Authentication of Cranberry-Based Foods and Dietary Supplements by MALDI-TOF MS

ASMS 2021

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Introduction

Cranberry (*Vaccinium macrocarpon* Aiton) is an economically important fruit crop that is marketed as a food, beverage and dietary supplement. The health benefits associated with consumption of cranberry products are attributed to the presence of A-type proanthocyanidins (PAC). Cranberry products are susceptible to adulteration with lower cost sources of PAC. We have worked closely with AOAC to identify stakeholder concerns, set SMPR guidelines, and developed an **AOAC First Action Method (2019.05)** to identify A-type PAC in cranberry-based foods and dietary supplements by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS).

Methods

- PAC isolated from cranberry and apple fruit were mixed to obtain 21 different ratios (0-95%) by weight.
- MALDI-TOF analysis was performed on an Autoflex Max (Bruker Daltonics) in positive ionization reflectron mode (800 – 3500 Da).
- Samples (0.5 μL) were spotted on the stainless steel target followed by addition of 1.0 μL of the matrix 2,5-dihydroxybenzoic acid (DHB).
- Deconvolution of overlapping isotope distributions of PAC at each degree of polymerization was accomplished by methods of matrix algebra.
- Statistical treatment using advanced in-house developed **Polyphenol Fingerprinting™**, such as principal component analysis (PCA) were utilized for the discrimination/classification of the samples.

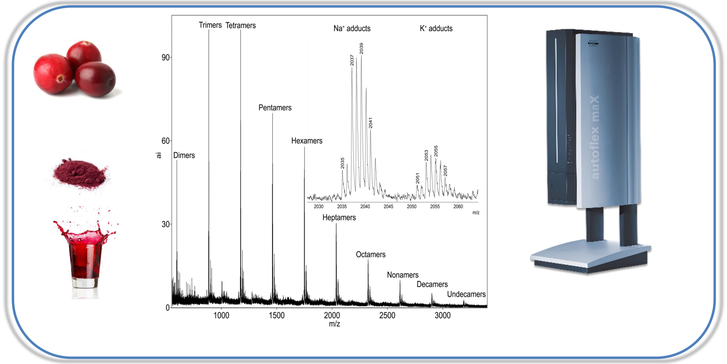

Fig. 1: MALDI-TOF mass spectrum of cranberry proanthocyanidins in positive reflectron mode, showing a series from dimers to undecamers.

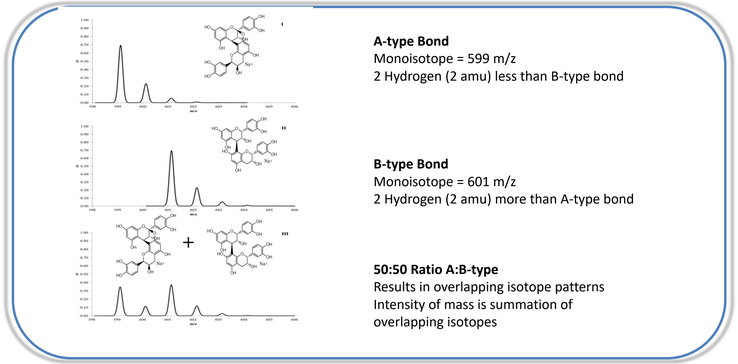

Fig. 2: . Isotopic distribution of procyanidin A2 (I), procyanidin B2 (II) and 1:1 ratio of procyanidins A2 and B2 (III) .

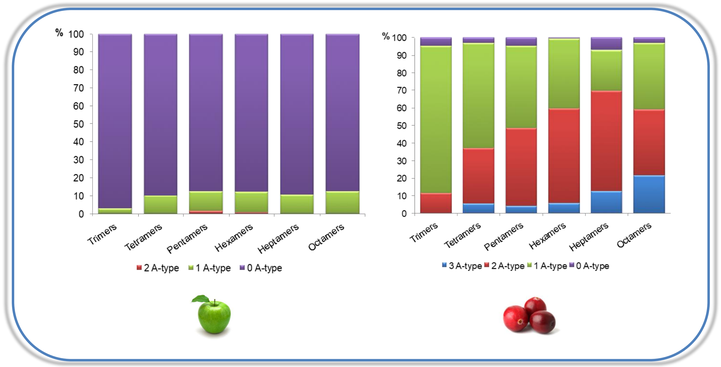

Fig. 3: Deconvolution by methods of matrix algebra to determine percentage A-type to B-type interflavan bonds of apple and cranberry proanthocyanidis.

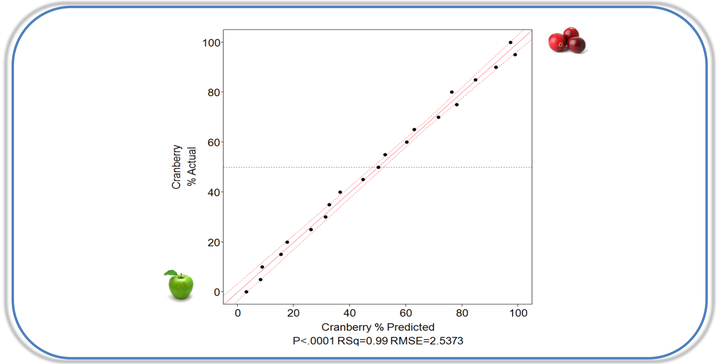

Fig. 4: Deconvolution of MALDI-TOF MS of 21 different ratios of isolated cranberry and apple PAC showing predicted percentage cranberry PAC is within 3.9% of actual mixed ratios.

Results

- A reliable AOAC First Action MALDI-TOF MS Method (2019.05) for identifying A-type PAC bonds with probability >90% and confidence of 95% was developed.
- The combination of the MALDI-TOF MS and in-house developed methods of chemometrics, can be applied for reliable detection of cranberry PAC adulteration down to 3.9%.
- MALDI-TOF mass spectrometry is the analytical technique of choice for characterizing PAC structural heterogeneity (interflavan linkages and flavan ring substitutions) that are unique to authentic fruits and botanicals.

References

- Esquivel-Alvarado *et. al* Journal AOAC International. 2021. 104(1):223-231
- Esquivel-Alvarado *et. al* Food Chemistry. 2021; 336:127667

Conclusions

- MALDI-TOF mass spectral Polyphenol Fingerprinting™, enables reliable detection of cranberry PAC adulteration.
- MALDI-TOF MS can be applied to a wide variety of fruits, and botanicals to substantiate authenticity and consistency in manufacturing.
- MALDI-TOF MS technique presented is shown to be a powerful analytical technique for detection of cranberry adulteration in the food, beverage and dietary supplement markets.

MALDI / Polyphenol Fingerprinting™