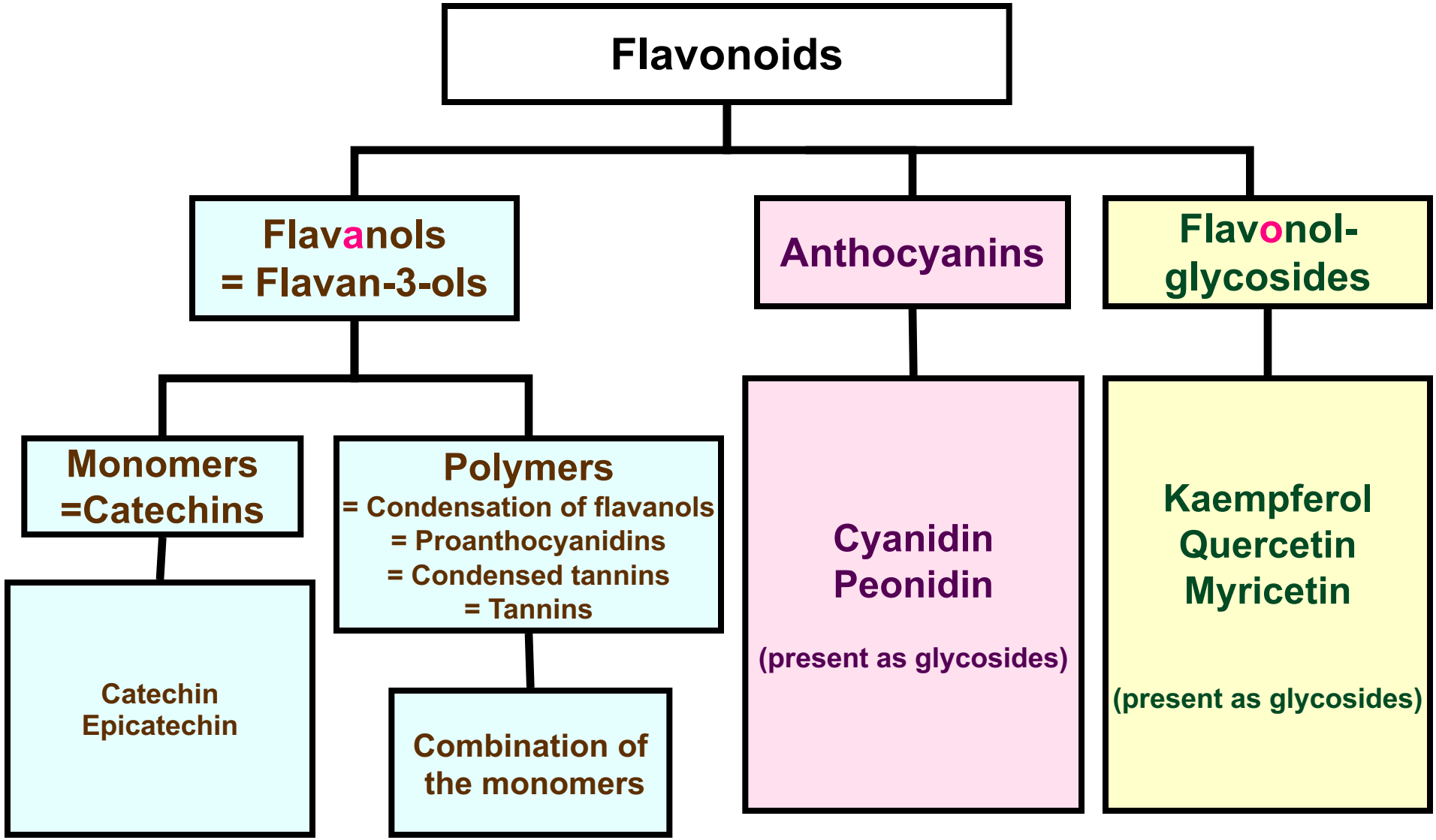


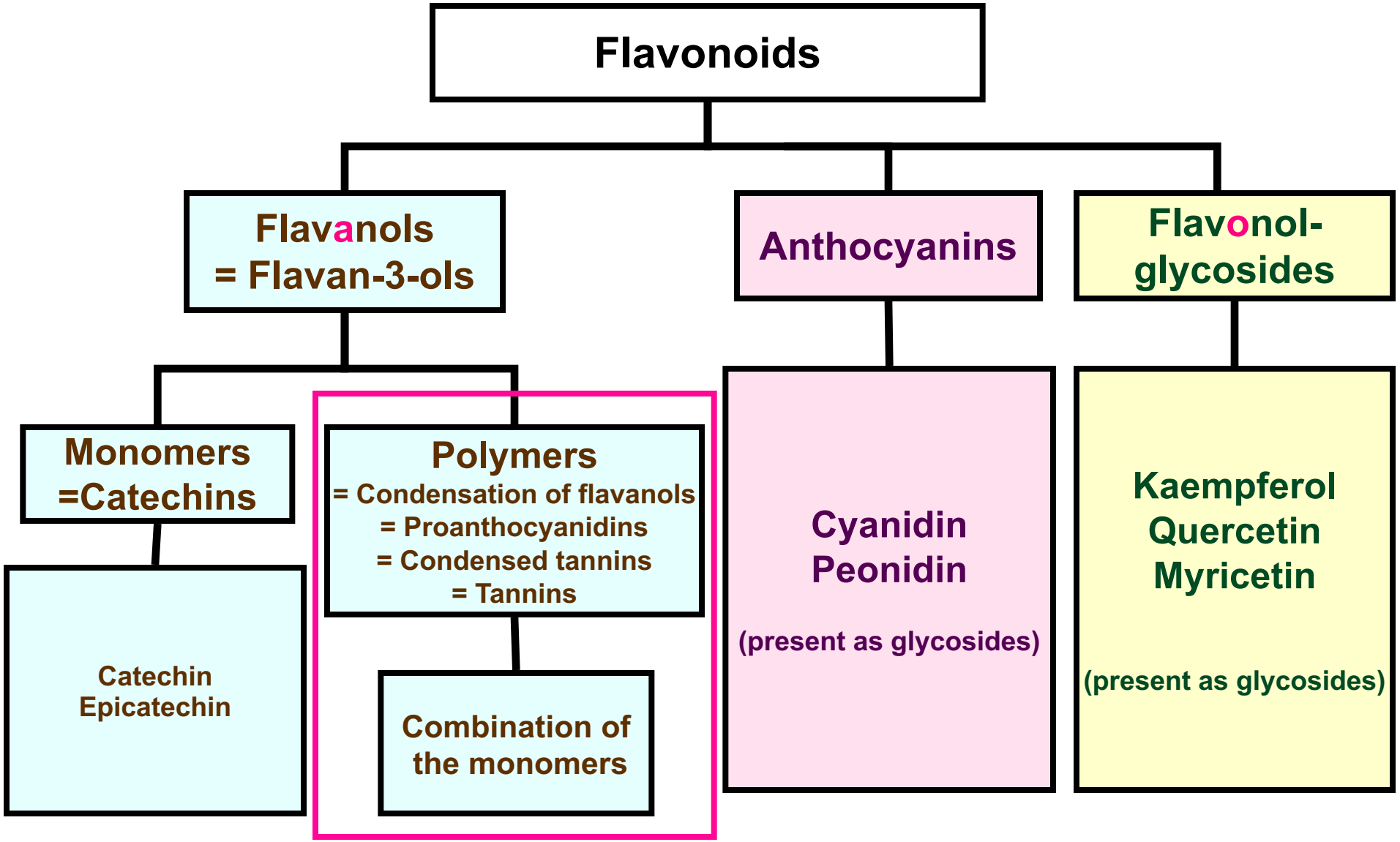
Cranberry juice cocktail anthocyanins =
~ 1 mg / 100 mL

Flavonol-glycosides



R_1=H	R_2=H	Kaempferol
R_1=OH	R_2=H	Quercetin
R_1=OH	R_2=OH	Myricetin


Flavonoids
Flavanols
= Flavan-3-ols
Anthocyanins
Flavonol-
glycosides
Monomers
=Catechins
Polymers
= Condensation of flavanols
= Proanthocyanidins
= Condensed tannins
= Tannins
Cyanidin
Peonidin
(present as glycosides)
Kaempferol
Quercetin
Myricetin
(present as glycosides)
Catechin
Epicatechin
Combination of
the monomers


Flavonoids
Flavanols
= Flavan-3-ols
Anthocyanins
Flavonol-
glycosides
Monomers
=Catechins
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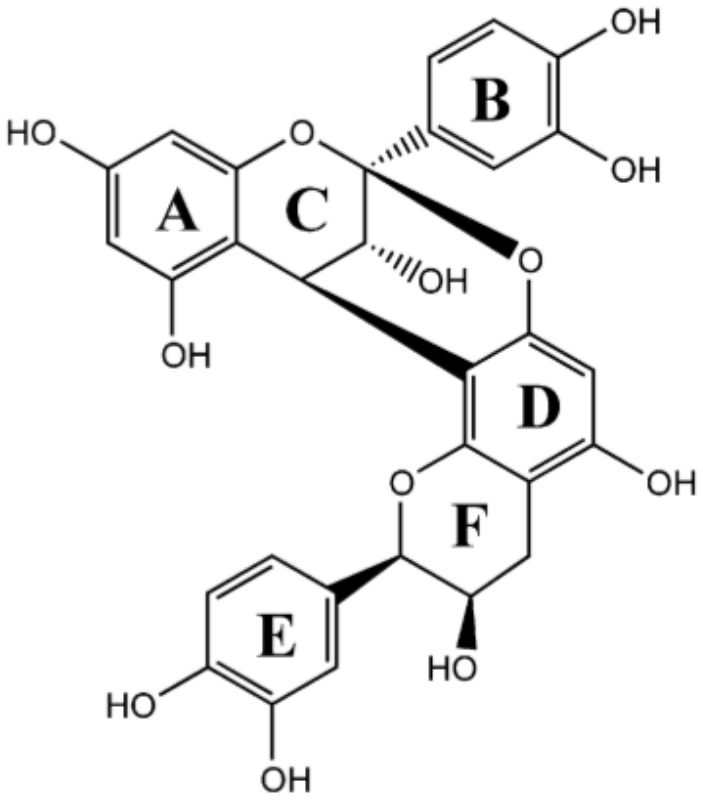
Cyanidin
Peonidin
(present as glycosides)
Kaempferol
Quercetin
Myricetin
(present as glycosides)
Catechin
Epicatechin
Combination of
the monomers

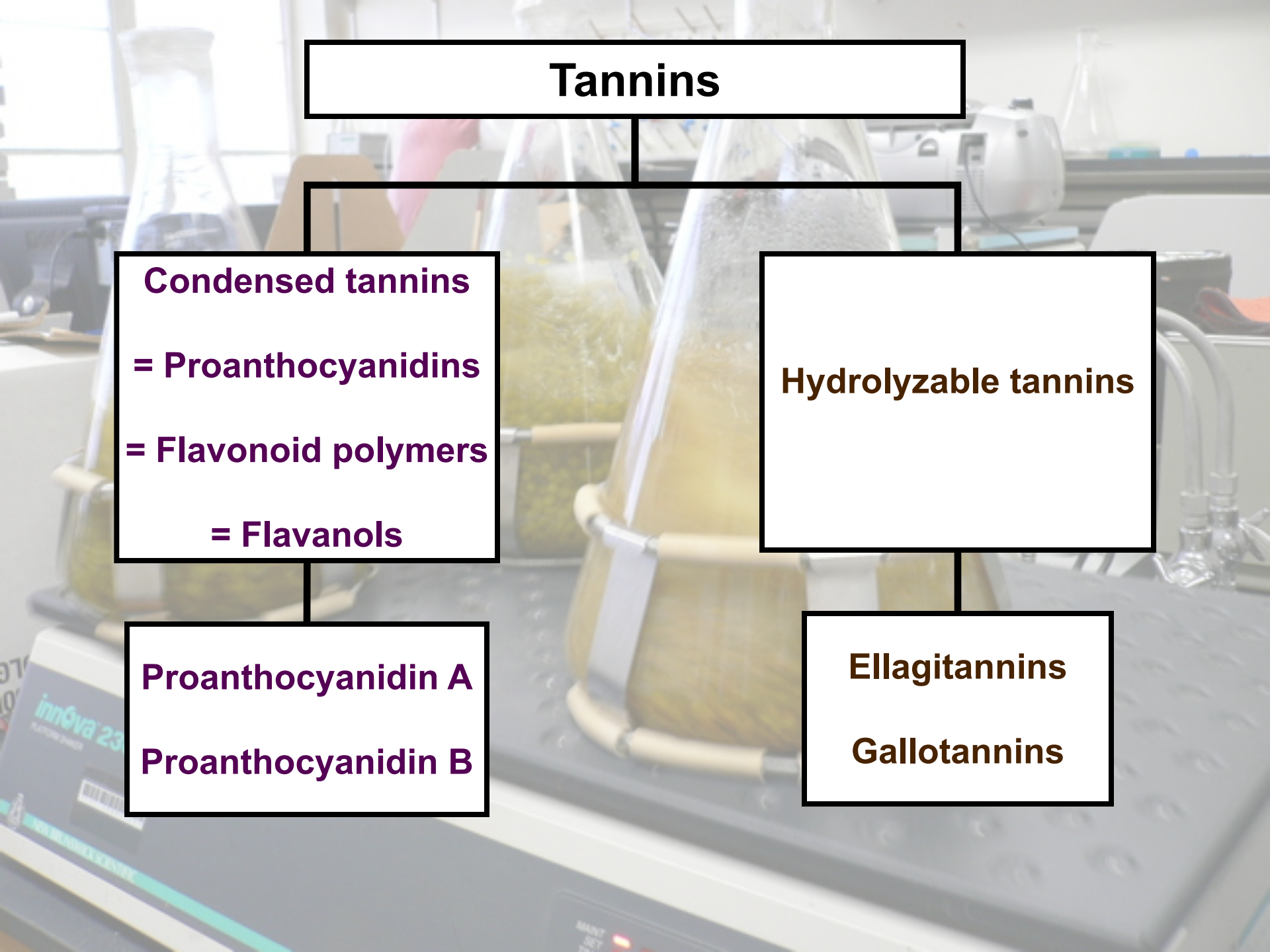
Cranberry supplement

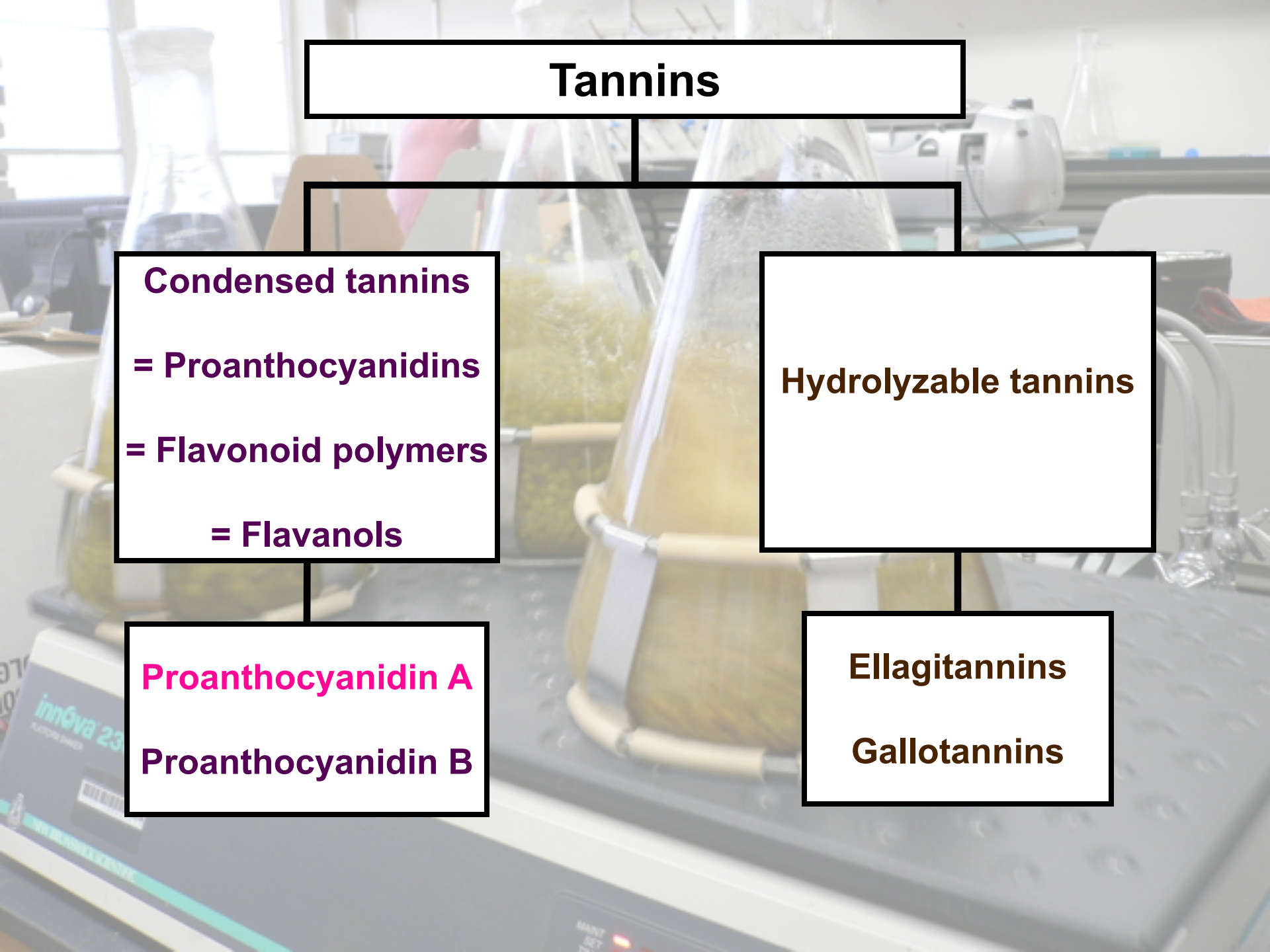

THE NEXT
SUPERFOOD
WAS DISCOVERED
IN 1647.
With proanthocyanidins that have kept
skin young for 371 years, no fruit on earth
takes care of you like a cranberry.
THE NECESSARY, LEGENDARY,
EXTRAORDINARY CRANBERRY
Ocean Spray

Proanthocyanidin = Procyanidin = PAC = PAs

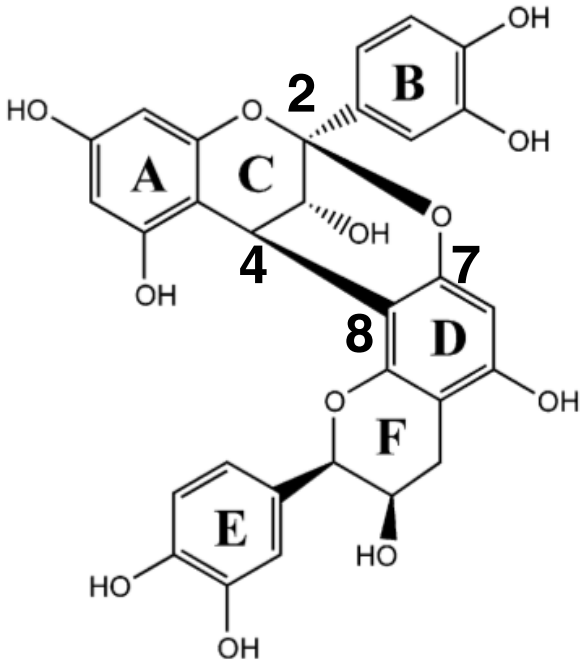


A2

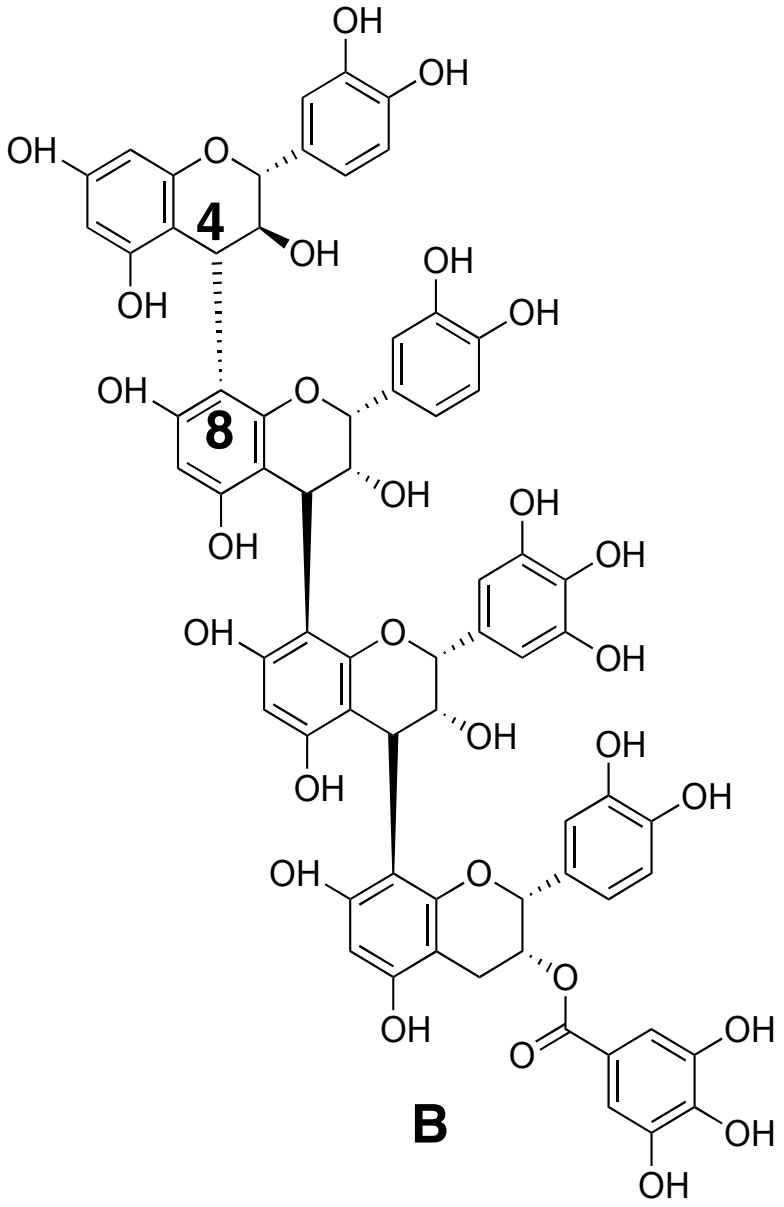

Tannins
Condensed tannins
= Proanthocyanidins
= Flavonoid polymers
= Flavanols
Hydrolyzable tannins
Proanthocyanidin A
Proanthocyanidin B
Ellagitannins
Gallotannins


Tannins
Condensed tannins
= Proanthocyanidins
= Flavonoid polymers
= Flavanols
Hydrolyzable tannins
Proanthocyanidin A
Proanthocyanidin B
Ellagitannins
Gallotannins

Proanthocyanidin A2 vs B

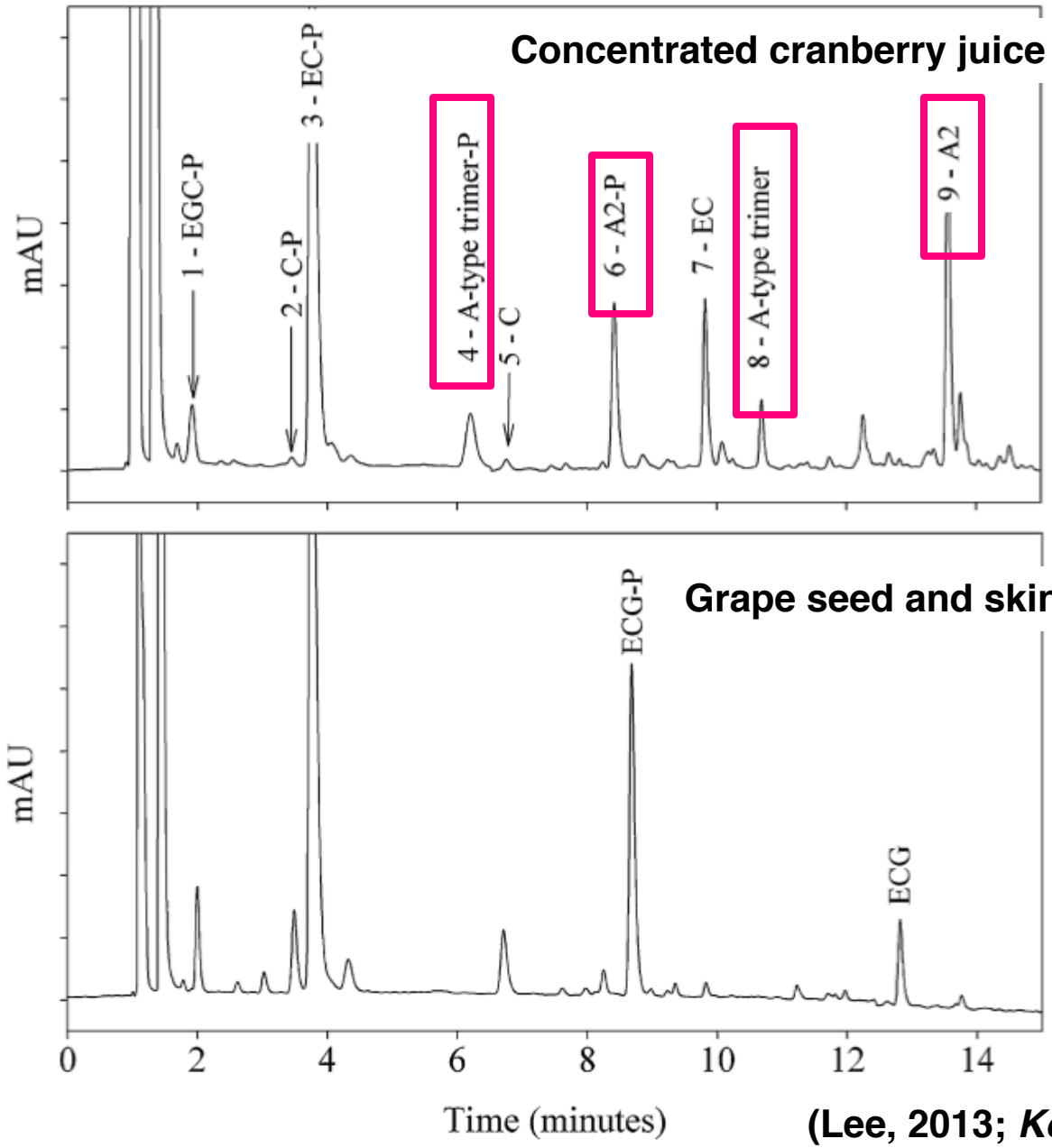


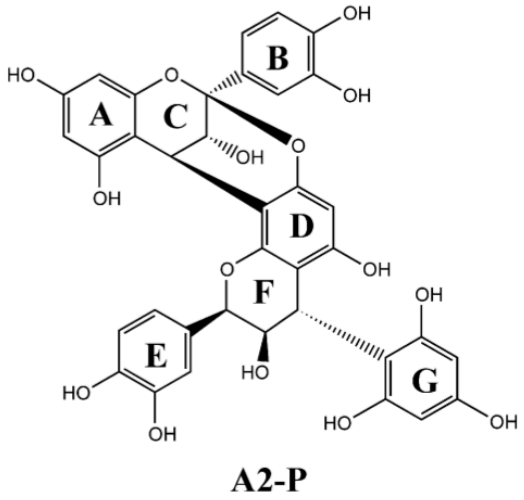
A2

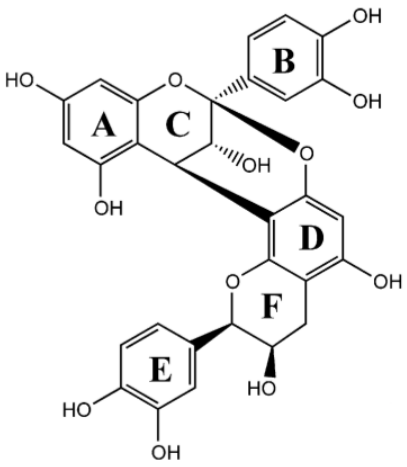


B

Cranberry proanthocyanidin A2 content

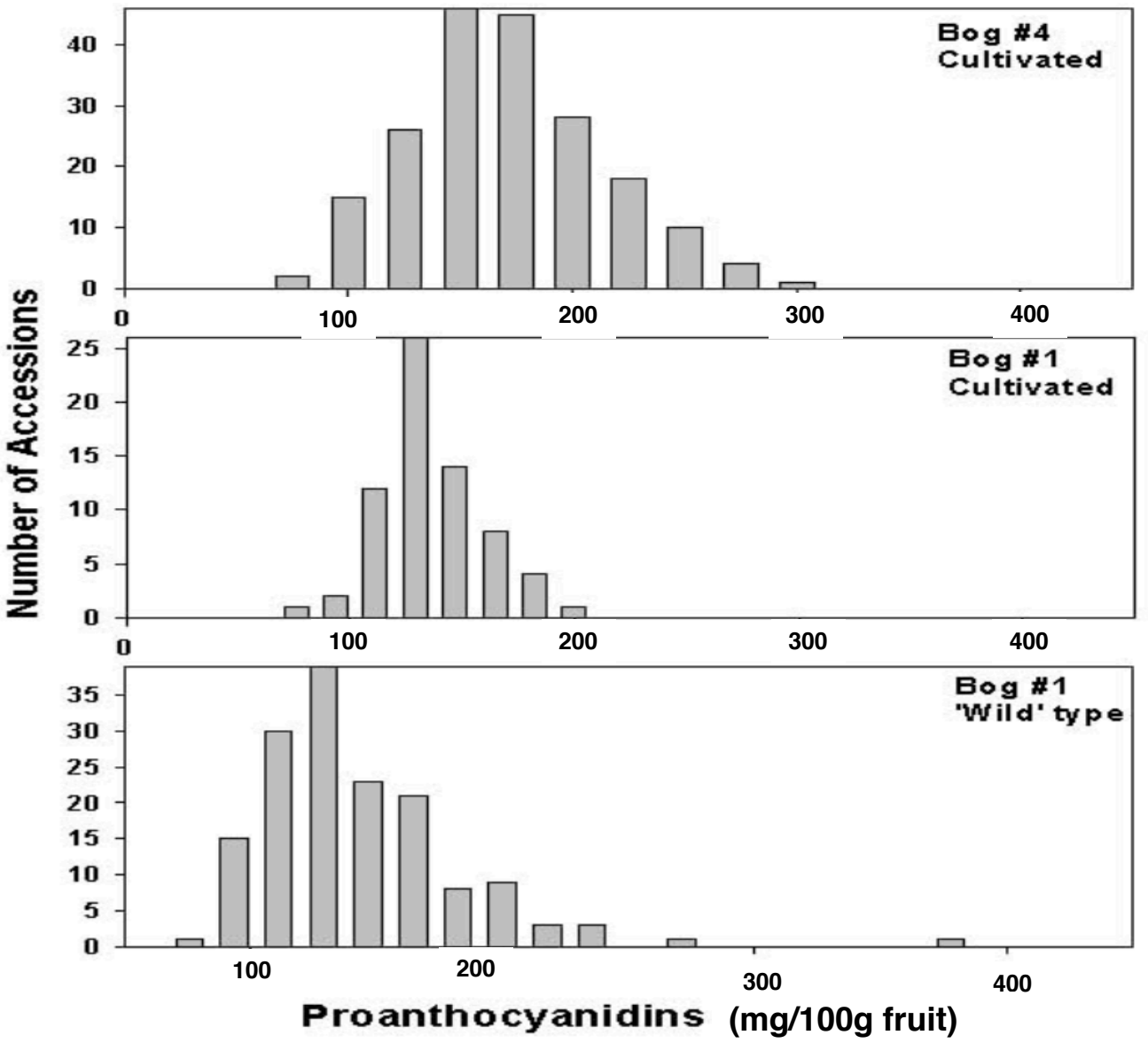






(Lee, 2013; *Koerner*, Hsu, Lee, & Kennedy, 2009)

Proanthocyanidin levels



(Vorsa and Johnson-Cicalese, 2007)

Proanthocyanidin levels among American cranberry, European cranberry, and lingonberry

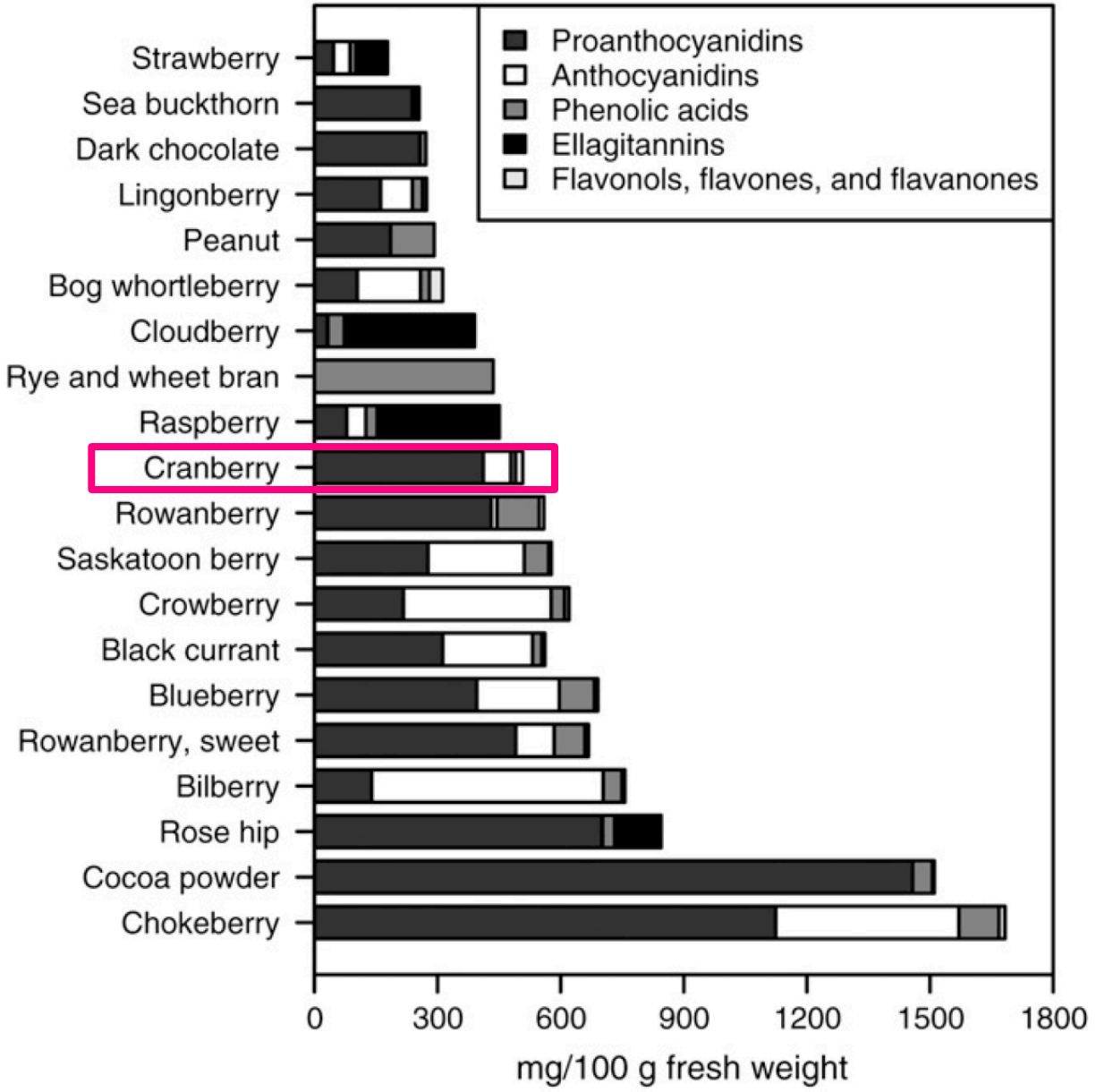
Table 2. Concentrations of Procyanidin A2 (mg/100 g) and A-Type Procyanidin Dimers (m/z 575) and Trimers m/z 863 (mg A2 equiv/100 g) in Fresh Berry Samples

			mg (A2 equiv)/100 g fresh weight (FW)[a]									
peak[b]	RT (min)	compd	*V. macrocarpon* (mixed)	*V. macrocarpon* (Ben Liar)	*V. macrocarpon* (Grygleski)	*V. macrocarpon* (Stevens)	*V. macrocarpon* (Pilgrim, CA)	*V. macrocarpon* (Pilgrim, PL)	*V. oxycoccus* (EU)	*V. oxycoccus* (PL)	*V. vitis-idaea* (EU)	*V. vitis-idaea* (CN)
6	19.81	dimer 1	0.12 ± 0.02	0.10 ± 0.02	0.13 ± 0.02	0.13 ± 0.01	0.10 ± 0.03	0.20 ± 0.04	0.18 ± 0.02	0.09 ± 0.02	5.94 ± 0.79	1.77 ± 0.20
8	21.30	A2	4.57 ± 0.34	4.14 ± 0.37	4.66 ± 0.78	4.71 ± 0.12	4.10 ± 0.12	5.49 ± 0.61	0.21 ± 0.03	0.13 ± 0.02	2.11 ± 0.27	7.98 ± 0.72
sum of A-type dimers (m/z 575)			4.69 ± 0.36	4.24 ± 0.39	4.79 ± 0.80	4.84 ± 0.13	4.20 ± 0.15	5.69 ± 0.65	0.39 ± 0.05	0.22 ± 0.04	8.05 ± 1.06	9.75 ± 0.92
1	14.99	trimer 1	nd	nd	nd	nd	nd	nd	nd	nd	1.55 ± 0.22	0.29 ± 0.07
2	17.31	trimer 2	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.01	0.05 ± 0.00	0.08 ± 0.01	0.11 ± 0.01	0.28 ± 0.05	0.09 ± 0.01	1.03 ± 0.16	0.32 ± 0.02
3	17.45	trimer 3	0.68 ± 0.06	0.62 ± 0.06	0.67 ± 0.08	0.68 ± 0.04	0.71 ± 0.10	1.05 ± 0.14	0.20 ± 0.01	0.05 ± 0.01	0.22 ± 0.03	0.98 ± 0.12
4	18.59	trimer 4	1.82 ± 0.16	2.35 ± 0.32	3.30 ± 0.41	2.83 ± 0.30	2.49 ± 0.34	2.96 ± 0.49	nd	nd	0.82 ± 0.14	3.18 ± 0.77
5	19.60	trimer 5	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	nd	nd	1.10 ± 0.18	0.27 ± 0.05
7	20.85	trimer 6	0.04 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.07 ± 0.02	nd	nd	3.40 ± 0.45	0.60 ± 0.11
9	21.80	trimer 7	1.03 ± 0.08	1.14 ± 0.15	1.35 ± 0.21	1.37 ± 0.10	1.17 ± 0.18	1.40 ± 0.20	nd	nd	0.29 ± 0.04	1.59 ± 0.33
10	23.10	trimer 8	0.98 ± 0.09	1.04 ± 0.11	1.43 ± 0.015	1.29 ± 0.09	1.09 ± 0.13	1.35 ± 0.22	nd	nd	1.60 ± 0.31	0.46 ± 0.08
sum of A-type trimers (m/z 863)			4.66 ± 0.42	5.30 ± 0.67	6.93 ± 0.88	6.32 ± 0.55	5.62 ± 0.78	6.99 ± 1.09	0.48 ± 0.09	0.14 ± 0.02	10.01 ± 1.53	7.69 ± 1.55

[a]Values are given as the mean ± standard deviations (n = 6). Procyanidin A2 calibration curve was used for quantification. nd, not detected. [b]Peak numbers of trimers refer to Figure 2.

(Jungfer et al., 2012)

Compared to others. . .



(Ovaskainen et al., 2007)

Phenolic Distribution in Cranberry

Skin:
- Flavanols and their polymers
- Anthocyanins
- Cinnamic acids
- Flavonols
- Stilbenes

Pulp:
- Cinnamic acids
- Benzoic acids

Seed:
- Flavanols and their polymers

Thank you!

USDA - ARS

OR cranberry growers' association

WA cranberry growers' association

British Columbia cranberry growers' association

Pacific Northwest Cranberry Congress

Cassie Bouska - OSU