

## Distribution of the Volatile Fraction in Different Tissues of *Capsicum* fruits

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### SUMMARY

Paprika and chile peppers (*Capsicum spp.*) are one of the most versatile vegetables in the World. They are used in a plethora of recipes to which they contribute with their particular flavour (DeWitt and Bosland, 2009). In this respect, because of their relatively low levels in sugars and organic acids, flavour in *Capsicum* pods depends mainly on two factors: pungency (in chile peppers) and volatile fraction (both chile peppers and paprika) (Rodríguez-Burruezo *et al.*, 2010). Pungency has been largely studied, while reports in volatiles are considerably lower although in the last years they are increasing (Rodríguez-Burruezo *et al.*, 2010). In this respect, it is known that capsaicinoids, the compounds responsible for pungency, accumulate mainly in the placenta (and veins) and seeds (Bosland and Votava, 2000). By contrast, the distribution of volatiles in *Capsicum* pods is unknown. In this contribution we present the preliminary results of the first study focused on the distribution of volatiles in the unripe (green) fruits of several *Capsicum* cultivars. For the present experiment 15 plants from 6 *Capsicum* cultivars (5 *C. annuum*: California Wonder, Serrano, Chile de Arbol, Cayenne, Pasilla; and 1 non-pungent *C. chinense*: Ají Dulce) were grown in Valencia (Spain) under greenhouse in the Spring-Summer growing season 2010. For each cultivar, we analyzed 5 3-grams samples (from 3 different plants each). Samples were subjected to head space solid phase microextraction (HS-SPME, trapped on fiber 50/30  $\mu$ M DVB/CAR/PDMS (Supelco, Bellefonte, PA, USA)). Volatile fractions were analyzed by GCMS (Trace GC-Ultra/ Polaris Q, Thermo Fisher, USA), equipped with an Thermo TR5 ms fused silica capillary column (5%-phenyl-95%-dimethylpolysiloxane, 30 m, 0.25 mm i.d., 0,25  $\mu$ m film). The column was programmed from 100°C at a rate of 5°C·min<sup>-1</sup> to 250°C. Helium was utilized as carrier gas at a flow of 1 mL·min<sup>-1</sup>. Transfer line was maintained at 220°C. The detection by the mass spectrometer was performed in the electron impact (EI) mode (70 eV ionization energy). The acquisition was performed in scanning mode (mass range  $m/z$  35-350 a.m.u.). Identification of individual volatiles was done by comparing their mass spectra and corresponding retention time with commercially available reference substances (Fluka, Deisenhofen; Sigma-Aldrich, Munich; Germany), and synthesized compounds and by comparison with the NIST-Library. A total of 37 volatiles were identified in the volatile fraction of the studied cultivars. To simplify the interpretation of results most individual volatiles were grouped into chemical families: terpenoids, esters, and alkanes; with the exception of 3-isobutyl-2-methoxy pyrazine (nitrogen-sulphur compound), commonly known as bell pepper pyrazine, and methyl salicylate (phenol derivative). Our findings revealed considerable difference among cultivars in the content of volatiles and, also that, in most cases, placenta/seeds accumulate higher

levels of volatiles than fruit flesh. Thus, in terms of total volatiles, Cayenne, followed by Aji Dulce and Serrano showed the highest levels in both flesh and placenta/seeds, while the lowest values corresponded to California Wonder and Pasilla (Tab. 1). Furthermore, all cultivars showed higher total volatiles in placenta/seeds than flesh, although the difference depended greatly on the cultivar. Thus, placenta/sedes levels in Serrano, Chile de Arbol, Cayenne, and Aji Dulce were 5 to 10-fold those recorded in flesh fruit (Tab. 1). The study of group of compounds revealed that terpenoids were the most abundant compounds in all cultivars, although remarkable levels of esters in Cayenne and Aji Dulce and alkanes in Serrano and Cayenne were found (Tab. 1). The levels of the bell pepper pyrazine were considerably lower (Tab. 1), as usual in this compound, although its extremely low odour threshold make it one of the most important volatiles for paprika aroma, particularly when green (Rodríguez-Burruezo *et al.*, 2010). Methyl salicylate was only found in Chile de Arbol in both flesh and placenta/seeds, and very low levels in the flesh of California Wonder and Pasilla (Tab. 1). In most cases, as found for total volatiles, each compound or groups of compounds appeared at higher levels in the placenta/seeds than flesh. In this respect, esters levels of Cayenne in placenta/seeds were almost 20-fold those of the flesh ( $43.7$  vs.  $792.4 \times 10^6$ ) (Tab. 1). The contrary was only found in volatiles found at low levels, which could be mainly due to small errors in the estimates (e.g. methyl salicylate in Chile de Arbol or bell pepper pyrazine in Pasilla) (Tab. 1).

Tab. 1  
Tissue distribution (Fl: flesh vs.PI/S: placenta and seeds) of the main groups of volatiles and individual volatiles in *Capsicum* cultivars. Content of volatiles expressed as mean peak area  $\times 10^6$

Compounds <sup>1</sup>	California W		Serrano		Chile Arbol		Cayenne		Pasilla		Aji Dulce	
	Fl	PI/S	Fl	PI/S	Fl	PI/S	Fl	PI/S	Fl	PI/S	Fl	PI/S
Terpenoids	55.2	72.7	10.8	48.7	51.3	284.9	242.1	938.9	29.6	23.8	12.0	154.0
Esters	--	--	1.1	14.0	--	--	43.7	792.4	--	--	95.6	894.7
Alkanes	1.7	14.5	92.3	610.9	5.9	9.34	179.3	854.0	17.4	33.7	8.1	41.2
3-IsB-2M Pyr	0.7	1.6	0.5	tr	0.7	2.3	tr	tr	0.4	0.2	--	--
Methyl Sal	tr <sup>2</sup>	--	--	--	6.6	3.6	--	--	0.4	--	--	--
TOTAL	59.2	89.1	105.7	683.9	65.8	300.2	518.5	2596.2	49.8	59.8	115.7	1089.8

<sup>1</sup> 3-IsB-2M Pyr: 3-isobutyl-2-methoxy pyrazine (bell pepper pyrazine), Methyl Sal: methyl salicylate. <sup>2</sup>tr: traces ( $< 0.1 \times 10^6$  peak area).

**Keywords:** *Capsicum* peppers, volatiles, fruit tissues, genotypic diversity

Aknowledgements. This work has been partially financed by INIA through Project RTA2010-00038-C03-03.

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