Practical and Effective Strategies to Debitter the HLB-affected Citrus Fruits and Juices

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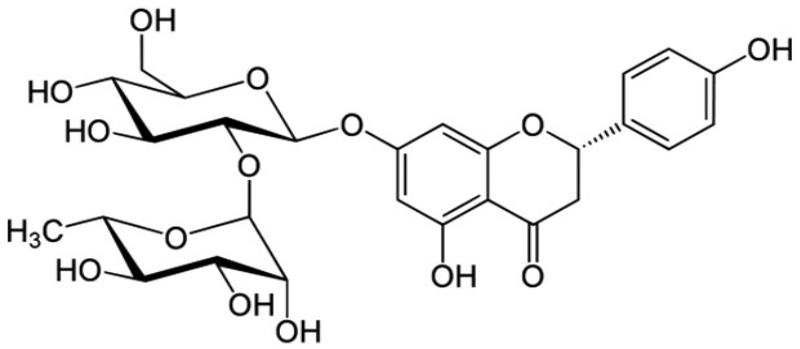
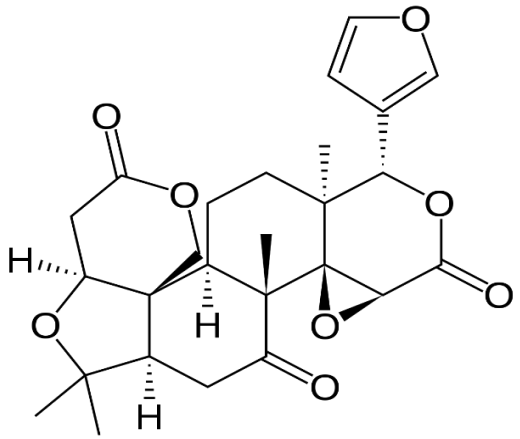
Bitter compounds in grapefruit fruits and juice



Naringin

Account for about 85% of bitterness
100 to 800 µg/mL in commercial grapefruit juices
Taste threshold: 20 µg/mL in water

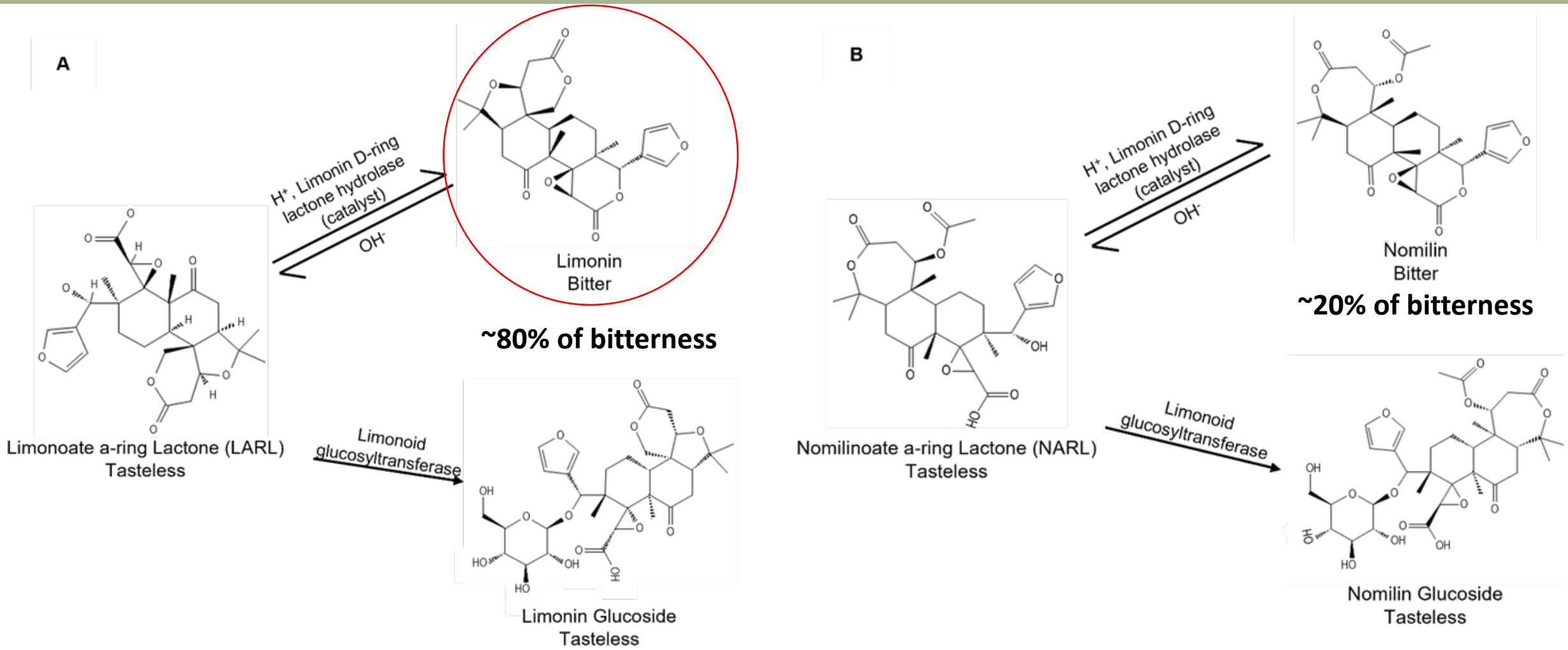


Limonin

Account for 15% of bitterness
7.0-10 µg/mL in commercial grapefruit juices
Taste threshold: 4.7 µg/mL in water

P. S. Jourdan et al. 1982; Dante G. Guadagni et al. 1973

Release of bitter compounds in oranges



V. P. Maier, G. D. Beverly, 1968

Post-harvest debittering strategies

On the fruits

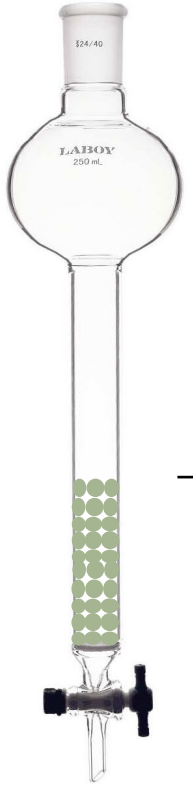
- Can we re-purpose the de-greening approaches (e.g., ethylene treatment) for debittering?
- We have tried and failed!

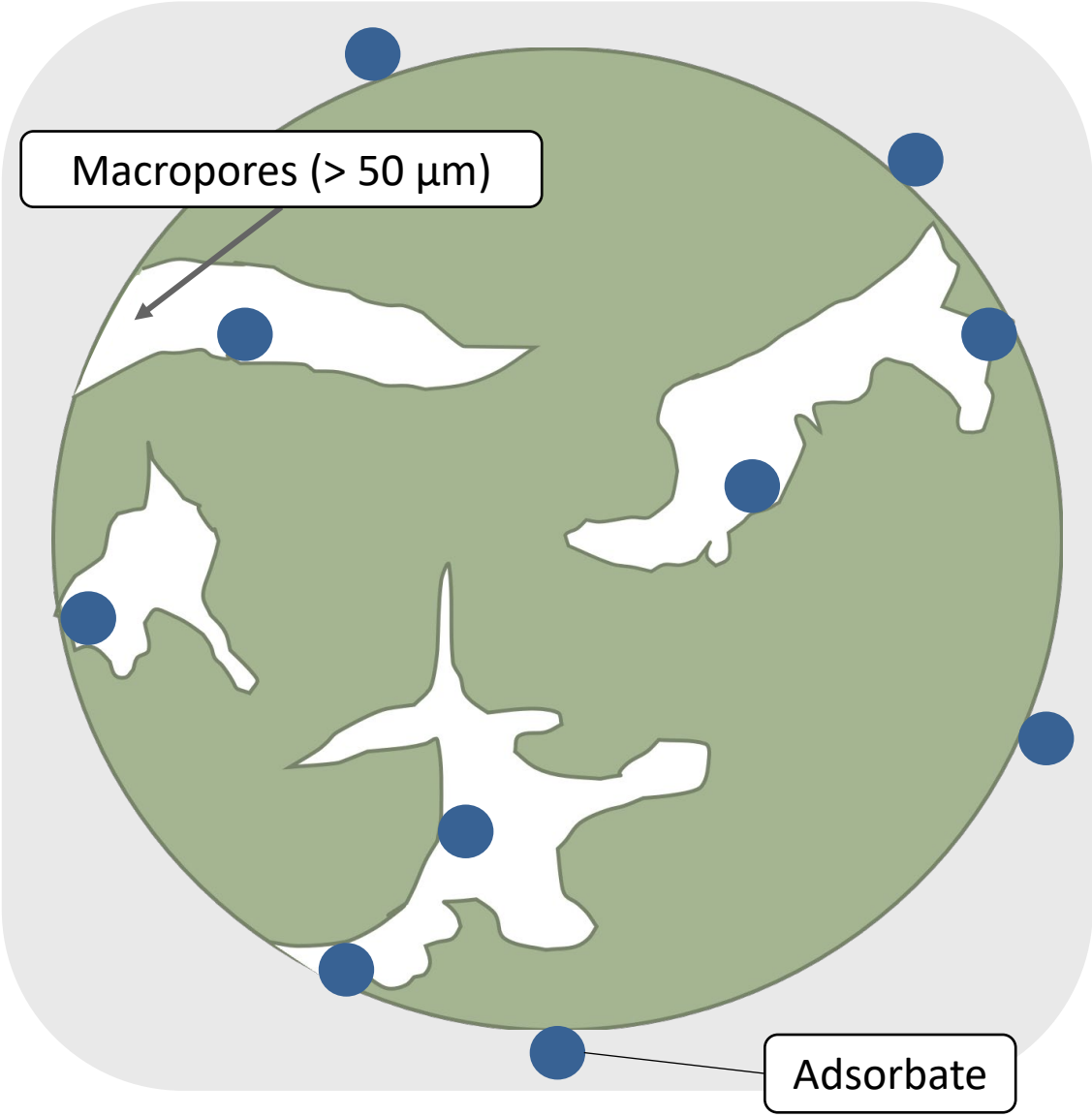
In the juice

- Adding sugar or syrup to the juice (non-starter!)
- Add NaOH to degrade limonoids (are you crazy!)
- Hydrolyze naringin using immobilized naringinase for grapefruit juice (academic value only)
- Partially mask the bitterness by adding β-cyclodextrin (0.5-2%) in the juice (academic value)
- Adsorption using synthetic polymeric resins (effective and practical)

Resin adsorption

PAD900 Resin beads



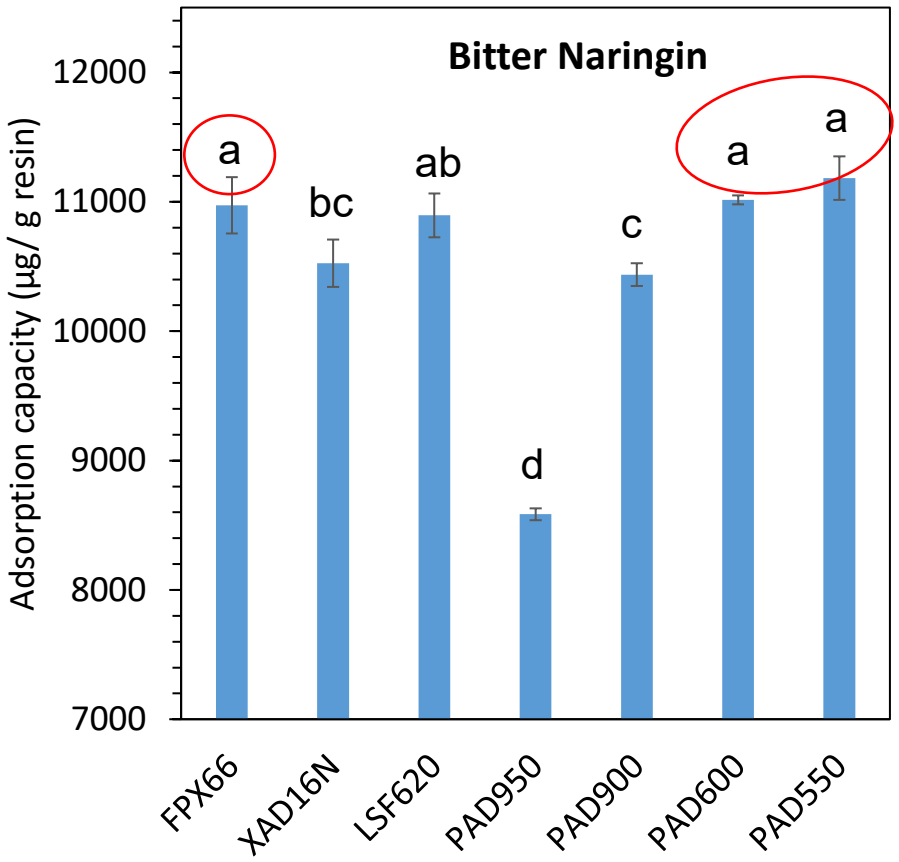


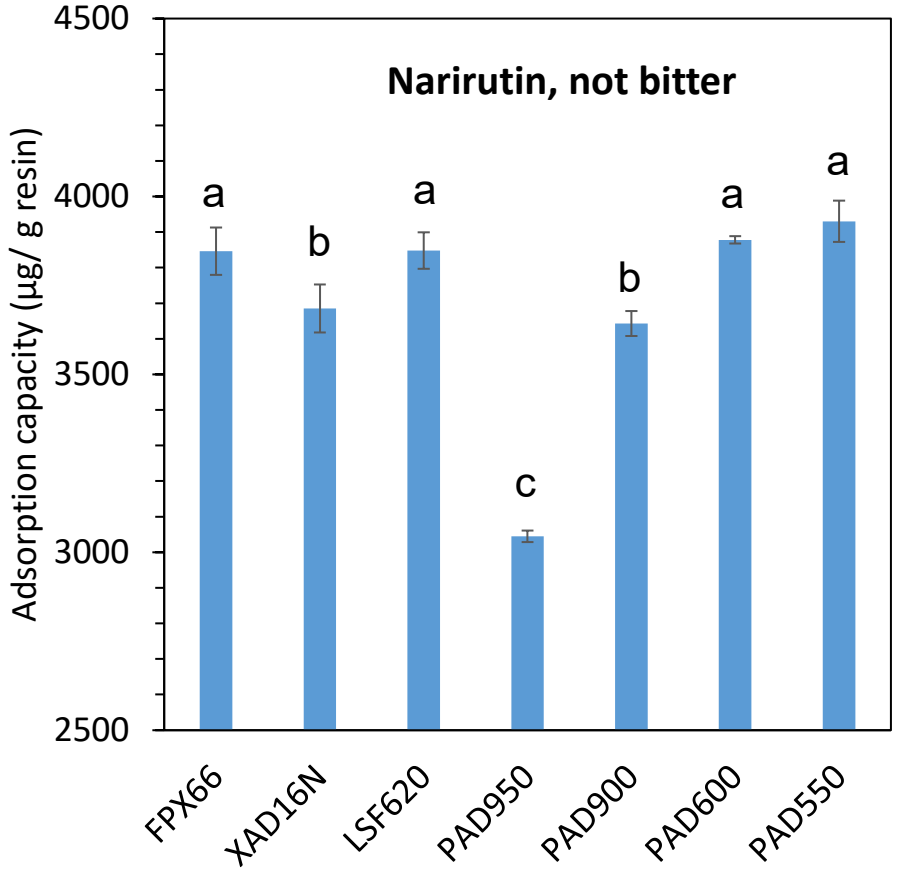
Resin options to debitter grapefruit juice

All approved for food processing

Resins	Chemical nature	Polarity	Surface area (m^2/g)	Mean pore diameter (Å)	Moisture Content (%)	Manufacturer
FPX66	polystyrene-divinylbenzene	nonpolar	700	200-250	80.9 ± 0.013	Dupont
XAD16N	polystyrene-divinylbenzene	nonpolar	800	150	82.2 ± 0.015	Dupont
LSF620	cross-linked styrene copolymers	nonpolar	1200	-	76.8 ± 0.15	Sunresin
PAD950	methylacrylic polymer	nonpolar	450	120	80.7 ± 0.011	Purolite
PAD900	polystyrene-divinylbenzene	nonpolar	850	200	83.3 ± 0.008	Purolite
PAD600	polystyrene-divinylbenzene	nonpolar	850	90	77.4 ± 0.019	Purolite
PAD550	polystyrene-divinylbenzene	nonpolar	950	130	77.2 ± 0.012	Purolite

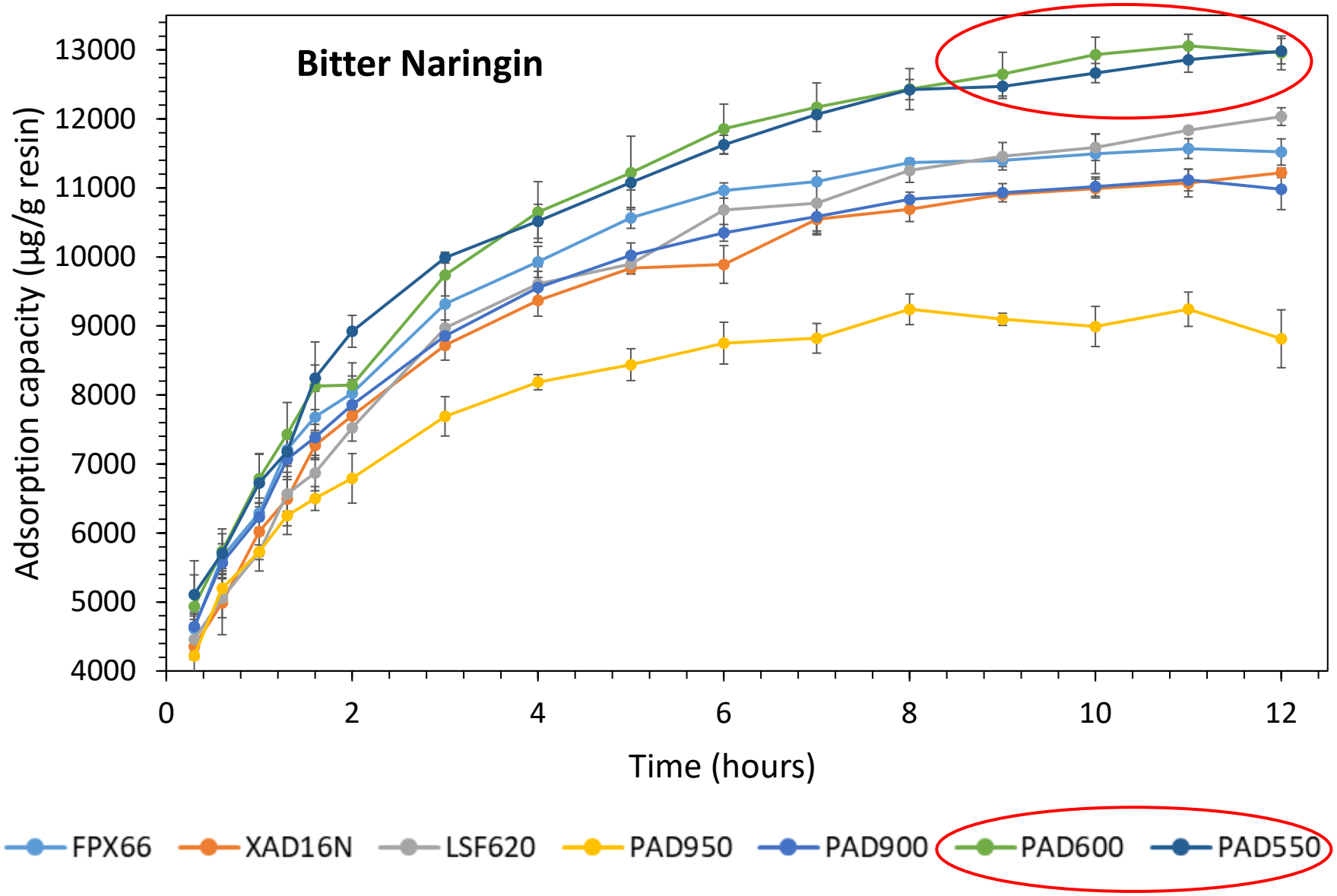
Static adsorption of bitter naringin in grapefruit juice



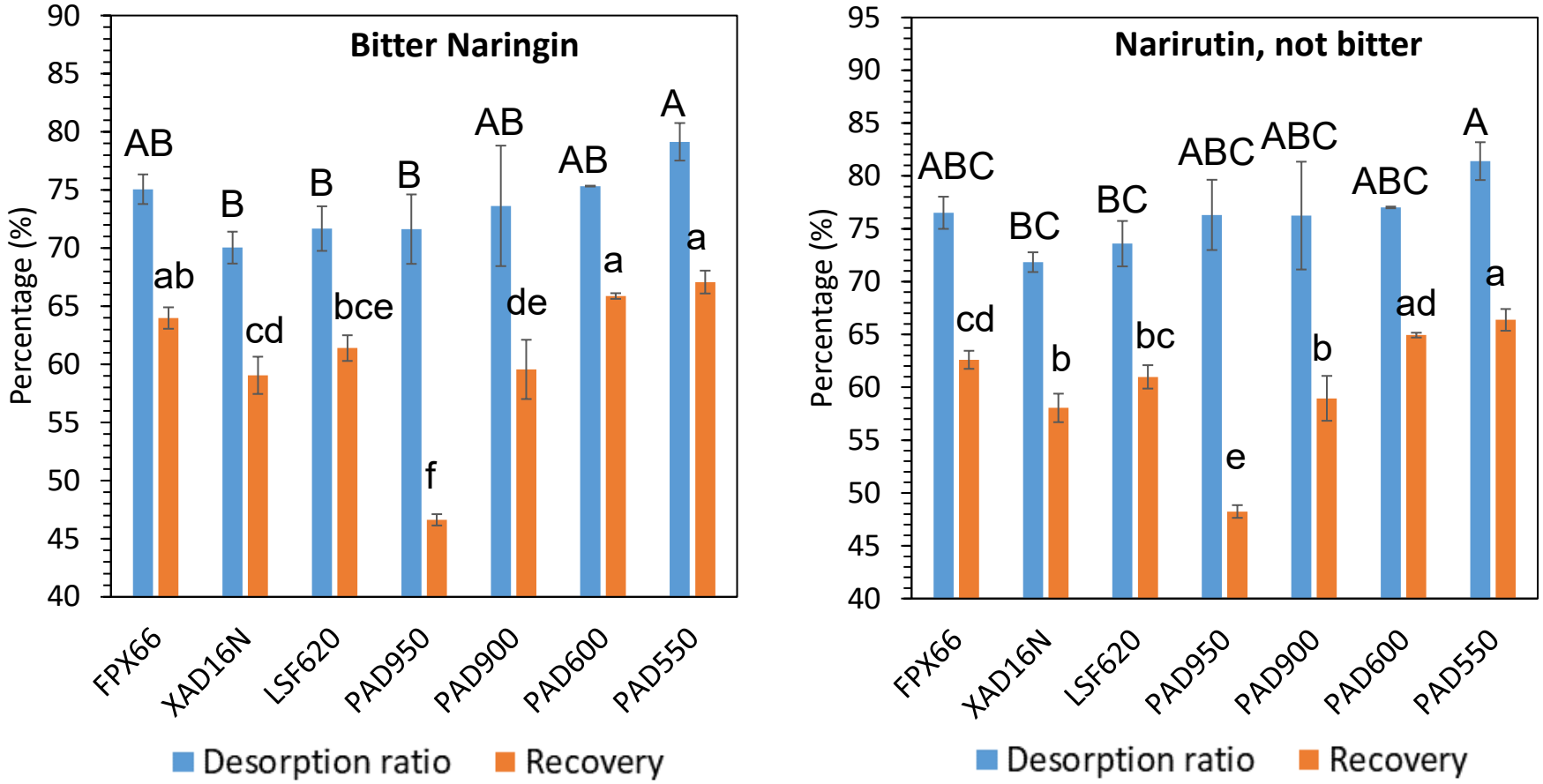


Adsorption capacity: the amount of adsorbate adsorbed per 1 g of dry resin weight

Kinetic adsorption of naringin in grapefruit juice over 12 hours



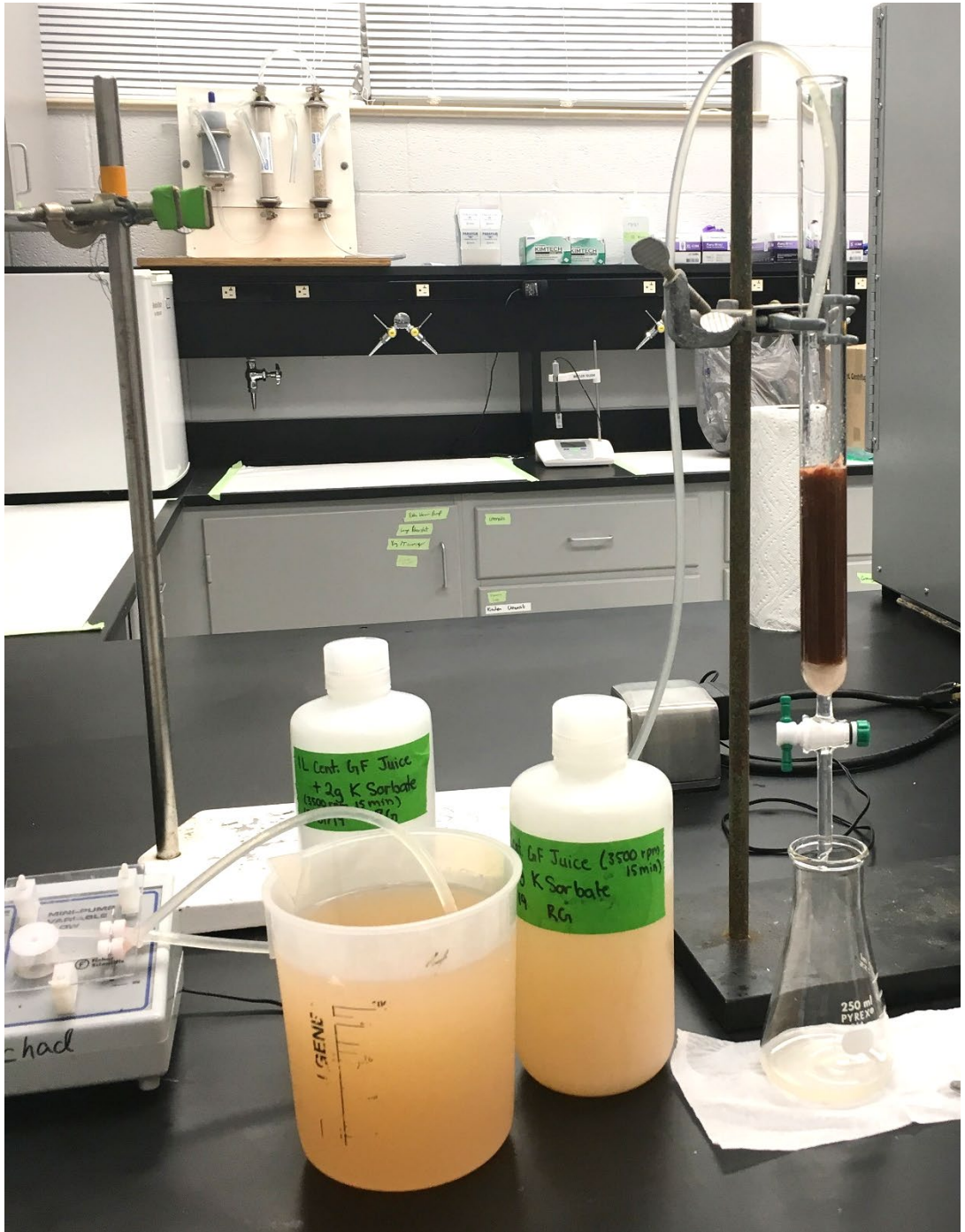
Static desorption by ethanol for grapefruit juice



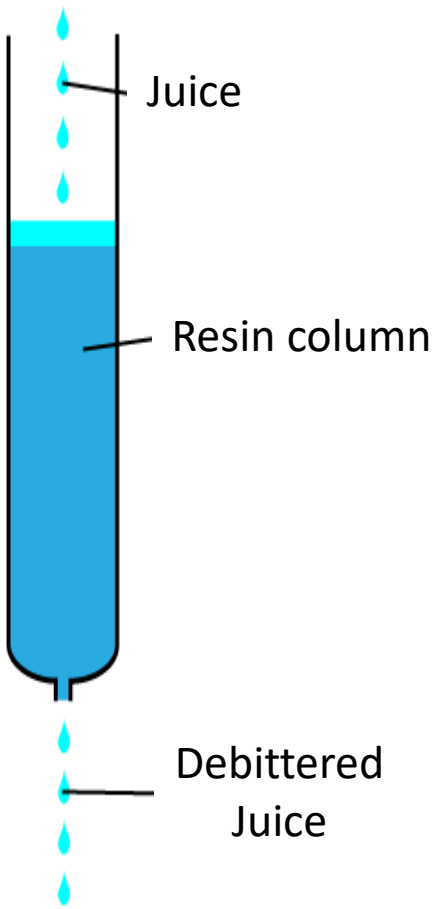
Desorption ratio: the percentage of the compound removed from the resin into the desorption solvent

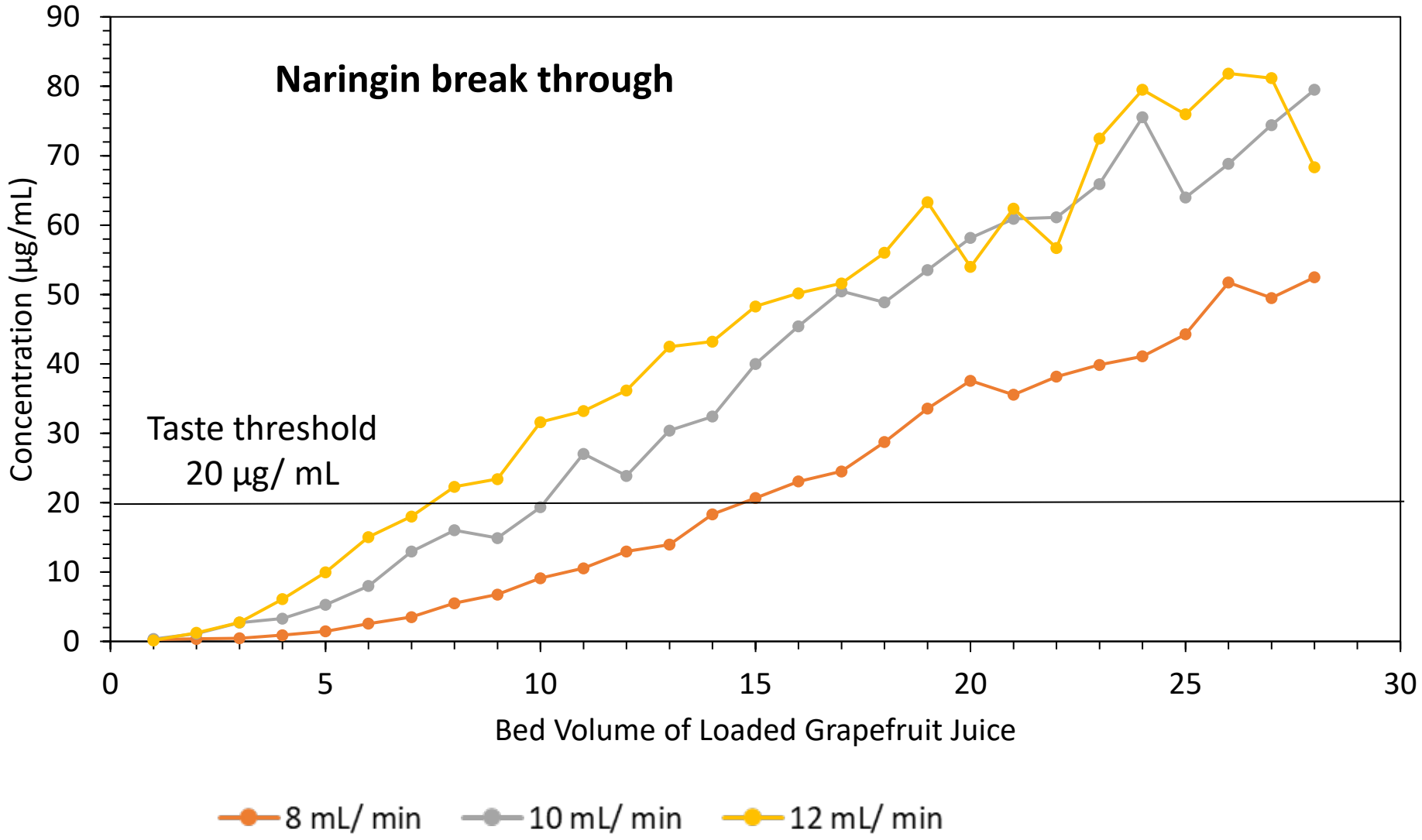
Recovery: the percentage of the compound recovered from the resin in the desorption solvent based on the initial concentration of the compound in the grapefruit juice

Adsorption and desorption on a fixed-bed Column

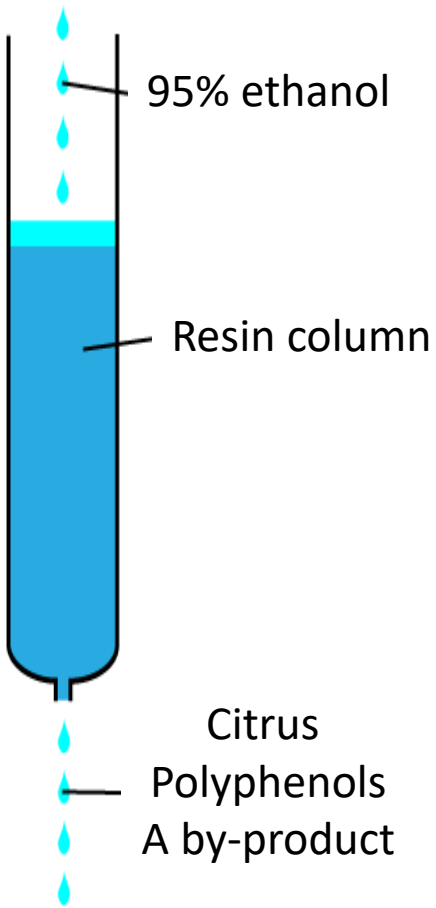


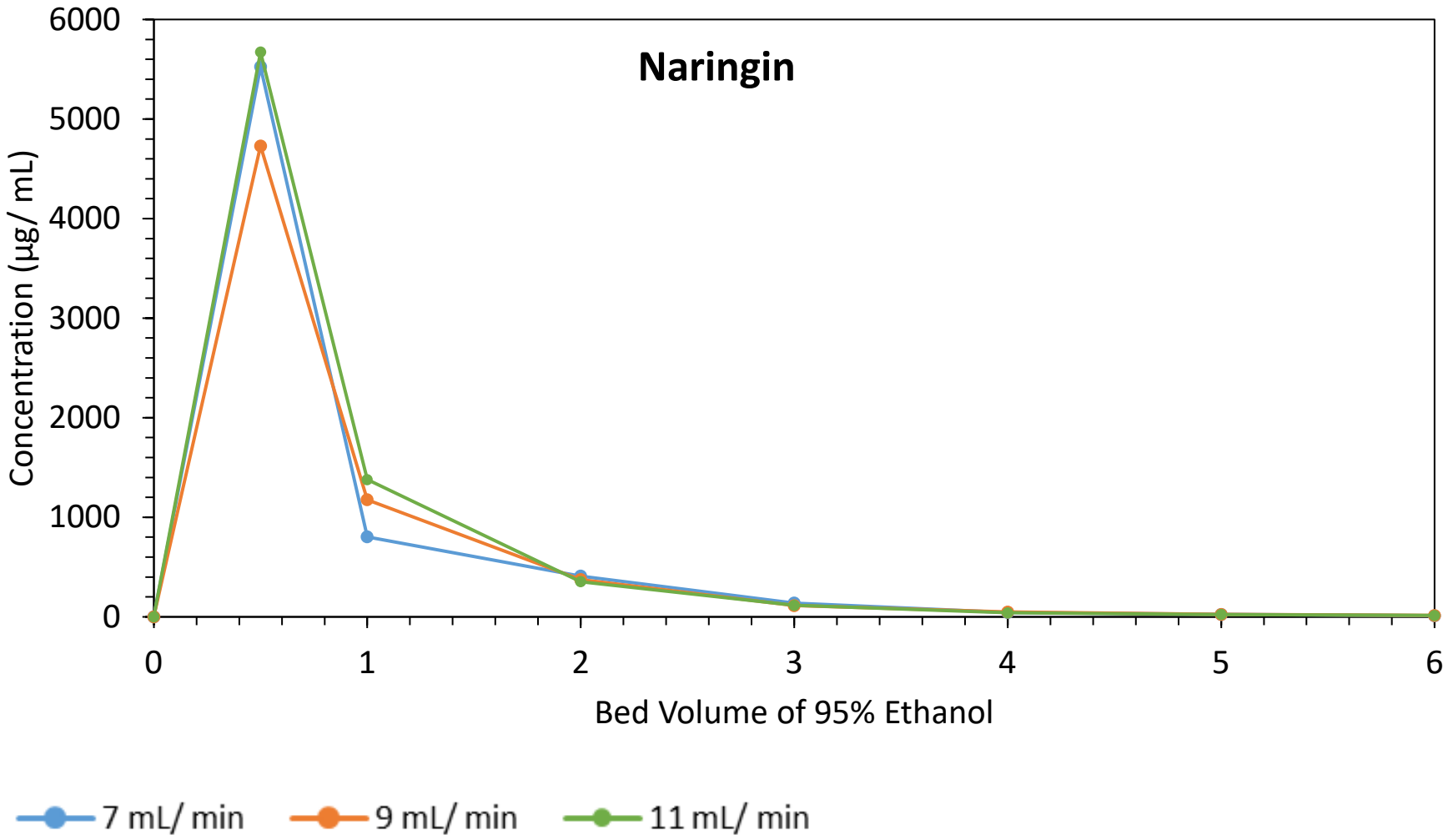
Dynamic break-through curve on PAD550 resin column





Dynamic desorption on PAD550 resin column





Performance of debittering on PAD550 resin column

2019 Grapefruit Juice	Untreated	Debittered
Naringin (µg/mL)	186.8 ± 6.59 a	17.82 ± 0.61 b
Narirutin (µg/mL)	77.22 ± 7.76 a	10.82 ± 0.90 b
Limonin (µg/mL)	6.90 ± 0.001	n.d.
Nomilin (µg/mL)	1.35 ± 0.035	n.d.
Bergamottin (µg/mL)	1.96 ± 0.12 a	0.80 ± 0.093 b
° Brix	9.2 ± 0.0 a	9.1 ± 0.058 b
pH	3.64 ± 0.006 a	3.62 ± 0.017 a

n.d. not detected and below the limit of detection of 0.37 µg/mL. Data are presented as mean ± standard deviation of triplicates. Means with different letters within each row are significantly different at $p \leq 0.05$.

Pilot test and taste panel results

2020 Grapefruit Juice	Untreated	Half debittered	Debittered
Overall Acceptability*	12.5 b	32.6 a	31.7 a
Bitterness Intensity*	37.4 a	27.5 b	17.9 c
Flavor Intensity*	36.4 ab	39.8 a	33.9 b
Rank#	162 a	97 c	125 b
Naringin (µg/mL)	111.2 ± 5.6 a	68.1 ± 4.4 b	13.1 ± 1.4 c
Narirutin (µg/mL)	39.38 ± 1.15 a	28.29 ± 8.08 a	8.21 ± 3.10 b
Limonin (µg/mL)	n.d.	n.d.	n.d.
Nomilin (µg/mL)	n.d.	n.d.	n.d.
° Brix	9.7 ± 0.058 a	9.5 ± 0.1 a	9.3 ± 0.058 b
pH	3.36 ± 0.006 a	3.38 ± 0.006 a	3.40 ± 0.006 b

Sensory results were from 64 panelists; *100-point intensity scale for overall acceptability, bitterness intensity, and flavor intensity; #rank from 1-3, the lowest value was most preferred. n.d. not detected and is below the limit of detection of 0.37 µg/mL. Chemical data are presented as mean ± standard deviation of triplicates; Means with different letters within each row are significantly different at $p \leq 0.05$.

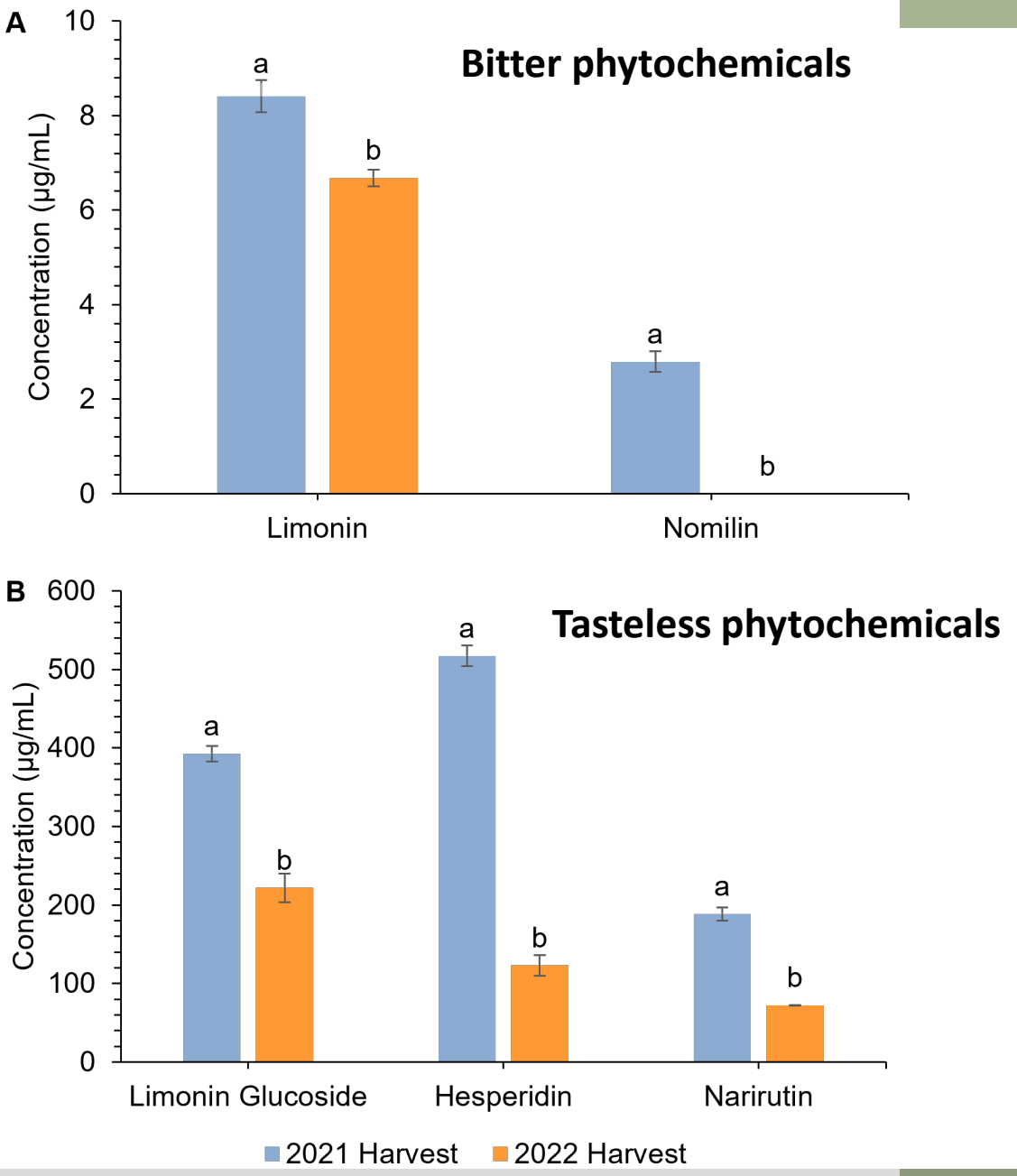
Grapefruit debittering summary

1. PAD550 and PAD600 resins showed higher adsorption capacity for naringin along with faster kinetics compared to other resins.

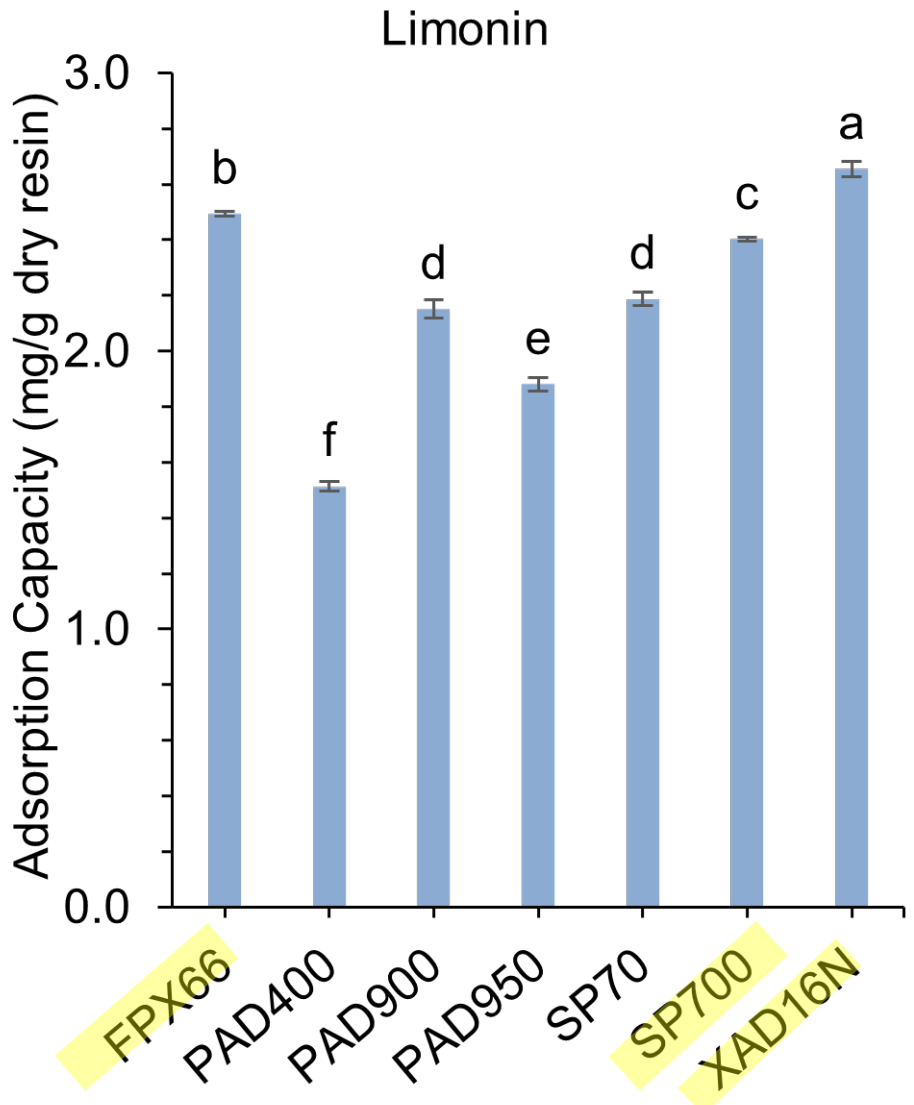
2. Debittering reduced the concentration of naringin and limonin to below their taste threshold.

3. The half-debittered juice was ranked as the most preferred by the taste panel likely because some degree of bitterness is expected for grapefruit juice.

Bitter and tasteless phytochemicals in Hamlin juice



Static adsorption of limonin in Hamlin juice

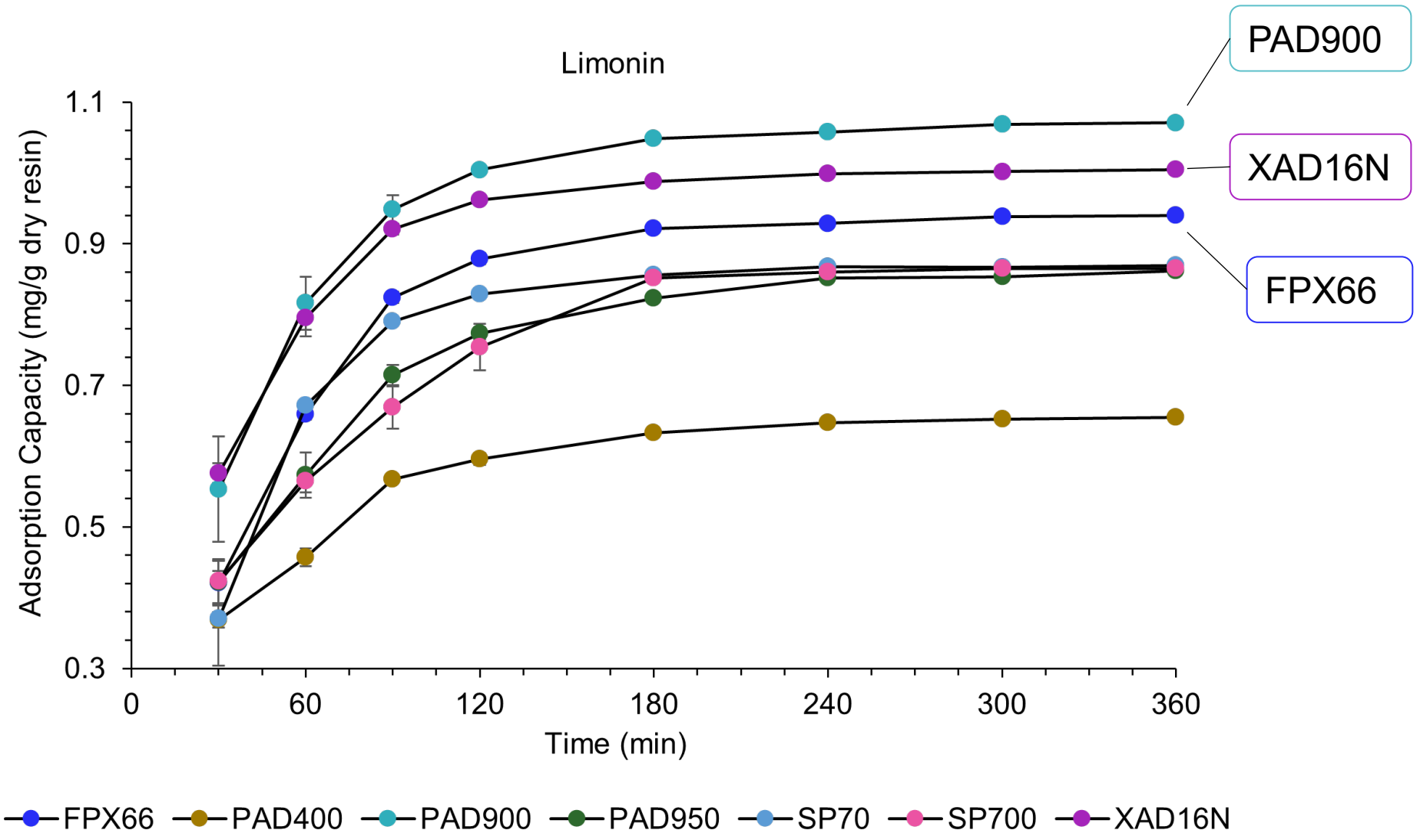


Physical Characterization of resins

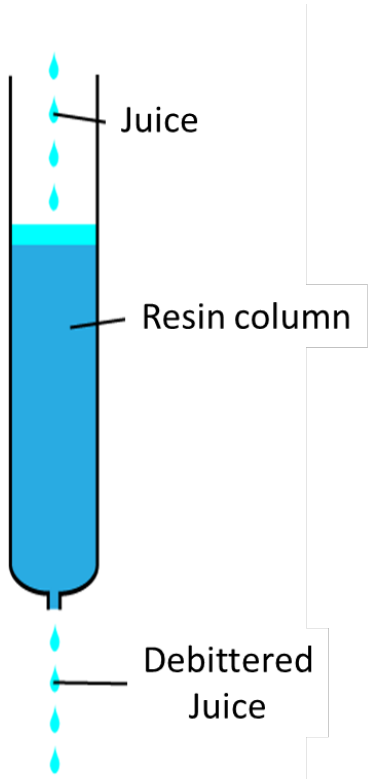
Resins	Matrix	Pore Diameter (A)	Surface Area (m^2/g)
FPX66	Polydivinylbenzene	250	700
PAD400	Polydivinylbenzene	360	700
PAD900	Polydivinylbenzene	220	850
PAD950	Polymethacrylic	120	450
SP70	Polydivinylbenzene	140	700
SP700	Polydivinylbenzene	180	1100
XAD16N	Polydivinylbenzene	150	800

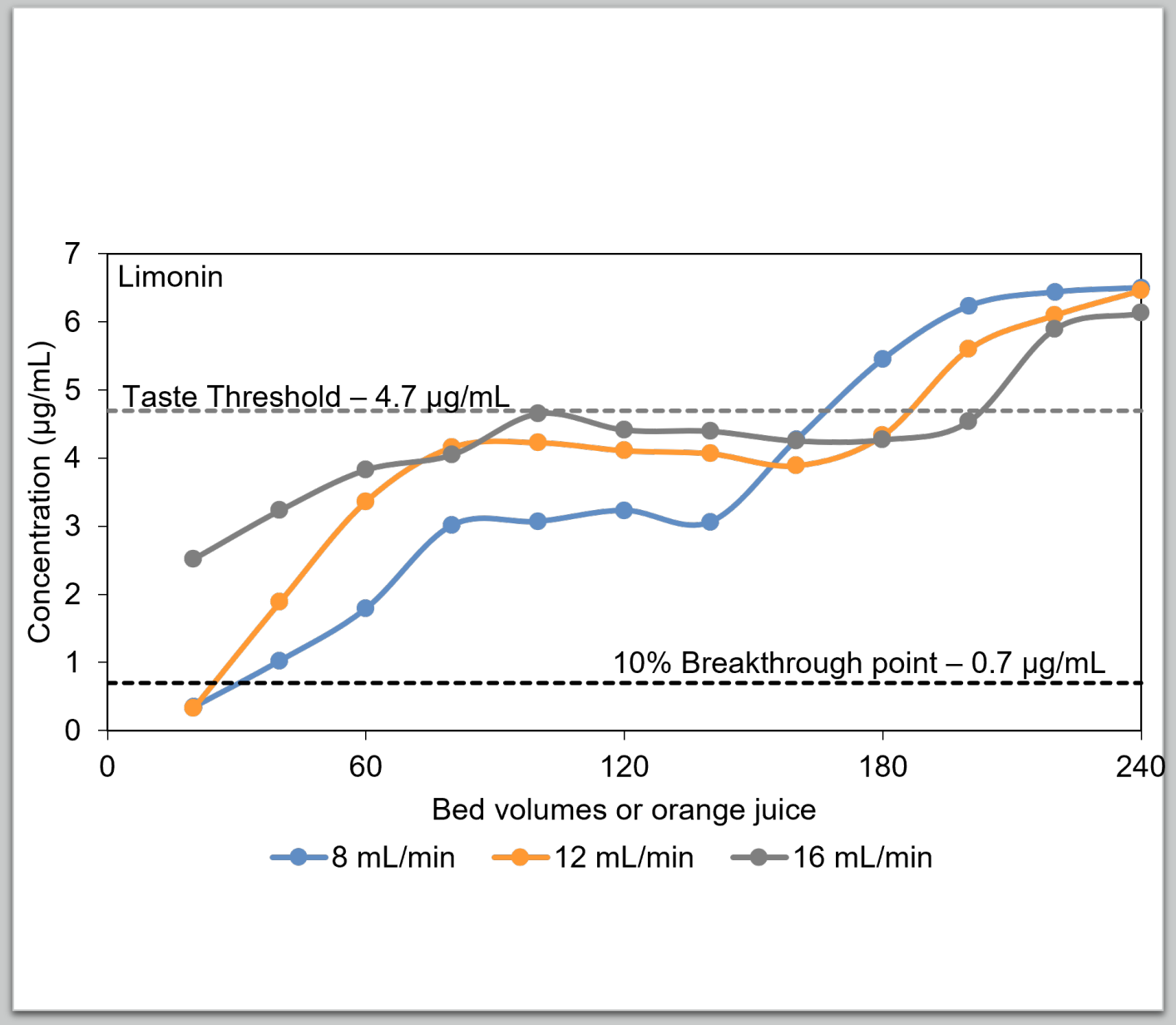
Significant Difference: $p \leq 0.05$, One way analysis of variance
Tukey Honestly Significant Difference

Adsorption kinetics of limonin in Hamlin juice

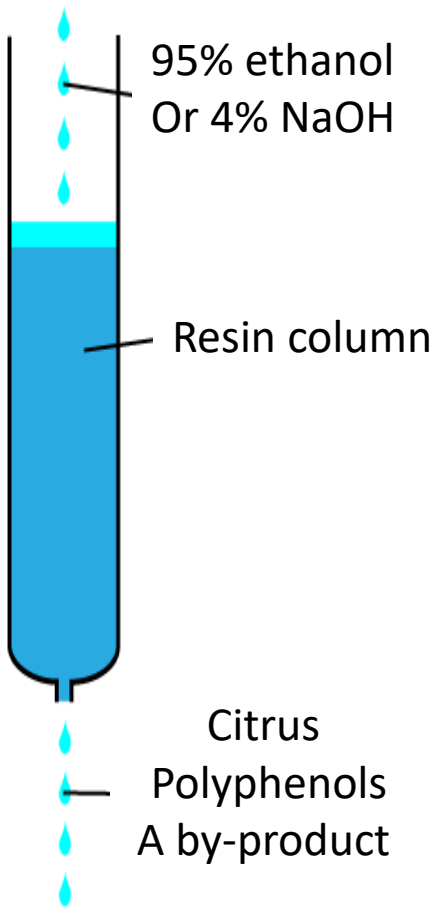


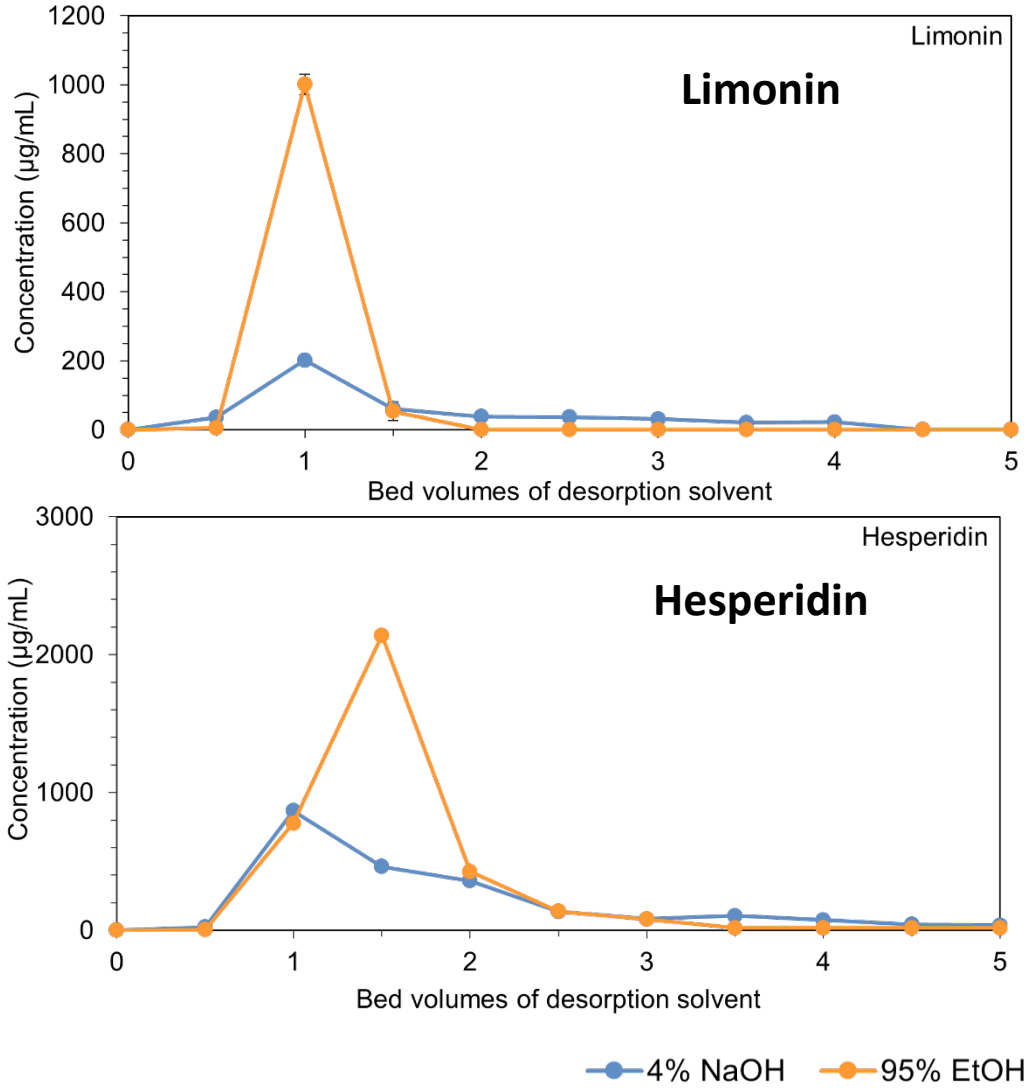
Limonin breakthrough on PAD900 resin column





Desorption of limonin and hesperidin





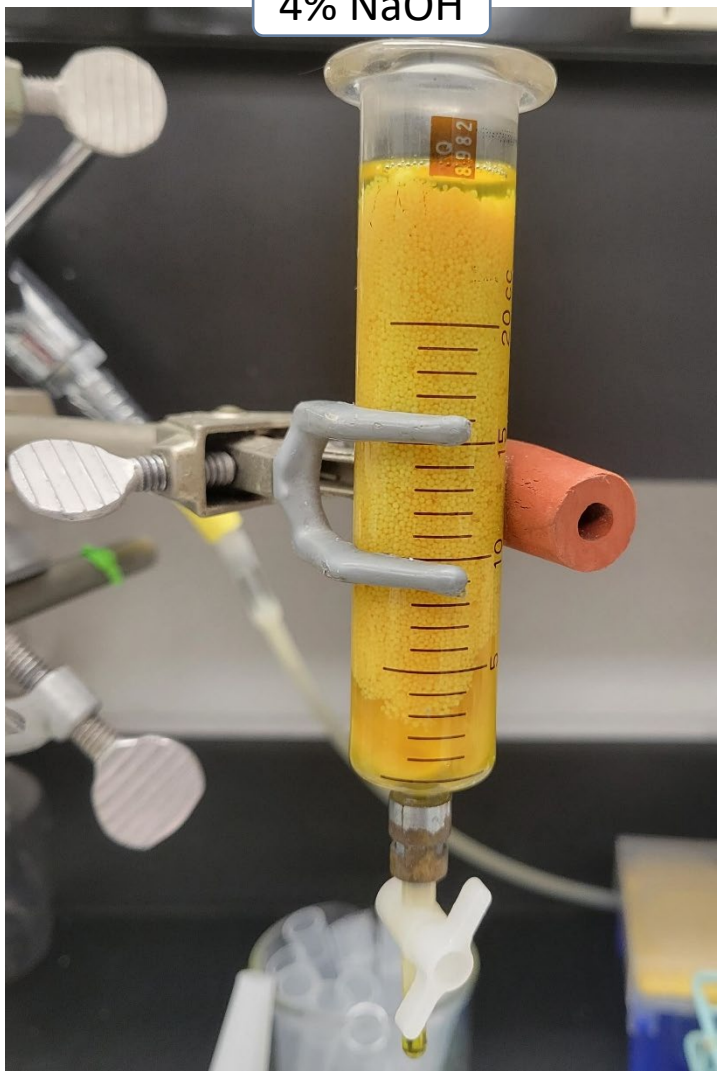
Resin desorption: ethanol *vs* NaOH

4% NaOH degrades citrus terpenoids and polyphenols, therefore, recovery of by-products is not possible.

These by-products can be recovered by ethanol desoption

EtOH

4% NaOH



Debittering performance of Hamlin juice

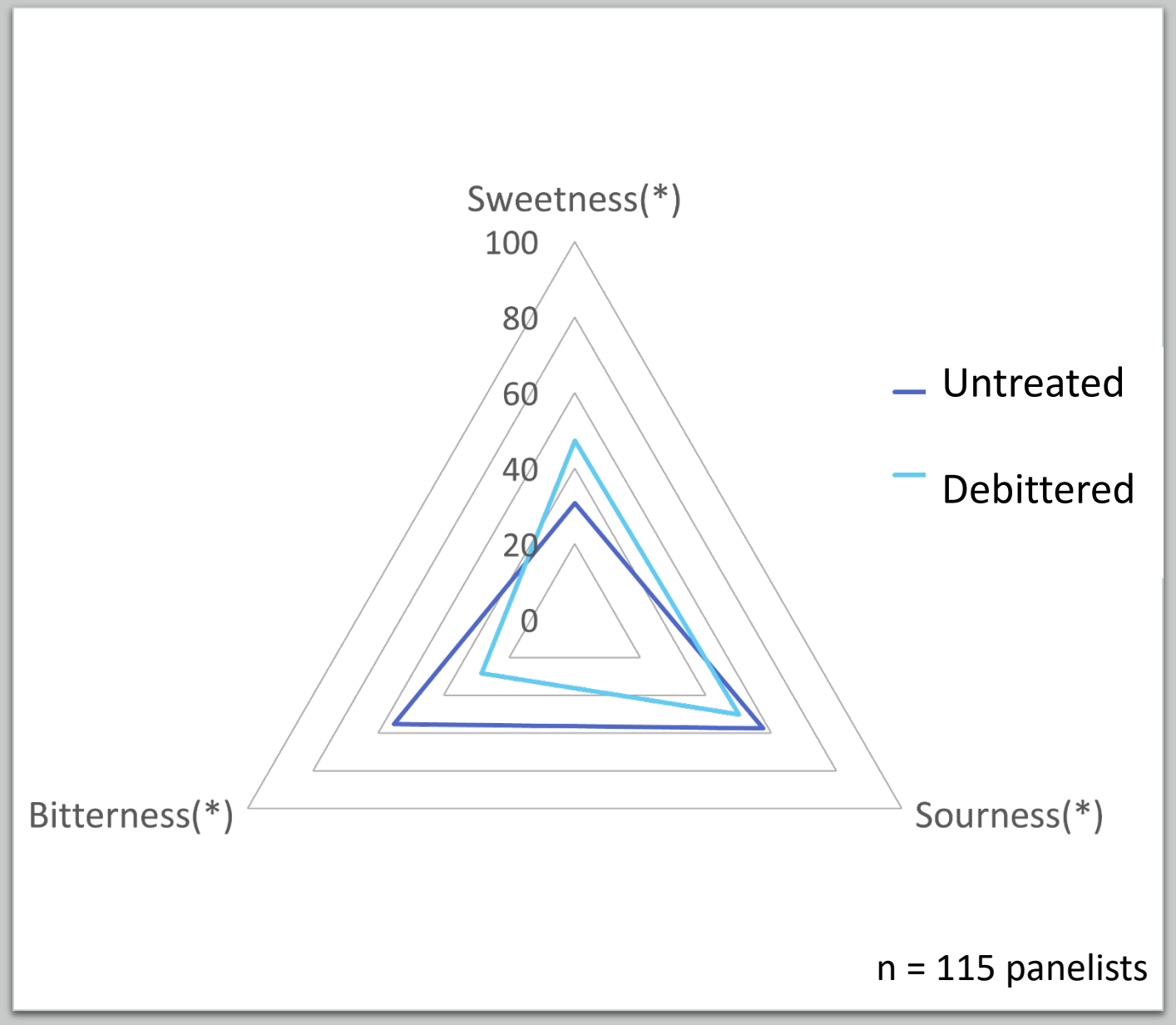
2022 Orange juice	Untreated	Debittered
Limonin (µg/mL)	6.68 ± 0.55	n.d.
Nomilin (µg/mL)	n.d.	n.d.
Limonin glucoside (µg/mL)	221.9 ± 18.0a	177.3 ± 6.8b
Hesperidin (µg/mL)	123.1 ± 12.9a	63.15 ± 9.68b
Narirutin (µg/mL)	72.28 ± 0.15a	46.65 ± 2.42b
Titratable acidity (% citric acid)	1.01 ± 0.03a	0.973 ± 0.030a
° Brix	8.43 ± 0.06a	8.43 ± 0.06a
pH	3.77 ± 0.01a	3.77 ± 0.01a

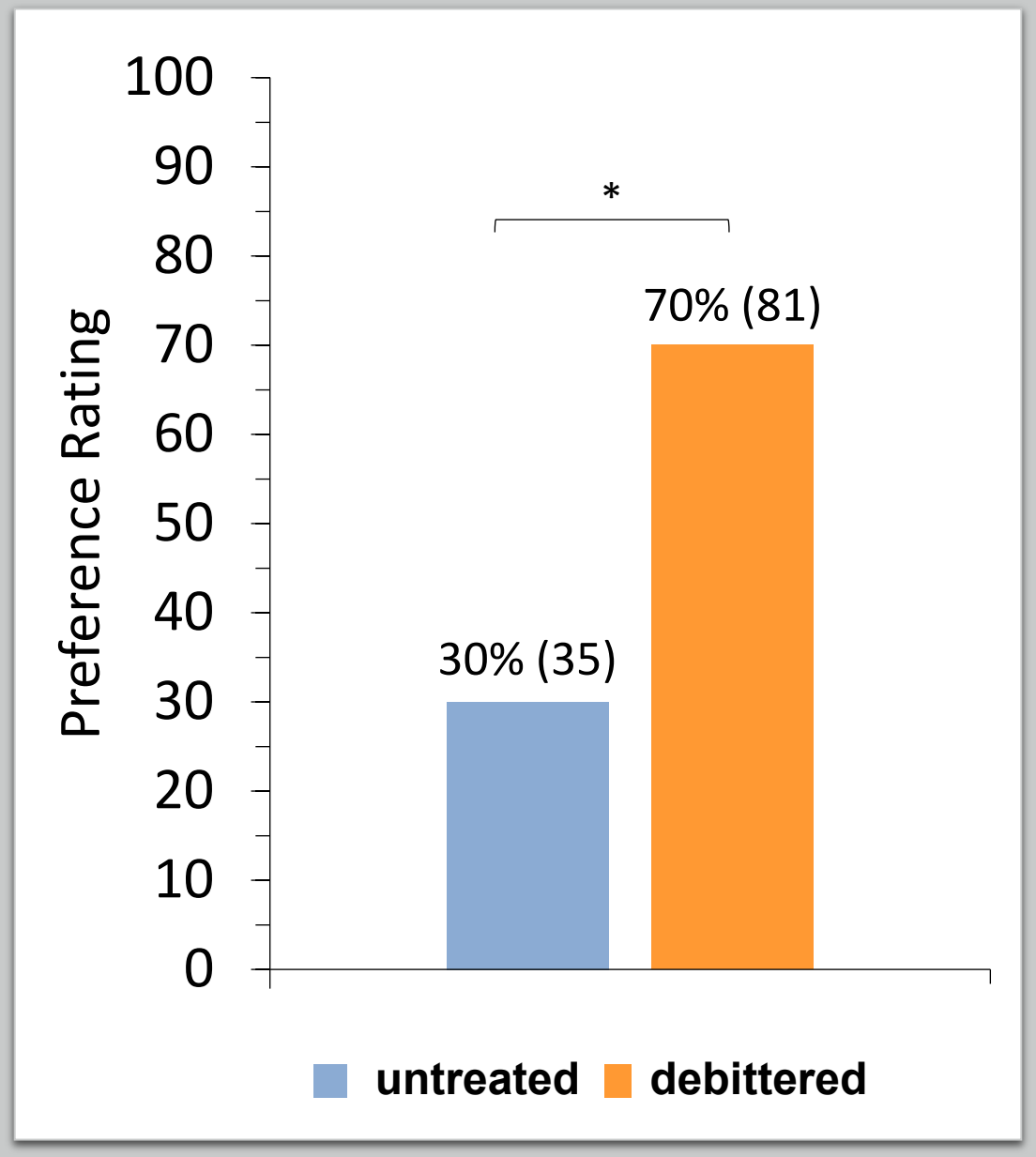
n.d. not detected and below the limit of detection. Data is presented as mean ± standard deviation of triplicates. Nomilin was below LOD of 0.63 µg/mL. Limonin was below LOD of 0.55 µg/mL.

Sensory tests

- Debittered perception:
  - Less bitter
  - Less sour
  - sweeter
- No significant difference in:
  - Brix
  - pH

Compound	Δ%
Limonin	- 77%
Hesperidin	- 56%





Preference

- 70% of consumers preferred debittered juice
- 30% of consumers preferred untreated juice
- The difference is significant ($p<0.05$)

Hamlin juice debittering summary

1. PAD900 resins showed higher adsorption capacity for limonin along with faster kinetics compared to other resins.

2. Resin adsorption reduced limonin content in orange juice from 7 µg/mL to less than 1.0 µg/mL and decreased tasteless compounds by at least 40%.

3. A consumer taste panel gave a higher overall liking and preference over untreated juice.

Acknowledgement

- Rachel Gordon and Taylor Washington, former MS students
- Wenyi (Chloe) Fu, doctoral student
- Specialty crop block grant by FDACS

Questions?