

“Quantità ed attività degli antiossidanti polifenolici della mela trentina”

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“Most nutritionists....are used to start from some general opinions taken for granted but being actually most debatable. First of all, it is generally assumed that all nutrients necessary for human health are really known. If health is defined as the highest level of physical and intellectual efficiency, this assumption is certainly not justified.”

“A second misconception underlies the widespread supposition that there be a sharp boundary between essential (indispensable) and non-essential nutrients. These arguments are not valid and can be refuted by a thorough examination of our vegetable food”

Joachim Kühnau, 1976

The Flavonoids: a class of semi-essential food components: their role in human nutrition. *Wld. Rev. Nutr.Diet.*, 24, 117-191

There are many compounds of plant origin biologically active in rather low concentrations which are so widely distributed in the vegetable world, and especially in our food plants, that a certain nutritive role and a “semi-essential” quality of these substances must be taken into consideration. This applies preferentially to the compounds with phenolic structure (...) and among them in the first line to the so-called flavonoids”

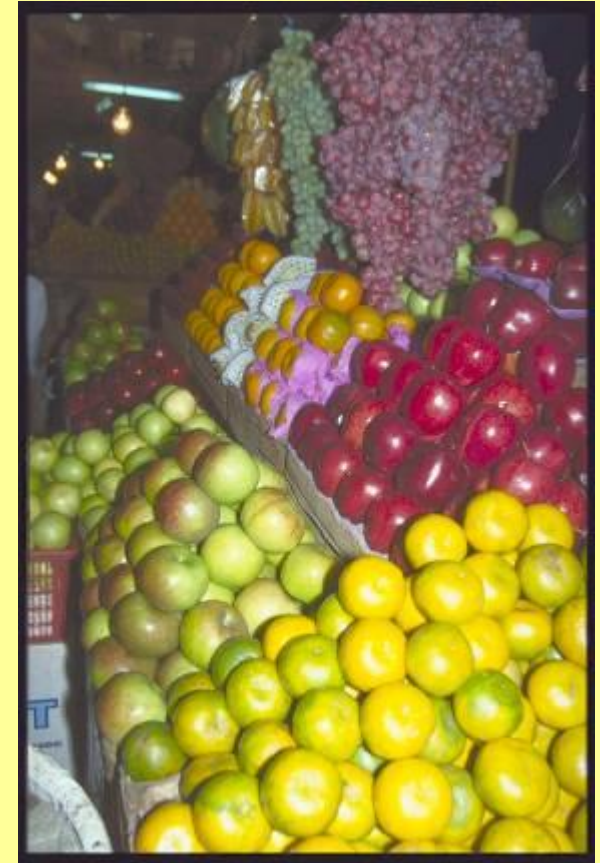
“The exact determination of the nutritional potency of flavonoids in vivo presents great difficulties due to the fact that a special experimental diet otherwise complete and palatable but totally devoided of flavonoids is not available”

Joachim Kühnau, 1976

The Flavonoids: a class of semi-essential food components: their role in human nutrition. *Wld. Rev. Nutr.Diet.*, 24, 117-191

Il consumo giornaliero di polifenoli, antiossidanti naturali che si ritiene giochino un ruolo protettivo sulla salute umana, è estremamente variabile in funzione del tipo di alimenti consumati

Nella dieta americana, è stato stimato intorno ad 1 g/die⁽¹⁾, valore tutt'ora ritenuto nel giusto ordine di grandezza ⁽²⁾

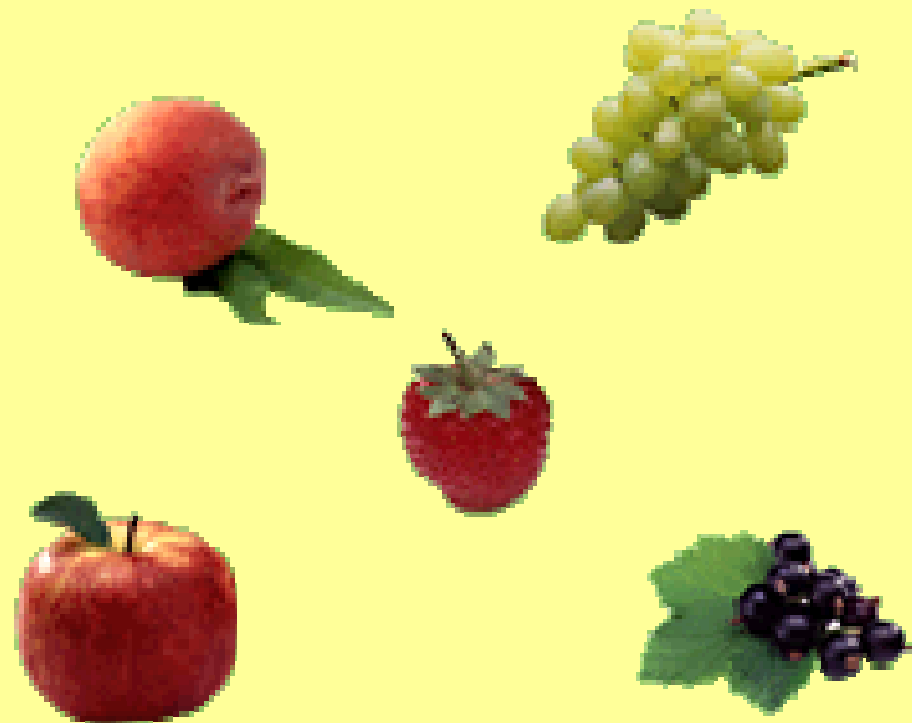


(1) Kühnau J., 1976, *World Rev. Nutr. Diet.*, 24: 117-191

(2) Scalbert & Williamson, 2000, *J. of Nutrition*, 2073S-2085S

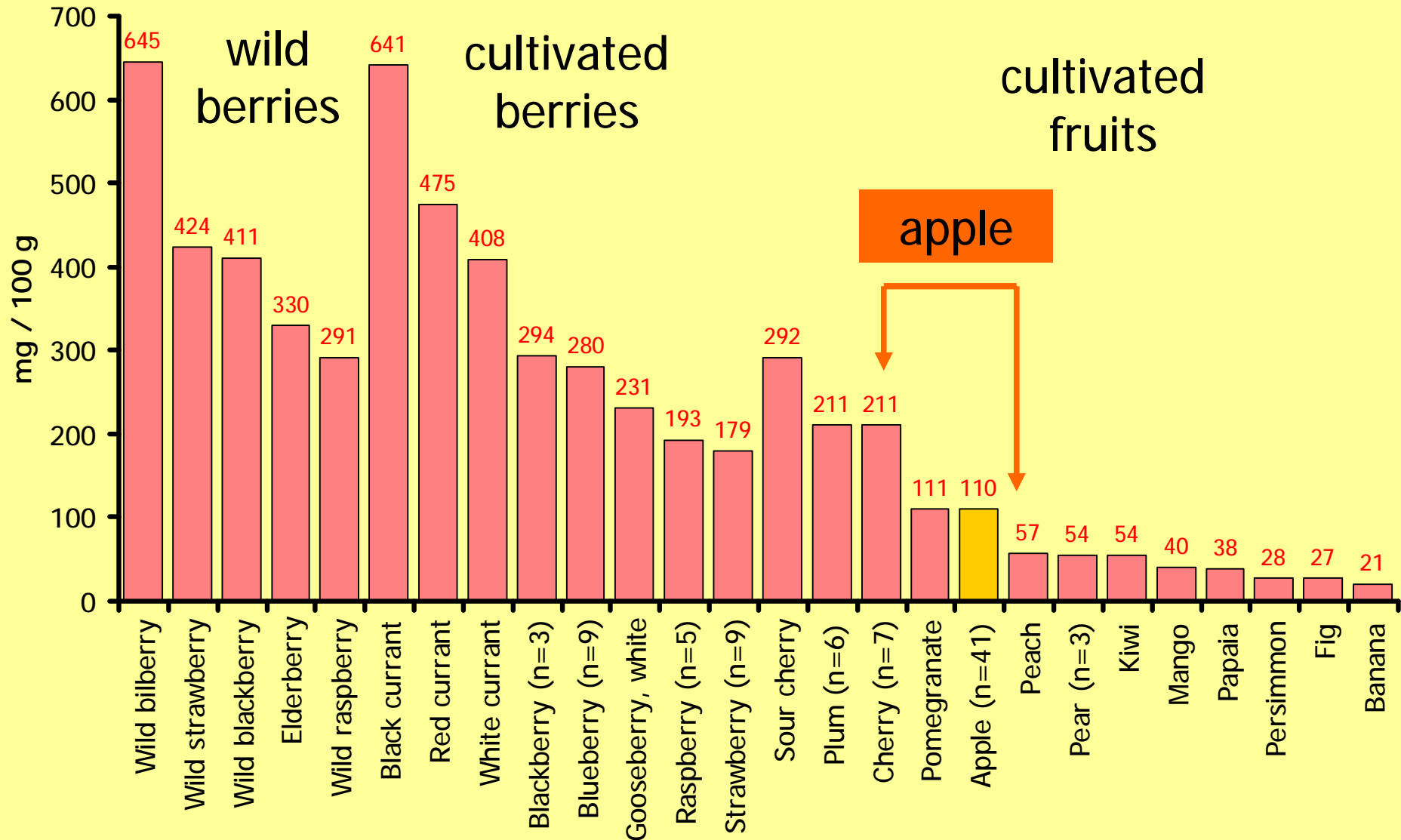


Quali frutti sono ricchi di polifenoli....?



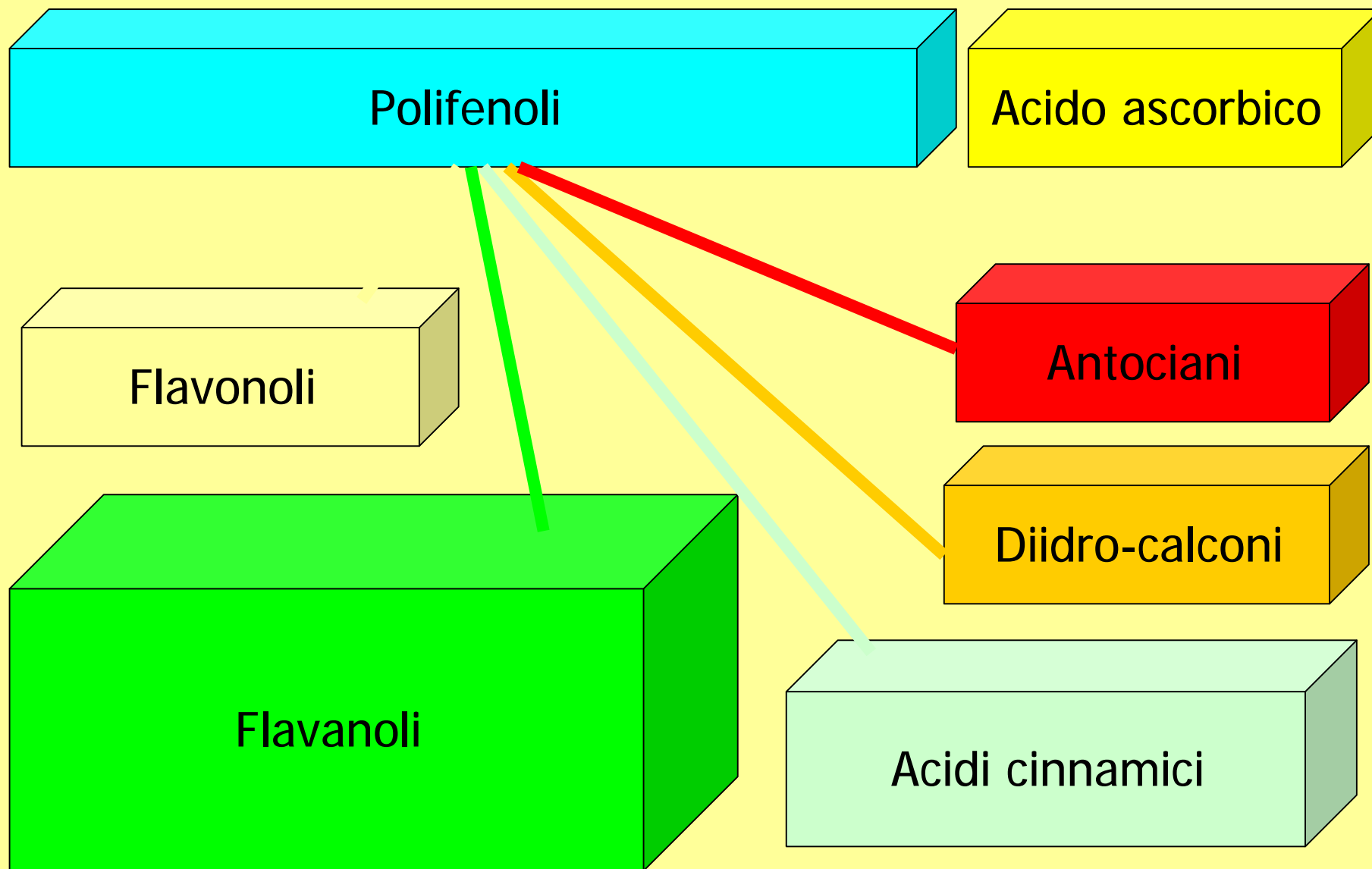


Frutta & polifenoli



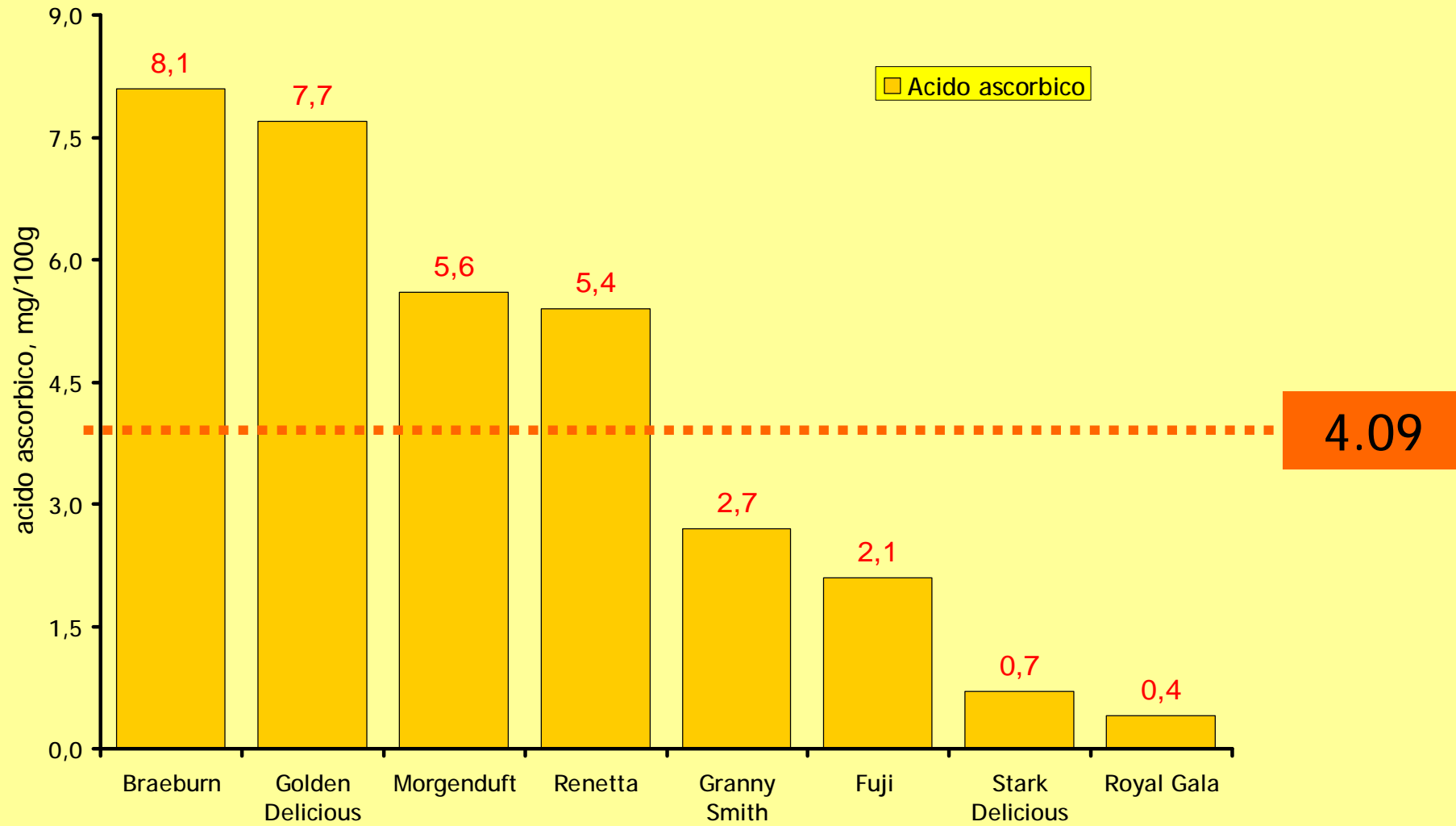
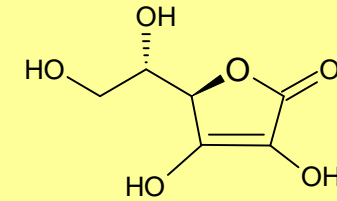


Gli antiossidanti nella mela





Acido ascorbico

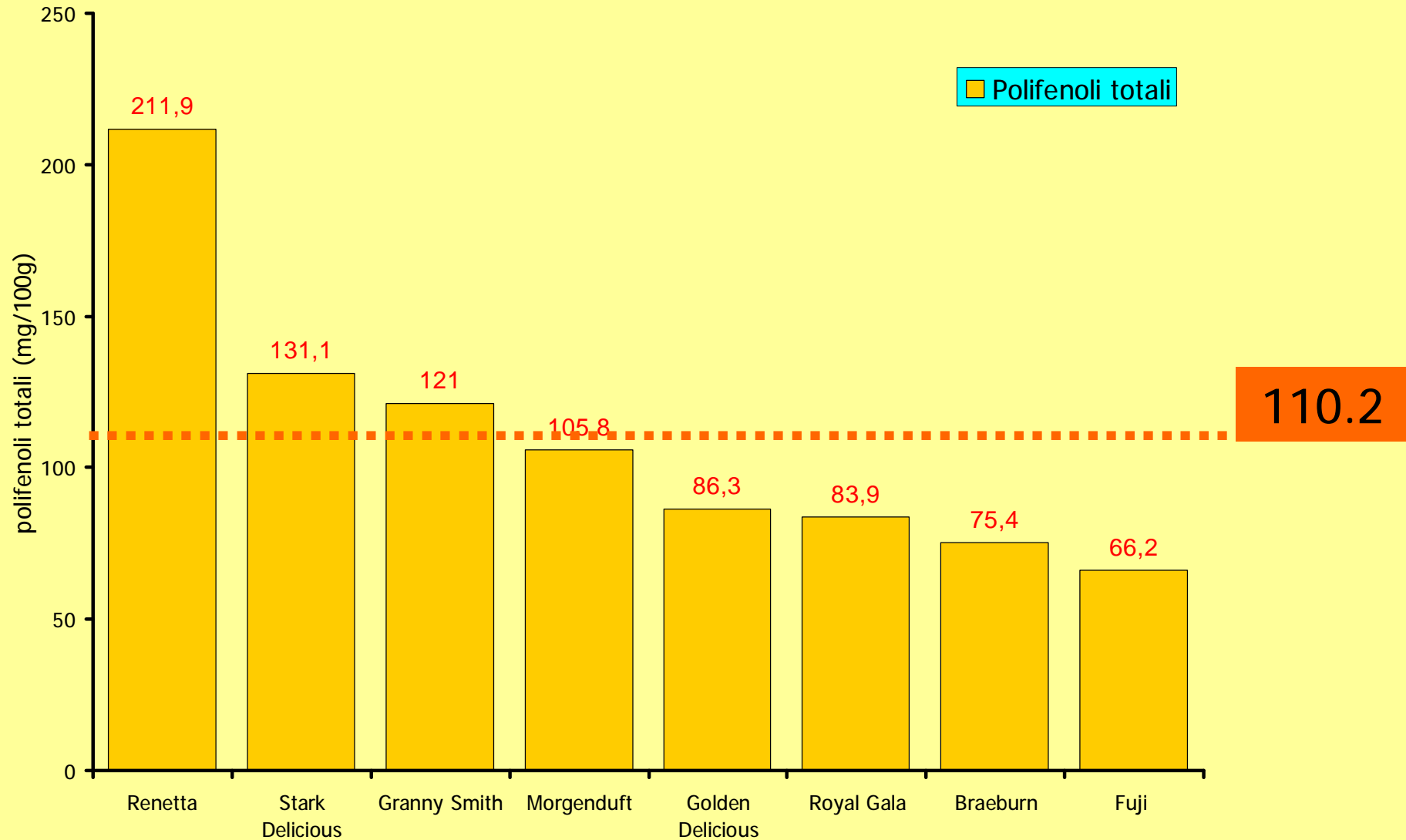


La mela ha una concentrazione media di polifenoli di ca. 110 mg/100 g ma sono tutte uguali?



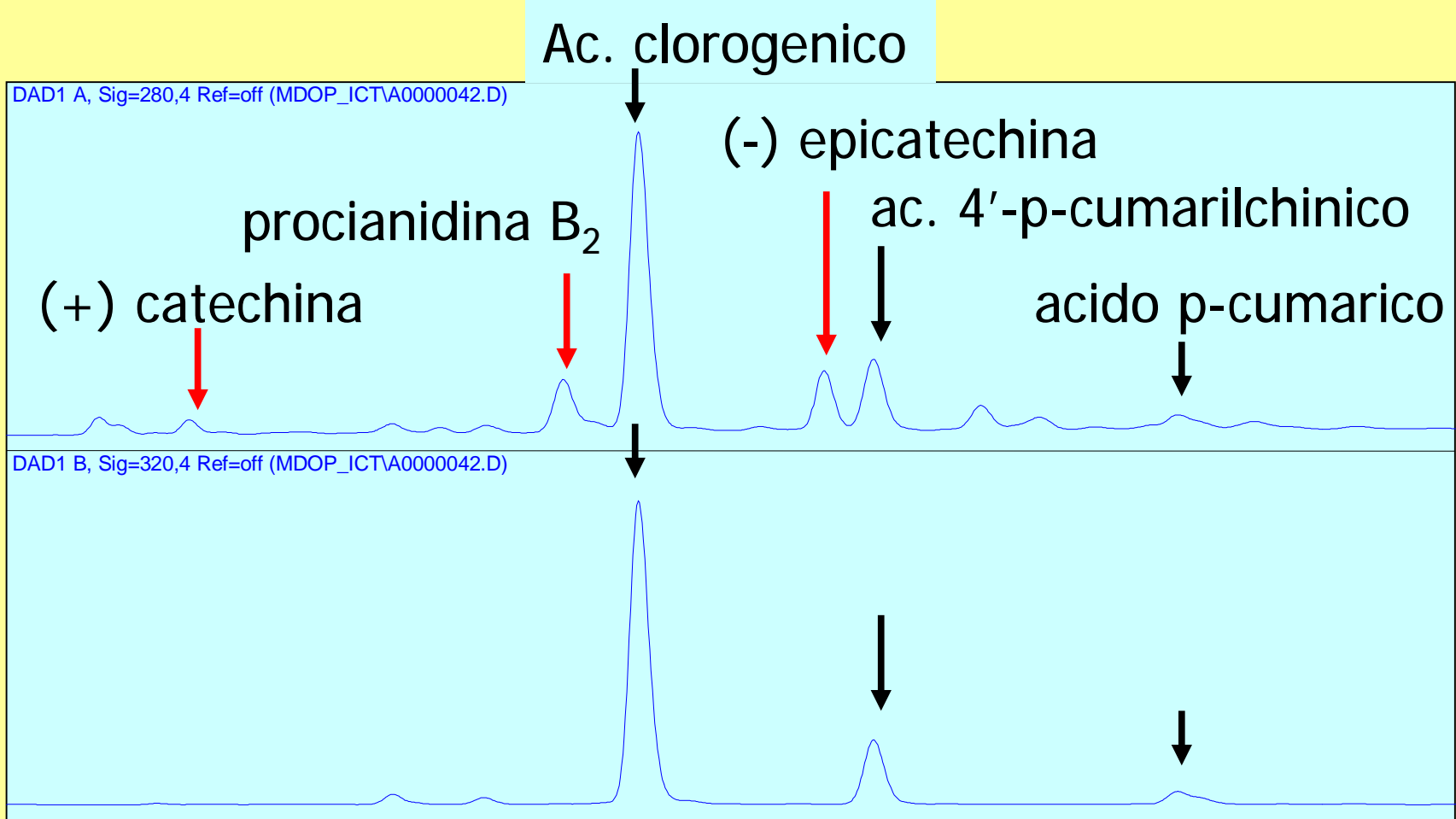


Polifenoli totali



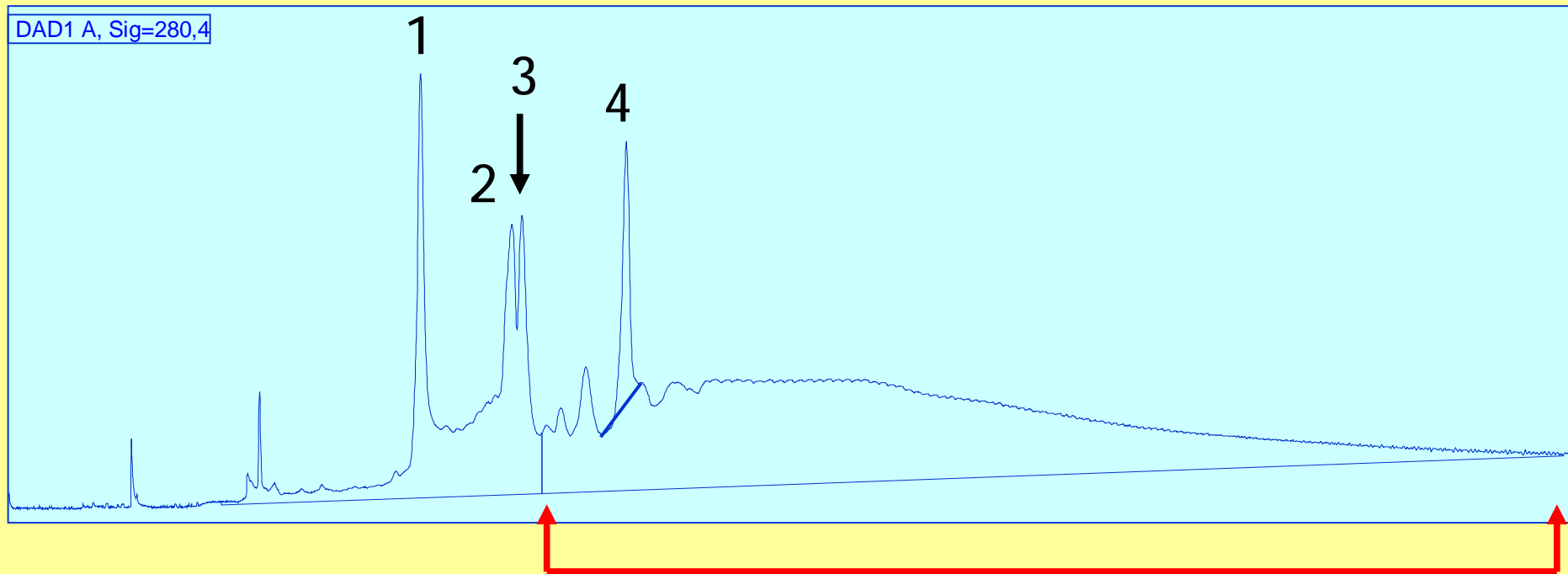
Flavanoli (I)

Acidi cinnamici

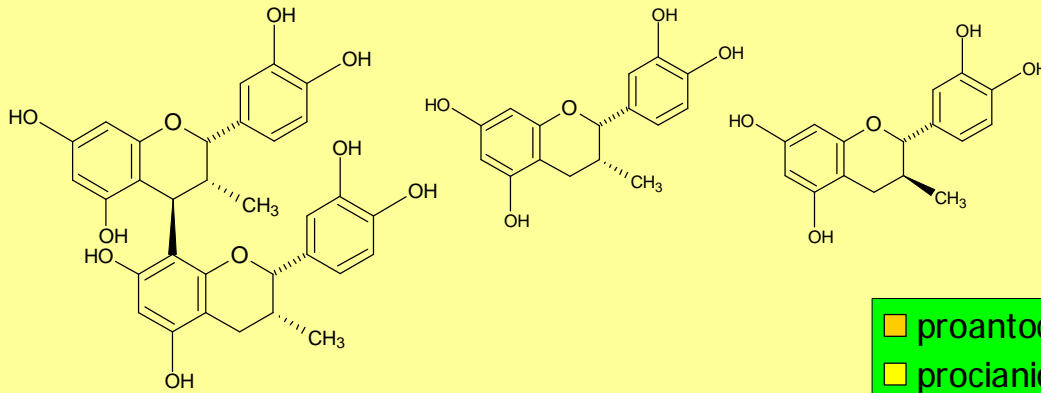


- 1 epicatechin & catechin
- 2 phloretin-2-xyloglucoside
- 3 procyanidin B₂
- 4 phloridzin

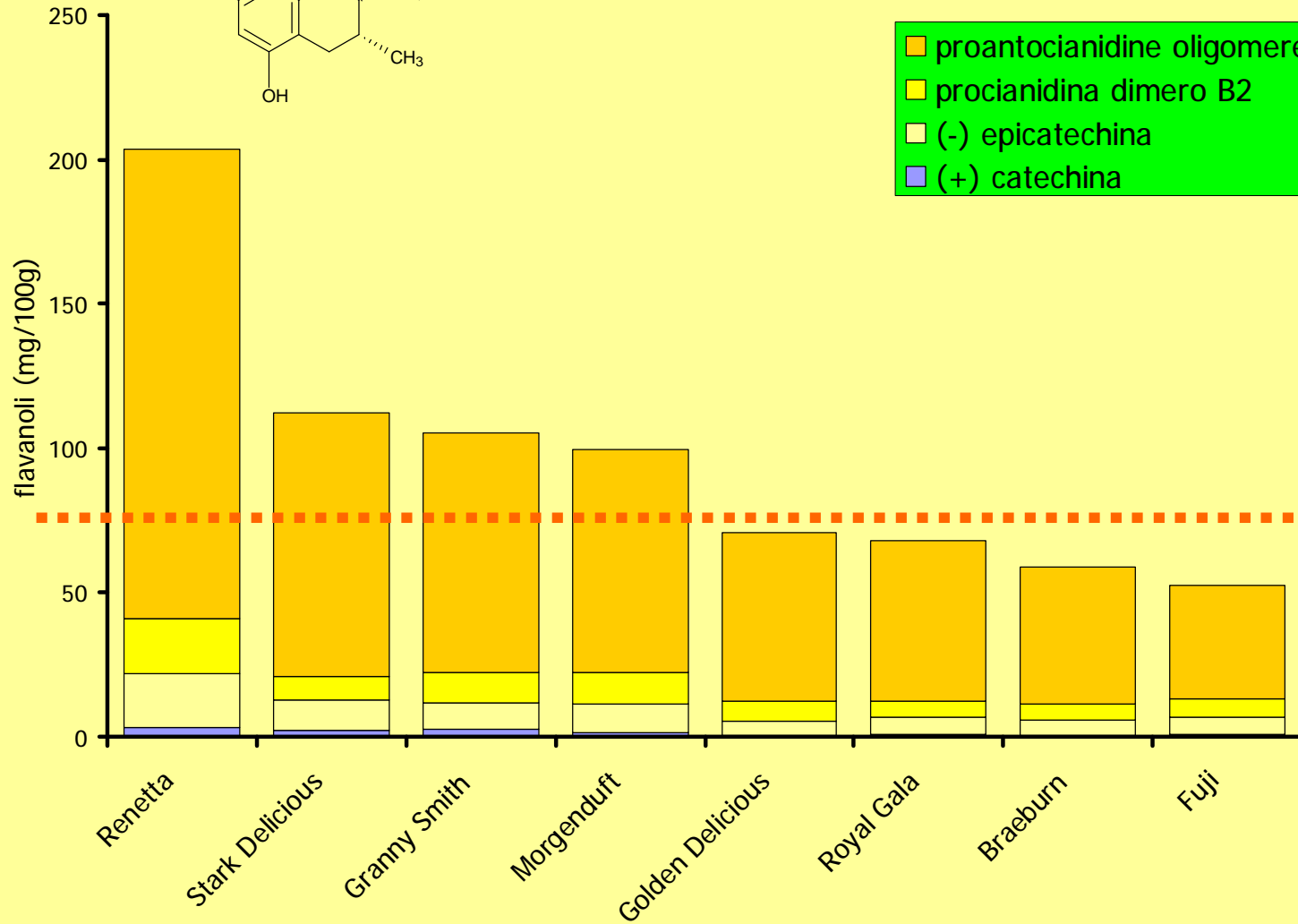
Flavanoli (II)



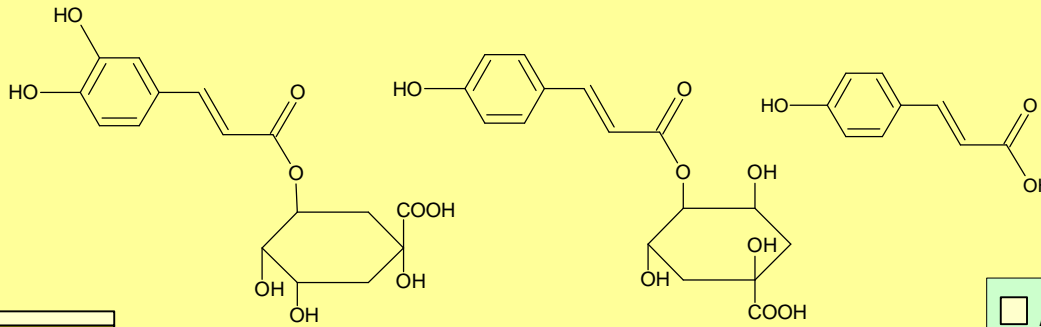
Proanthocyanidins (oligomers)



Flavanoli

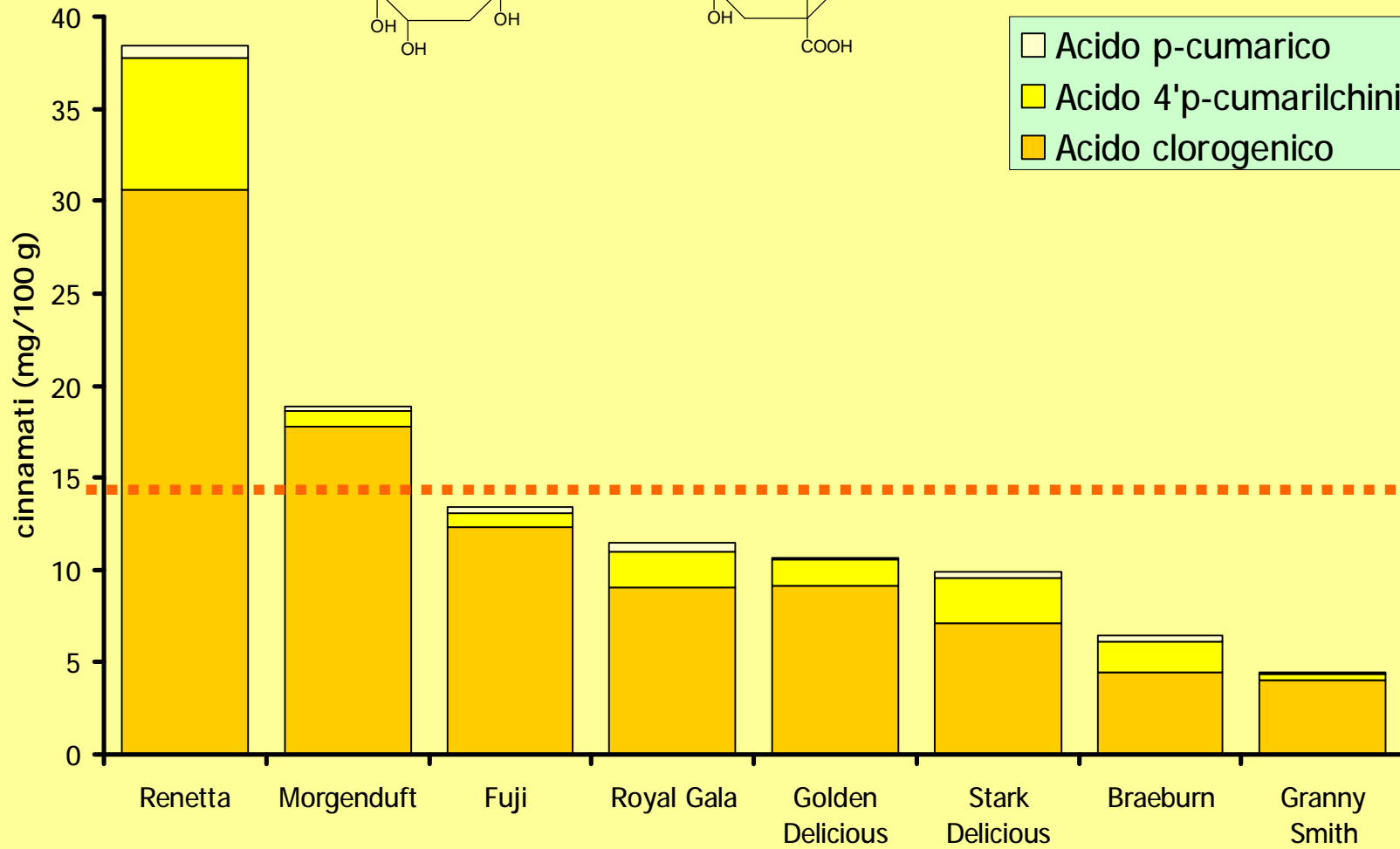


96.33



Acidi cinnamici

- Acido p-cumarico
- Acido 4'p-cumarilchinico
- Acido clorogenico



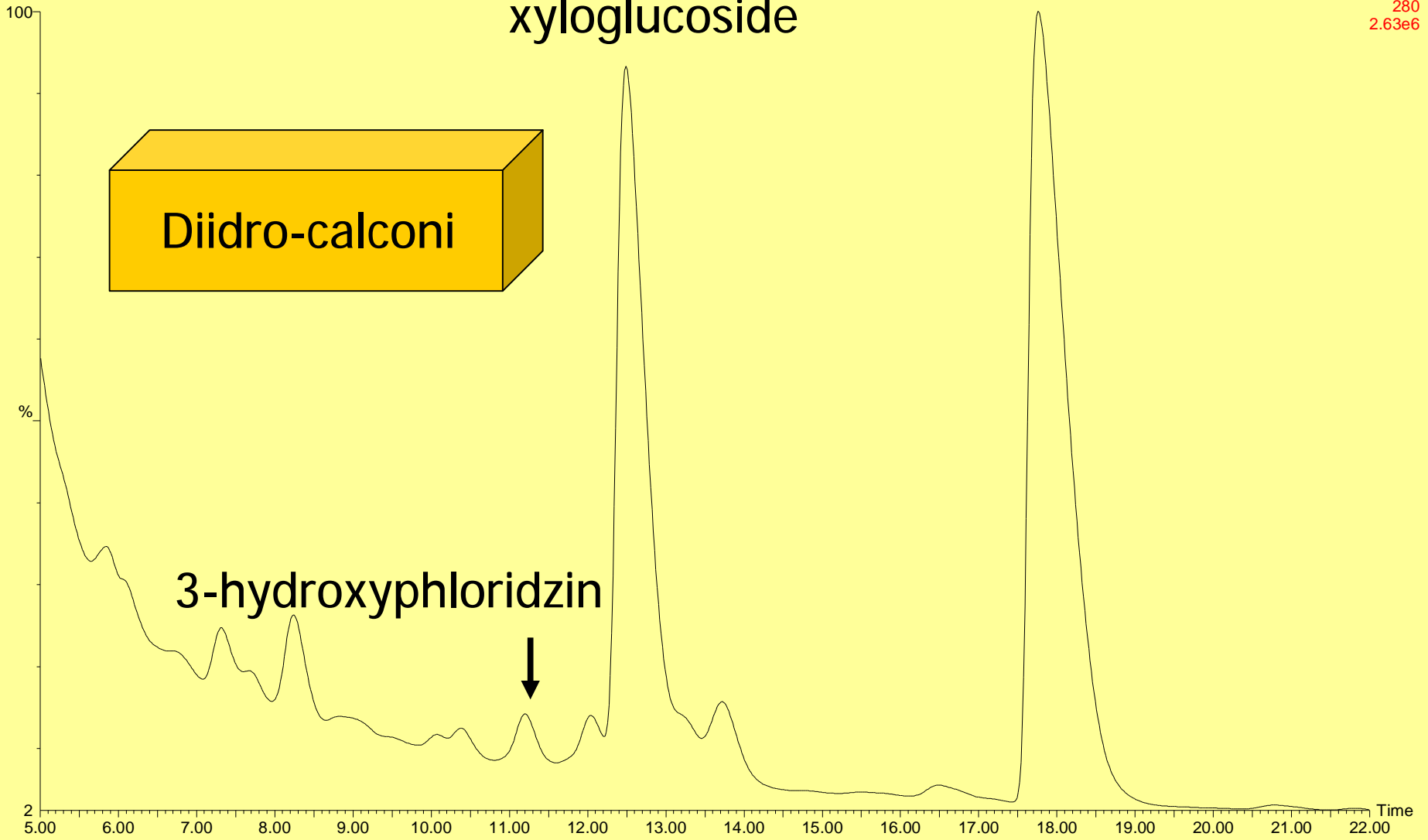
14.21

mix Renete, conc 100x
phlorizdin_mele Extr_5

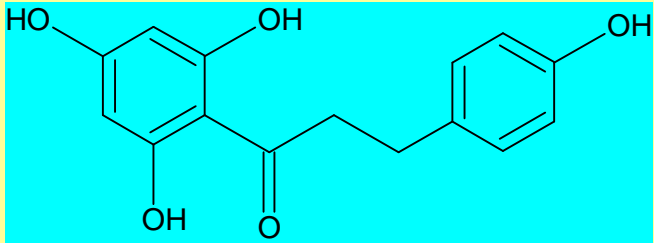
phloretin-2'-
xyloglucoside

phloridzin

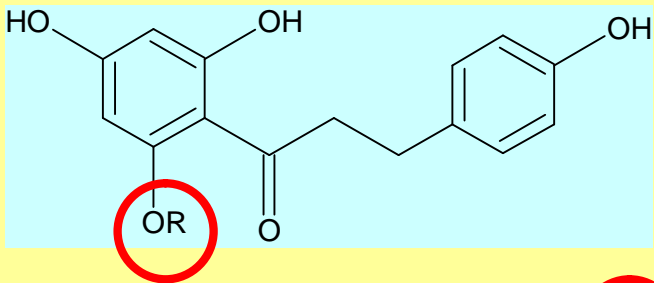
14-Oct-2002 13:57:29
10: Diode Array
280
2.63e6



Diidro-calconi

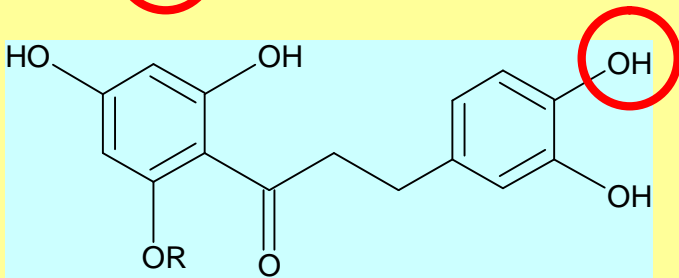


phloretin



phloretin-2'-glucoside (phloridzin)

phloretin-2'-xyloglucoside

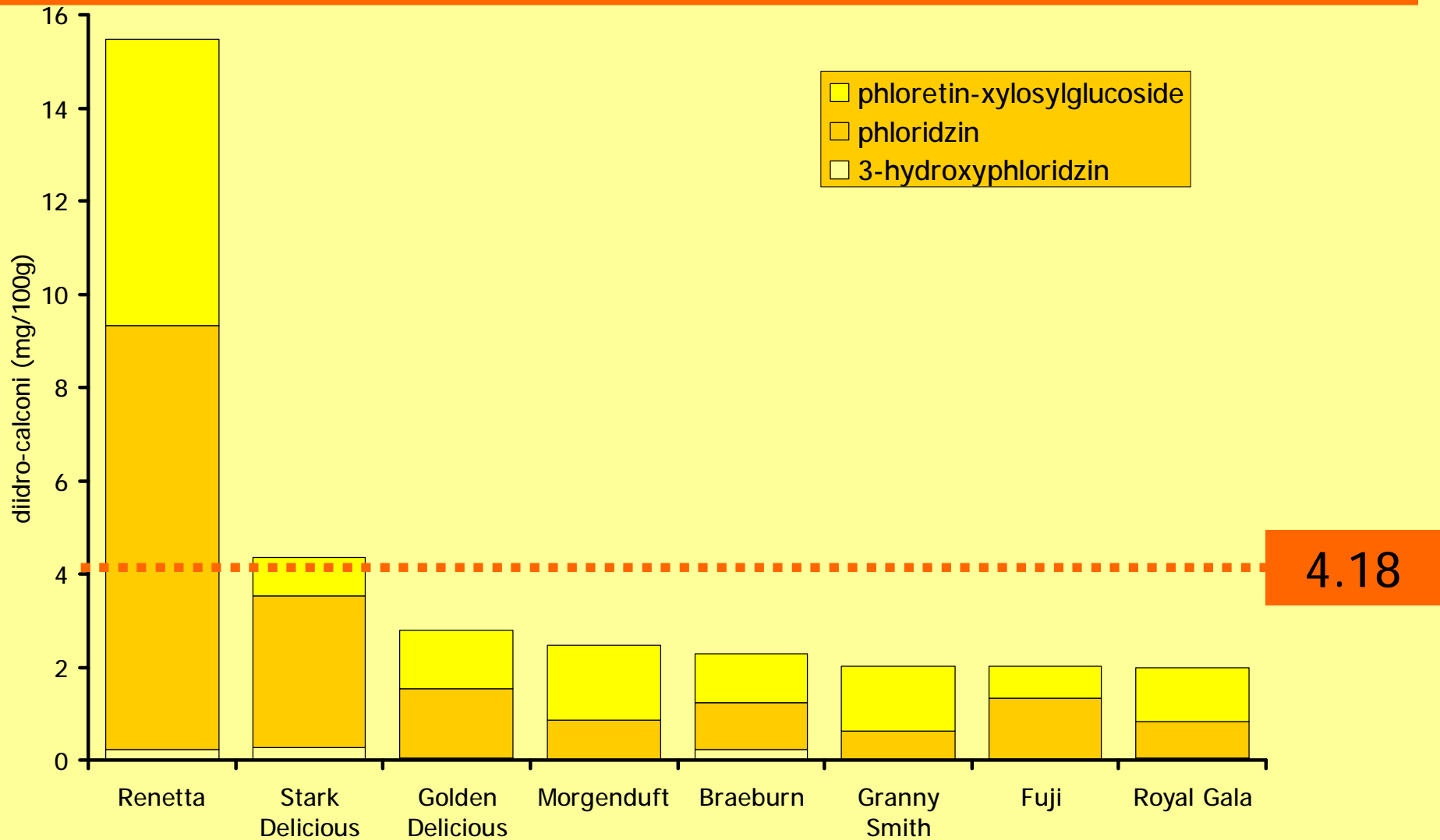


3-hydroxy-phloridzin

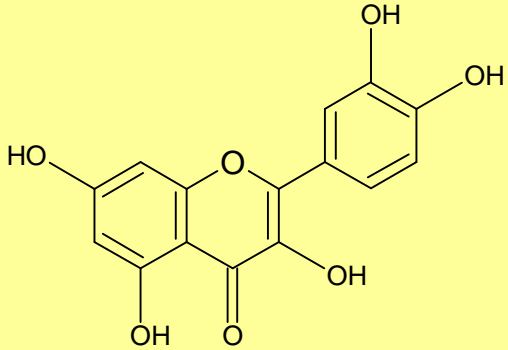




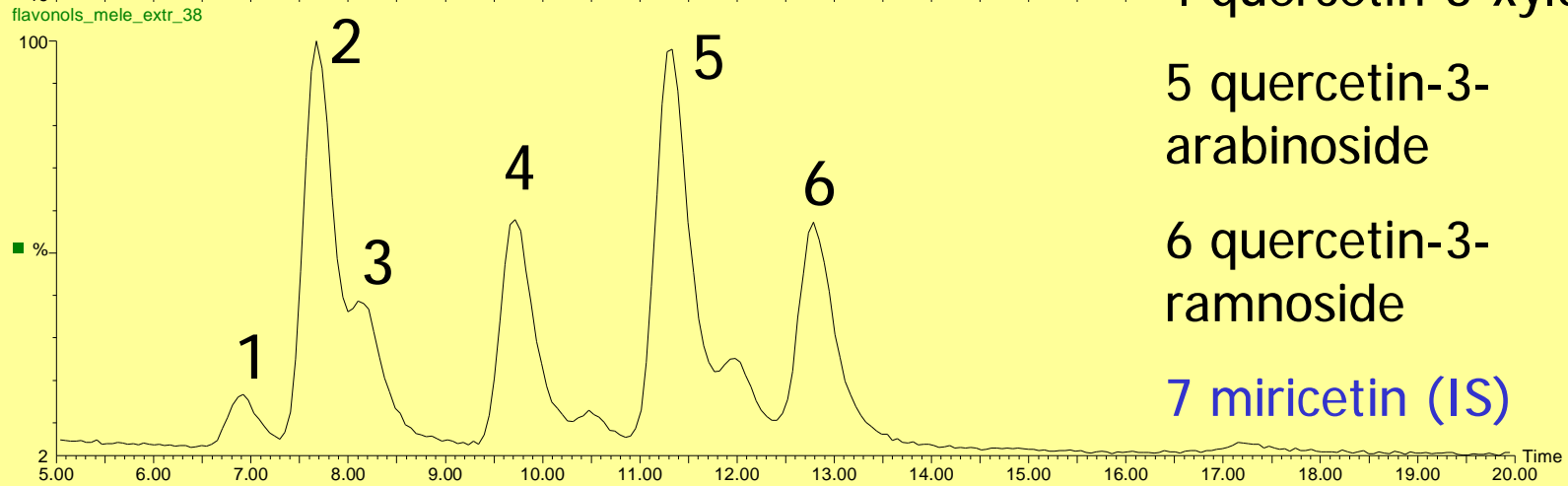
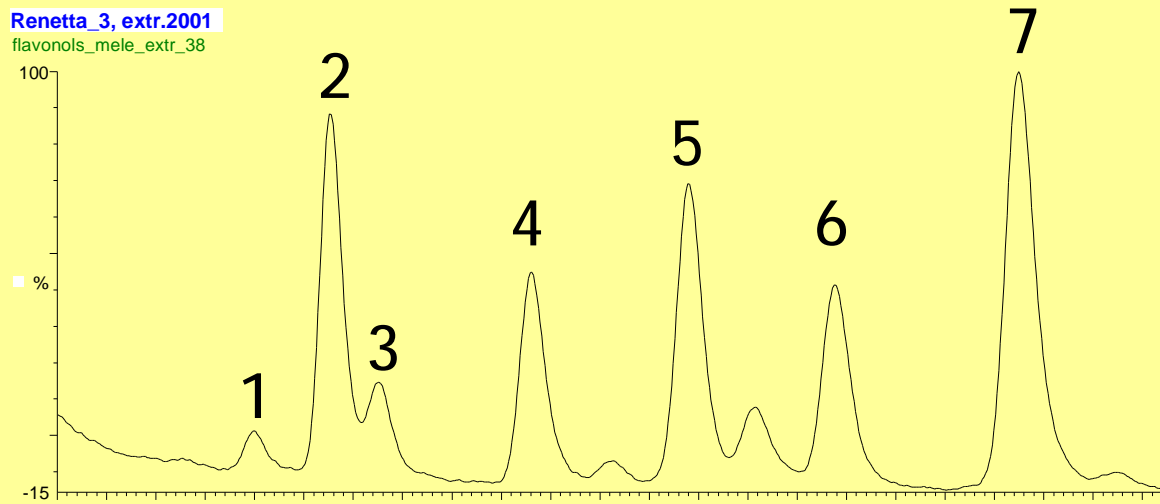
Diidro-calconi



Flavonoli



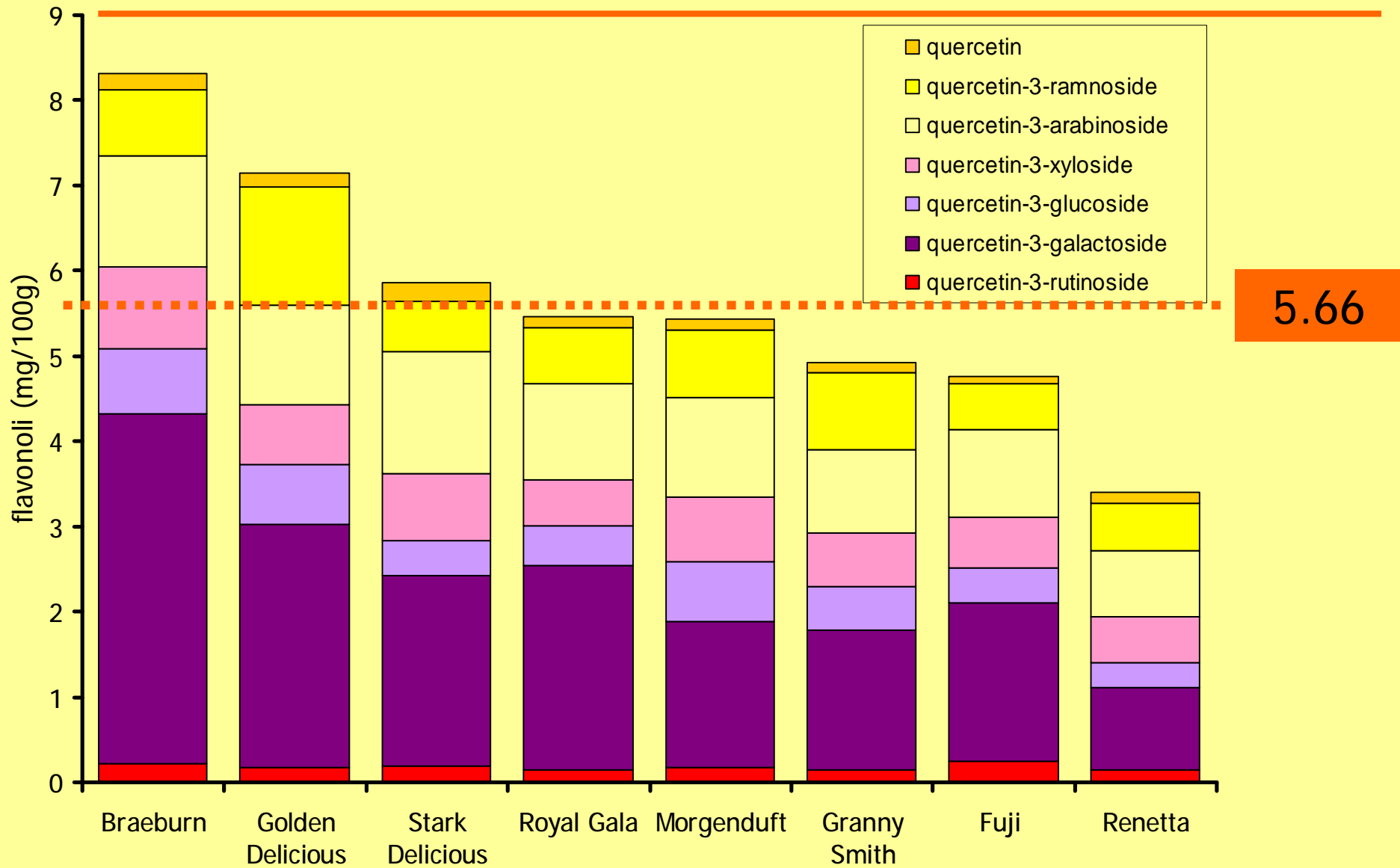
Renetta_3, extr.2001
flavonols_mele Extr_38



- 1 quercetin-3-rutinoside
- 2 quercetin-3-galactoside
- 3 quercetin-3-glucoside
- 4 quercetin-3-xyloside
- 5 quercetin-3-arabinoside
- 6 quercetin-3-ramnoside
- 7 miricetin (IS)



Flavonoli

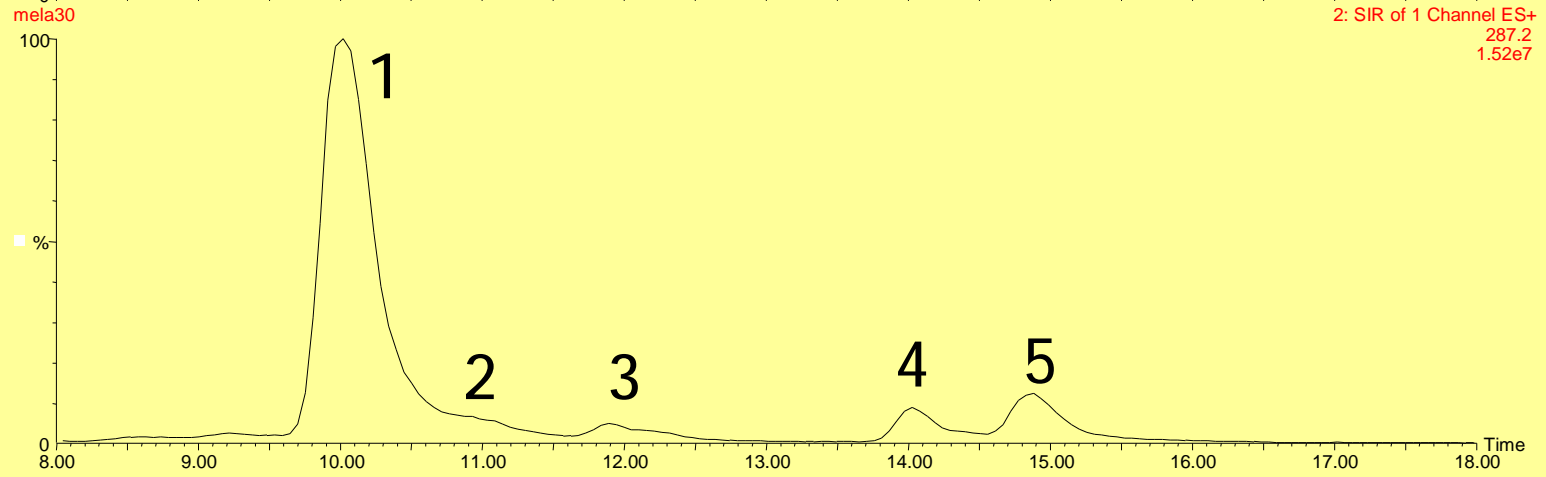
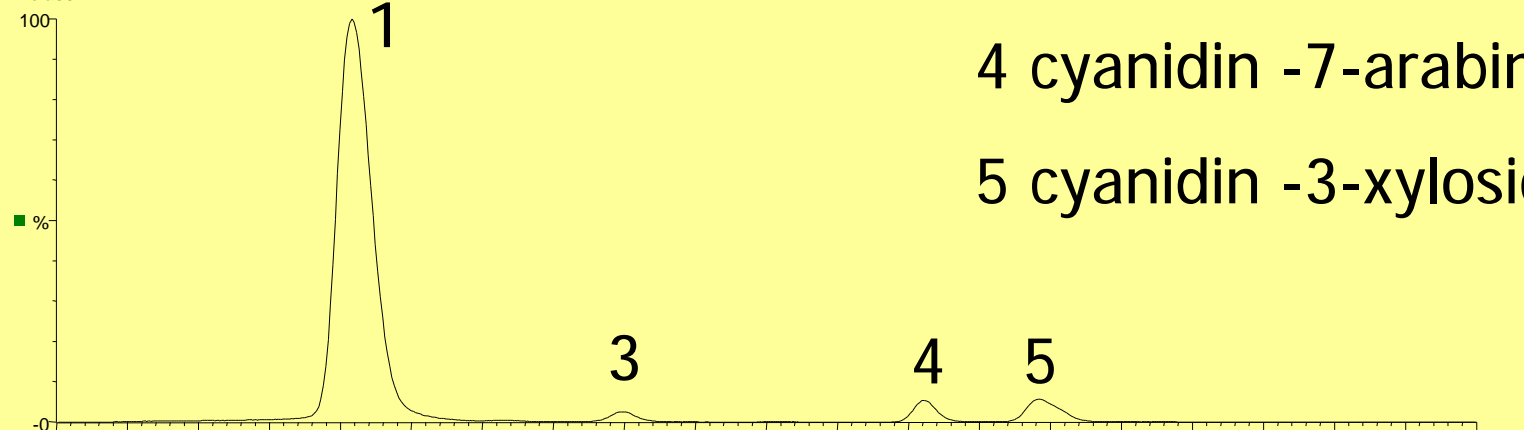


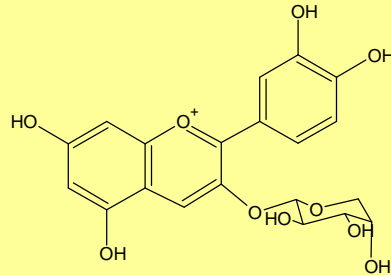
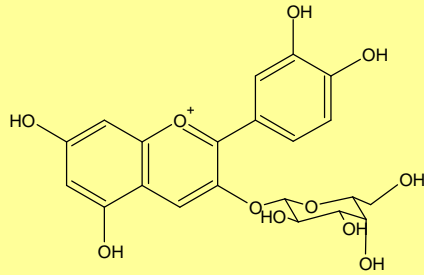
5.66

Antociani

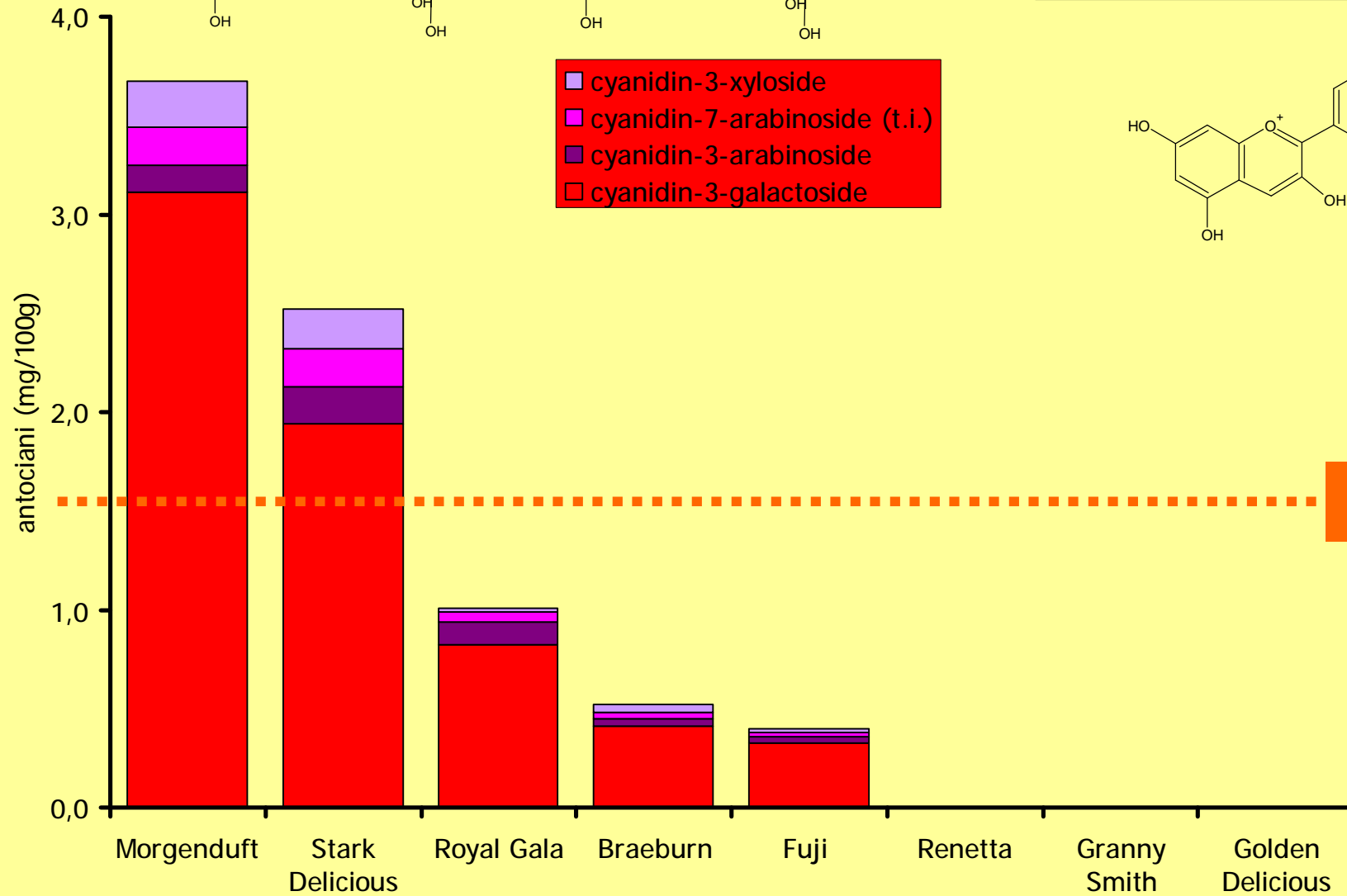
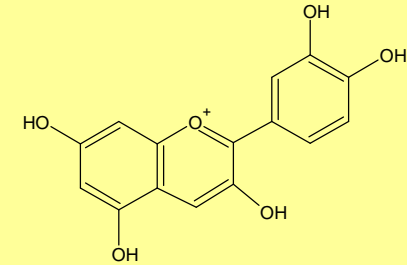
- 1 cyanidin-3-galactoside
- 2 cyanidin -3-glucoside (t.i.)
- 3 cyanidin -3-arabinoside
- 4 cyanidin -7-arabinoside
- 5 cyanidin -3-xyloside

35 Morgen, extr.2001 conc cca. 20x
mela30





Antociani

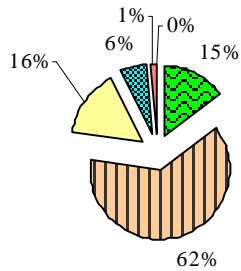


1.62

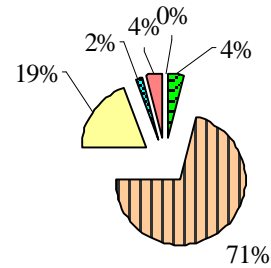


Composizione media delle varietà

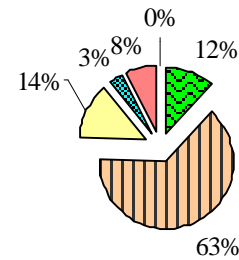
Renetta "media"



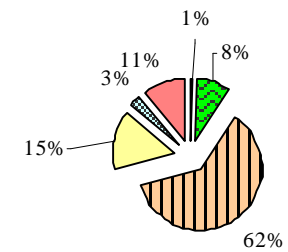
Granny Smith



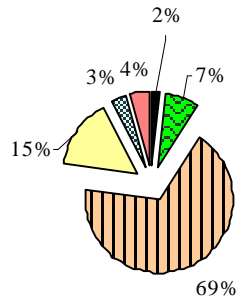
Golden Delicious



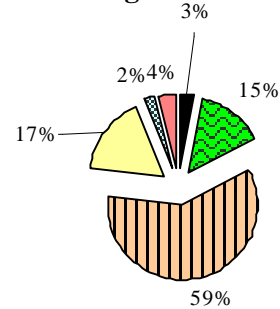
Braeburn



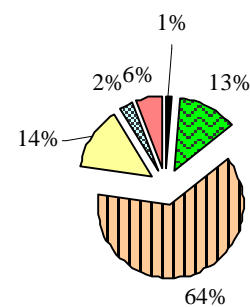
Red Delicious



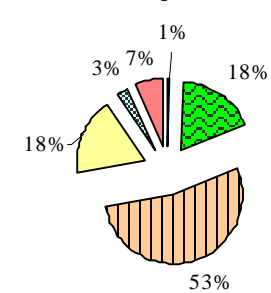
Morgenduft



Royal Gala



Fuji



- antociani
- acidi cinnamici
- proantocianidine oligomere
- flavan-3-oli
- diidro-calconi
- flavonoli

apporto medio giornaliero (mg) di antiossidanti naturali con il consumo di mele (esclusi trasformati)

| Nazione | Consumo giornaliero per abitante 2001 | acido ascorbico | polifenoli totali | flavanoli | acidi cinnamici | diidro-calconi | flavonoli | antociani (§) |
|----------------|---------------------------------------|-----------------|-------------------|-----------|-----------------|----------------|-----------|---------------|
| Francia | 72,1 | 2,95 | 79,4 | 69,4 | 10,2 | 3,0 | 4,1 | 1,2 |
| Italia | 67,3 | 2,75 | 74,1 | 64,8 | 9,6 | 2,8 | 3,8 | 1,1 |
| Germania | 96,4 | 3,94 | 106,2 | 92,9 | 13,7 | 4,0 | 5,5 | 1,6 |
| Regno Unito | 46,7 | 1,91 | 51,5 | 45,0 | 6,6 | 2,0 | 2,6 | 0,8 |
| Unione Europea | 77,8 | 3,18 | 85,7 | 74,9 | 11,1 | 3,3 | 4,4 | 1,3 |
| 1 porzione | 150 | 6,14 | 165,3 | 144,5 | 21,3 | 6,3 | 8,5 | 2,4 |
| 2 porzioni | 300 | 12,27 | 330,6 | 289,0 | 42,6 | 12,5 | 17,0 | 4,9 |

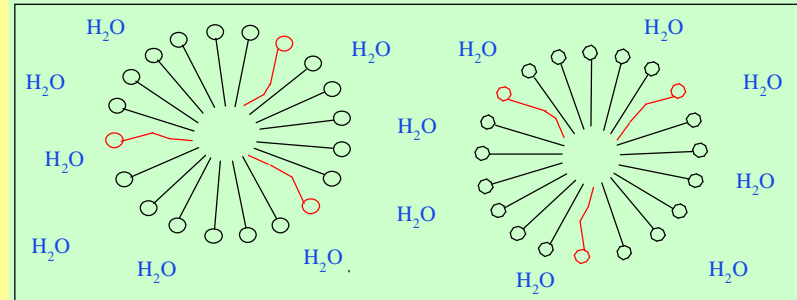
(*) fonte dati consumo per abitante: elaborazioni servizio statistico DG VI, da fonti diverse;

(§) media varietà rosse

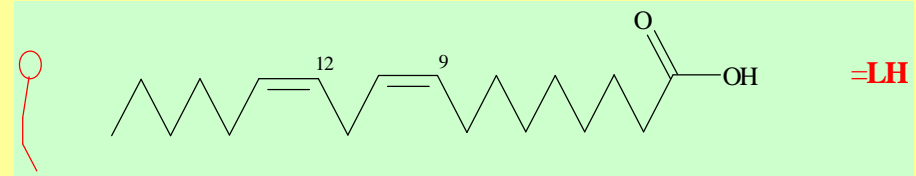


test in vitro per riprodurre i fenomeni di perossidazione che si verificano in vivo

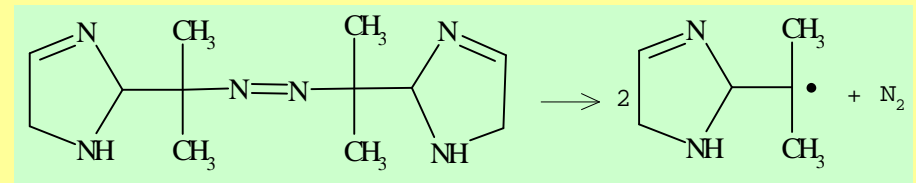
Sistema micellare



Substrato ossidabile: Acido linoleico

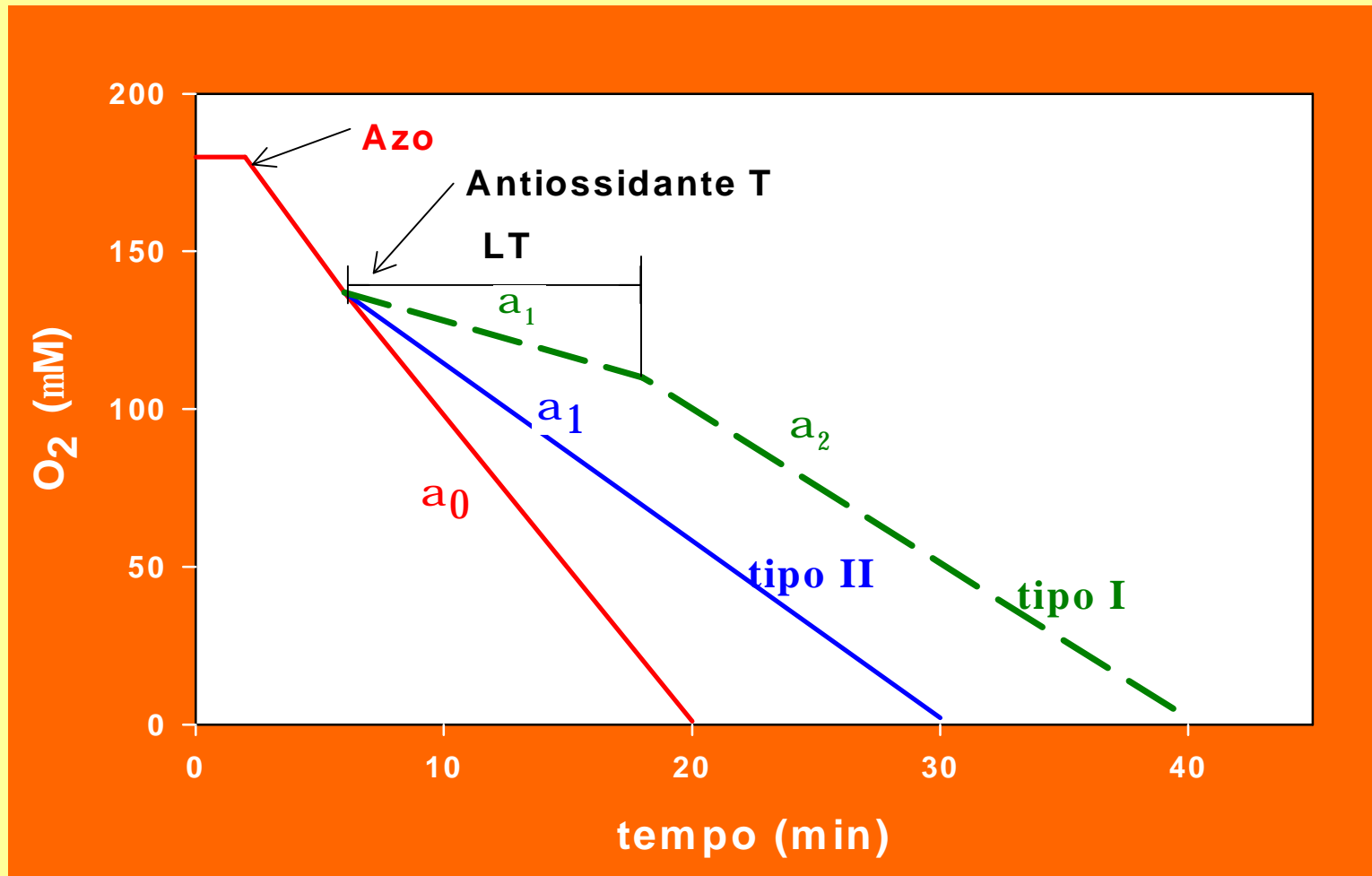


Iniziatore radicalico: ABIP



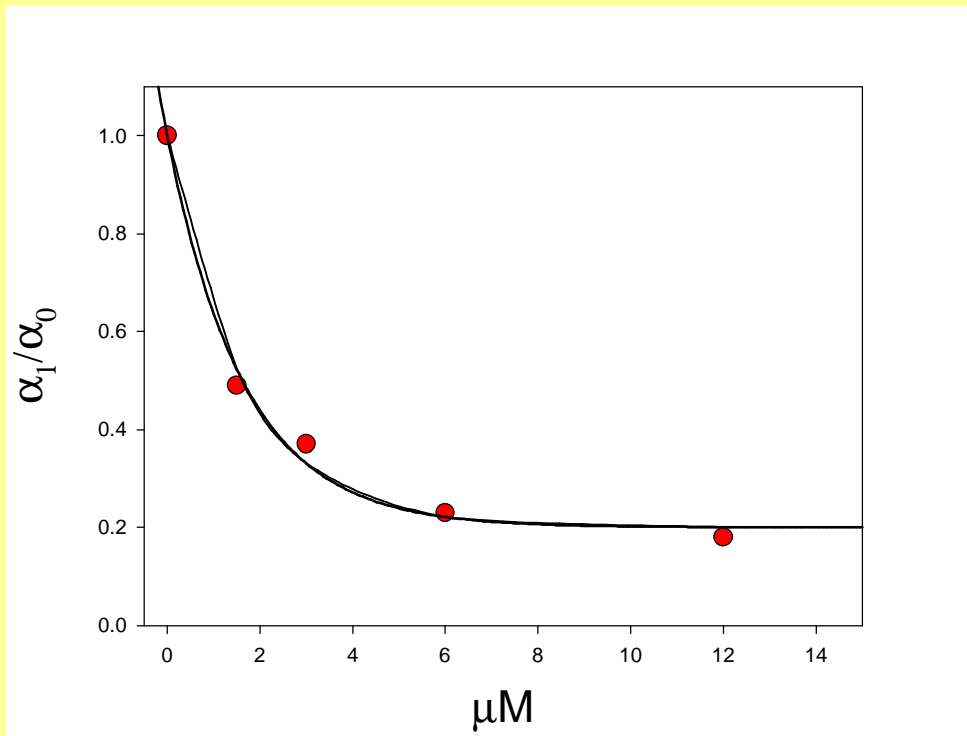


Le metodologie di indagine: il consumo di ossigeno per la misura dei fenomeni di perossidazione



Efficienza antiossidante (PRTE): $C_{1/2}$

(quantità di antiossidante necessaria per dimezzare il consumo di ossigeno dovuto alla perossidazione dell'acido linoleico)



se presenti più antiossidanti, vale l'additività

$$\frac{a_1}{a_0} = A + B \cdot e^{-\frac{(\ln 2) \cdot c}{c_{1/2}}}$$

$$A = \frac{a_1}{a_0} = \text{costante quando } c \rightarrow \infty$$

(A dipende dalla concentrazione di ABIP)

$$B = \frac{a_1}{a_0} - A \quad \text{per } c = 0$$

$$\frac{a_1}{a_0} = A + B \cdot e^{-\frac{(\ln 2) \sum_i c_i}{c_{i1/2}}}$$



Efficienza di sostanze pure

Composti di tipo I

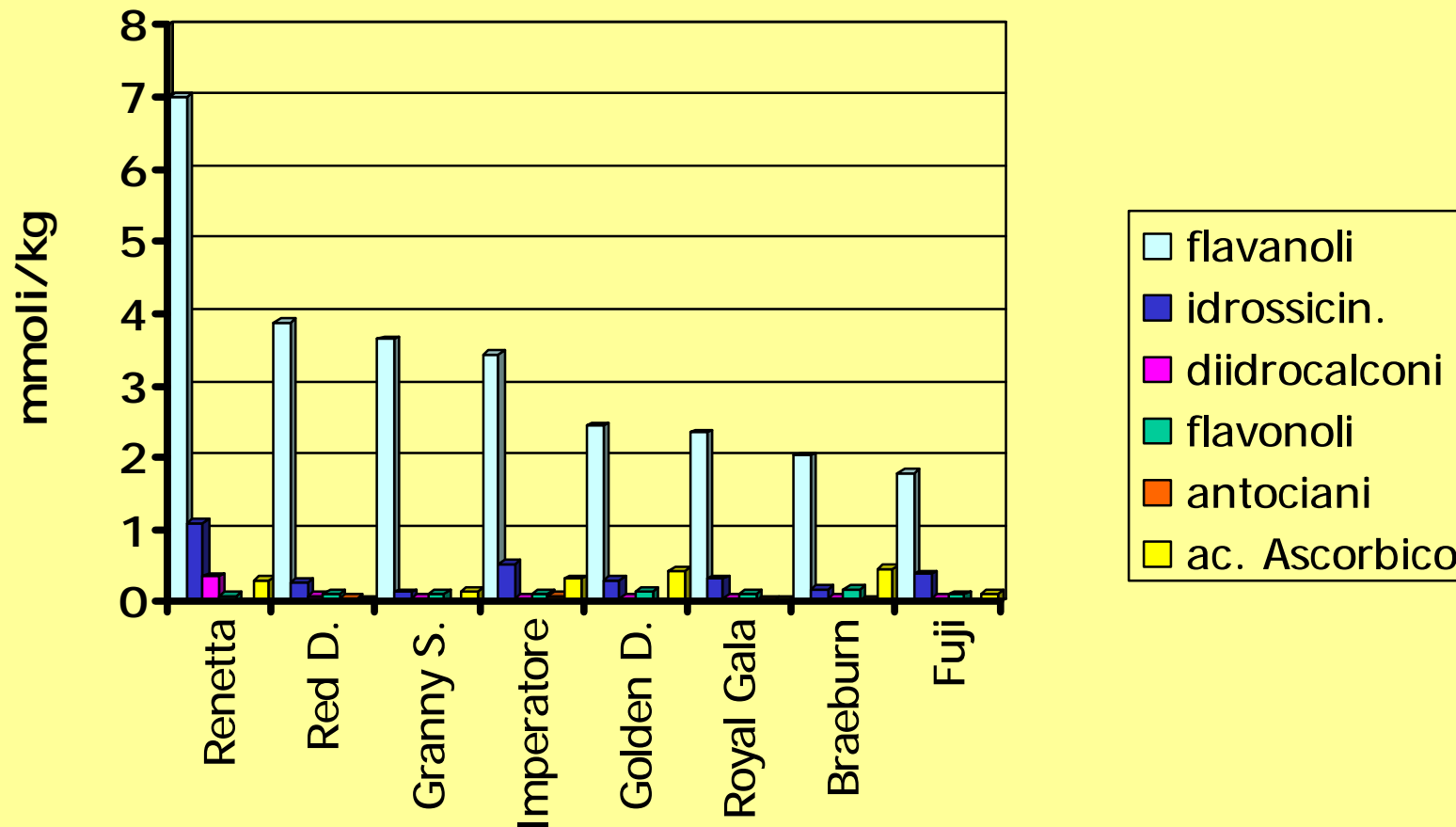
| Composto | $C_{1/2}$ (mM) | $(C_{1/2})^{-1}$ (mM) ⁻¹ |
|------------------|-------------------|--|
| delfinidina-3G | 0.8 | 1.25 |
| petunidina-3G | 1.0 | 1.0 |
| malvidina-3G | 1.2 | 0.83 |
| cianidina-3G | 2.5 | 0.40 |
| peonidina-3G | 5.8 | 0.17 |
| pelargonidina-3G | 6.4 | 0.16 |
| trolox | 1.1 | 0.91 |
| quercetina | 1.7 | 0.60 |
| miricetina | 0.7 | 1.43 |
| ac. ascorbico | 4.6 | 0.22 |

Composti di tipo II

| Composto | $C_{(1/2)}$ (mM) | $(C_{1/2})^{-1}$ (mM) ⁻¹ |
|------------------|---------------------|--|
| (+)-catechina | 11.1 | 0.09 |
| (-)-epicatechina | 12.1 | 0.08 |
| procianidina B3 | 11.8 | 0.085 |
| procianidina B4 | 8.7 | 0.16 |
| ac. clorogenico | 9.6 | 0.10 |
| ac. caffeico | 7.0 | 0.14 |
| phloridzin | 42.8 | 0.023 |
| t-resveratrolo | 2.5 | 0.40 |
| t-resveratrolo-G | 21.3 | 0.05 |
| t-piceide | 3.0 | 0.33 |

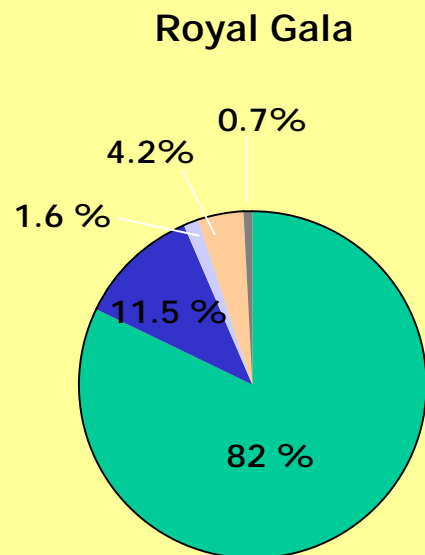
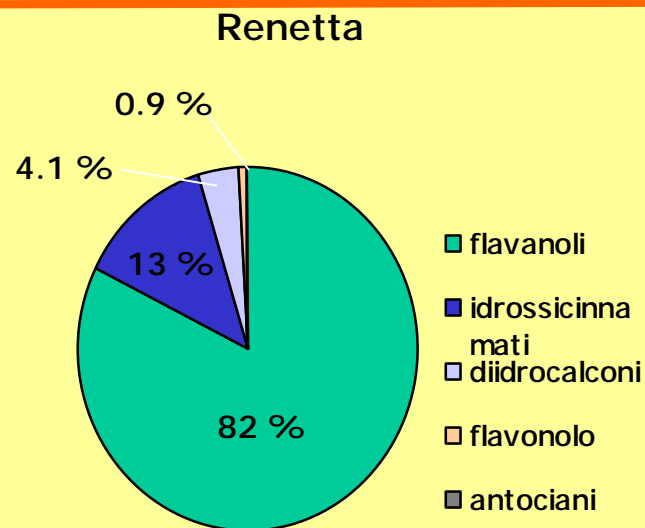


La conoscenza completa della composizione della mela è stata utilizzata per interpretare l'efficienza antiradicalica degli estratti delle diverse varietà.



Vrhovsek U., Rigo A., Tonon D., Mattivi F. (2004)
J. Agric. Food Chem., 52, 21, 6532-6538.

Composizione ed efficienza antiossidante di alcune cultivar di mela



| Cultivar | PT _{HPLC} (mmoli/Kg) | (C _{1/2}) ⁻¹ (L/g) | à _i C _i /C _{i 1/2} % |
|---------------|----------------------------------|--|--|
| Renetta | 8.52 | 1.64 | 52.9 |
| Red Delicious | 4.43 | 0.93 | 52.0 |
| Granny Smith | 3.92 | 0.93 | 47.0 |
| Imperatore | 4.22 | 0.96 | 55.7 |
| Golden Delic. | 2.96 | 0.75 | 59.0 |
| Royal Gala | 2.84 | 0.69 | 47.4 |
| Braeburn | 2.45 | 0.53 | 78.2 |
| Fuji | 2.34 | 0.68 | 43.5 |

Vanzani P., Rossetto M., Rigo A., Vrhovsek U., Mattivi F., D'Amato E.; Scarpa M. (2005) J. Agric. Food Chem., 53, 3377-3382.



.. Influenza della **esposizione al sole** sul contenuto di flavonoidi ed acido clorogenico nella buccia

(Awad et al., 2000, Sci. Hort, 249-263)

| | | Flavonoids and chlorogenic acid (mg/g dw) | | | | | |
|------------------------------|-------------------|---|-------------|-----------|------------------------|------------------|------------------|
| Fruit side | Cultivar | Cyanidin 3-galactoside | Phloridizin | Catechins | Quercetin 3-glycosides | Total flavonoids | Chlorogenic acid |
| Sun side | Jonagold | 0,81 | 0,81 | 0,90 | 12,14 | 14,66 | 0,20 |
| | Elstar | 0,63 | 0,52 | 1,83 | 6,38 | 9,36 | 0,04 |
| | Elshof | 1,04 | 0,54 | 2,27 | 7,00 | 10,85 | 0,06 |
| | Red Elstar | 1,41 | 0,44 | 1,87 | 5,29 | 9,01 | 0,05 |
| Shade side | Jonagold | 0,01 | 0,71 | 0,80 | 3,27 | 4,79 | 0,24 |
| | Elstar | 0,05 | 0,46 | 1,88 | 2,03 | 4,42 | 0,03 |
| | Elshof | 0,11 | 0,48 | 1,84 | 2,10 | 4,54 | 0,04 |
| | Red Elstar | 0,11 | 0,53 | 1,74 | 1,95 | 4,33 | 0,00 |
| <i>Mean</i> | <i>Sun side</i> | 0,97 | 0,58 | 1,72 | 7,7 | 10,97 | 0,09 |
| | <i>Shade side</i> | 0,07 | 0,54 | 1,57 | 2,34 | 4,52 | 0,08 |
| <i>F-test (for the mean)</i> | | ** | NS | NS | ** | ** | NS |

- Catechins = catechin + epicatechin;
- Quercetin 3-glycosides = quercetin 3-galactoside + quercetin 3-glucoside + quercetin 3-xyloside + quercetin 3-rhamnoside + quercetin 3-arabinoside
- Total flavonoids = cyanidin 3-galactoside, phloridzin, catechins and quercetin 3-glycosides
- NS - not significant; (**) significant at level P= 0.01



...influenza della **posizione della mela sulla pianta** sul contenuto di flavonoidi ed acido clorogenico nella buccia

(Awad et al., 2000, Sci. Hort, 249-263)

| Position | Flavonoids and chlorogenic acid (mg/g dw) | | | | | |
|---------------|---|-------------|-----------|------------------------|------------------|------------------|
| | Cyanidin 3-galactoside | Phloridizin | Catechins | Quercetin 3-glycosides | Total flavonoids | Chlorogenic acid |
| Top | 0,26 | 0,64 | 1,83 | 4,21 | 6,93 | 0,043 |
| Inner | 0,04 | 0,56 | 1,78 | 1,52 | 3,90 | 0,047 |
| North | 0,14 | 0,69 | 1,90 | 2,85 | 5,58 | 0,042 |
| South | 0,16 | 0,62 | 1,72 | 3,18 | 5,67 | 0,048 |
| East | 0,15 | 0,61 | 1,76 | 2,94 | 5,47 | 0,043 |
| West | 0,15 | 0,72 | 1,72 | 2,97 | 5,56 | 0,048 |
| <i>F-test</i> | *** | NS | NS | ** | ** | NS |

- Catechins = catechin + epicatechin;
- Quercetin 3-glycosides = quercetin 3-galactoside + quercetin 3-glucoside + quercetin 3-xyloside + quercetin 3-rhamnoside + quercetin 3-arabinsoside
- Total flavonoids = cyanidin 3-galactoside, phloridizin, catechins and quercetin 3-glycosides
- NS - not significant; (*), (**), (***) significant at levels P= 0.05, P=0.01 and P=0.001 respectively



.. influenza della **esposizione al sole** sulla concentrazione in **acido ascorbico** (mg/100 g) nelle differenti parti della mela **Granny Smith** (Simcic et al., 2001, COST 916 action: Molecular and genetic interactions involving phytochemicals, p.203-208)

SUNNY SIDE

SHADOW

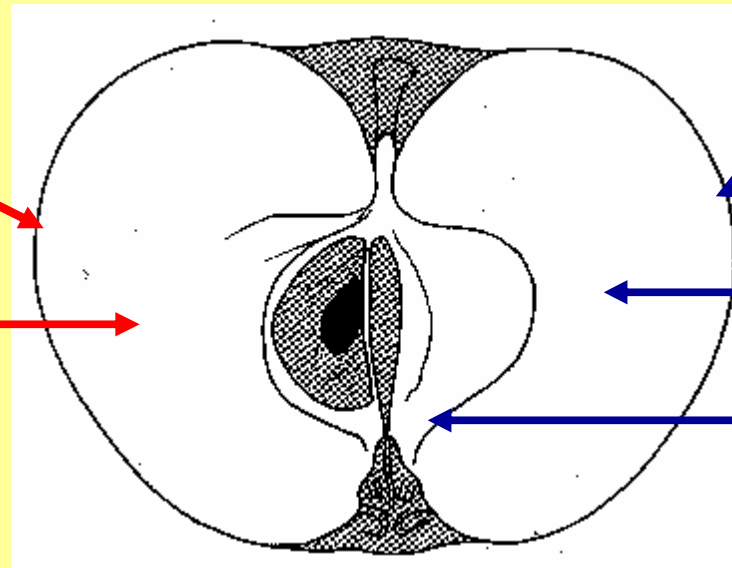
123.1 ± 21.3

8.4 ± 1.3

35.4 ± 12.3

4.1 ± 0.9

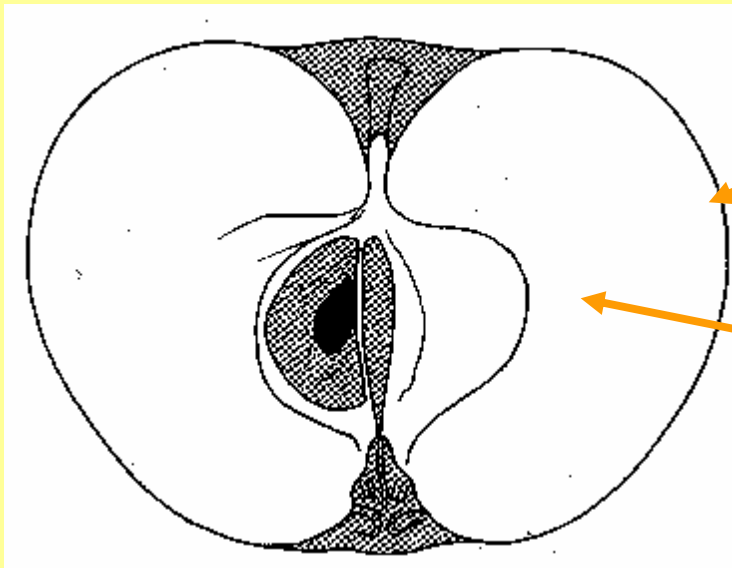
2.3 ± 0.8





Localizzazione delle catechine

- (-)-epicatechin
- (+)-catechin

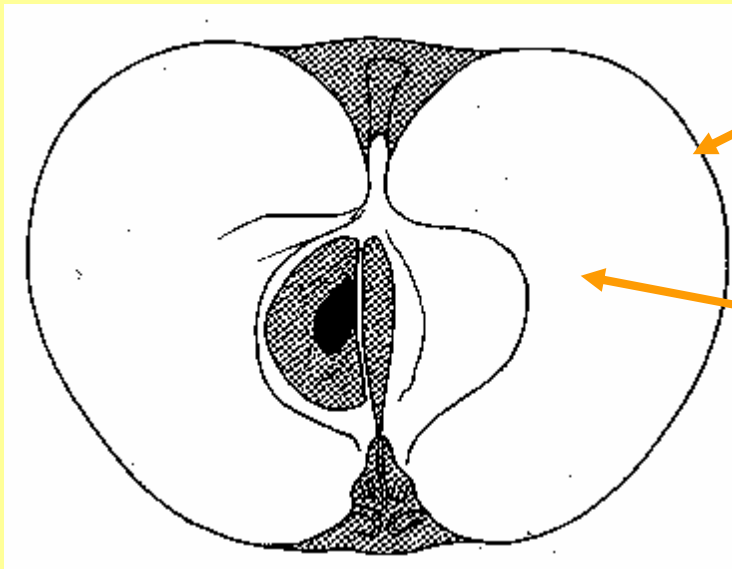


200-310 mg/kg

60-160 mg/kg



Localizzazione delle proantocianidine



1900-3400 mg/kg

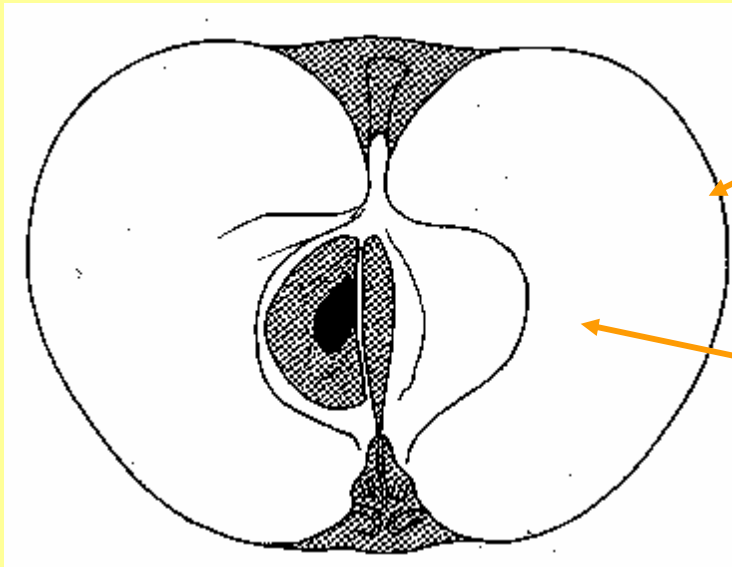
600-900 mg/kg

Proantocianidine oligomere:

elevatissime concentrazioni nella buccia, ma presenti in rilevanti concentrazioni anche nella polpa, il principale dimero (B2) costituisce circa il 10% del totale nella buccia, il 20% nella polpa



Localizzazione dei non-flavonoidi



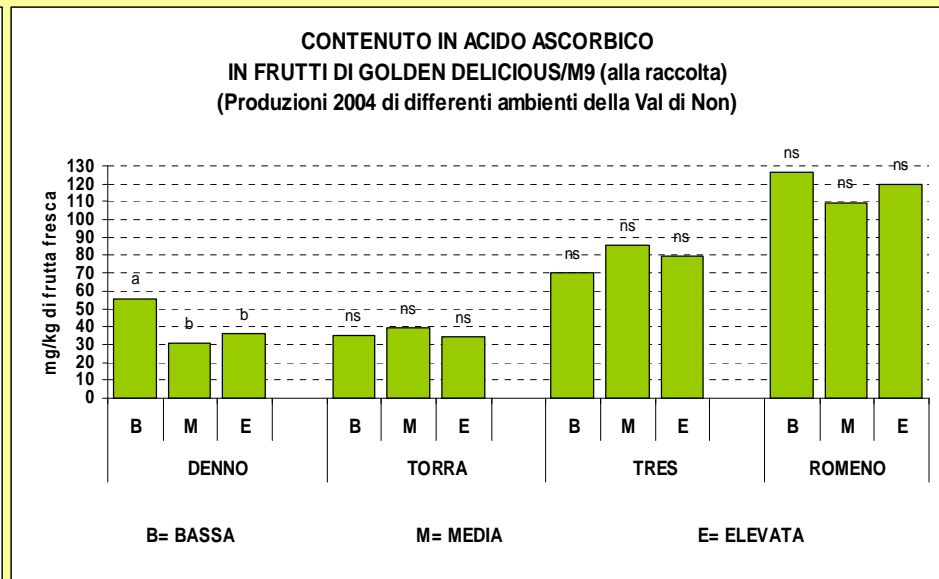
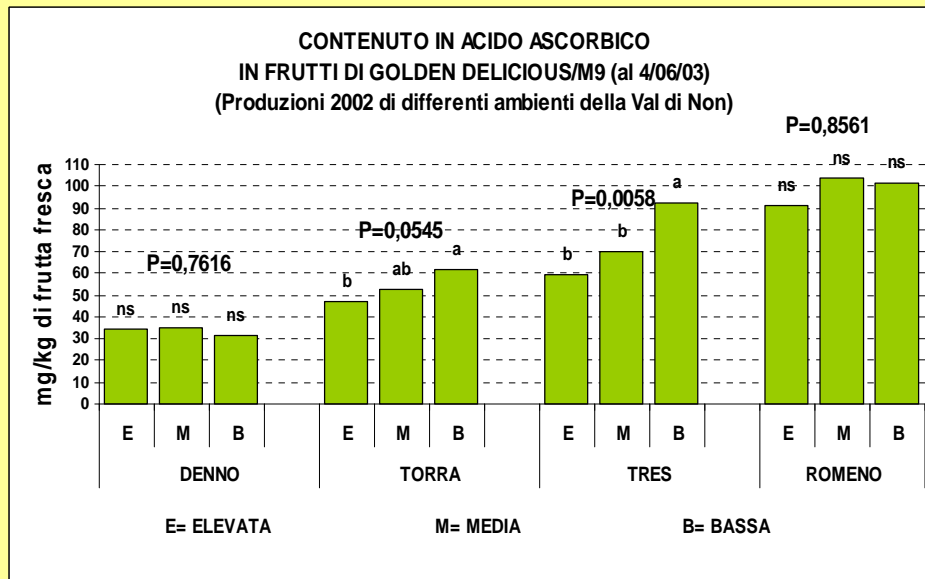
40-430 mg/kg

100-290 mg/kg

Hydroxycinnamic acids:
their concentrations in skin and cortex are
similar



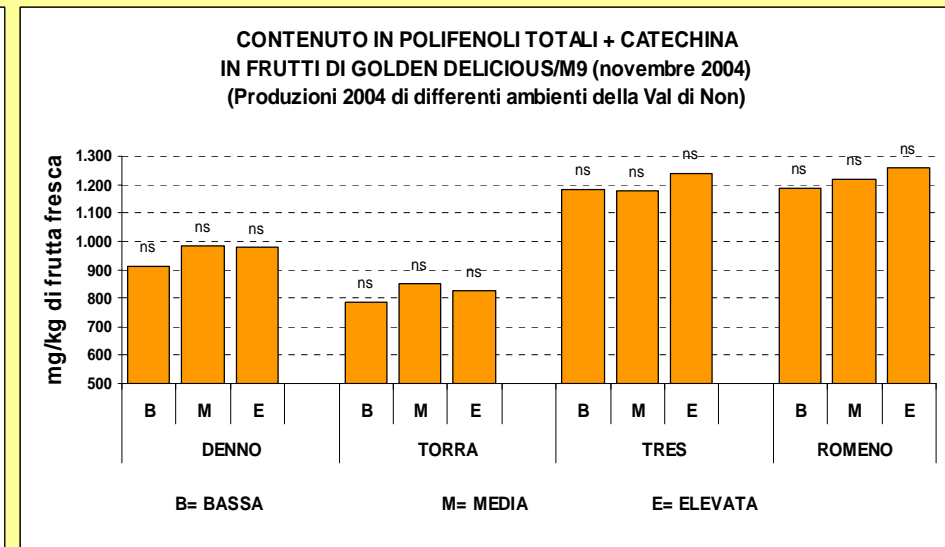
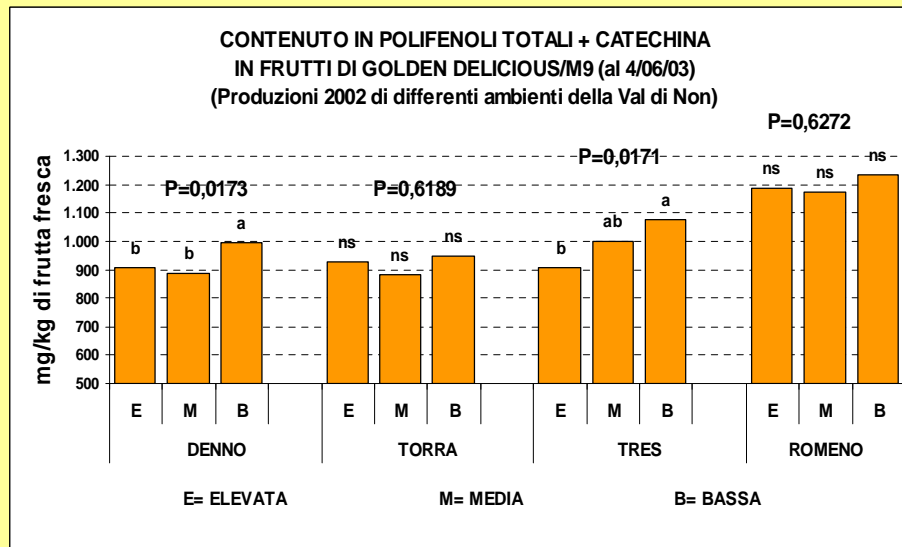
La mela di montagna è significativamente più ricca di acido ascorbico



Valori compositivi riscontrati in frutteti sperimentali tra 340 e 940 m.s.l.m.



La mela di montagna è significativamente più ricca di polifenoli



Valori compositivi riscontrati in frutteti sperimentali tra 340 e 940 m.s.l.m.



Influenza della conservazione sulla composizione di frutti della cv. Golden D. in differenti siti di produzione della Val di Non e da alberi a diversa carica

| Variabili | Livelli di Carica | Siti produttivi | | | | | | | |
|---|-------------------|-----------------|-------------------|----------------|----------------|----------------|---------------|----------------|-----------------|
| | | A (340) | | B (540) | | C (740) | | D (940) | |
| | | Racc. | F.C. ³ | Racc. | F.C. | Racc. | F.C. | Racc. | F.C. |
| Polifenoli (mg +- catechina/Kg di s. f.) | Bassa | 827 | 997 a | 789 | 949 | 934 | 1075 a | 1026 | 1234 |
| | Media | 735 | 886 b | 789 | 883 | 935 | 1002 ab | 990 | 1171 |
| | Elevata | 850 | 910 b | 826 | 930 | 912 | 907 b | 1078 | 1187 |
| | Av. R. | b 804 c | | b 802 c | | 927 b | | b1031 a | |
| | Av. F.C. | | a 931 bc | | a 921 c | | 995 b | | a 1198 a |
| Vitamina C (mg acido ascorbico/Kg di s. f.) | Bassa | 23 | 32 | 46 | 62 | 47 | 93 a | 111 | 101 |
| | Media | 33 | 35 | 34 | 53 | 58 | 70 b | 92 | 104 |
| | Elevata | 25 | 34 | 30 | 47 | 62 | 60 b | 83 | 92 |
| | Av. R. | 27 c | | b 37 c | | b 56 b | | 95 a | |
| | Av. F.C. | | 33 d | | a 54 c | | a 74 b | | 99 a |

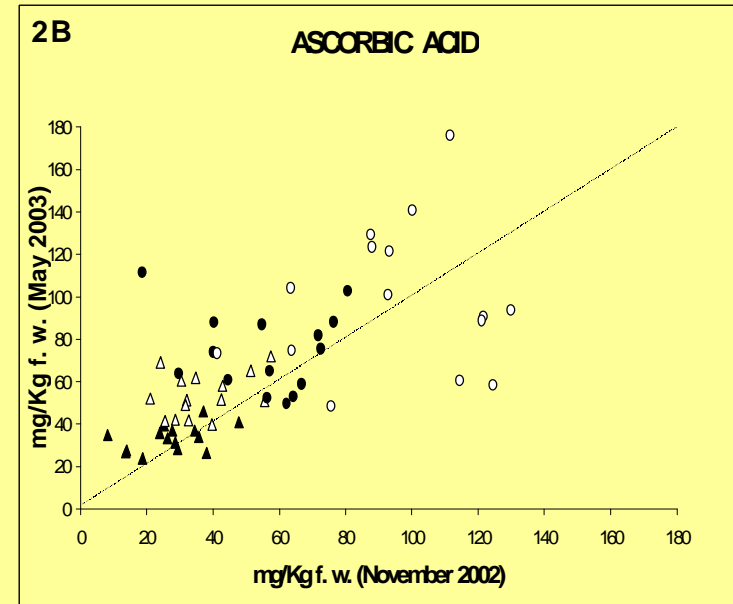
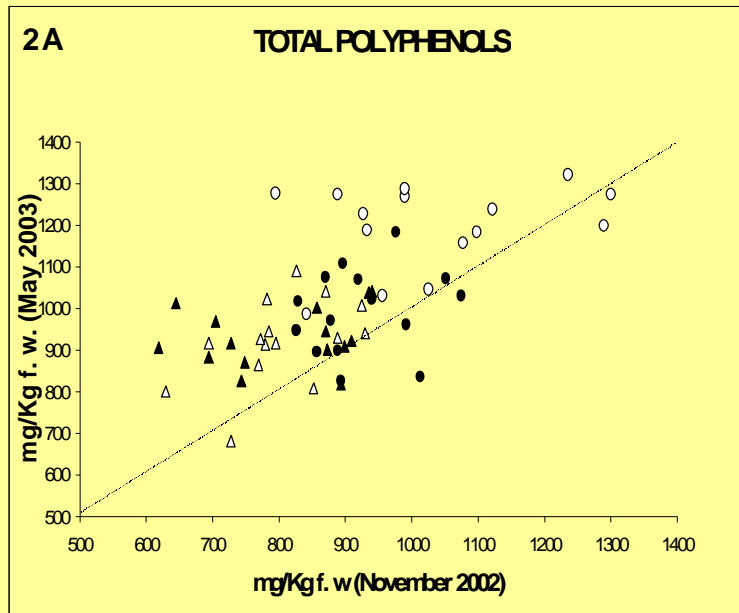
3 Racc. = alla raccolta (settembre 2002); F.C. = a fine conservazione (maggio 2003).

4 Medie in colonna con stesse lettere non sono significativamente diverse al Test di Duncan.

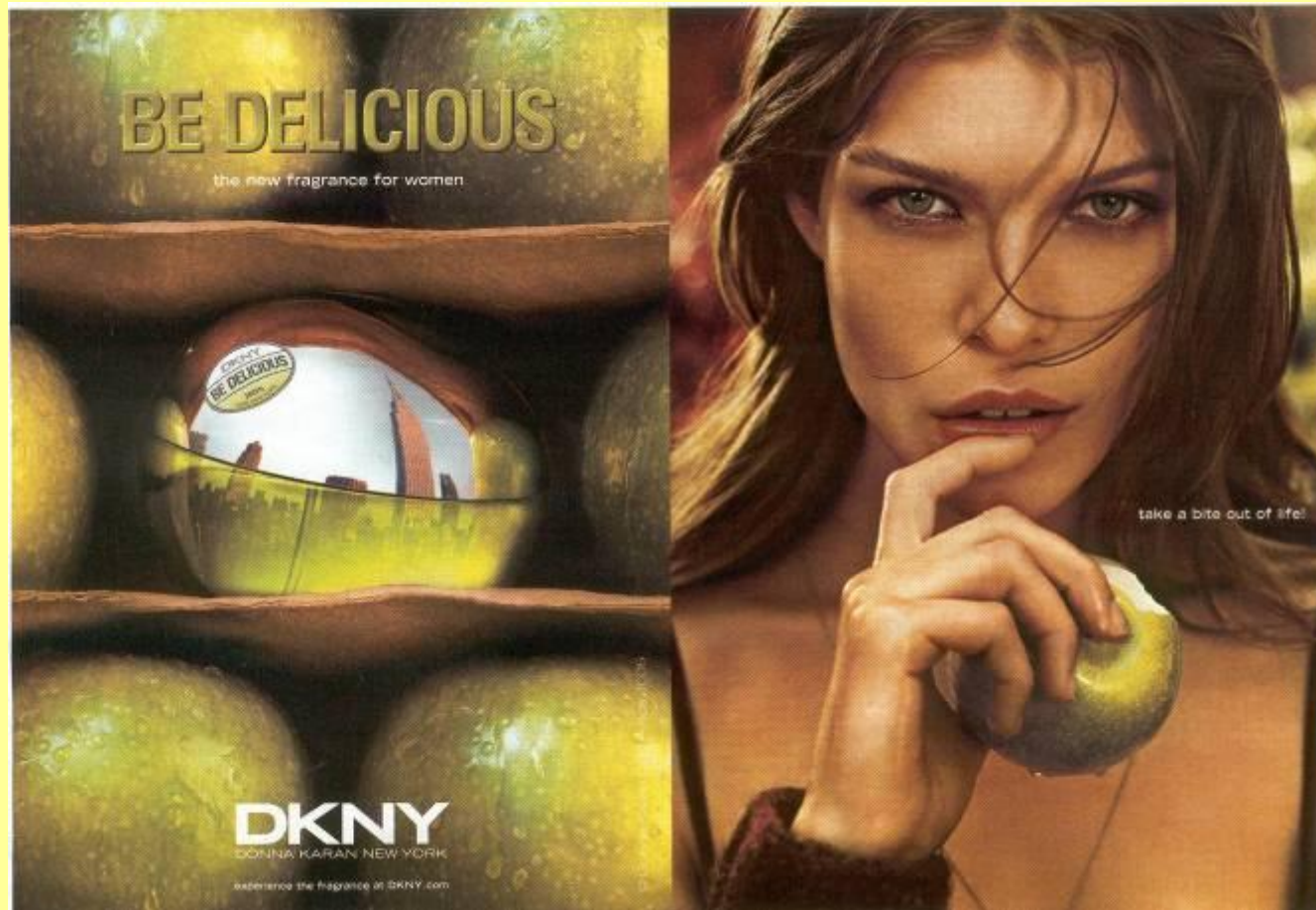
5 Av. R.= Indice medio alla raccolta; Av. F.C. = Indice medio a fine conservazione. Medie con stesse lettere sulla riga, ed in corsivo sulle colonne, non sono significativamente diverse al Test di Duncan.



Polifenoli totali alla raccolta e dopo 210 gg di conservazione in mele Golden Delicious, prodotte nei frutteti A-340 (p); B-540 (r); C-740 (l) e D-940 (•).



I polifenoli estraibili e l'acido ascorbico si sono significativamente accresciuti in conservazione, particolarmente con l'elevarsi della quota altimetrica del sito di produzione e con il contenimento della carica produttiva degli alberi.



Grazie per la vostra attenzione!