BEATRIZ CERVEJEIRA BOLANHO

CARACTERIZAÇÃO DE FARINHAS OBTIDAS DE SUBPRODUTOS DE PALMITO PUPUNHA

Londrina
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Tese apresentada ao Programa de Pós-Graduação em Ciência de Alimentos, nível Doutorado, da Universidade Estadual de Londrina, como requisito parcial à obtenção do título de Doutor (a) em Ciência de Alimentos.

Orientadora: Dra. Adelaide Del Pino Beléia

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Londrina, 8 de maio de 2014.

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"De tudo ficaram três coisas: A certeza de que estamos começando, a certeza de que é preciso continuar e a certeza de que podemos ser interrompidos, antes de terminar. É preciso fazer da interrupção um caminho novo, da queda um passo de dança, do medo uma escada, do sonho uma ponte, da procura um encontro". Fernando Sabino

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RESUMO

O Brasil é um dos maiores produtores e exportadores de palmito, cuja obtenção a partir da pupunheira *(Bactris gasipaes)* tem se intensificado nos últimos anos. No processamento, a extremidade inferior e as bainhas medianas são descartadas devido a sua estrutura fibrosa, o que corresponde a 46 % do peso da haste. Os objetivos deste trabalho foram investigar a estrutura e a composição das diferentes porções da pupunheira e caracterizar as farinhas obtidas dos subprodutos. Análises de composição química, de microscopia eletrônica, e de atividade de enzimas oxidativas foram realizadas nas diferentes porções da pupunheira e nas farinhas obtidas dos subprodutos: bainha mediana (FB) e porção caulinar (FC). A presença de antinutrientes e antioxidantes e as propriedades funcionais das farinhas foram investigadas. Realizou-se o fracionamento dos carboidratos e a análise dos monossacarídeos componentes de cada fração. A porção central da pupunheira (palmito comercializado em toletes) apresentou maior teor de proteínas, lipídios e amido. As porções descartadas (casca, bainha e porção caulinar) apresentaram elevado teor de fibras alimentares (59-83 %). As micrografias revelaram as características da pupunheira, com a presença de elementos fibrosos, vasos de xilema e floema, amiloplastos e cristais de oxalato de cálcio. Com a utilização de alta temperatura de secagem (90° C por 36 h) não foi possível detectar a atividade de enzimas oxidativas, porém houve maior escurecimento das farinhas, provavelmente devido a ocorrência de reações não-enzimáticas. Por isso, a temperatura de secagem foi definida a 60° C, pois a coloração mais clara contribui para a incorporação da farinha em alimentos. Em termos de fatores antinutricionais, a FB apresentou menor teor de ácido oxálico (84 $mg.100g^{-1}$) e taninos (295 $mg.100g^{-1}$) que a FC, porém similar teor de ácido fítico. As farinhas apresentaram elevado teor de fibras (62-71 %), principalmente insolúveis (59-69 %), cujos componentes majoritários são celulose e hemicelulose. Na FC foram encontrados os maiores teores de minerais, proteínas, lipídios, açúcares, compostos fenólicos e atividade antioxidante, enquanto a FB apresentou maior teor de fibras e carotenoides totais. A FC se destacou quanto às propriedades funcionais testadas, como solubilidade, viscosidade e absorção de água. As isotermas de sorção de água indicaram que a FB é mais higroscópica que a FC em umidade relativa de equilíbrio inferior a 50 %, e o contrário é válido para valores acima de 50 %. As frações extraídas com soluções alcalinas (0,1-4,0 M de hidróxido de sódio) apresentaram alto rendimento (21-22 %) e diferente composição monomérica, havendo elevadas concentrações de ácidos urônicos, arabinose, manose, galactose e xilose. Estas frações caracterizaram a presença de hemicelulose, com provável inclusão de cadeias de pectina. A fração péctica com o maior teor de ácidos urônicos foi obtida na extração com oxalato de amônio. Os altos rendimentos e teor de monômeros encontrados nas duas últimas frações (extraídas com NaOH 4M e resíduo insolúvel) caracterizam as fibras insolúveis - maior componente das farinhas - e está relacionado com o alto grau de complexidade da parede celular. Portanto, as farinhas produzidas apresentam potencial utilização na elaboração de produtos ricos em fibras.

Palavras-chave: Fibras alimentares. Microscopia. Propriedades funcionais. Fracionamento de carboidratos. Monossacarídeos.

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ABSTRACT

Brazil is one of the largest producers and exporters of heart-of-palm, and the production from peach palm *(Bactris gasipaes)* has increased in recent years. In the heart-of-palm processing, the stem part and the median sheaths are discarded due to their fibrous structure and they correspond to an average of 46 % of the rod weight. The aim of this work was to study the structure and composition of the different peach palm portions and characterize the flours produced from its by-products. Chemical composition, microscopic analysis and oxidative enzymes activity were investigated in the peach palm portions and in the flours obtained from by-products: median sheath (MSF) and stem portion (MS). The presence of antinutrients and antioxidants and the functional properties of the flours were analyzed. The carbohydrates fractionation and the monomeric composition of each fraction were researched. The central portion of peach palm (heart-of-palm) had the highest content of proteins, lipids and starch. The discarded portions (shell, median sheath and stem part) had high levels of dietary fibre (59-83 %). The micrographs showed the characteristics of peach palm parts, with the presence of fibrous elements, xylem and phloem vessels, amyloplasts and calcium oxalate crystals. With the application of a high drying temperature (90° C for 36 h) it was not possible to detect the activity of oxidative enzymes, but there was a darkening of the flours, probably due to the occurrence of non-enzymatic reactions. Therefore, the drying temperature was set at 60° C, because of the lighter color that facilitates flour incorporation into food products. In terms of anti-nutritional factors, MSF have lower content of oxalic acid and tannins than SF, but similar phytic acid content. The flours produced had high fibre content (62-71 %), mainly insoluble (59-69 %), whose major components are cellulose and hemicellulose. SF had the highest levels of minerals, proteins, lipids and sugars, as well as, higher content of phenolic compounds and antioxidant activity, while MSF have the highest content of fibers and carotenoids. The best functional properties were noted in SF, particularly solubility, viscosity and water absorption. The water sorption isotherms indicated that MSF is more hygroscopic than SF in equilibrium relative humidity lower than 50% and the opposite is valid for values above 50%. The fractions extracted with alkaline solutions (0.1-4.0 M of sodium hydroxide) showed high yield (21-22 %) and different monomeric composition, with elevated concentrations of arabinose, mannose, galactose and xylose. These fractions characterized the presence of hemicelluloses, with probably inclusions of pectic chains. The pectin fraction with the highest content of uronic acids was obtained by extraction with ammonium oxalate. The high yield and the high content of monomers found in the last two fractions (extracted with 4M NaOH and the insoluble residue) characterize the insoluble fibers - major component of the flours - and it was related to the high degree of complexity of the cell wall. Therefore the flours produced from peach palm by-products have potential to be incorporated in rich-fiber products.

Keywords: Dietary fibers. Microscopy. Functional properties. Carbohydrates fractionation. Monossacharaides.

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1 INTRODUÇÃO

O palmito é amplamente consumido no Brasil e sua comercialização tem se expandido no mercado internacional. A obtenção do palmito pode ocorrer a partir de várias espécies de palmeiras, sendo as mais exploradas pertencentes ao gênero Euterpe, que incluem o juçara *(E. edulis)* nativo da Mata Atlântica, e o açaizeiro (E. *olerácea)* nativo da Amazônia. Dentre as palmeiras cultivadas destacam-se a pupunheira *(Bactris gasipaes* Kunth), também nativa da Amazônia, porém em região mais abrangente, englobando as Américas Central e do Sul, e a palmeira real australiana *(Archontophoenix* spp), nativa do leste da Austrália (ANEFALOS; TUCCI; MODOLO, 2007).

Desde a década de 1970 o interesse de pesquisadores e produtores voltou-se para a pupunheira, como alternativa sustentável de cultivo para a produção de palmito. Essa palmeira apresenta características desejáveis quando comparada àquelas exploradas predatoriamente, tais como, crescimento acelerado, precocidade para o corte (2 anos) e farto perfilhamento (ANEFALOS; TUCCI; MODOLO, 2007).

A haste da pupunheira apresenta porções de diferentes diâmetros e texturas. Assim, um estudo aprofundando sobre a estrutura e a composição das distintas partes - casca, bainha mediana, porção caulinar e parte comestível (central e basal) - se faz necessário para diferenciar os tecidos componentes e direcionar sua aplicação.

Durante o processamento do palmito há um grande volume de resíduo que é descartado, constituído principalmente pela porção caulinar e por bainhas foliares, que submetidos a processo tecnológico adequado podem ser transformados em farinhas com potencial utilização em produtos de panificação. No entanto, a presença de enzimas oxidativas, como a peroxidase e a polifenoloxidase, pode dificultar o processamento destes subprodutos, já que estas enzimas são capazes de catalisar um grande número de reações, acarretando no escurecimento do tecido vegetal (CLEMENTE; PASTORE, 1998). O escurecimento não enzimático, como a reação de Maillard, também pode ocorrer durante a secagem em altas temperaturas.

Vários subprodutos agroindustriais vêm sendo estudados por se constituírem fonte de nutrientes, por apresentarem baixo custo e cujo descarte inadequado pode causar prejuízos ambientais. Entre os nutrientes, as fibras alimentares se destacam pelos efeitos benéficos à saúde humana, sendo crescente sua incorporação em alimentos. Os minerais são importantes por desempenharem diversas funções no organismo, porém sua disponibilidade pode ser afetada pela presença de alguns compostos quelantes, como ácido fítico, ácido

oxálico e taninos, considerados antinutrientes. Os resíduos agroindustriais podem apresentar ainda compostos bioativos como os carotenoides e os compostos fenólicos. A presença de polifenóis está muitas vezes relacionada com a atividade antioxidante, devido a sua interação com os radicais livres, diminuindo o efeito deletério destas moléculas instáveis. No entanto, estes dados não são conhecidos para os descartes provenientes da pupunheira, cuja produção tem crescido em algumas regiões do Brasil.

A parede celular das plantas possui estrutura complexa, formada por polissacarídeos, como celulose, hemicelulose e pectina, proteínas e compostos fenólicos (DA-SILVA; FRANCO; GOMES, 1997; McDOUGALL et al., 1996). O conhecimento destes componentes é importante uma vez que eles podem influenciar nas propriedades funcionais, como capacidade de absorção de água e volume de intumescimento. Além disso, o fracionamento dos carboidratos oriundos da parede celular fornece informações importantes sobre a composição deste material.

Dessa forma, é de suma importância estudar as farinhas obtidas de descartes da produção de palmito pupunha para direcionar sua aplicação em alimentos, bem como para ampliar o conhecimento sobre as características da pupunheira.

2 OBJETIVOS

2.1 GERAL

Estudar as diferentes porções da pupunheira *(B. gasipaes)*, produzir e caracterizar as farinhas obtidas dos subprodutos.

2.2 ESPECÍFICOS

- Analisar a composição e a estrutura das diferentes porções da pupunheira;
- Obter farinhas a partir dos subprodutos do palmito pupunha em diferentes temperaturas de secagem, e avaliar seu efeito na atividade de enzimas oxidativas e nas características de coloração do produto final;
- Caracterizar as farinhas produzidas quanto à composição, propriedades funcionais, capacidade de sorção de água, compostos bioativos, atividade antioxidante e compostos antinutricionais;
- Realizar o fracionamento dos polissacarídeos da parede celular e avaliar os monômeros presentes nas frações fibrosas.

3 REVISÃO BIBLIOGRÁFICA

3.1 PALMITO

As palmeiras, plantas características de paisagens tropicais, pertencem a uma das maiores famílias botânicas conhecidas mundialmente - Arecaceae (Palmae) - que dentre as inúmeras espécies, possuem aquelas que se sobressaem como plantas ornamentais, e outras que além deste aspecto, fornecem importantes produtos, como óleos, ceras, frutos, polpas, fibras e o palmito (YASUDA, 2005).

As principais palmeiras utilizadas para a produção de palmito no Brasil são *Euterpe edulis* (juçara), *Euterpe oleracea* (açaí), *Bactris gasipaes* (pupunha) e *Archontophoenix* spp (palmeira-real). Alguns fatores como abundância, palatabilidade, cor, formato, rendimento e facilidade de extração do palmito determinam a preferência de uma espécie em relação à outra (ANEFALOS; TUCCI; MODOLO, 2007).

O palmito é um produto de grande aceitação no mercado brasileiro e também muito apreciado em outros países como França, Japão, Itália, Estados Unidos, entre outros, sendo o Brasil um dos maiores produtores, consumidores e exportadores de palmito em conserva. Porém, a falta de qualidade do produto tem dificultado a exportação em larga escala (VIEIRA, 2006). No país, a produção de palmito atingiu 5.563 toneladas em 2011, sendo a região norte a maior produtora (IBGE, 2011).

O palmito pode ser definido como o produto constituído pela porção comestível de palmeiras, incluindo a gema apical e as regiões acima e abaixo, correspondente às folhas macias em crescimento e ao estipe da palmeira, contendo ainda partes fibrosas e não comestíveis (FAO/WHO, 2009).

Em função da grande extração clandestina de espécies nativas de palmito juçara e açaí, a partir do ano de 2000 foi firmado um acordo durante a realização do "Rio 92", que limitou a extração do palmito apenas em áreas cultivadas (AGROINFORME, 2005). Para o setor agroindustrial, apesar da elevação dos custos da extração de palmito em palmitais manejados, o produto apresenta maior padronização e qualidade. Além disso, o consumo de palmito tem crescido nos últimos anos, o que aumenta a procura por produtos com características sensoriais e sanitárias adequadas (SANTOS; JÚNIOR; NEVES, 2008).

3.1.1 Palmito Pupunha

A pupunheira *(Bactris gasipaes* Kunth) pertence à família das palmáceas, nativa dos trópicos úmidos americanos, cultivada por índios da América Central e da Amazônia desde aproximadamente 1545. Entretanto, sua origem exata é desconhecida, apesar do conhecimento de seu uso por índios que ocupavam as regiões desde o estado do Pará ao sul do México (CARMO et al., 2003).

Esta espécie é adaptada às condições amazônicas, porém pode ser cultivada em várias regiões brasileiras, como nos estados da Bahia, Espírito Santo, Rio de Janeiro, São Paulo, Paraná e Santa Catarina. No estado do Paraná, a região litorânea apresenta-se como uma área potencial para o plantio da pupunheira devido às condições climáticas favoráveis (altas temperaturas e alto índice pluviométrico). De 2004 a 2007 houve um aumento de 90 % da área cultivada nesta região. Já no noroeste do estado é necessário fazer uso de sistemas de irrigação para melhorar o desenvolvimento da pupunheira como vem ocorrendo no município de Mariluz (SANTOS; JÚNIOR; NEVES, 2008).

As condições ambientais adequadas para o desenvolvimento da pupunheira são temperatura média superior a 22°C e precipitação acima de 2000 mm anuais. Apesar de ser uma planta rústica e adaptada a solos ácidos e de baixa fertilidade, prefere os mais férteis, de textura média a leve, respondendo bem a calagem e a adubação. Além disso, a pupunheira não tolera solo mal drenado e sujeito a encharcamento, devendo ser evitado também solos compactados (BERGO; LUNZ, 2000).

O interesse no palmito pupunha iniciou a partir da década de 70, quando a exploração predatória da palmeira juçara na região sudeste do Brasil tinha alcançado o seu máximo e as reservas de palmito nativo já estavam bastante dilapidadas. A pupunheira se destaca pelo seu potencial para a exploração racional de palmito. O palmito produzido por esta palmeira, embora com características diferentes das espécies tradicionalmente usadas para a exploração de palmito (juçara e açaí) é bem aceito (GUERREIRO, 2002).

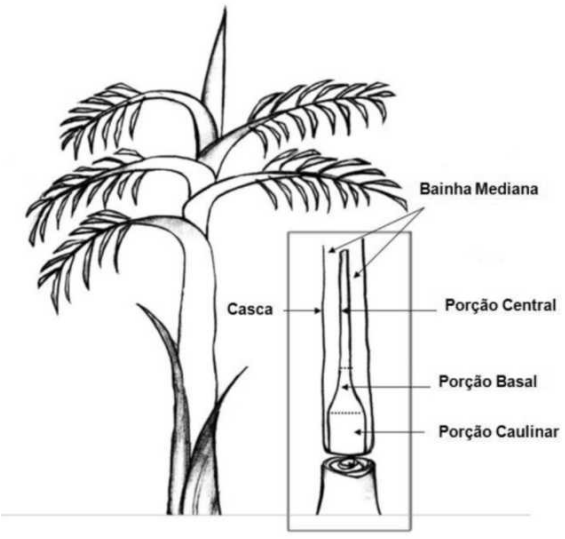
As principais características da pupunheira que interessam para a produção de palmito são: precocidade, o primeiro corte ocorre a partir de 18 meses após o plantio; perfilhamento da planta mãe, permitindo repetir os cortes nos anos subsequentes, sem necessidade de replantio da área; qualidade do palmito, o material geralmente apresenta comprimento de 40 cm e diâmetro entre 1,5 e 4 cm, sendo macio e de sabor agradável; lucratividade, em condições adequadas um hectare pode produzir de 5.000 a 12.000 palmitos por ano; facilidade nos tratos culturais e corte, uma vez que plantas selecionadas não

apresentam espinhos; e vantagens ecológicas, podendo a cultura ser conduzida a pleno sol, em áreas agrícolas tradicionais, sem nenhum dano às matas nativas, fator de grande apelo comercial, principalmente para a exploração do palmito visando o mercado externo (RESENDE; JUNIOR, 2004).

Em relação ao rendimento econômico, uma pesquisa realizada por Sampaio et al. (2007), revelou que as produções de palmito de pupunha e palmeira-real são viáveis economicamente, apresentando uma taxa interna de retorno de 53,27 % e 21,70 %, respectivamente. Essa diferença é decorrente da produtividade que, no estudo citado, foi de 13,5 t/ha/ano de palmito pupunha e de 8,5 t/ha/ano de palmito da palmeira-real, sendo mais um ponto positivo a ser considerado em relação ao plantio da pupunheira.

A pupunheira apresenta em sua constituição três camadas (bainhas): externa, mediana e interna, como ilustrado na Figura 1. A camada externa ou casca que envolve o palmito é fibrosa, de cor esverdeada a marrom, não é utilizada na industrialização do palmito, bem como a segunda camada, de cor mais clara, denominada bainha mediana ou semi-fibrosa. A parte interna ou "coração do palmito" contém menor teor de fibras, e corresponde à porção que produz o palmito em conserva. Esta porção ainda se divide em basal e central, sendo a primeira mais fibrosa que a segunda e por isso fornecem produtos de diferentes qualidades. A parte basal é geralmente comercializada em conservas no formato de cubos e a central na forma de toletes, a qual é mais tenra e tem maior valor de mercado. A porção abaixo da basal é denominada caulinar, a qual possui alto teor de fibras e textura inadequada para produção de conservas (SANTOS; JÚNIOR; NEVES, 2008).

Figura 1 – Pupunheira *(B. gasipaes)* e identificação das diferentes porções



Fonte: Marcos Rogério Rodrigues Silveira

Botanicamente o palmito pupunha é considerado uma gema apical, responsável pelo desenvolvimento da palmeira. É constituído de folhas ainda não desenvolvidas e imbricadas extraído do centro da parte cilíndrica. Este palmito apresenta diferenças em relação às outras espécies produtoras, como sabor adocicado e coloração mais amarelada. A haste da pupunheira apresenta formato cônico e as bainhas são mais grossas e curtas, o que implica em uma redução do diâmetro e do rendimento em comparação com o palmito juçara, além de uma maior desuniformidade de diâmetros. Com relação à composição física do palmito, 60 a 70 % é constituída por tecidos macios do estipe e 30 a 40 % por tecidos jovens de folhas (CARMO et al., 2003).

3.2 SUBPRODUTOS AGROINDUSTRIAIS

Nas indústrias de alimentos são conhecidos como resíduos ou subprodutos a parte da matéria-prima não utilizada no processamento do produto principal. Estima-se que a produção de resíduos agroindustriais é em torno de 250 milhões de toneladas/ano, os quais são compostos de celulose (20 a 60 %), hemicelulose (20 a 30 %) e lignina (15 a 30 %), variando a concentração de acordo com a matéria-prima (TAMANINI; HAULY, 2004).

De acordo com Laufenberg (2003), além de comprometer o meio ambiente, a não utilização de subprodutos representa uma grande perda de biomassa que poderia ser empregada na obtenção de produtos de alto valor. Atualmente, há uma tendência global de usar de forma eficiente os recursos naturais. A produção sustentável de alimentos e a valorização dos resíduos são questões que cada vez mais serão consideradas pelas agroindústrias (DHILLON; KAUR; BRAR, 2013).

Uma alternativa interessante consiste no aproveitamento integral de resíduos para a produção de alguns ingredientes passíveis de serem incluídos na alimentação humana. Tratase de uma proposta plausível e concreta, uma vez que esses resíduos representam uma fonte de materiais estratégicos para a indústria de alimentos (OLIVEIRA et al., 2002). Além disso, muitos subprodutos contem compostos funcionais interessantes, e podem ser empregados no desenvolvimento de produtos inovadores como as fibras usadas como matrizes para flavorizantes, corantes ou antioxidantes; pectinas e agentes geleificantes com propriedades específicas para aplicação em outros produtos e bioadsorventes que podem ser facilmente degradados após o uso (LAUFENBERG, 2003).

Em relação aos subprodutos gerados no processamento do palmito, sabe-se que durante a sua extração somente a porção interna presente no estipe é utilizada para a

comercialização, sendo o caule, as folhas, as cascas e as bainhas descartadas. Alguns estudos encontrados na literatura propõem alternativas para utilização das partes não destinadas a obtenção do palmito de diferentes espécies (VIEIRA et al., 2004; OLIVEIRA; TAVARES, 2005; ISRAEL, 2005; TONINI et al., 2007), sendo que alguns propõe a incorporação dos resíduos na formulação de produtos alimentícios (VIEIRA, 2006; GIORDANO, 2007).

3.3 ENZIMAS OXIDATIVAS

A peroxidase e a polifenoloxidase são oxirredutases consideradas as principais enzimas responsáveis pela deterioração da qualidade de frutas, vegetais, e produtos processados. Devido a isso, a presença destas enzimas deve ser investigada, pois as reações oxidativas e de biodegradação podem comprometer a vida útil de diversos alimentos (VALDERRAMA; MARANGONI; CLEMENTE, 2001).

A peroxidase (POD) é capaz de catalisar um grande número de reações oxidativas em plantas usando peróxido como substrato, ou, em alguns casos, oxigênio como um aceptor de hidrogênio. Em vegetais, a peroxidase induz a mudanças negativas de sabor durante a estocagem. É considerada a enzima vegetal mais estável ao calor e sua inativação tem sido usada como indicador de adequação do branqueamento de vegetais (FREITAS et al., 2008).

A polifenoloxidase (PPO) oxida compostos fenólicos na presença de oxigênio molecular, resultando na degradação de nutrientes. Durante a atuação desta enzima são formadas quinonas muito reativas, que interagem com outras moléculas, gerando inúmeros compostos de coloração escura. As PPOs podem ser diferenciadas quanto à isoformas, peso molecular, ponto isoelétrico e especificidade (GOULART et al., 2003).

Galdino e Clemente (2008) ao estudar a atividade das enzimas oxidativas em toletes de palmito pupunha encontraram que o pH mais adequado para extração da POD foi 5,5 e da PPO 6,5. Quando os extratos enzimáticos foram tratados em temperaturas de 65 a 80°C houve um decréscimo de 70 e 80 % em relação às atividades iniciais da POD e da PPO, respectivamente.

3.4 PAREDE CELULAR

Na estrutura da planta, a parede celular (PC) consiste em uma zona de fronteira entre cada célula, apresentando uma estrutura complexa e com diversas funções, tais como rigidez, definição do tamanho e formato das células, controle da expansão celular (permitindo que a pressão das células vizinhas não comprometa sua integridade) e proteção contra insetos e patógenos que causam a degradação dos polissacarídeos da PC (KEEGSTRA, 2010).

A parede celular é formada por um retículo de macromoléculas que representa um obstáculo ao movimento de moléculas grandes para dentro ou fora das células, o que impede a entrada e saída de moléculas como proteínas e ácidos nucleicos. As cargas negativas da parede retardam o movimento das partículas carregadas positivamente. Dessa forma, a parede celular funciona como uma barreira seletiva, controlando o transporte intracelular (BRETT; WALDRON, 1996).

Nos vegetais, a parede celular apresenta-se desuniforme, sendo sua composição, forma e tamanho dependente da função exercida por cada célula dentro do tecido vegetal. Todas as células vegetais apresentam parede celular primária e algumas desenvolvem parede celular secundária sobre a primária. Ambas as camadas contém celulose e hemicelulose, sendo que a primária também é composta por pectina, enzimas e proteínas estruturais, enquanto a secundária contém baixos teores de proteínas e pectina, e normalmente apresenta lignina (McDOUGALL et al., 1996; LEROUXEL et al., 2006).

3.4.1 Composição da Parede Celular

A parede celular possui estrutura complexa, constituída de multicomponentes formando um emaranhado de polissacarídeos unidos por ligações intermoleculares. Os polissacarídeos da PC são formados por quatro classes principais: celulose, polissacarídeos não celulósicos (PNCs), proteínas e compostos fenólicos (DA-SILVA; FRANCO; GOMES, 1997; McDOUGALL et al., 1996).

Em sua constituição a parede celular apresenta uma fase cristalina e uma fase amorfa. A fase cristalina apresenta composição química mais homogênea, composta por microfibrilas, sendo a celulose seu constituinte principal. As microfibrilas apresentam uma estrutura fina e longa, com moléculas de celulose alinhadas paralelamente umas as outras. A fase amorfa apresenta composição mais complexa, formada por polissacarídeos, proteínas e

compostos fenólicos, variando de acordo com a porção da parede, tipo de célula, estágio do ciclo celular e espécie. Esta fase também denominada matriz, apresenta variações quanto à estrutura e proporção dos polímeros presentes (BRETT; WALDRON, 1996).

A celulose é o principal constituinte da parede celular e é considerado o biopolímero mais abundante da Terra (LEROUXEL et al., 2006). É um polímero linear formado por unidades de glicose unidas por ligações P (1-4), cujas cadeias interagem por ligação de hidrogênio formando os agregados cristalinos (microfibrilas) (KEEGSTRA, 2010). O grau de polimerização varia de 2.000 a 6.000 na parede celular primária e pode atingir 15.000 na parede secundária (WALDRON; PARKER; SMITH, 2003). As microfibrilas são depositadas em torno das células e interligadas com hemiceluloses (LAGAERT; BELIÈN; VOLCKAERT, 2009).

Os PNCs são divididos em polissacarídeos hemicelulósicos e pectíneos. A hemicelulose compreende um grupo heterogêneo de polissacarídeos ramificados, presente nas formas solúveis ou insolúveis em água (DA-SILVA; FRANCO; GOMES, 1997; LEROUXEL et al., 2006; MUDGIL; BARAK, 2013). É constituída por monômeros como D-xilose, D-manose, D-arabinose e D-galactose, dentre outros, unidos por ligações P-1,4, e por ácidos urônicos. A hemicelulose pode ser classificada de acordo com o açúcar predominante na cadeia principal e na ramificação lateral, como por exemplo, xilanas, galactomananas, arabinoxilanas e galactosanas. A xilana é o principal polissacarídeo componente das hemiceluloses. Geralmente são extraídos dos polissacarídeos da parede celular usando soluções alcalinas após a remoção da pectina (DA-SILVA; FRANCO; GOMES, 1997; McDOUGALL et al., 1996; BRETT; WALDRON, 1996).

A rede de celulose e hemicelulose está embebida numa matriz gelatinosa de pectina, classe mais complexa dos polissacarídeos da parede celular (LAGAERT; BELIÈN; VOLCKAERT, 2009). A pectina encontra-se em toda parede celular primária e em sua composição há polissacarídeos ricos em ácido galacturônico, ramnose, arabinose e galactose, contribuindo para a firmeza e estrutura das plantas. As moléculas de ácidos galacturônicos possuem cargas negativas, o que promove sua alta capacidade de hidratação e de ligação com cátions bivalentes (BRETT; WALDRON, 1996; WALDRON; PARKER; SMITH, 2003).

As substâncias pécticas são formadas por duas frações interligadas: a ramnogalacturonana e a homogalacturonana. A primeira é um heteropolímero, cuja estrutura principal é constituída por repetidas unidades de ácido galacturônico ligado à ramnose e cadeias laterais consistindo de arabinose e galactose, a qual não interage com o íon Ca^{++}. Por outro lado, a homogalacturonana é um homopolímero formado por unidades de ácido

galacturônico e possui capacidade de ligar íons Ca++, o que tem importância tecnológica devido à capacidade de aumentar a viscosidade e formar gel. Este grupo pode ser dividido em ácido péctico ou poligalacturônico, os quais possuem todos os grupos carboxílicos das unidades de ácido galacturônico livres e ácido pectínico, quando os grupos carboxílicos estão esterificados com o metanol. O grau de esterificação da pectina depende da fonte e do método de extração (DA-SILVA; FRANCO; GOMES, 1997).

Além dos polissacarídeos, a parede celular apresenta proteínas estruturais que desempenham papel importante na sua arquitetura através das ligações cruzadas formadas com outros componentes (BRETT; WALDRON, 1996). Na parede celular ainda podem ser encontradas enzimas como peroxidase, invertase, celulase, pectinase, fosfatase ácida e pectina metilesterase (HUISMAN; SCHOLS; VORAGEM, 1998). As enzimas apresentam diversas funções incluindo degradação da parede celular e suas alterações durante o crescimento, desenvolvimento, maturação e senescencia (WALDRON; PARKER; SMITH, 2003).

Entre os compostos fenólicos encontrados na parede celular, se destaca a lignina, um polifenol altamente insolúvel, formado pela polimerização de três alcoóis: álcool coniferil, álcool trans-p-coumaril e álcool trans-sinapil. Estes alcoóis mantêm uma extensa rede de ligações cruzadas dentro da parede celular, com eliminação de água, o que lhes confere elevada resistência. Além disso, a lignina pode apresentar ligações covalentes com polissacarídeos de forma direta com resíduos de açúcares ou indiretamente via ácido ferúlico esterificado (McDOUGALL et al., 1996; BRETT; WALDRON, 1996; DA-SILVA; FRANCO; GOMES, 1997).

3.4.2 Fracionamento da Parede Celular

O fracionamento da parede celular é uma técnica utilizada para conhecer a composição das diferentes frações de polissacarídeos extraídos. A proporção e a estrutura dos polissacarídeos podem variar com o tipo celular e com a taxonomia da planta. Além disso, dependendo do tipo celular, outros componentes podem estar presentes como a lignina e as proteínas. O conhecimento da composição da parede celular é importante por estar relacionado com a digestibilidade do material ou com a sua qualidade de cozimento (SUN et al., 2006; BRETT; WALDRON, 1996).

A extração dos polissacarídeos pode ser realizada a partir do material finamente moído e pela extração com solventes orgânicos são removidas as moléculas de baixo peso molecular. Este material é deslignificado para aumentar a extração dos

polissacarídeos, quando necessário. A separação do amido também pode ser realizada utilizando dimetil sulfóxido (DMSO). A pectina é solubilizada em uma série de extrações com agentes quelantes como oxalato de amônio, EDTA (ácido etilenodiamino tetracético) ou CDTA (ácido ciclohexano diamino tetracético). As frações de hemicelulose podem ser separadas utilizando variadas concentrações de hidróxido de sódio (NaOH) ou potássio (KOH). Além disso, muitas vezes adiciona-se boroidreto de sódio para reduzir algumas reações como a P-eliminação. A celulose, por ser insolúvel nos solventes utilizados, é recolhida como última fração. A quantificação dos monossacarídeos que compõe as diferentes frações pode ser realizada por cromatografia gasosa, líquida ou de troca iônica, geralmente de alta eficiência. A despolimerização dos polissacarídeos é realizada por hidrólise ácida, baseado na quebra das ligações glicosídicas por ácidos fortes em temperaturas elevadas (CUI, 2005).

3.5 FIBRAS ALIMENTARES

As fibras alimentares (FAs) são constituintes da parede celular de vegetais e podem ser definidas como macromoléculas que não são digeridas no intestino delgado humano (MUDGIL; BARAK, 2013). FA constituem um complexo grupo de compostos químicos heterogêneos, englobando substâncias como a celulose, hemicelulose, pectinas, gomas, mucilagens, amido resistente, entre outros polissacarídeos, e a lignina. Estas substâncias conseguem atingir o intestino grosso, onde são fermentadas, podendo apresentar diferentes propriedades dependendo da fonte, processamento e destino após sua passagem no trato digestivo (THARANATHAN; MAHADEVAMMA, 2003; GUILLON; CHAMP, 2000).

As FAs são reconhecidas por seu papel na diminuição do risco de muitas doenças tais como, cardiovasculares, diabetes mellitus, câncer de cólon, constipação e diverticulite. Além disso, o consumo de alimentos ricos em fibras fornece benefícios à saúde, diminuindo o nível de lipídios no sangue e a velocidade de absorção de nutrientes, aumentando o volume do bolo fecal e o tempo do trânsito intestinal (THARANATHAN; MAHADEVAMMA, 2003). As fibras são conhecidas como prebióticos, uma vez que promovem o desenvolvimento de bactérias benéficas no intestino (MUDGIL; BARAK, 2013). Estudos têm demonstrado que fibras de diferentes fontes exercem distintos efeitos metabólicos e fisiológicos, e pode estar relacionado principalmente com as suas propriedades físicas e químicas (GUILLON; CHAMP, 2000). A recomendação do consumo de fibras por dia é de 25g para mulheres com menos de 50 anos, 21g para mulheres acima de 50 anos, 38g

para homens com menos de 50 anos e 30g para homens acima de 50 anos (FOOD AND NUTRITION BOARD, 2001).

As fibras podem ser classificadas quanto a sua solubilidade em água. As insolúveis são compostas por celulose, lignina e algumas hemiceluloses, formando uma matriz complexa. Elas são empregadas em suplementos dietéticos ou em alimentos funcionais, tais como pães e biscoitos. Já as fibras solúveis em água são constituídas por pectinas, gomas, mucilagens e algumas frações de hemicelulose. Apresentam elevada viscosidade quando dissolvidas em água, o que contribui para melhorar o trânsito intestinal e consequentemente geram inúmeros benefícios à saúde. Ao serem incorporadas aos alimentos, as fibras solúveis desempenham propriedades funcionais, como espessante e geleificante (THARANATHAN; MAHADEVAMMA, 2003; THOMPSON, 2000).

A capacidade de hidratação das fibras alimentares é importante tanto para o desempenho de seus efeitos fisiológicos, como de suas propriedades funcionais. Entre as propriedades de hidratação estão: capacidade de intumescimento (volume ocupado por um peso conhecido de fibra); retenção de água (volume de água retido por um determinado peso de fibra) e absorção de água (cinética do movimento da água em condições pré-estabelecidas), as quais dependem da composição físico-química e estrutural das fibras. As duas primeiras análises fornecem informações importantes sobre a hidratação das fibras e influenciam a sua aplicação em alimentos. Já o índice de absorção de água promove um maior conhecimento acerca do comportamento das fibras após a incorporação aos alimentos. Alguns processos como moagem, secagem, cozimento e extrusão além de modificar as propriedades físicas da matriz, afetam sua capacidade de hidratação (GUILLON; CHAMP, 2000).

Assim, o emprego das fibras alimentares em formulações alimentícias pode melhorar suas propriedades como capacidade de retenção de água e/ou de óleo, capacidade emulsificante, entre outras, além de ocasionar mudanças na consistência, textura, comportamento reológico e características sensoriais (ELLEUCH et al., 2011).

Devido à importância das fibras do ponto de vista fisiológico, tecnológico e econômico há uma tendência em procurar novas fontes deste componente, bem como métodos para aprimorar sua funcionalidade. A obtenção de novas fontes de fibras é importante para formular os produtos funcionais, os quais além de fornecer nutrientes podem afetar positivamente algumas funções biológicas, melhorando a saúde ou reduzindo o risco de doenças. É importante que os produtos com esta alegação, garantam que os efeitos benéficos sejam produzidos na quantidade em que são consumidos (RODRIGUEZ; MEGÍAS; BAENA, 2003).

Muitos subprodutos da agroindústria são ricos em fibras e podem ser utilizados como fontes deste componente para incorporação em alimentos processados. Eles podem ser empregados como substitutos parciais de farinhas ou gordura, e assim promover maior retenção de água ou óleo, estabilizar emulsões, etc. No entanto, o nível máximo de adição destas fibras em alimentos deve ser estudado, pois podem ocorrer alterações indesejadas na cor ou textura dos produtos (MUDGIL; BARAK, 2013).

3.6 COMPOSTOS ANTIOXIDANTES

Os antioxidantes podem ser definidos como substâncias que retardam, previnem ou impedem as reações oxidativas ou como moléculas capazes de interagir com radicais livres, sem comprometer a sua estabilidade química. Há dois grupos de antioxidantes conhecidos, os enzimáticos e os não-enzimáticos. Neste último grupo, encontram-se os compostos fenólicos e os carotenoides, amplamente distribuídos nos alimentos e que podem contribuir para minimizar os efeitos deletérios dos radicais livres à saúde humana (CAROCHO; FERREIRA, 2013).

Os compostos fenólicos são metabólitos secundários sintetizados pelas plantas, formados a partir dos aminoácidos fenilalanina e tirosina e são constituídos por anéis aromáticos com um ou mais grupos hidroxilas substituintes. Os fenólicos enquadram-se em diversas categorias, como fenóis simples, ácidos fenólicos (derivados de ácidos benzóico e cinámico), cumarinas, flavonóides, estilbenos, taninos condensados e hidrolisáveis, e ligninas. Nos alimentos, os compostos fenólicos contribuem com o amargor, adstringência, cor, sabor, odor e estabilidade oxidativa (NACZK; SHAHIDI, 2004).

Os compostos fenólicos são conhecidos por sua atividade antioxidante (AA), que se deve às suas propriedades redutoras e estrutura química (SOUSA et al., 2007). Estes compostos pertencem à categoria de antioxidantes primários, ou seja, eles atuam na fase terminal da reação em cadeia, doando hidrogênio ou elétrons aos radicais livres, convertendo-os em produtos mais estáveis. Um dos fatores mais importantes ao avaliar a AA destes compostos é a estabilidade ou reatividade dos radicais antioxidantes formados após a sua ação, havendo a necessidade de deslocalização do elétron no anel aromático, gerando estruturas de ressonância (MADHAVI; DESHPANDE; SALUNHE, 1995).

Além de atuarem como antioxidantes primários, Naczk e Shahidi (2004) afirmaram que estes compostos são capazes de interceptar oxigênio singlete, prevenir a iniciação da reação em cadeia sequestrando os primeiros radicais formados, tais como

hidroxila, podem ainda quelar íons metálicos impedindo sua ação catalisadora e decompor os produtos primários da oxidação para espécies não reativas.

Por outro lado, os carotenoides pertencem a um grupo de pigmentos naturais sintetizados pelas plantas e alguns micro-organismos. Eles desempenham importantes funções na fotossíntese, auxiliando a captação de energia luminosa e a fotoproteção dos tecidos vegetais, pela inativação de espécies reativas de oxigênio formadas pela exposição à luz e ao oxigênio. Na dieta humana assumem o papel de precursores da vitamina A (CAROCHO; FERREIRA, 2013).

A função antioxidante dos carotenoides, bem como seu papel na diminuição do risco de certos tipos de câncer, pode ser devida tanto a sua função de pró-vitamina A como por sua habilidade de reagir com radicais livres. Além disso, acredita-se que a atividade antioxidante dos carotenoides está relacionada com a habilidade de interagir com os radicais peroxil antes da sua propagação na peroxidação lipídica. Estudos tem confirmado que a atuação dos carotenoides como antioxidantes ocorre tanto *in vitro* como *in vivo,* com destaque para o P-caroteno. O potencial antioxidante desenvolvido pelos carotenoides depende da sua estrutura química e concentração, presença de oxigênio e de outros antioxidantes (CAROCHO; FERREIRA, 2013; DIMAKOU; OREOPOULOU, 2012).

3.7 ANTINUTRIENTES

Antinutrientes são compostos conhecidos por sua capacidade de interferir na absorção de determinados compostos, como minerais e proteínas. Os mais conhecidos são o ácido fítico, o ácido oxálico e os taninos (GUPTAA et al., 2005).

3.7.1 Ácido Fítico

O ácido fítico (AF) está amplamente distribuído na natureza, na forma de ácido livre, fitato ou fitina dependendo do pH fisiológico e dos metais que formam os sais (TSAO; ZHENG; LU, 1997). Na maioria dos cereais e oleaginosas, o fitato está localizado em corpos proteicos, complexado com as proteínas ou com minerais, principalmente os cátions potássio, magnésio, cálcio, ferro e zinco (LIU, 1997; LIU; CHENG; ZHANG, 2005).

A habilidade do ácido fítico quelar íons metálicos di e tri valentes, tais como Ca, Mg, Zn e Fe, possibilita a formação de compostos com baixa solubilidade, que não são totalmente absorvidos pelo intestino (LIU, 1997). A associação do fitato com proteínas pode

formar complexos insolúveis, que só são dissolvidos em pH abaixo de 3,5, afetando sua atividade biológica e digestibilidade (KUMAR et al., 2010).

Durante o processamento dos alimentos e também no trato gastrointestinal, o inositol hexafosfato pode ser parcialmente defosforilado, formando penta, tetra e tri-fosfato, pela ação das fitases endógenas, que são encontradas na maioria das plantas (ZHOU; ERDMAN, 1995). Estes derivados têm capacidade de interagir com metais similares ao hexafosfato, porém a força da ligação depende do número de fosfatos desprotonados da molécula. Esta degradação é de suma importância nutricional, pois a diminuição da ligação do AF com minerais promove maior solubilidade quando os grupos fosfatos são removidos do anel inositol, consequentemente aumenta a biodisponibilidade dos íons (SANDBERG, 2002).

O AF tem sido considerado um antinutriente devido ao seu efeito inibitório na bioviabilidade dos minerais, através do seu poder quelante. Porém, esta propriedade confere ao AF a função de antioxidante, por sua capacidade de quelar o ferro, bloqueando todas as possibilidades de ligação e impedindo que este mineral catalise a formação de hidroxilas. O Fe^{2}+ é o responsável por produzir as espécies reativas de oxigênio e causar a peroxidação lipídica, enquanto Fe é relativamente inerte. Muitos processos biológicos resultam na formação de Fe^{2+}, a presença do AF pode acelerar a redução do ferro, originando o Fe^{3+}. Portanto, o AF presente nos alimentos pode protegê-los contra a formação de radicais livres (ZHOU; ERDMAN, 1995).

3.7.2 Taninos

Os taninos pertencem ao grupo de compostos flavonóides, com estrutura básica, C6-C3-C6, que inclui os mais diversos e numerosos compostos fenólicos de plantas (DESHPANDE; CHERYAN; SALUNKHE et al., 1986). A maioria dos fenóis comuns em plantas não são considerados tóxicos em quantidades e condições normais, com exceção dos fenóis poliméricos denominados taninos, que possuem habilidade de complexar e precipitar proteínas de soluções aquosas (SALUNKHE; CHAVAN; KADAM, 1990).

A habilidade de formar complexos com vários tipos de moléculas é o principal impacto dos taninos na nutrição. São considerados potentes inibidores de enzimas, devido à sua complexação com proteínas enzimáticas, podendo ainda interagir com carboidratos, membrana celular de bactérias e íons metálicos (LEINMULLER; KARL-HEINZ, 1991). Segundo Haslam (1996), dentre todos estes efeitos, a complexação dos

taninos com proteínas é o principal efeito biológico, o qual envolve ligações de hidrogênio e depende do pH do meio, sendo portanto reversível.

Apesar de existirem fatores antinutricionais atribuídos aos taninos, há relatos sobre possíveis efeitos benéficos, quando ingeridos em quantidades moderadas (10 a 40 g/Kg de matéria seca). Alguns destes efeitos são: atividade antioxidante; atividade anticarcinogênica; diminuição da pressão sanguínea e também ação bactericida e fungicida (VIEIRA, 2006).

3.7.3 Ácido Oxálico

O ácido oxálico ($C_2H_2O_4$) é o ácido dicarboxilíco mais simples e o mais oxidado composto orgânico formado em vegetais. Este composto pode formar complexos com o cálcio, altamente insolúveis, conhecidos como cristais de oxalato de cálcio. A combinação entre fatores genéticos e ambientais desempenham papel importante na definição da forma, tamanho, quantidade e função do cristal formado. As formas mais comuns que os oxalatos de cálcio podem assumir são: prismáticas, estiloides retangulares alongados, feixes de agulhas denominados ráfides, pequenos cristais angulares, e cristais multifacetados conglomerados conhecidos como drusas. Estes cristais de cálcio desempenham uma série de funções nas plantas, como armazenamento e regulação do nível de cálcio e atuação no mecanismo de defesa (FRANCESCHI; NAKATA, 2005).

O ácido oxálico (AO) está amplamente distribuído em alimentos de origem vegetal e devido à formação de sais de cálcio insolúveis é considerado um fator antinutricional, interferindo na absorção de cálcio pelo organismo humano. O tratamento térmico ou cozimento tem mostrado grande eficiência em reduzir os níveis de oxalato, devido a sua solubilidade em água quente, o que torna os alimentos mais seguros para o consumo. Isto é importante por causa do efeito deletério que o AO apresenta a saúde humana, pois além de diminuir a absorção de minerais, sua presença está relacionada à formação de cálculo renal (GUPTAA et al., 2005).

No homem, os oxalatos urinários podem ser formados durante o metabolismo do ácido ascórbico e da glicina, ou por fontes de ácido oxálico provenientes da dieta (THOMPSON; FRANKOS; HANSON, 1989). As principais fontes de AO são os vegetais, principalmente os folhosos, como espinafre e ruibarbo, e as sementes. Em casos extremos, a ingestão e absorção de altas concentrações de oxalatos pode ser letal por causar oxalose, ou seja, deposição de oxalato de cálcio nos tecidos. A ingestão de doses moderadas

de ácido oxálico pode levar a formação de cálculo renal, devido a sua absorção e excreção na urina (HOLMES; KENNEDY, 2000). Para pessoas nesta condição, recomenda-se uma ingestão máxima de 50 a 60 mg de oxalato por dia (CHICAGO DIETETIC ASSOCIATION, 2000).

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4 MATERIAL E MÉTODOS, RESULTADOS E DISCUSSÃO

Esta seção foi dividida em 3 artigos científicos apresentados a seguir.

4.1 ARTIGO CIENTÍFICO 1

O Artigo Científico 1 foi publicado no periódico *Food Science and Technology Research,* volume 19, número 6, páginas 1061-1069. 2013.

Peach palm *(Bactris gasipaes* kunth) characterization and the potential of by-products flour processing

Peach palm characterization and the potential of by-products processing

Beatriz C Bolanho[1]*, Eliane DG Danesi[1], Adelaide P Beléia[2]

Abstract: The peach palm cultivated for the industrial canning of heart-of-palm has different portions whose utilization can be maximized. The aim of this work was to evaluate the composition and structure of all portions of peach palm rod and to investigate the possible utilization of the by-products for flours processing. The central edible portion had the highest content of protein, fat, starch and the lowest level of dietary fiber. The highest content of oxalic acid was found in the shell. The tissue is formed by fibrous elements, xylem and phloem vessels, amiloplasts and calcium oxalates in druses and raphides. Although the oxidative enzymes of by-products were inactivated during drying at 90° C for 36 h, the color parameter indicated that the flours should be dried at 60° C. The median sheath flour had a lower content of oxalic acid and tannins than the stem flour, but similar content of phytic acid.

Keywords: Chemical composition. Enzymatic browning. Micrographs. Dietary fiber. Antinutrients

Introduction

The peach palm *(Bactris gasipaes* Kunth), known in Brazil as *pupunheira,* is a specie of native palm that grows in the tropical forest and it is now being cultivated. All the peach palm portions can be utilized although the fruits and the heart-of-palm are the most

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important economically. Among cultivated species for the production of heart-of-palm, the peach palm stands out because it is an excellent alternative for sustainable production (Galdino and Clemente, 2008).

The palm is generally multistemmed and after the harvest for heart-of-palm, offshoots will grow providing another crop in the future. The edible portion, known as heart-of-palm or *pupunha,* is appreciated for its flavor and texture and is described by Mora-Urpi *et al.* (1997) as "the tender internodes which extended from the apical meristem down to 10-25 cm bellow; the tender tubular part composed of immature leaves wrapped within the tender petiole sheaths; the tender immature leaves above the enveloping sheath". The heart-of-palm can be divided into basal and central, the first part is used to make a product cut into cubes due its lower quality (less tender, more fibrous) while the central part is commercialized in cylindrical form, generally processed and sold in glass containers (Egea *et al.,* 2012).

The peach palm has 3 to 4 sheaths that surround the edible portion, the external sheath or shell is green and the internal sheaths are lighter in color (Figure 1). At harvest the rods are cut and a stem part below the edible portion as well as enveloping sheaths are eliminated during the peach palm processing. The sheaths and the stem portion generate a large volume of discarded material which has negative impact in the environment.

There are many studies of peach palm (Galdino and Clemente, 2008; Egea *et al.,* 2012; Yuyama *et al.,* 1999; Monteiro *et al.,* 2002) but no one described its composition and structural characterization of all its parts. Besides the peach palm tissues characterization, there is a need to improve the utilization of its by-products generated during the canning process. The sheaths and the stem portion can be processed into flours that have a potential market as a new food ingredient rich in dietary fibers (DF). However, during the processing of the flours browning can occur darkening the product and limiting its utilization.

The use of peach palm by-products can be maximized through an understanding of their chemical composition and structure that will allow the implementation of diverse processing strategies for the development of economically alternative products. The aim of this work was to evaluate the composition and the microstructure of all portions of the cut peach palm rod and of the processed by-products (sheaths and stem) flours, investigating their oxidative enzyme activity, types of mineral inclusions and antinutrients composition.

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Material and Methods

Material

The rods of peach palm were obtained in Mariluz/PR/Brazil from a commercial crop for heart-of palm processing. Reagents utilized in the analyses were of analytical grade.

Peach palm portions characterization

After harvesting the different parts of peach palm shell, median sheath, stem and edible portions (basal and central) of different rods were separated and subjected to weighing to calculate the yields.

The proximate composition (moisture, ash, protein, fat) and the determination soluble (SDF) and insoluble dietary fiber (IDF) of the fresh portions of the peach palm were determined according to AOAC (2002). The total dietary fiber content (TDF) was obtained by summing the SDF and IDF values.

Oxalic acid was determined by titration of the extract with 0.02 M KMnO4, and the percentage of oxalic acid calculated by multiplying titrate volume in mL by 1.8 (Moir, 1953).

Starch granules from fresh samples were isolated after triturating the samples with cold water at 5^{o} C and sieving though 48 and 100 mesh to separate the fibers. The starch suspension was decanted for 12 h, centrifuged at 1700Xg for 15 min, washed with water and ethanol and dried at 35^{o} C (Rocha *et al.,* 2008). The dried samples were coated with gold in the Sputter Coater (Baltec-Balzers SCD 050) and the images were obtained in scanning electron microscopy (SEM - FEI model Quanta 200).

The different portions of peach palm fresh were observed by SEM. The samples were fixed in a solution of 2 % (v/v) glutaraldehyde and 3 % (v/v) //-formaldehyde in 0.2 M phosphate buffer (pH 7.2) for 24 h. After this period the samples were fixed in 2 % (v/v) osmium tetroxide, dehydrate in ethanol aqueous solutions from 70 to 100 %, dried in the Critical Point Dryer (CPD 030, Baltec-Balzers) and coated with gold in the Sputter Coater.

Preparation of peach palm by-products flours

The peach palm flours were obtained from the median sheaths and stem portion discarded in the processing of the canned products and classified as median sheath flour (MSF) and stem flour (SF). The external shell was not used for flour production due to its green color. The processing started with the separation of the various parts, washing, cleansing, cutting and drying in an oven with forced air circulation (Marconi, MA 035) at 60, 75 and 90^{o} C for 36 h. The dried material was ground in a knife mill type Willye (SOLAB, SL-031), passed through a set of sieves from 25 to 100 USS/ASTM, subjected to vibration for 10 min, and the flour of 100 mesh-passed particle size was analyzed.

Oxidative enzyme activity and color parameters

The oxidative enzyme activity of raw material (median sheath and stem portion) and flours produced was investigated. The peroxidase (POD) and polyphenol oxidase (PPO) were extracted using 100 mM sodium phosphate buffer in pH 5.5 and 6.5, respectively. The samples were filtered and centrifuged at 7.000Xg for 20 min at 4^{o} C (Galdino and Clemente, 2008). The same extraction was used for the flours prepared and dried at different temperatures.

The POD activity was determined using 0.2 M phosphate buffer (pH 6.0), 0.5 % guaiacol, 2 mL of the enzyme extract and 0.08 % H_2O_2 (freshly prepared). The PPO activity measurement was done using 0.1 M catechol as substrate. Readings were taken at one minute intervals in a Spectrophotometer (Biochrom Libra 522) at 470 and 425 nm, respectively. Both activities were followed for 10 min and the enzyme activity calculated by equation 1 (Ferhman and Diamond, 1967).

$$EU = \frac{(\Delta Abs \times 1000)}{\Delta t \times b \times V} \quad (1)$$

Where EU - enzymatic unity (AAbsmL'min"^{1}); AAbs - absorbance change during the reading; At - time variation (min); *b* - optical path (1 cm) and *V* - sample volume (mL).

To monitor the drying process of the flours at different temperatures the final moisture and color were determined. The color characteristics of the flours were defined by the parameters of CIE-Lab, L* (lightness), +a* (red) -a* (green), and +*b** (yellow) -*b** (blue) using the colorimeter Color Reader CR-10, Konica Minolta. *C** (Chroma, color saturation) was obtained according Equation 2 (Giese, 2000) and *H* (hue angle) was calculated according to Equation 3 when positive results were generated for the first quadrant (+a*, +b*) and followed Equation 4 when negative values of *a** and positive values of *b** were obtained (second quadrant) (Mclellan *et al.,* 1995).

$$C^* = (a^{*2} + b^{*2})^{1/2} \quad (2)$$

$$H(h^o) = \tan^{-1}(b^*/a^*) \quad (3)$$

$$H(h^o) = 180 + \tan^{-1}(b^*/a^*) \quad (4)$$

The best temperature for production of flour with lightest color was applied to dry the peach palm discarded portions and to study the yield and the antinutritional compounds.

By-products flours characterization

The yield of stem flour (SF) and median sheath flour (MSF) of peach palm (dried at 60°C for 36 h) was gravimetrically determined by the relationship between the weight of the material before and after drying in an oven with air circulation and grinding (100 mesh-passed).

The antinutrient components evaluated were phytic acid, oxalic acid and tannins. The extraction of phytic acid (PA) was carried out according to Thompson and Erdman (1982), and after digestion and appropriate dilution of the samples, the phytic phosphorous (PP) was colorimetric determined in a spectrophotometer UV-VIS at 820 nm using the factor 3.55, related to 28.2 % of phosphorus present in PA molecule, to convert phytic phosphorous values into phytic acid values. Phosphorus standard curve was a solution of K_2HPO_4 with P concentrations varying from 1.25 to 12.5 u^'mL"[1] (Chen *et al.,* 1956).

Tannins components were extracted with 80 % (v/v) acetone aqueous solution. A volume of 0.5 mL of the extract was mixed with 3 mL of vanillin-HCl (0.5 % (w/v) vanillin, 4 % (v/v) HCl) and the absorbance was measured at 500 nm in spectrophotometer, using the 4 % (v/v) HCl solution as blank. The results were expressed as

catechin equivalent, based on a standard curve of D-catechin with concentrations between 0.2-2.0 mg'mL^{-1} (Prince *et al.,* 1978).

The oxalic acid content was determined as previously described (Moir *et al.,* 1953).

The microstructure of peach palm by-products flours were visualized by SEM after coating with gold in the Sputter Coater.

Statistical analysis

The chemical analyses were carried out in three individual samples and the results were expressed as mean ± standard deviation in wet basis (w.b.) or dry basis (d.b.). ANOVA and Tukey's test were performed using the Statistica software version 6.0 (StatSoft, Inc.).

Results and Discussion

Characterization of peach palm portions

The average weight of the peach palm rods as harvested was 6.3 kg. The most valued product in the market is the heart-of-palm obtained from central portion due to its appreciable texture; however, its yield is the lowest (8.1 g'100g^{-1}) of the cut rod when compared to the discarded portions (Table 1). The basal and central edible portions have similarly yield, amounting to 16.5 g'100g^{-1} of the harvested peach palm stem, while the inedible stem portion had a higher yield (29.1 g'100g^{-1}) and median sheaths comprised 16.7 g'100g^{-1} of the peach palm rod. The most external sheath (shell) was discarded because of the undesirable color, corresponding to 37.5 g'100g^{-1} of the residue. Despite the large volume of waste still generated the use of the median sheath and stem for flour production decreases in 45.8 g'100g^{-1} the total of discharges generated in heart-of-palm processing.

The edible portions had higher moisture content (approximately 90 g'100g^{-1}) than the sheath (86.6 g'100g^{-1}) and shell (81.3 g'100g^{-1}) (Table 1). The canned products of heart-of-palm may be the basal (cubes) or the central portion (cylinders), and these had higher ash content (8.2 g'100g^{-1} d.b.) than the other parts of peach palm. The central portion had the highest level of protein (24.9 g'100g^{-1} d.b.), and crude fat (5.5 g'100g^{-1} d.b.) than the other portions and whose values are similar to that found by Mora-Urpi *et al.* (1997).

The content of protein, fat and ash increased from the stem to the central part, while TDF content was lower in central (48.2 g'100g^{-1} d.b.) than in basal (54.1 g'100g^{-1} d.b.) and stem portion (58.9 g'1OOg^{-1} d.b.). The shell had the highest level of IDF (80.2 g'1OOg^{-1} d.b.) and lower SDF content (2.4 g'1OOg^{-1} d.b.), followed by the median sheath portion (66.1 and 2.6 g'1OOg^{-1} d.b., respectively). The stem and basal portion has similar IDF content (approximately 52.O g'1OOg^{-1} d.b.), which was higher than the value found in central portion (41.O g'1OOg^{-1} d.b.). The level of IDF decreased and the level of SDF increased from stem to central portion, which corresponds to the most tender texture of edible portion, especially the central portion that is the most desirable in the canning industry, having the greatest market value. Yuyama *et al.* (1999) found similar content of IDF in heart-of-palm *(B. gasipaes)* fresh (44.7 g'1OOg^{-1} d.b.) and higher content of SDF in the cooked product (9.2 g'1OOg^{-1} d.b.) than the values found in this study.

Various compounds including cellulose, hemicellulose, pectin, gum, resistant starch, inulin, lignin and others compose the dietary fiber fraction of foods. Total DF is divided into two fractions, one of which is soluble in water at 1OO^{o} C and it is chiefly involved in the lowering effects on blood cholesterol and glucose by reducing intestinal absorption, whereas the fraction insoluble in water is more effective in intestinal regulation. The consumption of foods with high dietary fiber content is important due to the effect in prevention of several diseases such as colon cancer, coronary heart disease, obesity, diabetes and gastrointestinal disorders (Elleuch *et al,* 2O11; Scheneeman, 1987).

The FDA (Food and Drug Administration) recommended for adults the consumption of 25 g of DF per day. Considering the high moisture content of the edible peach palm portions, it would be necessary to consume a large amount of peach palm products to reach the daily demand of DF. The drying process concentrates this component, which is especially important in peach palm by-products, they are not used in the canning process due their undesirable texture and this alternative makes the process more feasible economically. Moreover, the use and application of by-products is important to minimize the impact of the discards in the environment.

The starch yield was higher in the edible central portion (8.9 g'1OOg^{-1} d.b.) than in basal (3.O g'1OOg^{-1} d.b.) and the other portions (Table 1). These values are lower than the ones observed in black beans, chick peas, lentils, navy and pinto beans, whose values varied between 2O to 37 g'1OOg^{-1} (Hoover and Ratnayake, 2OO2).

The shell has higher level of oxalic acid content (13.1 mg'1OOg^{-1} w.b.), followed by the stem portion (11.2 mg'1OOg^{-1} w.b.), basal portion (8.4 mg'1OOg^{-1} w.b.),

central portion (7.6 mg'1OOg^{-1} w.b.) and median sheath (6.7 mg'1OOg^{-1} w.b.). Chai and Liebman (2OO5) observed higher levels of oxalic acid in hazelnuts (222 mg'1OOg^{-1} w.b.), pine nuts (198 mg'1OOg^{-1} w.b.), peanuts (14O mg'1OOg^{-1} w.b.), soybeans (56 mg'1OOg^{-1} w.b.) and black beans (72 mg'1OOg^{-1} w.b.). Oxalic acid is a common constituent of plants, and several species accumulate high levels of it, that has strong chelating ability with multivalent cations, and is considered an antinutrient (Massey *et al.,* 2OO1).

Microstructure of peach palm portions, starch and by-products flours

Stems of palms are stiff fibrous elements immersed in parenchymatous tissue, but we examined the younger tissues still covered by the protective sheaths cut from the top of the stem. Sample preparation for SEM resulted in elimination of most of the protoplasm from the cells and the observation was done on the remaining solids components and the structure formed by the cell walls and vascular bundles.

The stem portion (bellow the heart-of-palm) (Figure 1) had xylem and phloem vessels surrounded by parenchyma cells (Figure 2 A, B, C). The cell wall of parenchyma tissue is relatively thin and formed of cellulose and hemicellulose, with a layer of pectic substances. Around the vascular tissues some parenchyma cells may develop a secondary wall or become lignified and fibers are visible surrounding the vessels (Figure 2 C). In general these vessels exhibited scalariform thickening in lateral wall (Figure 2 A) characterized by the deposition of lignin and hemicelluloses (Rudall, 2007).

The epidermis cells adaxial to the external sheath portion (Figure 2 D) are elongated, irregular and have depressions on the edges of the cells; the stomata appear above the epidermis. Uzzo (2008) analyzing the leaves of king palm noticed that they are hypostomatic, so present only in the lower epidermis, arranged in discrete rows with irregular distribution. According to Passos and Mendonça (2006) tetracytic stomata, formed by a pair of guard cells, a pair of subsidiary cells parallel, and with ends containing two further subsidiary cells, polar, smaller and rounded, is commonly found in palms. Around the stomata it was observed the presence of wax crystals (Figure 2 G).

In the median sheaths cells it was noted the presence of leucoplasts (Figure 2 F), which are plastids responsible for nutrients synthesis. Parenchyma cells and sclerenchyma fibers were observed in median sheath (Figure 2 H). This tissue is the most resistant and specialized among support tissues and fibers were the main component of this portion, as described in the proximate composition. The cell walls of sclerenchyma have the

property of elasticity and mechanical support for the vascular bundles (Rudall, 2007; Trigiano and Gray, 2005).

In the basal portion phloem and xylem vessels are surrounded by fibrous sheaths with lignin (Figure 2 I), which were not observed in the central portion (Figure 2 K). The edible portions had higher number of leucoplasts (Figure 2 J, L) than the other portions, probably amyloplast due to the similarity to starch granules isolated (Figure 3 A). The presence of this reserve polysaccharide in the younger portions of peach palm (heart-of-palm) is an important characteristic of this plant and corresponds to the starch quantified 8.9 g'100 g^{-1} d.b. in central portion of peach palm, while in the other portions the values varied between 0.6 to 3.0 g'100g^{-1}d.b.

The starch granules isolated from peach palm were observed by SEM and the image (Figure 3 A) showed rounded, small and irregular granules with diameters varying from 0.7 to 5.1 urn. Fibers were still visible indicating that the isolation of the starch retained some of this material. The starch granule is characteristic of a botanical source and it can be used for plant identification.

The micrographs showed calcium oxalates crystals in two different formats. In shell, stem part and median sheath there were druses crystals (Figure 2 E, F) whereas the edible portions had raphide crystals (Figure 2 J, L). These crystals are commonly observed in palms of Arecaceae and in other monocotyledons (Dahlgren and Clifford, 1982). The presence of inclusions in parenchyma of sheath is similar to that was observed by Simas *et al.* (2010) referred to as druses that contain multiple crystals of calcium oxalate. The druses are multifaceted conglomerate crystals often single, but also multiple per cell. The raphide crystal is a needle-shaped calcium oxalate crystal, often with grooves along its sides, that occurs as bundles of hundreds to thousands in the vacuole of a cell. Particular specie will form only a certain crystal type or subset of crystal morphologies. This is important because it indicates that the cells and the genetics of the particular species forming these crystals control the morphology.

The oxalate crystals formation is a normal physiological process found in all major groups of photosynthetic organisms. There are numerous hypotheses regarding crystal function in plants, including calcium regulation, plant protection, detoxification, ion balance, tissue support/plant rigidity, and even light gathering and reflection. The crystals found in edible portion of peach palm (raphides) perform a dual function, initially Ca regulation in mature state, and a defense mechanism (Franceschi and Nakata, 2005).

The micrographs of flours revealed the fibrous tissue disorganization due to the milling processing. The SF images (Figure 3 B, C) reveal residues of parenchyma and sclerenchyma, and some vessels of xylem, as well as observed in MSF images (Figure 3 D, F). These micrographs indicated that fibers are the main component of the flours and the effect of cutting, drying and milling in the peach palm portions.

Oxidative enzyme activity and color parameters

The SF dried at 90^{o} C had the lower moisture content (6.0 g'100g^{-1}) than the stem flours dried at 60 and 75^{o} C, whereas in the MSF the final moisture content did not differ among the drying temperatures used, varying from 5.5 to 6.7 g'100g^{-1} (Table 2). In both flours the initial moisture content decreased approximately 92 %.

It was known that POD performs single-electron oxidation on a wide variety of compounds, but this activity is limited due the low level of hydrogen peroxide in vegetal tissue, which can be produced by PPO. Although a possible synergistic effect between these enzymes cannot be excluded, the main enzyme responsible for browning is PPO (Tomas-Barberan and Espin, 2001), whose activity varied from 1.3 to 3.2 AAbs'min'mL^{-1}, while POD activity varied from 8.6 to 44.4 AAbs'min'mL^{-1} in inedible portions of peach palm fresh and dried in different temperatures. Galdino and Clemente (2008) found higher activity in edible portions of peach palm, 257.2 and 3.1 AAbs'min'mL^{-1} for POD and PPO.

The PPO activity was higher in SF dried at 60^{o} C (3.2 AAbs'min'mL^{-1}) than in fresh portion and SF dried at 75^{o} C (2.1 and 1.8 AAbs'min'mL^{-1}, respectively). It was also higher in fresh median sheath (1.5 AAbs'min' mL^{-1}) and in MSF dried at 60^{o} C (1.7 AAb s'min'mL^{-1}) than the value in MSF dried at 75^{o} C (1.3 AAbs'min'mL^{-1}). The highest POD activity was found in the flours dried at 60^{o} C. The decrease of moisture content in the flours resulted in relatively higher PPO and POD enzyme activity in the extracts, before there was heat inactivation. However, higher drying temperatures decreased the oxidative enzyme activity and it was not detected in the extracts of flours dried at 90^{o} C. Galdino and Clemente (2008) tested the thermo stability of PPO and POD extracted from heart-of-palm, also noted a gradual decrease in enzyme activity with increasing temperature. The oxidative enzyme activity may change according to age/harvesting-time, environmental conditions and genetic factors of the plants.

The color parameter brightness (L*) of SF and MSF after drying at 60^{o} C was not different from the one of the fresh portions, however these values decreased with the

increasing drying temperatures (Table 2). The color parameters a*, *b** and *H* had a gradual change with the drying temperature, which was more pronounced in the flours dried at 90° C, whose brown color stood out over the cream color of the fresh portions. The peach palm fresh portions and the flours dried at 60 and 75° C have hue angle closer to 90° which is in the yellowness quadrant (Table 2). Furthermore, higher drying temperatures caused an increase in Chroma values (C*) indicating opacity increase. The lightest color of flours obtained at 60° C is interesting to facilitate their addition in food, like bakery products.

Due to the decrease in oxidative enzyme activity and the increase in the darkening of the flours with the increase of temperature, non enzymatic browning can be the main cause of the dark coloration found in the flours processed at high temperature. The browning could be from Maillard reaction, which occurs by the interaction between amino acids and reducing saccharides or from caramelization of saccharides in drying conditions. The temperature of 60° C was chosen to dry the peach palm residue, because at this temperature the color was similar to the fresh product and the lower temperature minimize energy consumption, promoting an economical process and preserving nutrients of the raw material.

Flours Characterization

The peach palm by-products were milled into flours of different particle sizes. The SF and MSF of 100 mesh-passed particle size had the highest yield 39.7 g'100g^{-1} and 52.1 g'100g^{-1}, respectively, and better technological properties (data not shown), so they were chosen for the study. This particle size of the flours studied is similar to the value commonly found in wheat flour (80 mesh-passed), thus SF and MSF can be an alternative ingredient to be used in bakery products with high fiber content.

The tannin content of SF (295.4 mg'100 g^{-1}) was higher than that in MSF (255.5 mg'100 g^{-1}). Tannins belong to the group of polyphenols and the interaction of these compounds with proteins form complexes which can decrease the solubility of proteins. The complex formed can become less susceptible to proteolyses than the same proteins isolated, they impair starch and disaccharide assimilation and interact with proteases inhibiting their activity (Reddy *et al.,* 1985). However, phenolic compounds may interact with free radicals and reduce the risk of certain diseases, acting as antioxidants (Sreerama *et al.,* 2012).

There was no difference in phytic acid (PA) content among the flours studied. Similar values of these compounds were verified in king palm flour 762.5 mg'1OOg^{-1} for phytate and 281.8 mg'1OOg^{-1} for tannins (Vieira *et al,* 2OO9).

PA is considered an antinutrient because of their inhibitory effect on the bioavailability of minerals through its chelating power. However, this property confers to PA antioxidant function, due to its ability to chelate iron, blocking all the possibilities of bonds and preventing the mineral to catalyze the formation of hydroxyl groups. The chelating potential of PA may result in benefits to the human health, such as lowering cholesterol and triglycerides, preventing heart disease, kidney stones and certain types of cancers such as colon (Jenab and Thompson, 2OO2).

The oxalic acid content was higher in SF (84.1 mg'1OOg^{-1}) than in MSF (57.4 mg'1OOg^{-1}), lower than that found in buckwheat flour (269 mg'1OOg^{-1}) and soybean flour (183 mg'1OOg^{-1}) and higher than that observed in barley flour (56 mg'1OOg^{-1}), corn flour (54 mg'1OOg^{-1}), dark rye (51 mg'1OOg^{-1}) and semolina (48 mg'1OOg^{-1}) (Chai and Liebman, 2OO5). In extreme cases, the consumption of foods containing oxalate may lead to a condition known as oxalosis caused by calcium oxalate deposited in tissues. Food with moderate doses of oxalate may lead to the development of kidney stones (Holmes and Kennedy 2OOO), and for persons that already have this condition the Chicago Dietetics Association (2OOO) recommends a maximum intake of 5O to 6O mg of oxalate a day.

Conclusions

In peach palm portions the content of protein, fat, ash and starch increased from the stem to the central edible portion, while TDF decreased. The high level of SDF and lower content of IDF in the central portion corresponded to most desirable texture of this portion used to make canned products. The tissue is formed mostly by fibrous material and there are different types of mineral inclusions as visualized in the SEM micrographs. The flours produced from the discarded portions in the canning processing can have an alternative use in food industry as fibrous material of light color. The lightest flour was obtained in the drying process conducted at 6O° C although not all the oxidative enzymes were inactivated. Phytic acid was similar in both flours, but SF had higher levels of oxalic acid and tannins than MSF.

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Table 1 – Weight and starch yield, proximal composition and oxalic acid content of peach palm (*Bactris gasipaes*) parts

	Weight yield (g-lOOg^{1} w.b.)	Starch yield (g100g^{-1} d.b.)	Moisture (g-100g-^{1})	Ash (g 100g^{-1} d.b.)	Protein (g 100g^{-1} d.b.)	Fat (g 100g^{-1} d.b.)	TDF (g 100g^{-1} d.b.)	IDF (g100g^{-1} d.b.)	SDF (g 100g^{-1} d.b.)
	37.5±4.3^{a}	0.6±0.0^{d}	81.3±1.1^{c}	3.8±0.1^{c}	3.9±0.2^{e}	1.9±0.2^{c}	82.6	80.2±0.9a	2.4±0.1^{c}
	16.7±1.8 ^{c}	1.0±0.1^{cd}	86.6±2.9^{b}	4.3±0.2^{c}	6.3±0.3^{d}	2.5±0.1^{c}	68.7	66.1±1.9^{b}	2.6±0.2^{c}
	29.1±2.9 ^{b}	1.6±0.1^{c}	89.2±0.2^{ab}	6.8±0.2^{b}	11.2±0.9^{c}	2.6±0.1^{c}	58.9	54.9±3.1^{c}	4.0±0.2^{b}
	8.4±1.2 ^{d}	3.0±0.2^{b}	90.3±0.1^{a}	8.2±0.3^{a}	18.8±0.3^{b}	4.4±0.4^{b}	54.1	48.8±2.4^{c}	5.2±0.4^{b}
	8.1±1.1^{d}	8.9±0.5^{a}	90.7±0.3^{a}	8.2±0.7^{a}	24.9±0.5a	5.5±0.5a	48.2	41.0±2.0^{d}	7.1±0.4a

Mean values in the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$). TDF - Total dietary fiber; IDF -Insoluble dietary fiber; SDF - Soluble dietary fiber; OA - Oxalic Acid.

Table 2 – Moisture, polyphenol oxidase and peroxidase activity, and color parameters of fresh parts of peach palm (stem and median sheath) and flours dried at different temperatures

Fresh part/ Dried part	Moisture (g'100g^{-1})	PPO (AAbs' min$^{'}$mL^{-1})	POD (AAbs' min$^{'}$mL^{-1})	L*	a*	
Stem	89.4±0.1^{a}	2.1±0.1^{b}	30.5±0.9^{b}	85.7±0.7^{a}	-3.4±0.3^{d}	21.3
SF - 60°C	7.2±0.2^{b}	3.2±0.2^{a}	39.7±0.9^{a}	85.9±1.0^{a}	-2.0±0.1^{c}	23.6
SF - 75°C	7.0±0.3^{b}	1.8±0.1^{b}	14.0±0.6^{b}	83.6±0.3^{b}	-0.3±0.1^{b}	25.6
SF - 90°C	6.0±0.2^{c}	ND	ND	65.4±0.3^{c}	6.9±0.2^{a}	28.6
Median sheath	84.0±0.1^{a}	1.5±0.1^{ab}	37.3±1.2^{b}	89.1±0.9^{a}	-1.3±0.1^{d}	12.0
MSF - 60°C	6.7±0.3^{b}	1.7±0.1^{a}	44.4±1.5^{a}	87.9±0.3^{a}	2.1±0.1^{b}	21.4
MSF - 75°C	6.1±0.4^{b}	1.3±0.1^{b}	8.6±0.5^{c}	82.8±0.4^{b}	1.2±0.1^{c}	25.3
MSF - 90°C	5.5±0.2^{b}	ND	ND	64.0 ±1.2^{c}	6.9±0.3^{a}	28.7

Mean values in the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$). SF - stem flour; MSF - median sheath flour; PPO - polyphenol oxidase; POD - peroxidase; ND - not detected.

Table 3 – Phytic acid, tannins and oxalic acid content of the peach palm by-products flours

Component	SF (mg-lOOg^{1} w.b)	MSF (mg-lOOg^{1} w.b)
Phytic acid	666.7±20.9^{a}	634.7±17.9^{a}
Tannins	295.4±12.6^{a}	255.5±15.0^{b}
Oxalic Acid	84.1±3.5^{a}	57.4±4.2^{b}

Mean values in the same line followed by the same letter are not significantly different ($p < 0.05$). SF - stem flour; MSF - median sheath flour.

Fig. 1 – Peach palm (*Bactris gasipaes*) and the identification of its portions

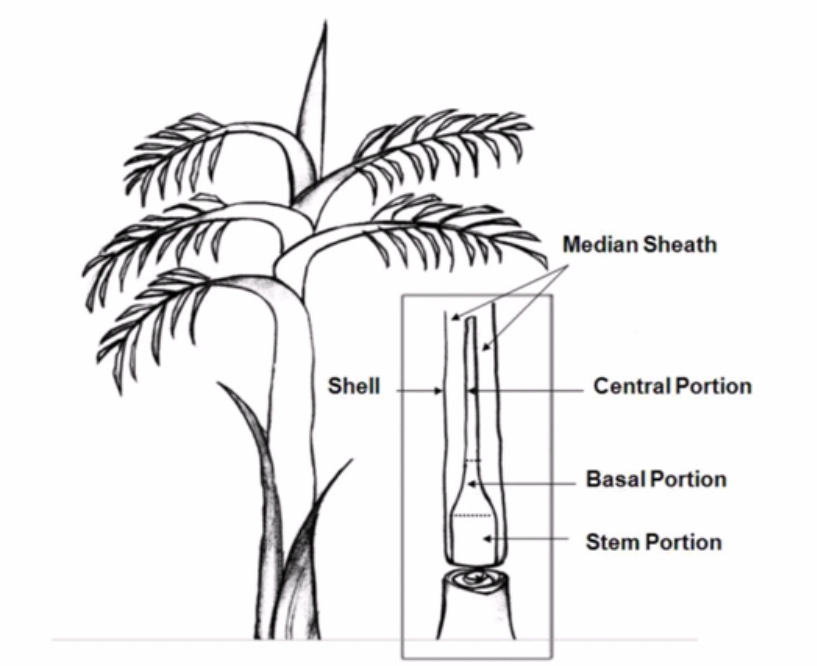


Fig. 2 – Peach palm portions microstructure: stem (A, B, C); shell (D, E); median sheath (F, G, H); basal portion (I, J); central portion (K, L). Xy: xylem; Ph: phloem; RC: raphid crystals; St: stomata; Dc: druse crystals; Lc: leucoplast

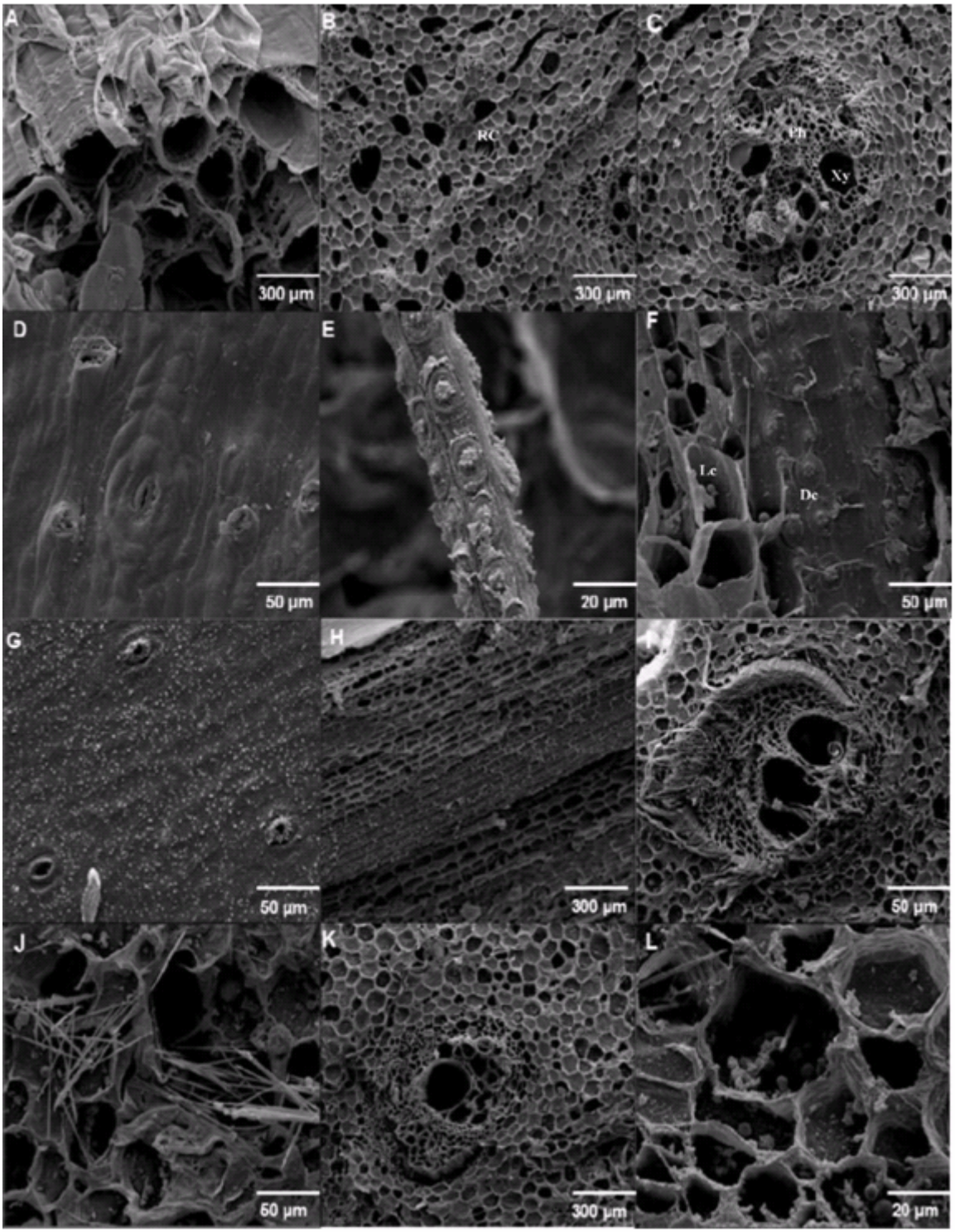
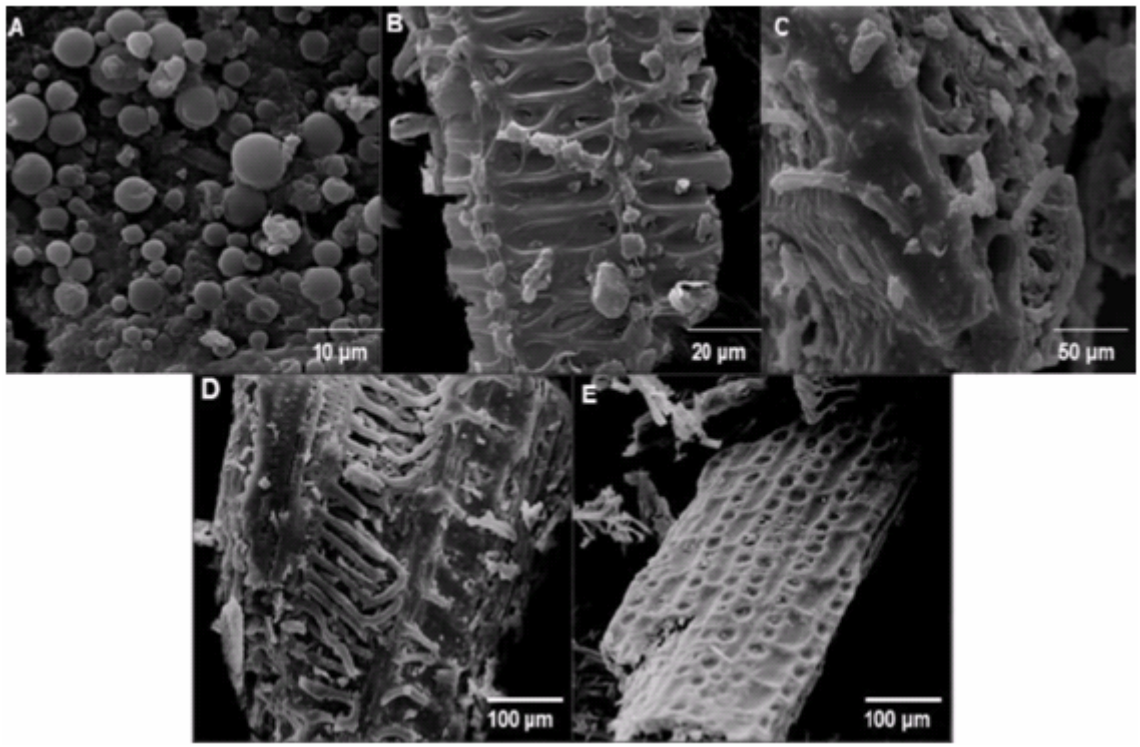


Fig. 3 – Microstructure of starch and peach palm by-products flour: starch extracted from central portion (A); stem flour (B, C); median sheath flour (D, E)



4.2 ARTIGO CIENTIFICO 2

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Characterization of peach palm *(Bactris gasipaes* Kunth) by-products flours as a new food ingredient

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Running title: Characterization of peach palm by-products flours

Summary: Flours production from unused parts of peach palm rods harvested for heart-of-palm is an alternative to add value to the canning industry. The aim of this work was to evaluate the composition, physicochemical and antioxidant properties and water sorption isotherms of flours produced from median sheath (MSF) and unused stem part (SF) of peach palm. The main component of the flours was dietary fibre, especially insoluble fibre. SF had higher content of ashes (50.61 gkg), proteins (98.40 gkg), lipids (23.22 gkg) and saccharides (157.07 gkg) than MSF. There was higher carotenoid content in MSF and higher content of phenolic compounds in SF. This flour also had the highest antioxidant activity in ABTS+, DPPH' and FRAP methods. The SF stands out due to the physicochemical properties: water solubility, water absorption, swelling and viscosity. The isotherm indicated that MSF is more hygroscopic than SF for relative humidity of equilibrium lower than 50 % and the contrary is valid for values higher than 50 % with final moisture content of 268 gkg^{-1} and 325 gkg^{-1} of water, respectively.

Keywords: Chemical composition. Flour. Dietary fibre. Minerals. Antioxidant activity. Physicochemical properties.

The peach palm *Bactris gasipaes* Kunth is a multistemmed Amazonian tropical palm that has economic potential related to its fruits and heart-of-palm production. The heart-of-palm (locally known as *palmito)* is appreciated by many consumers and it can be obtained from various species of palms. Among the cultivated palms, peach palm, known in Brazil as *pupunha,* stands out as an alternative crop for heart-of-palm production. Currently the sustainable production is increasing due to the depletion of extractive material, intense

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supervision of the remaining plants in nature and the high value of the product. This palm has all the desirable characteristics when compared to those of predatory exploitation and advantages such as rapid growth, early maturity for cutting (2 years) and growth of stems from offshoots [1].

The palm stem has three layers (sheaths): external, middle and heart-of-palm. The outer layer that surrounds the palm stem is fibrous, of green or brown colour, while the second layer called median or semi-sheath is lighter in colour and the central core, known as heart-of-palm, is attached to a slightly more fibrous cylindrical base with a larger diameter (both edible) (Fig. 1).

The heart-of-palm is the main product of peach palm and its processing generates a large volume of waste from unused parts such as sheaths (external and median) and a stem part, which is cut together with the heart-of-palm but not used for canning because of its toughness. These by-products of peach palm represent approximately 84 % of the harvested plant weight. To minimize the impact of the discarded parts of the peach palm in the environment, an alternative is to produce flours from the median sheaths and the unused stem part. By-products, obtained specially from fruit and vegetable processing are gaining attention as novel and economic sources of healthy functional ingredients. They can be used to create products which contain value added materials, such as dietary fibre or bioactive compounds. The production and addition of such nutrients to foods can be costly for the producer but may have a positive impact on the health of consumers and on the environment [2].

By-products having high dietary fibre content could be used in bakery products, dairy, jams, processed meats, canned or dried soups, where they can alter textural properties, avoid syneresis and improve shelf-life while benefiting the consumer. Fibre intake has a positive impact in human health and as they can act by slowing the hydrolysis, digestion and absorption in the small intestine, increasing the volume of stools and reducing the levels of glucose and cholesterol absorbed from the lumen [3]. Among the associated phytochemicals the antioxidant compounds are important due the ability to scavenge free radicals, which are involved in oxidation of bio molecules, damaging cells and causing tissue alterations [4]. Besides the nutritional characteristics, it is important to evaluate the functional properties of the flours to direct its application in food products, as well as, to study their water adsorption ability, which may limit its shelf life.

The aim of this work was to characterize the flours produced from peach palm byproducts, evaluating composition, physicochemical and antioxidant properties, and water sorption isotherms, as a possible new source of dietary fibre.

Material and Methods

Peach palm by-products flour production

The peach palm flours were produced from the median sheaths and parts of the unused stem, harvested in a heart-of-palm farm in Mariluz, Paraná, Brazil, which were subjected to washing, cleansing, cutting and drying in an oven with forced air circulation at 60^{o} C for 36 h (MA 035, Marconi, Piracicaba, Brazil). The dried material was ground in a knife mill type Willye (SL-031, Solab, Piracicaba, Brazil) and passed through a set of sieves with particle separation from 150 um to 600 um, subjected to vibration for 10 minutes. The flours from median sheath (MSF) and stem part (SF) of peach palm with particle size of 150 um were used in the analysis.

Proximate and mineral composition

MSF and SF were analysed for chemical composition: moisture (method 925.09), ash (method 923.03), protein (method 920.87), crude fibre (method 978.10) and fat (method 920.85) according to AOAC [5]. Glucose, fructose and saccharose were extracted with hot water and the content was estimated using Enzytec™ (n° E1247, R-Biopharm, Darmstadt, Germany).

Uronic acids were analysed following the recommendations of SIMAS et al. [6]. The samples were dissolved in water (0.5 $mgml^{-1}$) and hydrolysed with sulphuric acid and then the reaction was carried out with 0.1 % m-hydroxydiphenyl dissolved in 0.5 % sodium hydroxide. The absorbance was read in spectrophotometer (700 Plus, Femto, São Paulo, Brazil) at 520 nm. A standard curve with different concentrations of galacturonic acid (10-60 $ug\text{-}ml^{-1}$) was used for the calculation of uronic acid content.

Minerals were analysed in atomic absorption spectrophotometer (AAnalyst 200, PerkinElmer, Waltham, Massachusetts, USA) after nitro perchloric acid digestion (HNO_3:$HClO_4$/3:1) and appropriate dilution.

Dietary fibre and its components

The determination of soluble (SDF) and insoluble dietary fibre (IDF) was according to gravimetric enzymatic method 991.43 AOAC [5]. The total dietary fibre was obtained by summing SDF and IDF content. Resistant starch was determined according to method 2002.02 of AOAC [7] and after enzymatic hydrolysis the glucose content was detected with a glucose oxidase kit, supplied by Bioclin (Belo Horizonte, Brazil).

Acid detergent fibre (ADF) and neutral detergent fibre (NDF) were measured according to the Van Soest system [8] and the lignin content was determined after hydrolysis with 72 % sulphuric acid [9]. The content of lignin, cellulose and hemicellulose were calculated from the contents of NDF and ADF.

Total carotenoid, total phenolic compounds and antioxidant activity

The carotenoid content was determined according to the methodology described by RODRIGUEZ-AMAYA and KIMURA [10]. The antioxidant extraction was carried out using 80 % ethanol [11] and the ethanol extract was used for the determination of total phenolic content using Folin-Ciocalteau method [12]. The content of phenolic compounds was determined using a standard curve prepared with gallic acid (Sigma, New Orleans, Louisiana, USA) and expressed in milligrams of gallic acid equivalent (GAE) per kilogram.

The scavenging activity of DPPH' radicals (2, 2-diphenyl-1-picrylhydrazyl, Sigma-Aldrich Chemical, St. Louis, Missouri, USA) was determined according to BRAND-WILLIAMS [13] and the ferric reduction power (FRAP) of the extracts was assessed following the methodology described by BENZIE and STRAIN [14]. The calibration curves were linear between 100 $umoll^{-1}$ and 1000 $umoll^{-1}$ of Trolox (6-hydroxy-2, 5, 7, 8-tetramethylchromane-2-carboxylic acid, Sigma-Aldrich Chemical). The antioxidant capability of the extracts with $ABTS^{4"}$ free radical (2, 2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid, Sigma-Aldrich Chemical) was carried out according to THAIPONG et al. [15]. A standard curve with different concentrations of Trolox was used for the calibration (from 100 $umoH^{-1}$ to 2000 $umoH^{-1}$). All the results were expressed as Trolox equivalent (in millimoles of Trolox per kilogram).

Physicochemical properties

The pH was measured with a potentiometer (PG 2000, Gehaka, São Paulo, Brazil) using 10 g of sample suspended in 100 ml of water. The bulk density was measured through the relation between weight and volume using a graduated cylinder [16].

To determine the swelling volume of the particles (SVP) 1 g of sample was mixed with excess of distilled water and stirred for 2 h. After complete decantation, the volume occupied by the sample in the beaker was named swelling volume, expressed in millilitres per gram of dry matter (d.m.) [17].

The water solubility index (WSI) of flours was evaluated according to AZIZ et al. [18] and the results expressed in grams of soluble solids per kilogram. The water absorption index (WAI) was measured weighing 2 g of sample in centrifuge tubes, adding 20 ml of water and stirred continuously in a shaker. The mixture was centrifuged at 3000 g for 10 min, the supernatant was discarded and the residue weighed. WAI was obtained by the weight ratio between the wet sediment and the dry matter. The result was expressed in grams of water absorbed per gram of dry matter. The oil absorption index (OAI) was determined the same way as the water absorption, using commercial soybean oil [17].

To measure the viscosity, three percentages of the flours suspensions (4, 5 and 6 %) was analysed using the Viscometer Model DVII (Brookfield, Middleboro, Massachusetts, USA) with spindle number 1 (0.05 Hz to 1.00 Hz) at a constant rotational frequency of 0.05 Hz and 0.10 Hz.

Water sorption isotherm

The water sorption isotherm of SF and MSF was determined using an Aquasorp (Decagon Devices, Pullman, Washington, USA) at 25° C with relative humidity of equilibrium (RHE) between 10 % and 85 % that corresponds to water activity between 0.10 and 0.85. The water content was expressed in grams of water per kilogram in dry basis.

Statistical analysis

Analyses were done in three individual replicates and the results were expressed as mean ± standard derivation. The variance analysis ($p<0.05$) and correlations tests

($p<0.05$) were performed using the software Statistica version 6.0 (StatSoft, Tulsa, Oklahoma, USA).

Results and Discussion Proximate and Mineral Composition

SF had higher ash content than MSF (Tab. 1) but lower than those reported by HELM et al. [19] for flour produced from the uvarana palm *(Cordyline spectabilis)* by-products 84.6 gkg^{-1}. Protein and lipid content were higher in SF than in MSF, the values of protein were higher than that found by SIMAS et al. [6] in the leaf sheath flour of king palm (35 gkg^{-1}). The lipid content in SF and MSF was similar to that found in field pea flours (19 gkg^{-1}) [20].

Glucose was the most abundant saccharide in the flours of SF and MSF, followed by fructose, reducing saccharides that may participate in browning reactions, like Maillard reaction, during cooking in dehydration conditions or during drying of the material. ABOUBAKAR et al. [21] found in taro *(Colocasia esculenta)* flours values ranging from 135 to 267 gkg^{-1} of reducing saccharides. SF had higher content of saccharose than MSF. The total of glucose, fructose and saccharose in SF and MSF corresponds to 157 and 119 gkg^{-1}, respectively. These saccharides are probably present in tissues conducting nutrients to the apical meristem of peach palm, with a higher content for the younger tissue of the stem flour.

Saccharides and uronic acids are the most abundant soluble components of plant cells. The uronic acid content was higher in SF than in MSF, which was lower than in oat straw (16.7 gkg^{-1}), barley (18.2 gkg^{-1}), canola (68.5 gkg^{-1}) and mustard (82.1 gkg^{-1}) [22]. The uronic acid content in the flours is consistent with the occurrence of pectin, a component from the primary cell wall and middle lamella.

SF with higher ash content than MSF had higher content of minerals with exception of calcium, copper and manganese (Tab. 1). Mg, Fe, Mn and Cu content in the flours was lower than that found by SIMAS et al. [6] in king palm flour and the content of Ca and Zn in MSF was close to the reported by these authors. Major macro elements in the flours were potassium and calcium. Calcium is important to protein structuring of RNA and DNA and its deficiency may lead to osteoporosis [23].

Among the micro elements, manganese and zinc were found in high levels. These minerals are components of a number of enzymes acting as essential activators in metabolic reactions and they are very important elements for reproduction and growth [24].

The availability of the minerals present in the flours depends on the presence of antinutrients and digestibility.

Dietary fibre and its components

In the flours total dietary fibre (TDF) content was higher than the crude fibre content, or the residue remaining after the chemical decomposition by sulphuric acid and/or sodium hydroxide, which does not include water-soluble fibre.

The flour obtained from the median sheath of peach palm showed higher DF content than the flour produced from the stem (Tab. 2). There was higher content of soluble fibre in SF, since it is a younger tissue and a higher content of insoluble fibre in MSF, the older protective tissue. The content of SDF and IDF was similar to the reported by AZIZ et al. [18] for banana pseudo-stem flour (25.8 and 545 g-kg^{-1}). The SF also had TDF content similar to the cited by HELM et al. [19] for the uvarana palm flour.

SF and MSF can be considered a source of DF, a class of compounds which include a mixture of carbohydrates such as cellulose, hemicellulose, pectin, gum, resistant starch, inulin, which are associated with lignin and other compounds not classified as carbohydrate (polyphenols, saponins, cutin, phytate and resistant proteins). This group is important not only to help slow the hydrolysis, digestion and absorption in the small intestine, but also by increasing the volume of the stools, stimulate the fermentation process and reduce the levels of glucose and cholesterol absorbed from the lumen [3]. FDA (Food and Drug Administration) recommended for adults the consumption of 25 g of dietary fibre per day [25]. Thus, to reach the demand of the daily consumption of DF, it would be necessary an intake of approximately 40.4 g of SF or 35.1 g of MSF.

DF being the main component of the flours indicates that they can participate in the development of a potential large market of fibre-rich products. By-products have traditionally been undervalued; however there is a trend to find new sources of dietary fibre that can be used as ingredients in the food industry. Fibres provide many functional properties that affect the technological function of foods, like consistency, texture, rheological behaviour and sensory characteristics, moreover, the by-products rich in fibres can be used for economical and technological purposes, for example, as bulking agent or fat substitute [2, 3, 26].

Fibres are becoming one of the most visible ingredients in today's marketplace, and they can be incorporated in dairy products, breakfast cereals, baked goods,

pasta, cereal bars, snacks, nutritional supplements and others. Manufactures are finding that incorporating fibre into their products is a good way to make them healthier and subsequently more appealing to health-conscious consumers. Besides the nutritional aspect, the fibres addition should not adversely affect the sensory characteristics of the product and for this reason should be light in colour, tasteless, and not perceived in the mouth when added to products [26].

The percentage of resistant starch (RS) did not differ between the flours. RS represents a portion of starch which is not digested in the small intestine of healthy human, in other words, it is not subject to the action of amylase enzymes, but is fermented by the colonic micro flora, with similar health benefits as the dietary fibre [27].

MSF had higher percentage of acid detergent fibre and neutral detergent fibre than SF. AZIZ et al. [18] observed similar levels of ADF and NDF in flour of banana pseudo-stem to those found in SF. The acid detergent solution dissolves the cellular content, hemicellulose and soluble minerals, leaving a residue consisting of fibrous cellulose, lignin, and also a percentage of insoluble proteins and minerals, while the neutral detergent solution does not dissolve the hemicellulose. Thus, determination of ADF is related to the cellulose content and NDF is associated with the content of hemicellulose in the sample.

The content of cellulose, hemicellulose and lignin were higher in MSF than in SF in agreement as previous determined as insoluble DF. According to AZIZ et al. [18] the banana pseudo-stem flour contained 274 gkg^{-1} of cellulose and 119 gkg^{-1} of hemicellulose, similar to that found in SF.

The major components of DF in the flours studied were cellulose and hemicellulose, amounting 340 gkg^{-1} in SF and 485 gkg^{-1} in MSF, which together with pectin and lignin form the cell wall of plants. SF is produced from a younger tissue with more saccharides and lower content of fibres and non-lignified tissues than MSF, which is more related to structuring and protection of the rod. Lignin was the minor component of the dietary fibres in SF and MSF, this can be explained by the fact that lignification occurs only in specialized cells, increasing the resistance of the cell wall against mechanical, chemical and enzymatic degradation [28].

Total carotenoids, total phenolic compounds and antioxidant activity

The MSF had higher content of carotenoids, but lower content of phenolic compounds than SF (Tab. 3). SIMAS et al. [6] found lower content of phenolic compounds in

the king palm flour obtained from leaf sheath (1270 mg-kg^{-1}). RODRIGUEZ-AMAYA et al. [29] found 900 ug-kg^{-1} of a-carotene and 160 ug-kg^{-1} of P-carotene in heart-of-palm *(B. gasipaes)* after boiling. Carotenoids are pigments widely distributed in nature being important for its pro-vitamin A activity. However, recent studies showed that carotenoids also exhibit antioxidant mechanism, through its interaction with free radicals, providing protection against oxidation *in vitro* and *in vivo* [29].

The antioxidant activity (AA) measured by DPPH', ABTS^{4}" and FRAP methods (Tab. 3) indicated that the mechanisms involved in these *in vitro* reactions can be performed by the components of the flours. SF had higher antioxidant potential (1.36 - 15.27 mmol-kg^{-1}, expressed as Trolox equivalents) than MSF (0.88 - 14.98 mmol-kg^{-1}), which is probably related to the higher content of phenolic compounds. The antioxidant activity demonstrated by the flours in DPPH' assay was close to the reported by RAGAEE et al. [30] in rye whole flour (12.17 mmolkg^{-1}).

The phenolic content of the flours has a positive correlation with the antioxidant activity ($r>0.93$, $p<0.05$). Currently it has been attributed to free radicals the source of many health problems, since these unstable molecules are formed during the use of oxygen by the body which can start a chain reaction producing free radicals (FR). Antioxidants, like the phenolic compounds, interact with these reactive species, making it possible to prevent some damage to human cells. The role of antioxidants involves the donation of electrons or the transfer of hydrogen atoms to free radicals, without compromising the stability of their molecules. Moreover, they are capable to inhibit lipid peroxidation *in vitro* through the capacity of sequester FR or chelate metals [4].

Therefore, the antioxidant activity demonstrated by *in vitro* methods indicate that the compounds present in MSF and SF can interact with FR and help in human diseases prevention. However, the *in vivo* efficacy and the dilution or reprocessing of such products at the moment of consumption will influence the real content and the antioxidant potential of the compounds present in these flours.

Physicochemical properties

The SF and MSF had pH of the suspension 6.02 and 5.76 and density 0.39 gml^{-1} and 0.40 gml^{-1}, respectively. BENITEZ et al. [16] found similar values of bulk density in onion by-products (0.3-0.4 gml^{-1}). According to these authors the bulk density depends on the structural characteristics, the particle size and their distribution.

The water solubility index associated with carbohydrates and some proteins, ranged from 135.13 to 173.31 gkg^{-1} in MSF and SF, respectively. These values were similar to the found in field pea (137 gkg^{-1}) and pigeon pea (206 gkg^{-1}) flours [20].

Water and oil absorption of SF and MSF were higher than the values found in field pea and pigeon pea flours [20]; bean flours [31] and cowpea, horse gram and chickpea flours [32]. The WAI is related to the ability of a substance to associate with water under specific conditions, with carbohydrates and proteins being the main components responsible for such property, due to the presence of polar or charged groups. In food processing this property influences functional and sensory properties [32]. The oil absorption is also an important functional property of flours, retaining the flavour and aroma compounds and it can be used in many food applications, like emulsion-type meat products. Proteins have in their composition lipophilic and hydrophilic portions and so are the most responsible for this property, because non polar amino acids may form interactions with the lipid hydrocarbon chain [33].

The values of WAI and OAI of the flours can be related to the content of dietary fibres and indicate that they can probably be used in many food applications. The DF has an important role in the hydration properties of flours, which is associated to the chemical structure of its components, porosity, particle size, pH, ionic strength, among others. Similarly the oil absorption capacity can be defined as the amount of oil retained by the fibres after stirring, incubation with oil and centrifugation. This property is related to surface characteristics of the particles that composes the sample and is associated with the charge density and the hydrophobic nature of the constituents [3].

Furthermore, the values of WAI and WSI suggests that these flours can act as hypoglycaemic agents and could be used in weight loss diets, because after consumption they likely form a tridimensional network with water, that prolong the satiety sensation and delay nutrient absorption [27].

The swelling volume of flours was 17.21 mlg^{-1} and 20.79 mlg^{-1} d.m. in MSF and SF, respectively. The SVP was positively correlated ($p<0.05$) with viscosity in all conditions tested.

The viscosity of the suspensions increased with the increase of flour concentrations, and the values were higher in SF than in MSF, ranged in SF from 26.85 mPA.s to 96.41 mPA.s and from 32.8 mPA.s to 173.35 mPA.s and in MSF from 13.04 - 26.76 mPA.s and 23.20 - 41.82 mPA.s at 0.05 and 0.10 Hz, respectively (Tab. 4). SIDDIQ et al. [31] found apparent viscosity ranging between 10 mPA.s and 60 mPA.s in selected dry been flours

(0.10 g-ml^{-1}), reaching the maximum value of 462 mPA.s for small red kidney bean flour dispersion at 0.30 g-ml^{-1}. According to these authors the particle size distribution can influence the viscosity of dispersion, since small particles tend to be more uniform and offer higher resistance due to the inter particle friction, resulting in high viscosity of dispersion. Solubility is another critical factor, which also influences the viscosity of dispersion, especially soluble fibre. The low solubility of the flours produced from peach palm by-products led to the deposition of particles over time, in spite of their small size. Therefore, the viscosity measurement was determined immediately after homogenization.

In this study the correlations between protein content with WAI, SVP and viscosity varied from 0.86 to 0.99 ($p<0.05$). Among saccharides, saccharose, fructose and glucose had positive correlations ($r>0.84$) for all physicochemical properties and viscosity ($p<0.05$), with the exception of no significant correlation between saccharose and OAI. The content of crude fibre, TDF, IDF, FDA, FDN, hemicellulose and cellulose in the flours were significantly correlated with WAI and SVP, with r values from -0.82 to -0.88 and from -0.89 to -0.93, respectively, with exception of FDA for WAI and of hemicellulose for SVP. Viscosity was also negatively correlated with these variables ($-0.91< r <-0.99$; $p<0.05$). On the other hand, soluble dietary fibre content has significant and positive correlations with WAI ($r = 0.94$), SVP ($r = 0.84$), viscosity ($r = 0.87$-0.92) and WSI ($r = 0.93$). This indicated that the high levels of SDF, protein, fat and saccharides improve the physicochemical properties, contrary to what occurs with the increasing values of crude or dietary fibre and its insoluble components. Overall, SF stood out in relation of its physicochemical properties due to its composition.

Water sorption isotherms

The experimental sorption isotherms (Fig. 2) indicated that MSF is more hygroscopic than SF for relative humidity of equilibrium (RHE) lower than 50 %, but the opposite is valid for RHE higher than 50%. The water adsorption of SF and MSF reached 325 gkg^{-1} and 268 gkg^{-1} of water d.b., in the maximum value of RHE measured 85 %. Similar values were found by RAO et al. [34] in quamachil aril powders.

The water adsorption occurs due to the presence of macromolecules like carbohydrates and proteins that have polar groups and can form hydrogen bonds with water. Probably the high fibre content in MSF promoted the high water adsorption up to 50 % of RHE. Above this value of RHE the higher content of saccharides contributed to the

hygroscopic behaviour of SF, which reached higher final humidity than MSF. Among the insoluble components of fibres, the hemicellulose content seemed to affect positively the water absorption, while, cellulose and lignin content affected negatively [35]. Although MSF had the highest content of hemicellulose, this flour also had the highest content of the other insoluble compounds.

Although there is no mathematical model adjusted to the experimental data, it is possible to note that the flours tend to gain moisture at RHE above 10 % and values above 60 % led to moisture content of the flours above 100 gkg^{-1} of water d.b., which is the limit value for storage of flours in general. Therefore, the packaging system used to storage these flours must maintain the RHE bellow 60 %.

Conclusions

SF had higher content of moisture, ash, proteins, fats and saccharides than MSF, however, MSF had higher amount of dietary fibre than SF, which is the most abundant component of the flours, basically formed by cellulose and hemicellulose. There was higher carotenoid content in MSF and higher content of phenolic compounds and antioxidant activity in SF. As a result of its composition, SF had better physicochemical properties than MSF, especially in WAI, SVP and viscosity. Above 60 % of RHE the flours reached more than 100 $g\text{-}kg^{-1}$ of water d.b. of water adsorbed, which can limit its shelf life, therefore it is indicated a package system that will protect the flours from the environment relative humidity.

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Fig. 1 – Peach palm (*Bactris gasipaes* Kunth) and the identification of its parts.

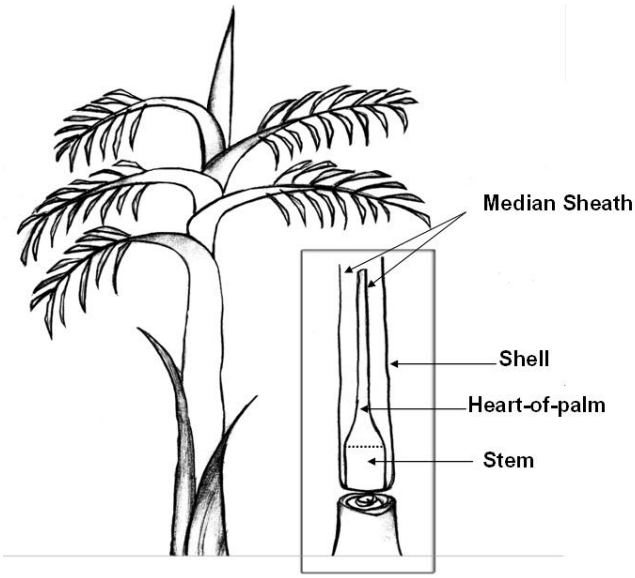
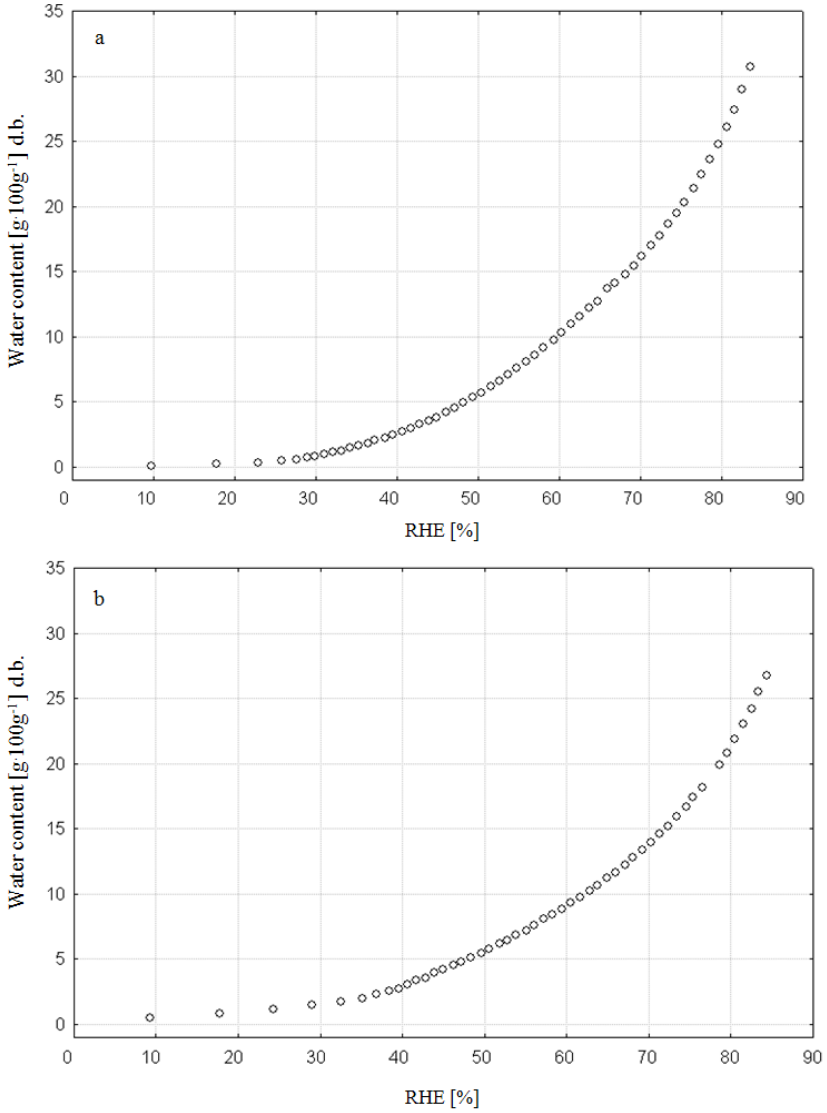


Fig. 2 – Adsorption isotherms: a, stem flour; b, median sheath flour.



Tab. 1 – Chemical, saccharides and mineral composition of flours obtained from peach palm by-products (wet basis).

Component	SF	MSF
Moisture and volatiles[1] [g·kg^{-1}]	61.62 ± 2.51^{a}	53.20 ± 3.40^{b}
Ash [g·kg^{-1}]	50.61± 0.90^{a}	43.82 ± 0.83^{b}
Protein[2] [g·kg^{-1}]	98.40 ± 1.12^{a}	68.62 ± 2.81^{b}
Crude fat [g·kg^{-1}]	23.22 ± 0.53^{a}	20.10 ± 1.02^{b}
Crude fibre [g·kg^{-1}]	219.55 ± 6.40^{b}	301.51 ± 7.03^{a}
Glucose [g·kg^{-1}]	64.41 ± 4.49^{a}	47.82 ± 3.60^{b}
Fructose [g·kg^{-1}]	46.76 ± 1.74^{a}	41.53± 1.70^{b}
Saccharose [g·kg^{-1}]	45.90 ± 2.72^{a}	30.10±1.04^{b}
Uronic acid [g·kg^{-1}]	15.92 ± 0.96^{a}	12.20±0.82^{b}
Mg [g·kg^{-1}]	3.90±0.02^{a}	2.62±0.06^{b}
Ca [g·kg^{-1}]	4.32±0.10^{b}	7.30±0.08^{a}
K [g·kg^{-1}]	14.77±0.10^{a}	11.76±0.09^{b}
P [g·kg^{-1}]	2.95±0.08^{a}	2.44±0.05^{b}
Fe [mg·kg^{-1}]	3.75±0.07^{a}	0.97±0.06^{b}
Cu [mg·kg^{-1}]	2.67±0.06^{b}	2.83±0.06^{a}
Mn [mg·kg^{-1}]	3.75±0.30^{b}	12.75±0.90^{a}
Zn [mg·kg^{-1}]	12.50±0.70^{a}	4.07±0.11^{b}

Means values in the same line followed by the same letter are not significantly different ($p \leq 0.05$).
Stem flour (SF), median sheath flour (MSF). 1 dried at 105º C, 2 conversion factor 6.25.

Tab. 2 – Total, soluble and insoluble dietary fibre, resistant starch, acid detergent fibre, neutral detergent fibre, cellulose, hemicellulose and lignin content of flours obtained from peach palm by-products (wet basis).

Component	SF [g·kg^{-1}]	MSF [g·kg^{-1}]
Total dietary fibre	619.42	711.84
Insoluble dietary fibre	587.21 ± 9.50^{b}	686.70 ± 6.94^{a}
Soluble dietary fibre	32.20 ± 2.82^{a}	25.14 ± 2.86^{b}
Resistant Starch	9.23 ± 0.44^{a}	8.15 ± 0.70^{a}
Acid detergent fibre	229.30 ± 10.27^{b}	332.94 ± 12.60^{a}
Neutral detergent fibre	345.74 ± 8.44^{b}	492.05 ± 11.41^{a}
Hemicellulose	116.43 ± 6.30^{b}	159.12 ± 10.42^{a}
Cellulose	223.61 ± 9.05^{b}	326.04 ± 7.41^{a}
Lignin	10.40 ± 1.16^{a}	15.92 ± 2.41^{a}

Means values in the same line followed by the same letter are not significantly different ($p \leq 0.05$).
Stem flour (SF), median sheath flour (MSF).

Tab. 3 – Total phenolic compounds, total carotenoids and antioxidant activity measured by DPPH·, ABTS·+ and FRAP methods in the flours produced from peach palm by-products (wet basis).

	SF	MSF
Total phenolic compounds [mg·kg^{-1}]	2698.60 ± 62.60^{a}	2332.82 ± 56.22^{b}
Carotenoids [µg·kg^{-1}]	349.63 ± 3.04^{b}	966.50 ± 5.02^{a}
DPPH$^{\cdot}$ [mmol·kg^{-1}]	15.27 ± 0.12^{a}	14.98 ± 0.06^{b}
ABTS$^{\cdot+}$ [mmol·kg^{-1}]	1.36 ± 0.05^{a}	0.88 ± 0.07^{b}
FRAP [mmol·kg^{-1}]	10.97 ± 0.30^{a}	8.59 ± 0.39^{b}

Means values in the same line followed by the same letter are not significantly different ($p \leq 0.05$).
Stem flour (SF), median sheath flour (MSF).
Total phenolic compounds are expressed as gallic acid equivalents. Antioxidant activity is expressed in Trolox equivalents.

Tab. 4 – Physicochemical and technological properties of flours obtained from peach palm by-products and viscosity in different percentages of flours suspensions (4, 5 and 6 %) and in two spindle velocities (0.05 and 0.10 Hz).

Property	SF	MSF
pH	6.02±0.01[a]	5.76±0.01[b]
Bulk density [g·ml^{-1}]	0.39±0.01[a]	0.40±0.01[a]
Water Solubility Index [g·kg^{-1}]	173.31±17.87[a]	135.13±13.03[b]
Water absorption [g·g^{-1}]	7.36±0.28[a]	6.60±0.20[b]
Oil absorption [g·g^{-1}]	3.58±0.09[a]	3.46±0.10[a]
Swelling volume [ml·g^{-1}]	20.79±0.91[a]	17.21±0.75[b]
Viscosity 4 %/0.05 Hz [mPA.s]	32.8±1.15[a]	23.2±2.13[b]
Viscosity 4 %/0.10 Hz [mPA.s]	26.85±0.84[a]	13.04±0.91[b]
Viscosity 5 %/0.05 Hz [mPA.s]	126.09±6.93[a]	31.64±1.27[b]
Viscosity 5 %/0.10 Hz [mPA.s]	91.28±5.64[a]	22.80±1.05[b]
Viscosity 6 %/ 0.05 Hz [mPA.s]	173.35±8.65[a]	41.82±3.56[b]
Viscosity 6 %/0.10 Hz [mPA.s]	96.41±4.14[a]	26.76±1.47[b]

Means values in the same line followed by the same letter are not significantly different ($p \leq 0.05$).
Stem flour (SF), median sheath flour (MSF).
Water solubility index, water absorption, oil absorption and swelling are expressed per gram of dry matter.

4.3 ARTIGO CIENTÍFICO 3

O Artigo Científico 3 será submetido a publicação no periódico *Carbohydrates Polymers.*

Carbohydrate composition of peach palm *(Bactris gasipaes* Kunth) by-products flours

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ABSTRACT: The flours obtained from peach palm by-products are rich in dietary fiber. The aim of this work was to investigate the carbohydrates present in the flours produced from the residual parts (stem and median sheath) of hearts-of-palm processing plant. The flours were submitted to fractionation that originated 5 polysaccharides portions, whose monomelic composition were determined. The fraction containing cellulose (S5) was the most abundant in the flours studied (26 - 28 $g.100g^{-1}$), followed by the sum of fractions (S2, S3 and S4) extracted with alkaline solutions (21 - 22 $g.100g^{-1}$). The S1 fraction contained the highest percentage of uronic acids, which characterizes the presence of pectic substances. Xylose and arabinose were found in high proportion in S2 and S3 fractions, characterized as hemicelluloses. The S4 and S5 fractions, rich in glucose, constituted the main portion of the cell wall material and correspond to the insoluble fraction of the dietary fiber.

Keywords: Fractionation. Cellulose. Hemicellulose. Pectin. Monomers.

1 INTRODUCTION

Brazil is one of the largest producers and consumers of heart-of-palm *(palmito)* of the world. Among the palm species, the peach palm *(Bactris gasipaes* Kunth) yields two food crops with commercial potential, the fruit and the heart-of-palm. The processing of heart-of-palm from *B. gasipaes* (locally known as *pupunha)* for the international market is expanding, because of the appreciated sensory characteristics of the product (Santos, Correa-Júnior, & Neves, 2008). However, the canning process generates a large amount of by-products due to the non uniform diameter and variable texture of the harvested rod. The by-products generated during the processing of the plant food result in economic and environmental problem due to the high volumes of discarded material and the cost of elimination (Mateos-Aparicio, Redondo-Cuenca, & Villanueva-Suarez, 2010a). The median

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sheaths that cover the heart-of-palm and the stem part located below the edible portion are peach palm by-products that correspond to an average of 46 % of the weight of the harvested rod. The flours produced from these parts have high level of dietary fiber (62 - 71 %), mainly insoluble fiber (59 -69 %) (Bolanho, Danesi, & Beleia, 2013; Bolanho, Danesi, & Beleia, 2014).

The interest in foods rich in dietary fiber has increased and the importance of this food component has led to the development of a large market for fiber-rich products and ingredients (Pszczola, 2008). The intake of foods with high DF content has been related to several physiological and metabolic effects: increase of the fecal bulk, provide a favorable environment for beneficial intestinal microflora multiplication, prevention and control of obesity, atherosclerosis, coronary heart diseases, colorectal cancer and diabetes (Vergara-Valencia et al., 2007).

DF is composed of cell wall polysaccharides (cellulose, hemicellulose, pectin) and lignin. Cellulose consists of glucose chains, with P-1,4 linkages with a high degree of polymerization. Hemicellulose is a heterogeneous group of branched polysaccharides that contain xylose, mannose, arabinose, galactose, uronic acids and others monosaccharaides. Pectin is the most complex polysaccharide with high level of galacturonic acid, rhamnose, arabinose and galactose (Brett & Waldron, 1996; McDougall, Morrison, Stewart, & Hillman, 1996).

The determination of the polysaccharides composition in the DF (pectin, cellulose and hemicellulose) is important to understand their physiological function, structure and organization in food products, and it allows a planned application in functional foods (Waldron, Parker, & Smith, 2003). Furthermore, studies on the characterization of neutral sugar composition of the major cell wall constituents are scarce. Therefore, the aim of this work was to evaluate the polysaccharides and monosaccharaides composition of peach palm by-product flours.

2 MATERIAL AND METHODS

2.1 PEACH PALM BY-PRODUCTS FLOUR PRODUCTION

The peach palm flours were produced from the median sheaths and parts of the unused stem, harvested in a heart-of-palm farm in Mariluz, Paraná, Brazil, which were subjected to washing, cleansing, cutting and drying in an oven with forced air circulation at

60° C for 36 h (MA 035, Marconi, Piracicaba, Brazil). The dried material was ground in a knife mill type Willye (SL-031, Solab, Piracicaba, Brazil) and passed through a set of sieves with particle separation from 150 urn to 600 urn, subjected to vibration for 10 min. The flours from median sheath (MSF) and stem part (SF) of peach palm with particle size of 150 um were used in the analysis.

2.2 POLYSACCHARIDES FRACTIONATION

The procedure of Seibel & Beléia (2008) was followed for the fractionation of the carbohydrates. The soluble sugars present in MSF and SF were subject to extraction with ethanol aqueous solution (80 %) for 20 min at 80° C with eventual shaking. The material was centrifuged at 8000Xg (Shimadzu, Himac CFD2, São Paulo, Brazil) and the supernatant was removed. This procedure was repeated 8 times. The precipitate was dried in an oven with forced air circulation at 40° C for 12 h (MA 035, Marconi, Piracicaba, Brazil) and weighed afterwards. The starch was removed from this material using 90 % DMSO (dimethylsulfoxide) with shaking at 200 rpm (Marconi, MA 830/A) for 24 h. The solution was centrifuged and the precipitated was dried and weighed (Seibel & Beléia, 2008). The glucose content of alcoholic and DMSO fractions were determined after acid hydrolysis, using an enzymatic kit of glucose oxidase (Biotécnica, Varginia, Brazil). The conversion of glucose into starch was made using the factor 0.9.

The S1 extraction, that solubilizes pectic substances, used 0.5 % ammonium oxalate with agitation in a magnetic stirrer at 80° C for 1 h. The material was centrifuged at 8000Xg for 15 min at 4° C. This procedure was repeated 3 times. The supernatants, containing the soluble pectin fraction, were combined and dialyzed against water (24 h) and distilled water (24 h). The precipitates of the soluble pectin were washed 3 times with distilled water, freeze dried (Telstar, LyoQuest, São Paulo, Brazil) and weighed.

To the remaining solid material it was added sodium chlorite (NaClO), glacial acetic acid, and deionized water for lignin removal. The mixture was placed in a water bath at 75° C for 2 h, the suspension was centrifuged at 8000Xg for 15 min at 4° C and the lignin in the supernatant fraction was dialyzed against water (48 h) and freeze dried.

The residue of lignin extraction was sequentially treated with 0.1, 1.0 and 4.0 M NaOH solution containing 3 mg/L of $NaBH_4$ (sodium borohydrate) for 1 h at 25° C with shaking at 200 rpm, consisting in S2, S3 and S4 fractions, respectively. The supernatants were neutralized with acetic acid, dialyzed against water (24 h) and distilled water (24 h) and

centrifuged at 8000Xg for 15 min at 4° C. The final supernatants were freeze dried and weighed and they contained the hemicelluloses with different degrees of polymerization.

To the final precipitate of hemicellulose extraction it was added the Updegraff reagent (5 % nitric acid and 15 % acetic acid). The mixture was placed in water bath at 100° C for 90 min with shaking every 15 min, and afterwards, it was centrifuged at 8000Xg for 15 min at 4° C. The supernatant was discarded and the precipitated was washed 3 times with distilled water, freeze dried and weighed. The remaining weight corresponds to the S5 fraction, mainly formed by cellulose.

2.3 MONOSACCHARAIDES AND URONIC ACID DETERMINATION

The monosaccharaides were determined according to Seibel & Beleia (2008) with some adaptations. The samples obtained from the fractionations were pre-hydrolyzed with 300 uL of 72 % sulphuric acid in a water bath at 30° C for 45 min. Distilled water (5.0 mL) was added to the samples and incubated in a water bath at 100° C for 3 h. Afterwards the material was neutralized with sodium hydroxide (NaOH) and subjected to salts removal with anionic resins (Dowex 1 x 8 50-100 mesh, Cl Form, Sigma-Aldrich) and cationic resins (Dowex 50w x 8 50-100 mesh, H Form, Sigma-Aldrich).

The samples were filtered (Millex-GV, PVDF hydrophilic membrane, 0.22 um pore size; Millipore, Billerica, MA, USA) and analyzed by high performance anion exchange chromatography (HPAEC-PAD, model ICS 5000). Aliquots (10 uL) of the filtrate were injected automatically and the carbohydrates were separated by CarboPac® PA1 analytical column (Dionex Corporation, Sunnyvale, CA, EUA) preceded by a CarboPac® PA1 guard column. The flow rate was of 0.7 mL min^{-1} at 25 °C with gradient elution of 19 mM of NaOH for 17.25 min and 1mM up to 22 minutes. After this first elution a washing step with 200 mM of NaOH for 10 min and a stabilization step with 19 mM of NaOH for 15 min were used before any other sampling. Chromatogram analysis was carried out using Chromeleon version 6.8 software (Dionex Corporation).

The standard curves were obtained with different concentrations of monosaccharaides: glucose (0.7 - 23 ug.mL"^{1}), galactose (0.8 - 7.0 ug.mL^{-1}), mannose (0.1 - 8 ug.mL^{-1}), arabinose (0.3 - 6.0 ug.mL^{-1}) and fucose (0.1 - 1.5 ug.mL^{-1}), all from Sigma-Aldrich (New Orleans, USA).

The uronic acid (UA) was determined in the hydrolysates by reaction with 0.15 % m-hydroxydiphenyl dissolved in 0.5 % sodium hydroxide. The absorbance was read in

a spectrophotometer (700 Plus, Femto, São Paulo, Brazil) at 520 nm. A standard curve with different concentrations of galacturonic acid (10 - 60 ug.mL^{-1}) was used for uronic acid content (Kintner &Van Buren, 1982).

2.4 STATISTIC ANALYSIS

The analyses were performed in triplicate and the results were expressed as mean ± standard deviation. ANOVA, Tukey's test and principal component analysis were performed using the Statistica software version 6.0 (StatSoft, Inc.).

3 RESULTS AND DISCUSSION

The ethanol fraction that contained the soluble sugars had 13.1 and 9.2 g.100g^{-1} of glucose in SF and MSF, respectively. The starch content varied from 2.2 to 2.5 g.100g^{-1}in the flours. These values are in accordance to that found by Bolanho et al. (2013) and Bolanho et al. (2014).

The polysaccharides fractions obtained from SF and MSF had similar yields (Table 1). The cellulose-rich residue (S5) is the main component of both flours (26.9 - 28.5 g.100g^{-1}) as also noted by Favaro, Beléia, Fonseca-Junior and Waldron (2008) in cell walls of cassava varieties. The residue fraction also corresponds to approximately 49 % of total cell wall polymers extracted, which is in accordance to the values found by Mateos-Aparicio et al. (2010a) (21.9 - 71.0 %) when analyzing the by-products okara, pea pod and broad bean pod. Cellulose forms about one third of dietary fiber in vegetables and it's insolubility in water helps the increase of fecal volume promoting regular bowel movements. Furthermore, the fermentation of cellulose by the beneficial microflora in the colon generates short-chain fatty acids important for the nutrition of the intestinal cells that line the lumen (Mudgil & Barak, 2013).

The delignification before the alkaline extraction yielded an estimated value of 10.1 g. 100g^{-1} in MSF to 15.7 g.100g^{-1} in SF, however these values are superestimated due to the solubility of carbohydrates (5 - 10 g.100g^{-1}), phenolic compounds and glycoproteins in sodium chlorite used in the extraction (Seibel & Beleia, 2008).

The hemicellulose released by saponification with 0.1 (S2), 1.0 (S3) and 4.0 M (S4) of NaOH constitute a significant part of whole cell wall polymers, totalizing 21.4 g.100g^{-1} in SF and 22.5 g.100g^{-1} in MSF. Similarly Gaspar, Juhasz, Szengyel, & Reczey

(2005) studying the effect of alkaline extraction in corn fiber obtained a total yield of 20.9 g. $100g^{-1}$. Hemicelluloses were extracted with increasing concentrations of alkali, the first removing the most soluble polysaccharides, the second extracting the low molecular weight polymers, and the third the high molecular weight hemicelluloses (Selvendran & O'Neill, 1987). Among these fractions S3 was the major fraction in the flours studied, whose concentration (7.9 - 9.5 g. $100g^{-1}$ of flour) was similar to the values found by Seibel and Beleia (2008) in fibers flours of soybean cotyledons (7.8 - 8.1 $g.100g^{-1}$). Hemicelluloses are important to intestinal regulation, help in increasing the number of beneficial bacteria in the gut and directly bind cholesterol, preventing its absorption from the intestine (Mudgil, Barak, & Khatkar, 2012).

Table 1 – Yield of polysaccharides fractions obtained from peach palm by-products flours

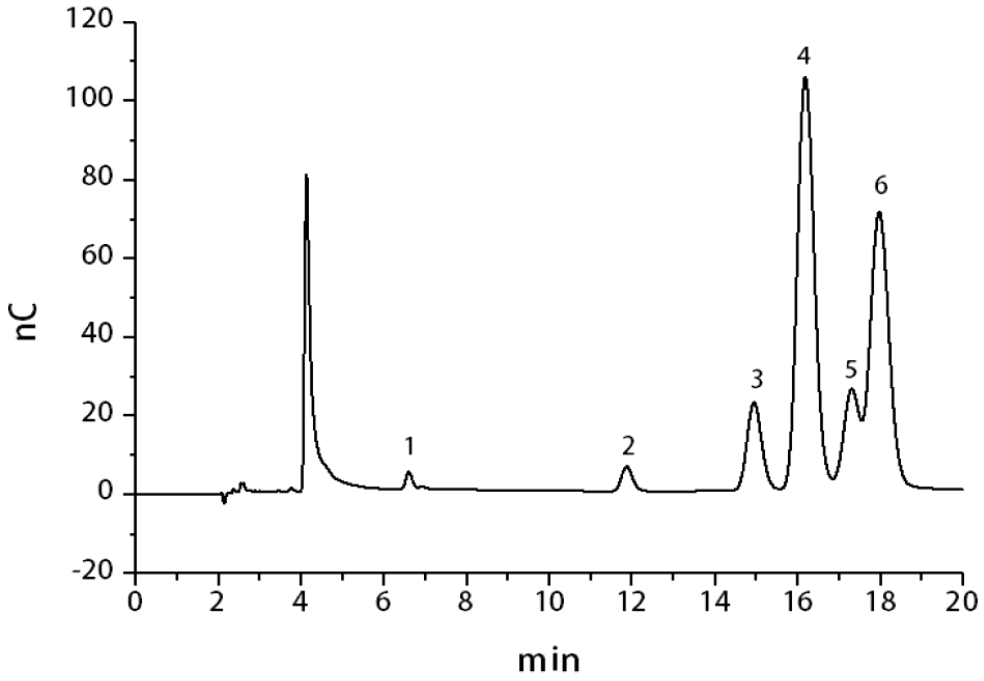
Flour	Fraction ($g.100g^{-1}$ of flour)				
	S1	S2	S3	S4	S5
SF	6.8±0.8[a]	8.1±1.1[a]	6.5±0.7[a]	7.9±1.0[a]	5.4±0.7[a]	26.9±3.3[a]
MSF	6.2±0.8[a]		9.5±1.1[a]	6.9±0.9[a]	28.5±3.7[a]

Means values in the same column followed by the same letter are not significantly different ($p < 0.05$).
SF (stem flour), MSF (median sheath flour), S1 (soluble fraction in ammonium oxalate), S2 (soluble fraction in 0.1 M NaOH), S3 (soluble fraction in 1.0 M NaOH), S4 (soluble fraction in 4.0 M NaOH), S5 (residual fraction).

The pectin extraction (S1) with ammonium oxalate was in order to cause minimal degradation and with a maximum chelating power of Ca and Mg that are complexed with the galacturonic acids. The values obtained for S1 fraction (6.5 - 6.8 $g.100g^{-1}$) were lower than that found by Seibel and Beléia (2008) in the cell wall of soy fiber flours (13.2 - 15.4 $g.lOOg^{-1}$). Pectic components can appear in other fractions, when the high ramified non-solubilized molecules are associated with other polymers (Mateos-Aparicio et al., 2010a). The pectin is a component of soluble fiber that can delay glucose and lipid uptake into the blood stream and reduces the serum cholesterol levels (McDougall et al., 1996).

Table 2 shows the monomeric composition of the isolated fractions. Glucose and uronic acids were the major monomers of polysaccharides fractions that can be formed by fucose, arabinose, rhamnose, galactose and mannose. Simas et al. (2010) observed that xylose and glucose were the main components of king palm flour. Fucose was only found in S4 while rhamnose was not detected in the materials analyzed. Fig. 1 shows a representative lution pattern in the HPAEC-PAD.

Fig. 1 – Separation of sugars in flour of peach palm by-products using high-performance anion-exchange chromatography associated with pulsed-amperometric detection (HPAEC-PAD).



Monosaccharides fucose (1), arabinose (2), galactose (3), glucose (4), mannose (5) and xylose (6) are shown with their respective retention times.

Table 2 – Monomeric composition of polysaccharides fractions obtained from peach palm by-products flours

Flour	Fraction	Neutral sugars (mg.g^{-1})						UA (mg.g^{-1})	Total (mg.g^{-1})
		Fuc	Ara	Gal	Glu	Man	Xyl		
SF	S1	nd	2.3±0.1^{f}	6.6±0.3^{cd}	33.1±2.7^{c}	2.5±0.1^{c}	nd	124.3±7.4^{a}	168.7
	S2	nd	14.3±0.7^{a}	7.4±0.3^{c}	6.4±0.3^{d}	nd	39.4±1.5^{c}	39.9±1.9^{bc}	107.4
	S3	nd	5.2±0.0^{c}	3.4±0.1^{e}	6.9±0.4^{d}	nd	100.8±8.9^{a}	36.3±1.6^{c}	152.6
	S4	1.7±0.1^{a}	3.6±0.1^{de}	14.1±0.2^{b}	68.4±0.2^{c}	24.3±0.2^{a}	47.5±4.6^{c}	21.3±0.7^{e}	180.9
	S5	nd	nd	nd	452.3±22.5^{a}	nd	nd	23.3±1.2^{de}	475.6
MSF	S1	nd	4.3±0.4^{de}	16.1±1.6^{a}	43.4±4.9^{c}	19.5±1.7^{b}	nd	131.4±5.6^{a}	214.8
	S2	nd	6.1±0.4^{b}	5.7±0.5^{d}	3.5±0.3^{d}	nd	17.2±1.5^{d}	48.9±1.6^{b}	81.5
	S3	nd	3.4±0.3^{d}	3.5±0.3^{e}	5.3±0.4^{d}	nd	64.9±0.3^{b}	30.7±2.0^{cd}	107.9
	S4	1.2±0.0^{b}	4.5±0.3^{d}	7.4±0.4^{c}	48.6±4.8^{c}	20.7±0.5^{b}	44.5±4.3^{c}	34.9±0.8^{c}	161.8
	S5	nd	nd	nd	356.3±25.4^{b}	nd	nd	15.7±1.4^{e}	371.9

Means values in the same column followed by the same letter are not significantly different ($p < 0.05$).
SF (stem flour), MSF (median sheath flour), Fuc (fucose), Ara (arabinose), Gal (galactose), Glu (glucose), Man (manose), Xyl (xylose), UA (uronic acids), nd (not detected), S1 (soluble fraction in ammonium oxalate), S2 (soluble fraction in 0.1 M NaOH), S3 (soluble fraction in 1.0 M NaOH), S4 (soluble fraction in 4.0 M NaOH), S5 (residual fraction).

It is known that pectin is mainly composed by chains of galacturonic acid with side chains of neutral sugars in different amounts depending on the pectin source

(Mudgil & Barak, 2013). Thus, the S1 fraction of SF and MSF has galacuronic acid as main component (61 -74 %), which is consistent with the presence of homogalacturonan. Mateos-Aparicio et al. (2010a) also found UA as the major monomer of S1 fraction of legume by-products (okara, pea pod and broad bean pod), with values ranging from 12.4 to 71.4 %. According to the authors, in this fraction of pea pod and bean pod, residues of rhamnose and fucose were not detected, as observed in the flours produced from peach palm by-products. The levels of mannose (2 - 9 %), galactose (4 - 8 %) and arabinose (1 - 2 %) may indicate the presence of mannans, galactans, arabinans and arabinogalactans.

The 0.1 M NaOH solution (S2 fraction) solubilized a mixture of polymers with a high concentration of xylose (21 - 37 %), and a lower concentration of glucose (4 - 6 %) demonstrating the occurrence of xylans, possibly along with xyloglucans, the most widespread neutral hemicellulose. Besides these monomers, arabinose (8 - 13 %), galactose (7 - 8 %) and UA (37 - 60 %) content suggest a mixture of pectic and hemicellulosic polymers. The uronic acids can be galacturonic or glucuronic acids, the first generally forms pectic molecules strongly bound or wrapped firmly in cellulose/hemicellulose network, while the second would probably be hemicellulose substituent (Huisman, Schols, & Voragen, 1998). The level of these monomers also indicates the presence of arabinans, galactans and arabinogalactans.

The increase in alkali concentration to 1.0 M for the extraction of S3 fraction, showed higher xylose concentration to 60 - 66 % in both flours, inferring a hemicellulose polymer rich in xyloglucans. It also had UA (24 - 28 %), glucose (4 - 5 %), galactose (2 - 3 %) and arabinose (3%), demonstrating the possibility of some pectin inclusion. The complex architecture of the cell wall, probably due to a high degree of ramification of the polysaccharides implies insolubility and association with other polymers (Ng, Parr, Ingham, Rigby, & Waldron, 1998). Mateos-Aparicio, Mateos-Peinado, Jimenez-Escrig, Ruperez (2010b) found values of 2.6 % for arabinose, 2.0 % for galactose, 1.0 % for glucose and 1.8 % of uronic acids in 1 M KOH soluble fraction of soybean by-products.

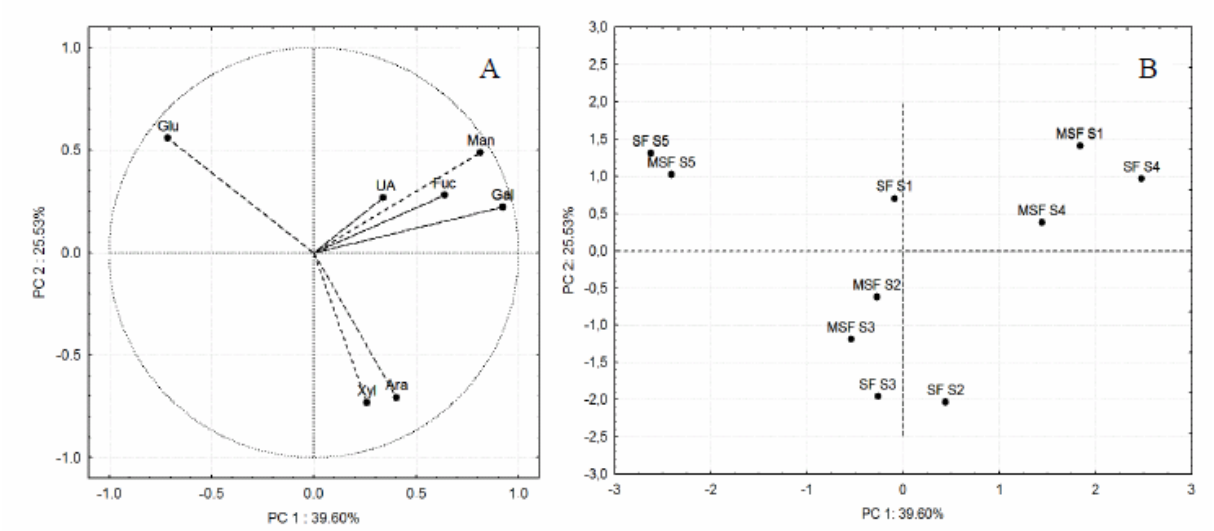
The S4 fraction (extracted with 4 M NaOH) probably has xyloglucans in lesser extent than S3 due to the lowest level of xylose (26 - 28 %). The xyloglucans of this fraction can have fucose in its composition (1 - 2 %). The content of mannose (12 - 13 %) and galactose (5 - 8 %) can indicate the presence of galactomannans. Some pentosans of arabinose and xylose and/or hexosan of galactose, mannose and glucose can also participate in the S4 fraction. The high content of glucose in S4 (30 - 38 %) also demonstrates the potential existence of glucose-rich neutral hemicellulose and/or some acid hemicellulose with

glucuronic acid, due the presence of UA (12 - 22 %). According to Redgwell et al. (2011), strong alkali can solubilize hemicelluloses or other polysaccharides which are strongly hydrogen bonded to the cellulose fibrils.

The fraction solubilized in the 4 M NaOH solution together with the final residue (S5) obtained after the acid hydrolyze allowed reaching the highest yield of monomers. This indicates that the complex structure of the cell wall of peach palm by-products prevents the total accessibility of the selected reagents for complete extraction of the various fractions. The cellulose-rich residue (S5) of the flours was formed mostly by glucose (95 - 96 %) and a low amount of uronic acids (4 - 5 %). Kosmala et al. (2013) found similar glucose content (333 $mg.g^{-1}$) in cellulosic residue of plum pomaces. Glucose was the main component of the final residue obtained by Favaro et al. (2008), Mateos-Aparicio et al. (2010a), and Shiga and Lajolo (2006), but these authors also found lower amounts of other sugars. The absence of additional monosaccharaides may be the result of Updegraff reagent, used to isolate this fraction. However, as described by Ramirez-Truquea, Esquivela and Carleb (2011) bonds between the cellulose and mannose or xylose may be extremely stable and difficult to cleave even by treatment with mineral acids, indicating that the S5 composition is characteristic of each material.

S4 and S5 fractions are predominantly considered insoluble DF, due to their composition and low solubility (Mateos-Aparício et al., 2010a). The high yield of these fractions and the high content of monomers allow us to conclude that the insoluble DF is the major component of the flours studied as also observed by Bolanho et al. (2014), that found values between 59 to 69 % of insoluble fibers in flours of peach palm by-products using the enzymatic-gravimetric method. Insoluble fibers are characterized by their porosity, low density and by the ability to increase fecal bulk. Fiber-rich by-products may be incorporated into food products as inexpensive, non-caloric bulking agents for partial replacement of flour, fat or sugar, as enhancers of water and oil retention and to improve emulsion or oxidative stabilities (Elleuch et al., 2011). Furthermore, there are few types of flours commercially available that can be added to food products to increase their fiber content at low cost.

Fig. 2 – Principal component analysis of the monomer components of by-products flours from peach palm: projections of the analyses (A) and samples (B).



SF S1 (soluble fraction in ammonium oxalate of stem flour), SF S2 (soluble fraction in 0.1 M NaOH of stem flour), SF S3 (soluble fraction in 1.0 M NaOH of stem flour), SF S4 (soluble fraction in 4.0 M NaOH of stem flour), SF S5 (residual fraction of stem flour), MSF S1 (soluble fraction in ammonium oxalate of median sheath flour), MSF S2 (soluble fraction in 0.1 M NaOH of median sheath flour), MSF S3 (soluble fraction in 1.0 M NaOH of median sheath flour), MSF S4 (soluble fraction in 4.0 M NaOH of median sheath flour), MSF S5 (residual fraction of median sheath flour).

Fig. 2 helps to understand the monomers distribution in the fractions obtained from flours of peach palm by-products. It shows that the principal components (PC) explained 65 % of the total variance. PC 1 was correlated to the sugars glucose, mannose, fucose and galactose, whereas PC 2 was characterized by the uronic acid, arabinose and xylose content (Fig. 2 A). Fig. 2 B illustrates that the S5 fraction of both flours studied, is allocated in the left and above of the graph due to its high glucose content. The S2 and S3 fractions of SF and MSF are closer (below in the graph) because of the xylose and arabinose level. S4 fractions of both flours are located right and above of the graph due to the high percentage of mannose, fucose and galactose. The high UA content of S1 fractions shifted them above in the graph, but S1 from SF is at the side left due to the high glucose content, and the same fraction from MSF is at right because of the high levels of mannose and galactose. Therefore, each fraction can be characterized by its main components and its profile is similar in the two flours analyzed.

This study contributes to the knowledge of cell wall polysaccharides composition of peach palm by-products, which have an environmental impact as waste for the food industries and that have a great potential as a fiber-rich ingredient. Furthermore, it is important to increase information and knowledge about this food crop genuinely national.

4 CONCLUSION

The flours produced from peach palm by-products have high level of non starch polysaccharides. Cellulose (S5 fraction) was the major polysaccharide of both flours and mainly formed by glucose. Hemicelluloses extracted in three fractions (S2, S3, S4) also have high yield in the flours studied. The S2 and S3 have high content of xylose and arabinose, whereas S4 has glucose, mannose and galactose as main components. The S1 fraction responsible for the extraction of the soluble pectin portion has the lowest yield in both flours and the highest concentration of uronic acid. The results showed that most monomers were obtained after the acid hydrolysis of the S4 and S5 fractions, indicating the difficulty of solubilizing the cell wall material, and these fractions constitute the insoluble dietary fiber - the main component - of by-products flours of peach palm.

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5 CONCLUSÕES GERAIS

- As porções da haste da pupunheira apresentaram diferentes composições, sendo que os subprodutos (casca, bainha e porção caulinar) se destacaram quanto ao elevado teor de fibras alimentares, principalmente insolúveis.
- As micrografias revelaram que a haste da pupunheira é formada por elementos fibrosos, cristais de oxalato de cálcio, e em algumas partes foram observados grânulos de amido.
- A secagem dos subprodutos foi feita a 60^{o}C, pois temperaturas superiores provocaram escurecimento das farinhas, o que dificulta a incorporação em alimentos.
- A farinha caulinar apresentou maior teor de cinzas, proteínas, lipídios, açúcares e compostos fenólicos, porém menor teor de fibra alimentar que a farinha de bainha mediana. As farinhas apresentaram similar teor de ácido fítico, porém diferente teor de taninos e ácido oxálico.
- A farinha caulinar se destacou por suas propriedades funcionais e por ser menos higroscópica que a farinha de bainha mediana em umidade relativa de equilíbrio abaixo de 50%, sendo o contrário válido para valores superiores.
- No fracionamento de carboidratos, o oxalato de amônio solubilizou a fração péctica, contendo o maior teor de ácido galacturônico. As soluções alcalinas menos concentradas (0.1 e 1.0 M) extraíram cadeias de hemicelulose compostas principalmente por xilose e arabinose.
- A fração celulósica foi a mais abundante nas farinhas e que juntamente com a fração extraída com NaOH 4.0 M representam o maior componente das farinhas - as fibras insolúveis.
- Portanto, as farinhas produzidas, se usadas como ingredientes apresentam potencial para a formulação de produtos alimentícios enriquecidos com fibras alimentares, além de minimizar o impacto ambiental do descarte dos subprodutos e valorizar a cadeia produtiva, com o aproveitamento integral da matéria-prima.