

Final Report for Hargreaves Plants

Blackberries: comparing Arkansas varieties with industry standards and wild blackberries.



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Summary:

- Ouachita and Apache consistently supply larger berries than other varieties.
- Early crop Apache, Ouachita and Navaho are sweeter and lower in tartaric acid than Loch Ness.
- Tartaric levels are generally lower in Apache, Ouachita and Navaho compared with other varieties, especially Loch Ness.
- °Brix levels are generally lowest in Chester and Loch Ness compared with other varieties throughout the season. Thus Arkansas varieties should taste significantly sweeter.
- The traditional blackberry varieties (Loch Ness and Chester) contain several different volatiles to Arkansas varieties, which could make the traditional varieties taste rather greener than the other varieties.
- The Arkansas varieties contain several different volatiles to traditional varieties, which could confer higher floral/fruity notes to the new varieties.
- Total quantities of flavour volatiles were highest in cv Ouachita, followed (at half the level) by Apache, then Loch Ness, Navaho and Chester in that order. Differences are significant between Ouachita and Navaho and Chester. One would expect this level

of difference to be noticeable: cv Ouachita should have a noticeably more intense flavour than other varieties, especially Chester.

- The wild variety had similar levels of total volatiles as Loch Ness and Apache. However, in the wild type there were more volatiles which would confer a fruity alcoholic aroma, and less green notes.

Conclusions:

- Apache, Ouachita and Navaho are generally the same weight or larger, and are sweeter and either less, or as acidic, as cvs Loch Ness and Chester.
- Overall, Arkansas varieties, especially Ouachita and Apache, had more flavour volatiles than Loch Ness and Chester.

Background: Blackberries are valued for their juiciness, flavour and 'healthiness'. All of these factors are linked together. The colour of the fruit is directly linked to 'healthiness': anthocyanins cause the deep black colour. Flavour is the result of a combination of sweetness (sugars), acids (citric and malic acid) and flavour volatiles. Most scientific studies looking at blackberry flavour analyse sugars, acids and volatiles.

Aims: To compare the Arkansas varieties of blackberry (Ouachita, Navaho, Apache) for flavour, with industry standard varieties Loch Ness and Chester. The latter are generally hard, acidic and generally used for cooking. The new varieties are dessert varieties: sweeter and better for eating.

Analysis:

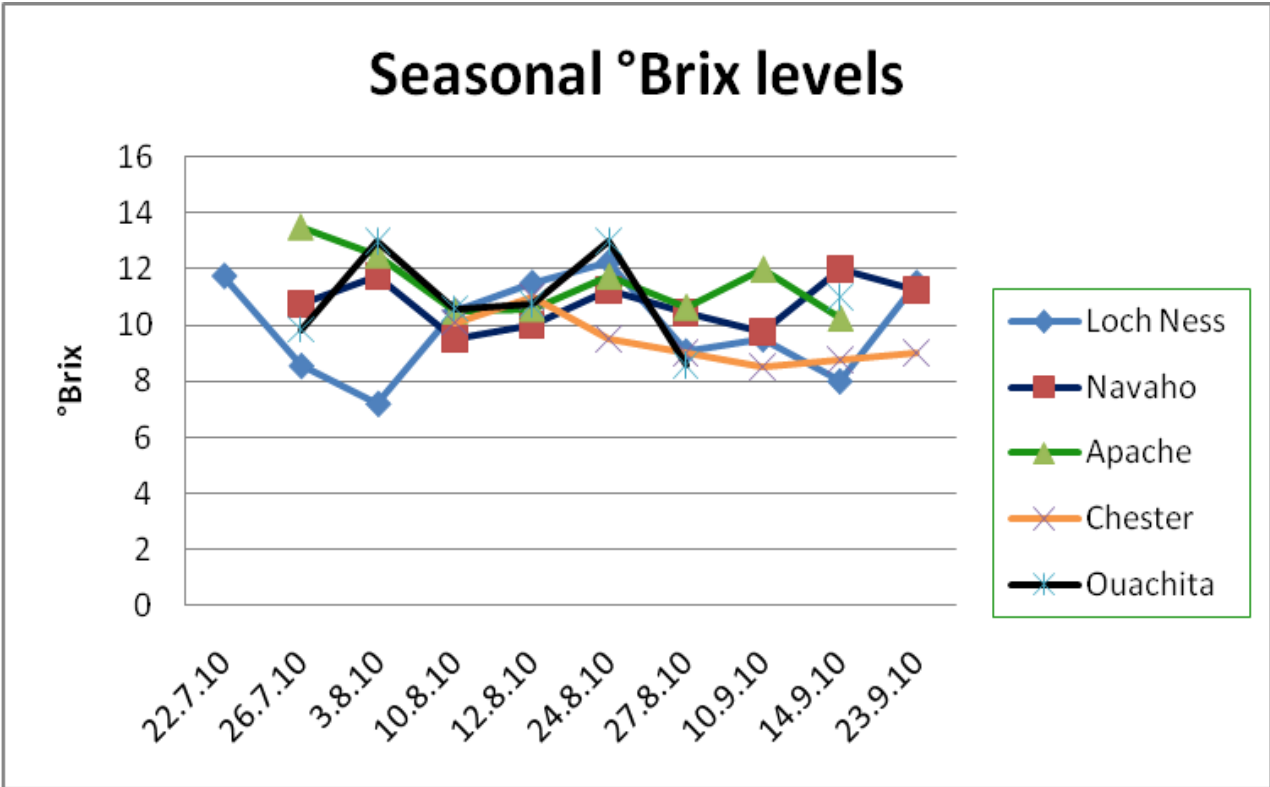
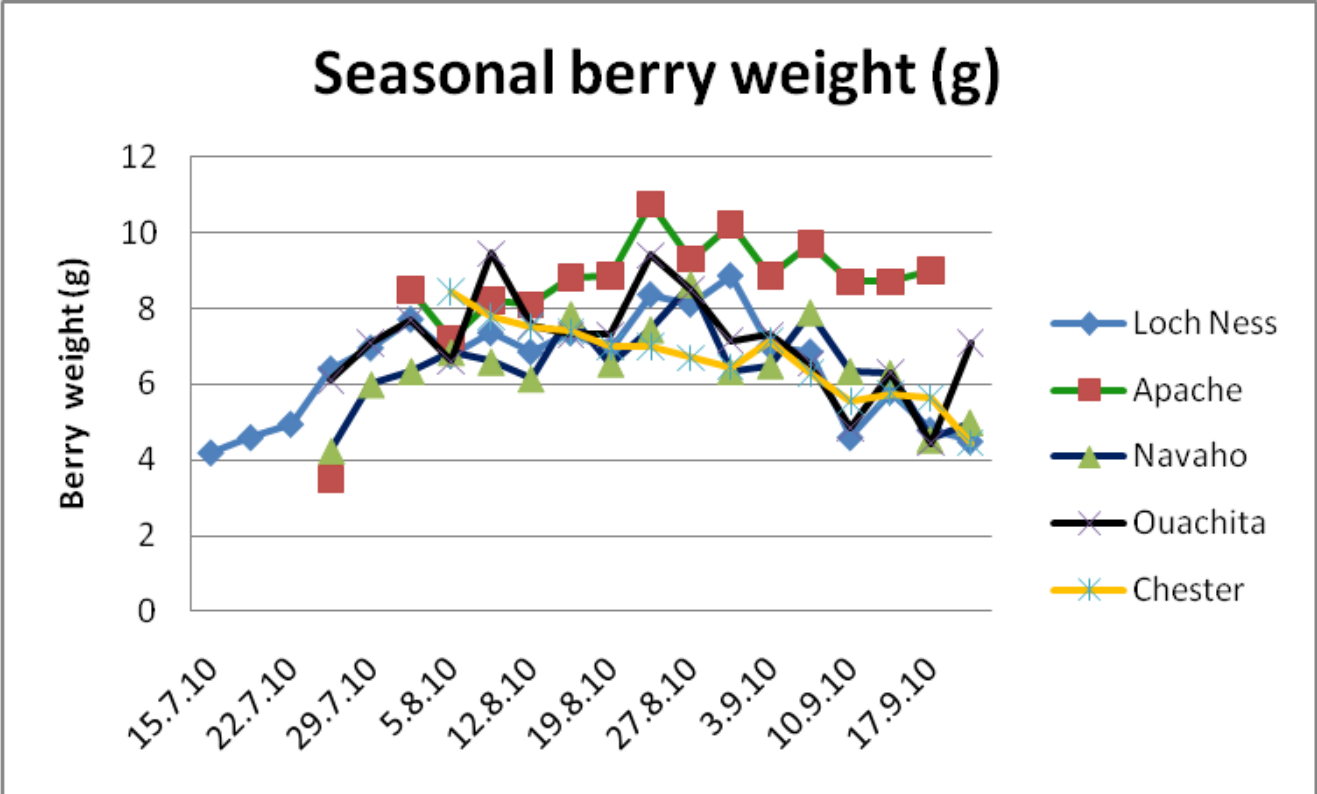
- **Sensory and °Brix analysis** was undertaken by Hargreaves Plants.
- **Flavour Analysis** was undertaken (x 3/sample) by an independent flavour analysis laboratory using an HP5890 Series II Gas Chromatograph with auto-injector, a HP5972 Mass Selective Detector, with Spectral Libraries: F&F Projects Ltd, NIST02 on a Stabilwax 30m, 0.25mm ID, 0.25µm df column using carrier Gas: Hydrogen. The oven was at 50°C for 5mins, 5 °C per min. to 150 °C, 10 °C per min. to 240 °C. Solid phase micro extraction fibres with 50/30µm DVB/Carboxen/PDMS coating were used to adsorb volatiles from 30g frozen blackberries defrosted at room temperature for 60 minutes. Brine (25% salt) was added then homogenised with a hand blender (Breville). 50g of this mix transferred to a SMPE bottle then headspace absorbed on to the SPME fibre at 75°C, stirred for 30 minutes with 2 minutes desorption in the GCMS injector.

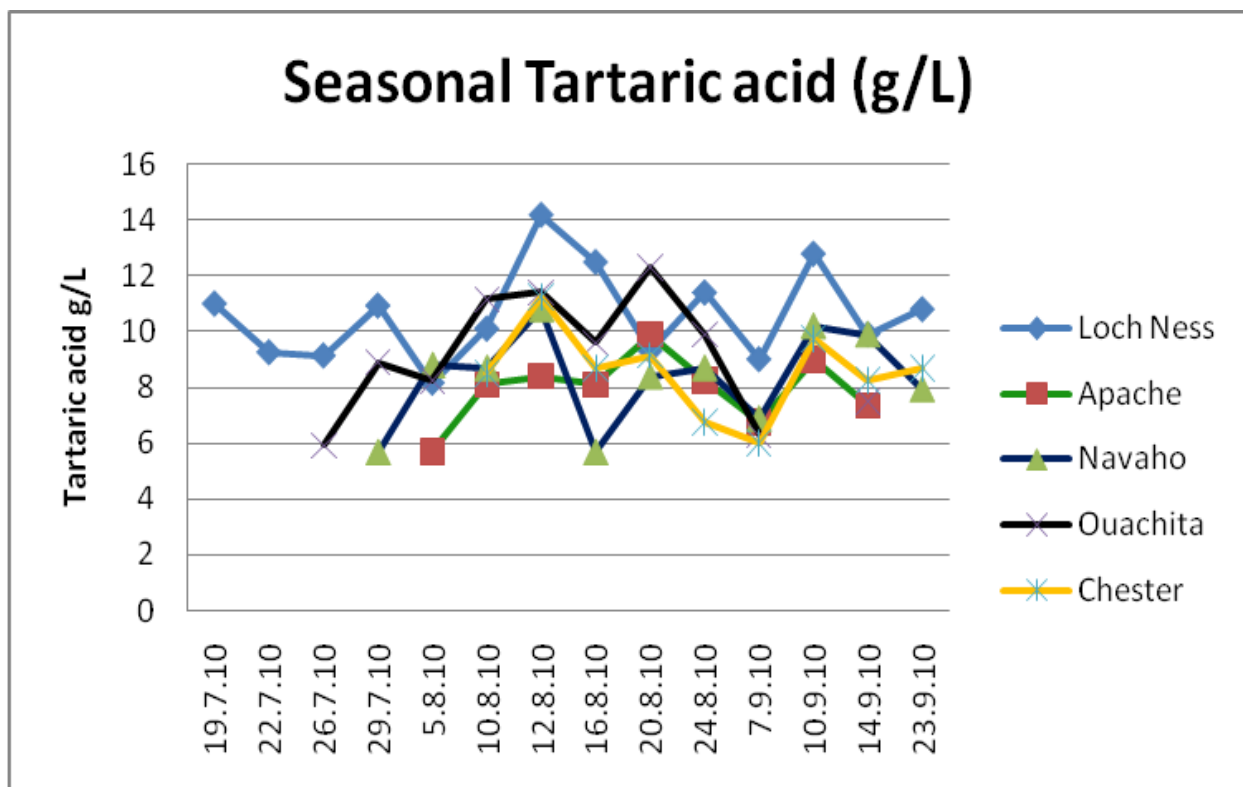
Results:

Cultivar	details	supplier	°Brix* av.	Tartaric acid av.* (g/L)	Description**	Av. wt./ berry* (g)
1.Ouachita	Mid-season florricane. 300-400 chilling hours.	Exclusive to Hargreaves Plants.	11	9.1	Blocky shape, compact drupelets. Glossy appearance. Easy to pick. High yield (comparable to Loch Ness). Flavour is low acid, pleasant sweetness, good blackberry flavour	7.1
2.Loch Ness	Main UK cv. Mid season.	Hargreaves Plants	10	10.6	Flavour is watery, bland, slight acid, low sugar.	6.3
3.Navaho	Mid-season florricane. 800-900 chilling hours.	Hargreaves Plants	10.7	8.3	Conic shape with compact drupelets, good cohesion. Glossy fruit. Flavour is slight astringency, variable acidity, slight sweetness, some fruity flavours.	6.3
4.Apache	Early season. 500+ hours chilling.	Hargreaves Plants	11.5	8.0	Flavour is very low acid, fruity with very pleasant blackberry flavour, high sugar.	8
5.Chester		Hargreaves Plants	9.4	8.6	Flavour is slight acid, astringent, some watery sweetness.	6.7

* See graphs below.

**From Hargreaves assessments and fliers supplied by Hargreaves Plants.





Comments:

- Ouachita and Apache consistently supply larger berries than other varieties.
- Early crop Apache, Ouachita and Navaho are sweeter and lower in tartaric acid than Loch Ness.
- Tartaric levels are generally lower in Apache, Ouachita and Navaho compared with other varieties, especially Loch Ness.
- °Brix levels are generally lowest in Chester and Loch Ness compared with other varieties throughout the season.

Conclusions: Apache, Ouachita and Navaho are generally the same weight or larger, and are sweeter and either less, or as acidic, as cvs Loch Ness and Chester.

Flavour volatiles

Scientists have identified up to 147 different flavour volatiles in blackberry fruits (Reineccius, 2010); some have listed 5-hydroxymethyl furfuryl as the primary blackberry-like aromatic compound. In a comparative study (Qian and Wang, 2005), the most abundant volatiles in 'Marion' blackberry were acetic, 2/3-methylbutanoic, hexanoic and decanoic acids, ethanol, and linalool, whereas the most abundant volatiles in 'Thornless Evergreen' were 2-heptanol, hexanol, octanol, α -pinene, nopol, and *p*-cymenol. Compared with 'Marion,' 'Thornless Evergreen' contained significantly more total volatiles, especially in alcohols, terpenoids, and phenols, whereas 'Marion' contained more organic acids. The compounds with the high odour activity values (OAV > 10) in 'Marion' were ethyl hexanoate, β -ionone, linalool, 2-heptanone, 2-undecanone, α -ionone, and hexanal. The compounds with the high odour activity values (OAV > 10) in 'Thornless Evergreen' were ethyl hexanoate, 2-heptanone, ethyl 2-methylbutanoate, 2-heptanol, 3-methylbutanal, α -pinene, limonene, *p*-cymene, linalool, *t*-2-hexenal, myrtenol, hexanal, 2-methylbutanal, and sabinene.

The aroma of key blackberry volatiles.

Volatile	Aroma	Volatile	Aroma
Acetaldehyde	Toppy, ethereal, fruity, almost a sensate at low levels as well as an odour. Citrusy and sharp in slightly higher doses.	Ethyl hexanoate	Powerful, diffusive, fruity-winey odor, suggestive of Green Apple, Banana, Pineapple, with a slightly floral undertone.
Acetic acid	Sharp, pungent. Acidic, astringent, vinegaric.	Beta-ionone	floral woody sweet fruity berry tropical beeswax
Methyl butyrate	Appley, sweet, diffusive, some ripe pear character.	Linalool	citrus floral sweet bois de rose woody green blueberry
Heptanone	Powerful, diffusive green-fatty, fruity. Reminiscent in dilution of ripe melon and some aspects of banana. (assuming 3-heptanone)	2-Heptanol	fresh lemon grass herbal sweet floral fruity green
Ethyl butyrate	Fruity, sweet, diffusive. Central to pineapple and other powerful fruit volatiles. Also suggestive of ripe banana.	Ethyl methyl butanoate	Central to the character of sweet, ripe orchard fruits. Extremely suggestive of red apple and ripe pear, also some more tropical almost pineapple character.

Blackberry fruit (frozen) were blended to produce a fruit 'smoothie', and the flavour volatiles were adsorbed onto solid phase microextraction fibres and then analysed by GCMS.

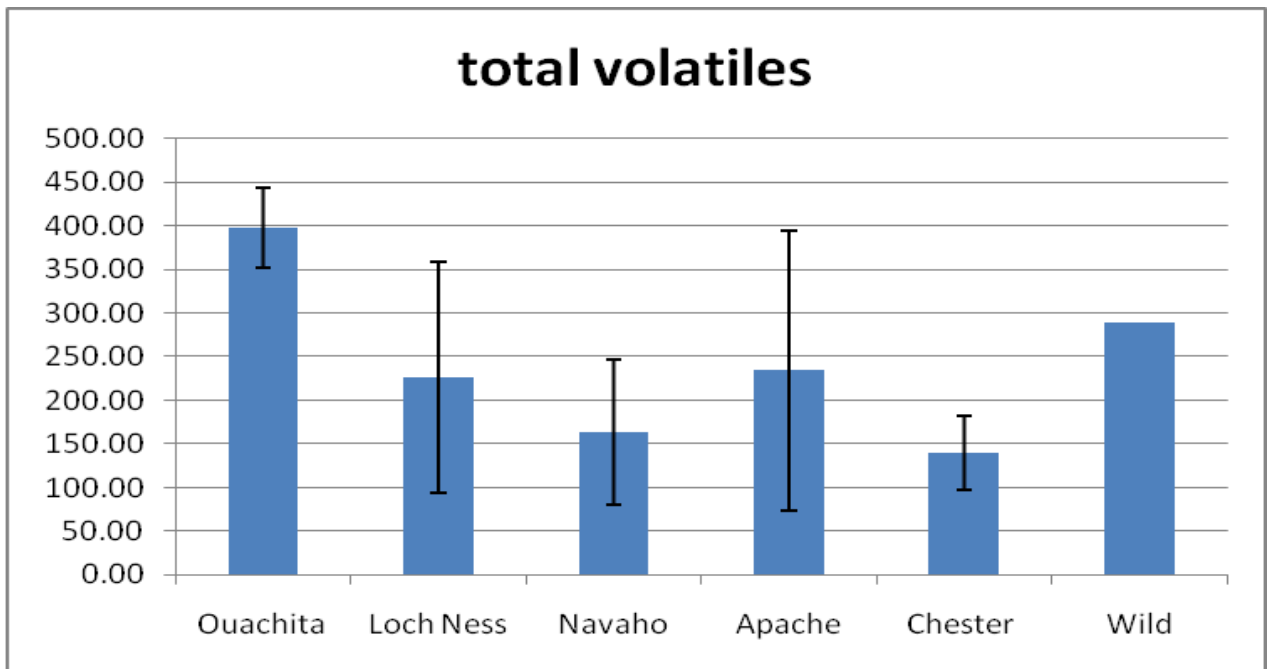
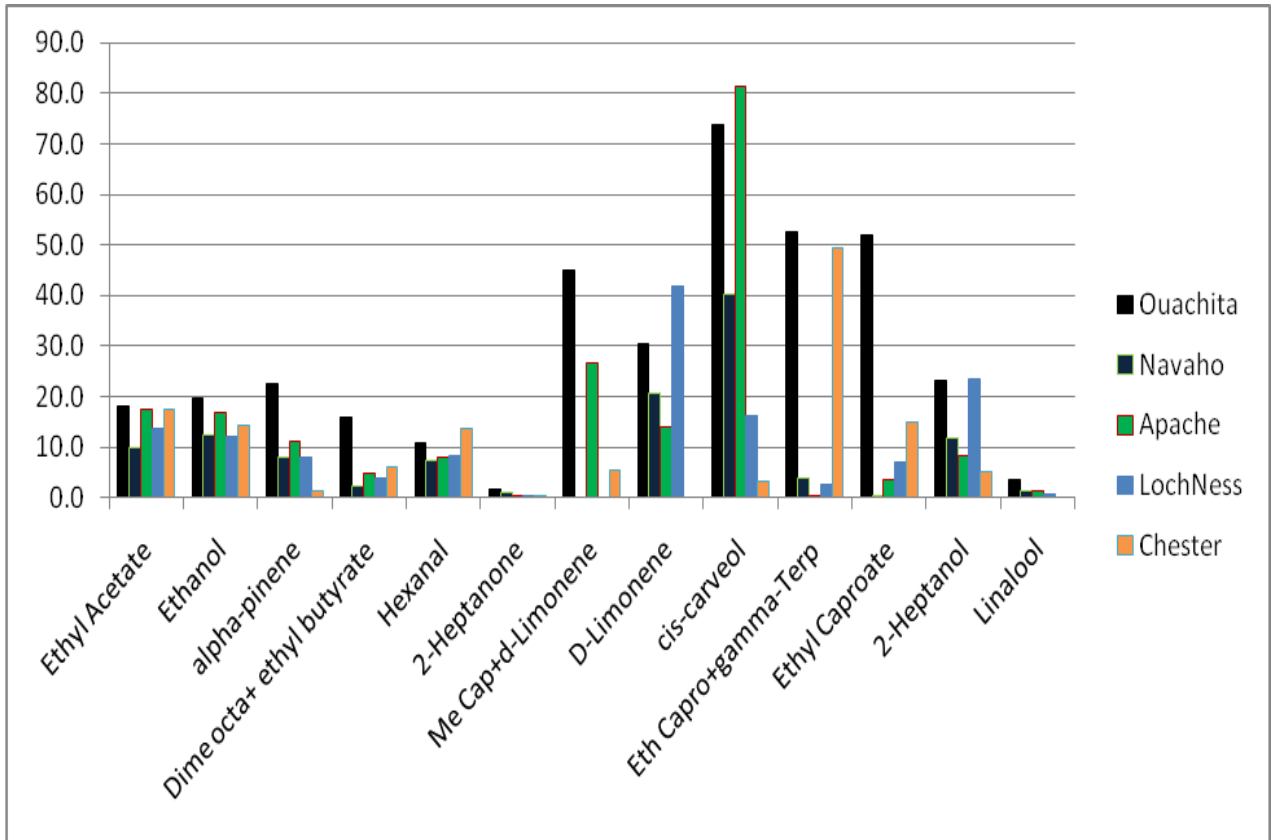
The wild fruit sample was not frozen and the fruits were very soft/ripe (very juicy).

Flavour volatile (area)	Ouachita	Navaho	Apache	Loch Ness	Chester	Wild
Acetaldehyde	2.4	0.4	1.0	1.8		
Methyl Acetate		0.3	1.0	0.6	0.9	10.84
Ethyl Acetate	18.2	10.0	17.5	13.8	17.6	65.1
Ethanol	19.9	12.4	17.0	12.3	14.4	52.8
Pentenal				6.6	5.2	
Methyl Butyrate	4.0	4.0	2.6		3.2	
Ethyl propionate						8.9
Propyl acetate						9.2
alpha-pinene	22.5	8.1	11.1	8.1	1.3	
Dimethyl octadiene + ethyl butyrate	15.8	2.3	5.0	3.9	6.2	
Dimethyl octadiene	4.2		1.1			
Isobutyl acetate						4.9
Ethyl Butyrate	7.5		2.1		13.3	2.7
Ethyl-2-Methyl Butyrate	0.6	0.4	0.5	0.2	0.5	0.6
Camphene	11.8	5.6	7.6	3.9	0.6	
p-Menth-3-ene + Ethyl Isovalerate	0.7	0.5	0.8	0.6	0.2	
Hexanal	11.0	7.5	8.2	8.4	13.6	4.1
beta-pinene	1.8	1.0	1.2	7.6		
isobutanol						2.8
2,6-Dimethyl-2,6-octadiene	5.4	0.4	2.9	2.0	1.2	
Isoamyl acetate						14.1
p-menth-1-ene	4.3	3.7	3.9	7.1	1.4	
beta-Myrcene	1.1	0.5	1.5	0.5	0.2	
alpha-terpinene	2.1	0.8	2.2	1.0	0.4	
2-Heptanone	1.8	0.9	0.4	0.5	0.5	4.4
Methyl Caproate + d-Limonene	45.1		26.5		5.5	
Methyl Caproate	13.1					
D-Limonene	30.4	20.8	14.0	41.8		
cis-carveol	73.9	40.3	81.2	16.2	3.4	
Isoamyl alcohol						16.3
tr-2-hexenal		6.9		6.4	5.2	2.5

Flavour volatile (area)	Ouachita	Navaho	Apache	LochNess	Chester	Wild
Ethyl Caproate + gamma-Terpinene	52.7	4.1	0.6	2.7	49.5	
Ethyl Caproate	52.0	0.5	3.5	7.1	15.0	3.0
gamma-Terpinene	5.3	0.9	3.4	3.4		
cis-beta-ocimene	13.4		5.8	1.8	2.3	
p-cymene	16.6	6.8	11.9	17.4	0.6	
Terpinolene + Hexyl Acetate	12.9	4.0	0.9	3.4	5.1	4.0
Terpinolene		6.6	7.7	12.2		
cis-3-hexenyl formate	0.4	0.2	0.1	0.4	0.2	
cis-3-hexenyl acetate	0.6	0.4	0.3	1.0	0.5	
2-Heptanol	23.3	11.8	8.4	23.6	5.2	19.9
tr-2-Hexenyl Acetate	6.7	1.5	1.1	6.4	4.3	
Ethyl-tr-2-Hexenoate	0.9			4.0		
1-Hexanol	5.9	4.1	3.1	4.8	5.4	38.0
1,3,8-p-Menthatriene	1.3	0.4	2.0	1.0		
cis-3-Hexenol	0.6				0.2	
Nonanal		1.1	1.8	1.0	1.6	
trans-2-hexenol	1.7	1.0	0.4	2.1	1.1	
hexyl butyrate				2.5	0.6	
p,alpha-Dimethylstyrene	7.9	3.2	5.9	3.5	0.2	
Ethyl Caprylate	3.0	0.7	0.7	2.4	1.7	0.4
Tetra-hydrolinalol	1.1	0.3				0.8
6-Methyl-5-Hepten-2-ol	0.4	0.5		0.3	0.3	2.0
trans-2-Hexenyl Butyrate				1.9	0.5	
Camphor	0.9	0.3	0.3	0.4		
Decanal	0.7	1.4	0.8	1.0	1.7	
Hydrocarbon (methyl pentene-like)	1.2	0.6	0.8	0.4	1.2	
Benzaldehyde	0.4			0.3	0.3	1.54

Flavour volatile (area)	Ouachita	Navaho	Apache	LochNess	Chester	Wild
Dihydrolinalol	1.7	0.5	0.4			1.1
Linalol + Octanol				0.5	0.2	
Linalol	3.6	1.4	1.3	0.6		0.62
1-Octanol	0.8	0.4	0.9	0.5		8.2
4-Terpinenol	0.9	0.5	1.3	0.9		
Thymyl Methyl Ether	0.5	0.3				
Methyl Benzoate	0.5	0.7			1.7	
Ethyl Caprate	0.4	0.2	0.2	0.2	0.1	0.5
Ethyl Benzoate	0.3	0.9			2.0	
trans-2-Hexenyl Caproate				1.4		
Verbenone	0.2			0.2		
Borneol	1.0	0.7	0.8	1.2		
Carvone	0.5	0.3	0.1			
Methyl Salicylate				0.7	0.3	0.6
Phenyl ethyl acetate						0.5
4-phenyl butanone						0.2
Phenylethyl alcohol						1.1
Myrtenol	0.5	0.3	0.2		0.4	
Ethyl Laurate	0.2			0.1		
p-Cymen-8-ol	1.5	0.8	2.0	1.3	0.1	

Comparison of flavour volatiles absorbed by SPME above blended blackberry samples.



Comments:

- The traditional blackberry varieties (Loch Ness and Chester) are the only varieties which contain pentenal (pungent green apple orange tomato), hexyl butyrate (green sweet fruity apple waxy soapy), 2-hexenyl butyrate (green orchid fruity apple grassy banana) and methyl salicylate (wintergreen, mint). *This could make these varieties taste rather greener than the other varieties.*
- The Arkansas varieties are the only ones which contain dihydrolinalol (bois de rose, woody citrus blueberry weedy) and also contain higher levels of linalool (citrus floral sweet bois de rose woody green blueberry). *This could confer higher floral/fruity notes to these varieties.*
- Total quantities of flavour volatiles were highest in cv Ouachita, followed (at half the level) by Apache, then Loch Ness, Navaho and Chester in that order. Differences are significant between Ouachita and Navaho and Chester. *One would expect this level of difference to be noticeable: cv Ouachita should have a noticeably more intense flavour than other varieties, especially Chester.* Levels of limonene, cis-carveol, gamma terpinene, ethyl caproate were comparatively high in Ouachita. *These could confer a green, freshness to the fruit.*
- Overall, Arkansas varieties, especially Ouachita and Apache, had more flavour volatiles than Loch Ness and Chester.
- The wild variety had similar levels of total volatiles as Loch Ness and Apache. However, in the wild type there was a complete lack of terpenes, which generally provide a 'green' flavour, a high level of 1-hexanol (which is fruity alcoholic in odour), and several fermentation compounds present including ethanol, ethyl acetate, isoamyl alcohol/acetate and phenyl ethyl alcohol /acetate. These provide a sweet fruity/floral flavour.

References

Qian, M. C. and Wang, Y. (2005), Seasonal Variation of Volatile Composition and Odor Activity Value of 'Marion' (*Rubus* spp. *hyb*) and 'Thornless Evergreen' (*R. laciniatus* L.) Blackberries. *Journal of Food Science*, 70: C13–C20.

Reineccius, G (2010). Flavor of small fruits. Chapter 1 in *Flavor and Health Benefits of Small Fruits*. ACS Symposium Series Washington DC.

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