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File: ■ Saw Palmetto (*Serenoa repens*, Arecaceae)
■ Isotopic Fingerprinting
■ NMR Analysis

HC 061891-597

Date: July 31, 2018

RE: Isotopic Fingerprinting and NMR Analysis Detects Designer Blends Made with Animal Fats Marketed as Saw Palmetto Extracts

Perini M, Paolini M, Camin F, et al. Combined use of isotopic fingerprint and metabolomics analysis for the authentication of saw palmetto (*Serenoa repens*) extracts. *Fitoterapia.* June 2018;127:15-19. doi: 10.1016/j.fitote.2018.04.011.

Saw palmetto (*Serenoa repens*, Arecaceae) berry extracts are widely used in dietary supplement products for urinary problems related to benign prostate hyperplasia. The geographic area where the saw palmetto tree naturally occurs is limited to the southeastern United States, and due to a limited supply, growing demand, and increasing prices, the appearance of vegetable oils, or mixtures of vegetable oils (e.g., canola, coconut, olive, palm, sunflower oils) with saw palmetto extracts marketed as authentic saw palmetto oil, has been observed.[1] The problem of saw palmetto adulteration is exacerbated in years when the harvest volume is low due to inclement weather conditions.

Over the past years, suppliers have noticed the sale of saw palmetto extracts that appeared to comply with the pharmacopeial fatty acid ratio requirements,[2,3] one of the main tests to detect saw palmetto extract adulteration. However, these ingredients sometimes failed other tests, such as color specifications, or limits on fatty alcohol and sterols.

The approach taken by the researchers from Indena, SpA (Milan, Italy), the Fondazione Edmund Mach (San Michele all'Adige, Italy), and the University of Eastern Piedmont (Novara, Italy), was to evaluate nine commercial extracts from suppliers outside Europe and North America and 30 authentic saw palmetto extracts by the fatty acid method of the United States Pharmacopeia (USP),[2] and by orthogonal methods, such as ^{1}H NMR and isotopic fingerprinting analysis with a subsequent statistical assessment by principal component analysis (PCA).

For the isotopic fingerprint analysis, the ^{14}C concentration, and the ratios of $^{87}Sr/^{86}Sr$, $^{13}C/^{12}C$, $^{18}O/^{16}O$, and $^{2}H/^{1}H$ were determined. The amount of ^{14}C in a sample is indicative of being derived from plants or from fossil-fuel (i.e., made by chemical synthesis). The strontium ($^{87}Sr/^{86}Sr$) ratio provides information about the nature of the soil and the climatic conditions from where the sample is obtained. The carbon ($^{13}C/^{12}C$) ratio can be used to distinguish among certain plant-derived materials since not all plants use the same photosynthetic pathways. As such, materials derived from corn or sugar cane have higher $^{13}C/^{12}C$ ratios than most of the

plants used medicinally. The oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) ratios are based on the local water composition, mainly influenced by precipitation in form of snow and rain in the area.

No differences were observed in the ^{14}C concentrations or the $^{87}Sr/^{86}Sr$ ratio among authentic saw palmetto extracts and the commercial samples. However, the $^{13}C/^{12}C$ ratio was slightly, but significantly lower in the commercial samples, suggesting adulteration. This was confirmed by the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios, which differed substantially from those of the authentic material. Comparison with $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios from various fats and oils suggested that six out of the nine commercial samples were derived from animal fats.

The gas chromatography with flame-ionization detection (GC-FID) analysis of the fatty acids with subsequent PCA led to a clustering of the six animal-derived ingredients with the authentic saw palmetto, suggesting that these ingredients were blended with the fatty acid composition of authentic saw palmetto in mind. Two of the three remaining commercial saw palmetto extracts clustered with coconut (*Cocos nucifera*, Arecaceae) and babaçu (*Attalea speciosa,* Arecaceae) oil, while one sample did not cluster with authentic saw palmetto extract nor with any of the vegetable oils.

A clear separation between adulterated and genuine saw palmetto extracts based on differences in the ^{1}H NMR metabolomics was also obtained for seven of the ten samples analyzed (apparently one additional commercial sample was evaluated by ^{1}H NMR). The remaining three commercial samples clustered closely to the authentic materials. It is not clear if the ^{1}H NMR approach would have been sufficient to detect the adulteration in these three cases, although a refinement of the statistical model may have provided more clarity on this.

—Stefan Gafner, PhD

References

[1]Gafner S, Baggett S. *Adulteration of Saw Palmetto (Serenoa repens) – Botanical Adulterants Bulletin.* Austin, TX: ABC-AHP-NCNPR Botanical Adulterants Prevention Program; Botanical Adulterants Bulletin. 2017;1-6.
[2]United States Pharmacopeial Convention. Saw Palmetto Extract. In: *United States Pharmacopeia and National Formulary* (*USP 41-NF 36*). Rockville, MD: United States Pharmacopeial Convention. 2018.
[3]The European Directorate for the Quality of Medicines & HealthCare. *European Pharmacopoeia* (EP 9.1). Sabalis serrulatae extractum. Strasbourg, France: Council of Europe; 2016:1509-1512.

Referenced article can be accessed at https://www.researchgate.net/publication/324690000_Combined_use_of_isotopic_fingerprint_and_metabolomics_analysis_for_the_authentication_of_saw_palmetto_Serenoa_repens_extracts.