

Effects of Stage of Maturity and Cooking on the Chemical Composition of Select Mushroom Varieties

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Select mushrooms were analyzed for proximate constituents and carbohydrate profiles either raw or cooked and at different stages of maturity. White button mushrooms (*Agaricus bisporus*) contained high concentrations of ash (12.5 and 11.9% for immature and mature mushrooms, respectively). Starch and total dietary fiber (TDF) concentrations were higher in maitake (*Grifola frondosa*) and shiitake (*Lentinus edodes*) mushrooms. Crude protein (CP) and acid-hydrolyzed fat (AHF) were highest in crimini (*Agaricus bisporus*) and white button and maitake mushrooms, respectively. Chitin concentrations were highest in portabella (*Agaricus bisporus*) and enoki (*Flammulina velutipes*) mushrooms (8.0 and 7.7%, respectively). Oligosaccharides were found in low concentrations in some mushrooms. CP and TDF accounted for 86.4 and 49.3% of mushroom organic matter. Cooking increased starch, TDF, and AHF but decreased CP and chitin concentrations. The chitin concentration increased with mushroom maturity. These results detail the complete carbohydrate profile of several important mushroom varieties.

KEYWORDS: Mushrooms; oligosaccharides; carbohydrate composition

INTRODUCTION

Mushrooms have been consumed by many cultures for centuries, not only for nutritive value but also for medicinal or functional purposes as well. As early as 100 AD, documentation of mushroom use to maintain health was recorded in China. Of the more than 10000 known species of mushrooms, approximately 700 are edible and more than 200 species are thought to have medicinal values. The majority of edible mushrooms, however, do not have medicinal values, and many medicinal mushrooms are not edible (1). Some edible mushrooms with medicinal or functional values include enokitake, maitake, shiitake, oyster, murrill, and yiner mushrooms (1, 2).

Nutritionally, mushrooms provide key nutrients and bioactive components such as high quality protein, some vitamins including riboflavin, niacin, and folates, minerals (potassium, phosphorus, magnesium, zinc, copper, and selenium), unsaturated fatty acids, and fiber (1–4). The primary bioactive components in mushrooms are polysaccharides and glycoproteins. Mushroom polysaccharides vary in chemical composition and physical properties. Two major types of mushroom polysaccharides include glucans and heteroglycans. Glucans vary in their glycosidic linkages and in side chain sugar constituents that may include arabinose, galactose, glucuronic acid, mannose, ribose, or xylose. Fucans, galactans, mannans, and xylans are heteroglycans, where the backbone is comprised of sugars other

than glucose. The side chain constituent sugars of heteroglycans may consist of arabinose, fucose, galactose, glucose, glucuronic acid, mannose, or xylose (3). Additionally, mushrooms contain another important polysaccharide, chitin. Chitin is composed of *N*-acetyl-D-glucosamine units and is the second most common biopolymer on Earth, found primarily in invertebrates, insects, marine diatoms, algae, fungi, and yeast (4). Chitin has valuable applications in chemistry, biotechnology, medicine, veterinary medicine, dentistry, agriculture, food processing, environmental protection, and textile production (5). A derivative of chitin, chitosan, obtained by deacetylation of chitin, is used as a dietary supplement claimed to lower cholesterol and promote weight loss, although data are contradictory (6, 7).

Mushroom consumption as a medicine has been well-established among various ethnic groups throughout the world. In many parts of Asia, Japan, China, and Mexico, mushrooms are believed to have curative attributes (3). Studies have demonstrated that the consumption of mushrooms or consumption of isolated bioactive constituents contained in mushrooms may promote health by improving immunity (8, 9), lowering blood cholesterol and lipids (10–15), reducing blood pressure (16–18), attenuating blood glucose (18–20), acting as a chemoprotectant (2, 21–23), and having antibiotic activity (24). It is important to note that many of these effects are dependent on the isolation of bioactive compounds, processing, and fruit maturity at time of harvest (2, 4).

The objective of this study was to analyze six mushroom species, commonly cultivated and consumed in the United

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States, at various stages of maturity, and four types in either raw or cooked form for their chemical constituents, with an emphasis on carbohydrates and chitin.

MATERIALS AND METHODS

Test Samples. Mushrooms (white button, crimini, portabella, maitake, shiitake, and enoki) were supplied by a single commercial grower. White button (*Agaricus bisporus*), crimini (*Agaricus bisporus*), portabella (*Agaricus bisporus*), maitake (*Grifola frondosa*), and shiitake (*Lentinus edodes*) mushrooms were obtained at two different stages of maturity (immature/mature). Immature mushrooms were harvested with gills covered by the veil. Immature mushrooms were typically smaller and contained more moisture as compared to mature mushrooms. Mature mushrooms were harvested when the gills were exposed after separation of the veil from the stem. White button, crimini, portabella, and enoki (*Flammulina velutipes*) mushrooms were analyzed in both raw and cooked forms. Maitake and shiitake mushrooms were analyzed in the cooked form only because these mushrooms are only consumed in a cooked form.

Chemical Analyses. All mushrooms were processed within 36 h of arrival from Phillips Mushroom Farms (Kennett Square, PA) and stored at 4 °C until further analysis. Upon arrival, mushrooms were weighed and the remaining growth medium was removed by rinsing in cold water. Initial fresh weights for immature white button, mature white button, immature crimini, mature crimini, immature portabella, mature portabella, and enoki mushrooms were 6.2, 6.2, 5.8, 5.8, 4.8, 3.2, and 1.2 kg, respectively. In addition, a second batch of mushrooms was weighed prior to cooking and following the cooking process. Cooking was accomplished by placing fresh mushrooms into boiling water for 10 min. After boiling, cooked mushrooms were strained to remove water and weighed until no differences in weight were observed. Cooking losses were determined by measuring differences in precooked and postcooked weights. The initial weights of mushrooms after cooking were 5.2, 4.7, 4.2, 4.3, 3.2, 2.3, 1.1, 3.2, and 3.4 kg for immature white button, mature white button, immature crimini, mature crimini, immature portabella, mature portabella, enoki, shiitake, and maitake mushrooms, respectively. Inedible stems of shiitake mushrooms were removed completely prior to analysis. Stems of portabella mushrooms were trimmed to a length of 1.3–2.5 cm, and enoki mushroom stems were trimmed to 2.5 cm. The remaining portions were used for sampling and analyses. Samples were dried in a 55 °C forced air oven prior to grinding to 2 mm. All samples were analyzed for dry matter (DM), organic matter (OM), and crude protein (CP) (25). The CP concentration was corrected for the nonprotein nitrogen present in chitin. The acid-hydrolyzed fat (AHF) (25, 26) concentration was measured in all samples because this procedure hydrolyzes and accounts for all fat associated with substrates and is, therefore, more accurate in quantifying the fat concentration (26) than is traditional crude fat analysis. Total starch and resistant starch (RS) were determined after hydrolysis with glucoamylase (27).

The β -glucan concentration was quantified following enzymatic hydrolysis with lichenase (50 U/mL; Megazyme, Bray County, Wicklow, Ireland) and β -glucosidase (2 U/mL; Megazyme) following AOAC methodology (25) with modifications for analysis of mushrooms according to Manzi and Pizzoferrato (28). Glucose released from β -glucan was quantified by glucose oxidase–peroxidase methodology according to AOAC (25), and samples were read on a Beckman DU 640 spectrophotometer at 450 nm (25, 28).

Chitin was determined by combining 80–120 mg of sample or 8–12 mg of chitin standard (Sigma; St. Louis, MO) with 0.4 mL of ethanol (50%) and 4 mL of phosphate buffer (50 mM, pH 6) in 50 mL flasks. Flasks were gently mixed prior to being placed in a boiling water bath for 15 min with gentle mixing every 5 min. The flasks were equilibrated at 50 °C for 5 min prior to the addition of 0.4 mL of lichenase (50.0 U/mL; Megazyme), followed by a 1 h of incubation at 50 °C with occasional mixing. Following the incubation, 10 mL of phosphate buffer (150 mM, pH 6) was added and the flasks were equilibrated at room temperature for 5 min. Chitinase (1 U/mL; Sigma) was added (1.0 mL), and the flasks were stoppered and incubated in a 37 °C water bath with consistent shaking for 7 days. Samples were boiled for 30

min, transferred to 50 mL volumetric flasks, brought to volume with distilled–deionized water, and filtered through Whatman #541 filter paper. At least 15 mL of filtrate was transferred to a Centiprep-10 centrifuge filter (10000 molecular weight cutoff; Amicon, Beverly, MA) and centrifuged at 2790g for at least 90 min at 25 °C. Structural components of chitin were quantified via high-performance liquid chromatography (HPLC) with a Dionex DX500 HPLC system consisting of an AS3500 autosampler, GP 50 gradient pump, and ED 40 pulsed electrochemical detector equipped with a gold working electrode, utilizing a CarboPac PA-1 column and guard. The mobile phase consisted of 40 mM sodium hydroxide at a flow rate of 1 mL/min with a postcolumn addition of 300 mM sodium hydroxide at 0.5 mL/min. The injection volume was 25 μ L, and detection of components was compared to an external standard with a regression factor equal to or greater than 0.9998.

Oligosaccharides (OSs), free monosaccharides, and free sugar alcohols were quantified via HPLC. Standards for quantification included sucrose, lactose, galactotriose, galactotetraose, cellobiose, cellotriose, cellotetraose, cellopentaose, raffinose, stachyose, verbascose, kestose, nystose, and fructofuranosylmaltose. Samples were homogenized with water and hot water extracted in an 80 °C water bath for 1 h. The incubation was followed by filtration through Whatman #541 filter paper and transferred to a Centiprep-10 centrifuge filter (Amicon, Beverly, MA). Samples were centrifuged at 2790g for at least 90 min at 25 °C, and the supernatant was used for chromatographic analysis. Eluted OSs and monosaccharides were quantified using the previously described Dionex DX500 HPLC system. Free monosaccharides were injected at a volume of 25 μ L, and OSs were injected at a volume of 10 μ L. All assays were conducted using a CarboPac PA-1 column and guard following methods cited by Smiricky et al. (29).

Total dietary fiber (TDF) and insoluble dietary fiber (IDF) were analyzed according to AOAC methodology (25). Soluble dietary fiber (SDF) was calculated as TDF minus IDF (30, 31). Monosaccharides associated with the TDF residue were quantified after a two-step sulfuric acid hydrolysis (32) using the previously described Dionex DX500 HPLC system and a 25 μ L injection volume. The degassed mobile phase consisted of water, at 1 mL/min, with postcolumn addition of 300 mM NaOH (0.5 mL/min) (33).

Uronic acids associated with TDF residue were analyzed after a two-step sulfuric acid hydrolysis. Uronic acids in the samples produced a pink chromogen, after reactions with sulfuric acid/tetraborate and *m*-hydroxydiphenyl reagent, that was read at 520 nm in a Beckman DU 640 spectrophotometer following procedures previously cited by Blumenkrantz and Asboe-Hanson (34).

Only one sample was collected from each mushroom type; therefore, statistical analysis could not be completed on the data set. However, to maintain quality control during chemical analyses, the error between duplicate samples was determined. If the error between duplicate samples was greater than 5%, the analysis was repeated.

RESULTS

Cooking Losses. On the basis of differences in weight before and after cooking, the greatest losses occurred in immature and mature white button mushrooms (33.4 and 32.6%, respectively). Crimini and portabella mushrooms also had high cooking losses of 31.2 and 29.2% and 30.5 and 28.1% for immature and mature crimini mushrooms and immature and mature portabella mushrooms, respectively. Maitake and enoki mushrooms had the lowest cooking losses of 16.0 and 10.6% and 11.8% for immature and mature maitake mushrooms and enoki mushrooms, respectively. Cooking losses were lower for mature mushrooms for all varieties (data not shown).

Proximate Analysis. Proximate analysis results for all substrates are presented in **Table 1**. DM concentrations were low, ranging from 5.3 to 11.4%. Enoki mushrooms contained more DM, on average (8.4%), as compared with the other types, while white button mushrooms contained the lowest DM concentrations. There was a wide range in OM ranging from

Table 1. Proximate Components in Select Mushroom Varieties

sample	form	DM basis (%)						
		DM	OM	CP	CP (chitin-N removed)	AHF	starch	NG-Starch
white button	raw	5.6	84.6	38.1	37.4	5.8	5.5	5.4
(immature)	cooked	6.3	90.3	37.5	36.9	7.2	13.6	13.5
white button	raw	5.5	85.1	37.5	37.5	5.5	7.8	7.7
(mature)	cooked	6.8	91.1	37.8	37.2	6.3	13.9	13.8
crimini	raw	6.7	85.7	44.8	43.6	5.8	8.0	7.9
(immature)	cooked	7.6	90.7	43.6	42.7	6.4	12.4	12.3
crimini	raw	6.3	86.0	42.2	41.1	5.3	8.9	8.5
(mature)	cooked	7.8	91.5	43.4	42.5	5.3	14.0	13.9
portabella	raw	6.4	85.7	39.9	37.4	4.7	9.5	7.9
(immature)	cooked	7.7	93.8	41.7	40.6	4.9	17.0	16.9
portabella	raw	7.0	87.4	42.4	39.1	5.0	7.0	6.3
(mature)	cooked	7.4	93.0	42.2	41.1	5.1	15.7	15.6
enoki	raw	11.4	91.2	23.2	20.0	3.3	11.9	11.5
	cooked	5.3	91.5	23.5	20.3	4.1	13.3	13.1
maitake (immature)	cooked	8.6	95.1	31.0	30.4	7.0	16.0	15.8
maitake (mature)	cooked	7.2	94.4	27.9	27.3	5.7	10.7	10.6
shiitake (immature)	cooked	7.9	95.4	30.0	29.1	4.3	21.3	21.3
shiitake (mature)	cooked	7.0	96.0	28.2	26.7	5.0	20.2	20.1

84.6 to 96.0%, with maitake and shiitake mushrooms containing high concentrations and white button mushrooms containing lower concentrations. On average, crimini mushrooms contained the highest concentrations of CP (43.5%) and enoki mushrooms contained the lowest concentrations (23.4%). The CP concentration corrected for chitin N was slightly less than uncorrected values. Fat concentrations were low in all mushroom types with enoki mushrooms containing the lowest concentrations (3.7%) while maitake and white button mushrooms contained the highest concentrations, on average (6.4 and 6.2% for maitake and white button mushrooms, respectively). Starch corrected for free glucose (NG-Starch) varied considerably among mushroom types. On average, shiitake mushrooms contained 20.7% starch as compared with white button mushrooms and crimini mushrooms that contained 10.1 and 10.7% starch, respectively.

On average, TDF was very high in mushrooms, particularly in maitake and shiitake mushrooms (54 and 55.6%, respectively). The lowest concentrations of TDF were analyzed in portabella and crimini mushrooms, containing 30.2 and 30.8% TDF, respectively (**Table 2**). IDF followed a similar pattern with maitake and shiitake mushrooms containing the highest concentrations of IDF and portabella and crimini mushrooms containing the lowest concentrations (**Table 2**). In contrast, SDF was low in mushrooms, with the highest concentrations detected in crimini and enoki mushrooms (3.0%) and the lowest concentrations detected in maitake and portabella mushrooms (0.9 and 1.2%, respectively).

After cooking, concentrations of proximate constituents, expressed on a DM basis, were increased in all samples (**Tables 1 and 2**). DM concentrations increased by approximately 17% after cooking for all mushroom types except enoki mushrooms, while OM increased by approximately 6% in all samples. In addition, starch, AHF, TDF, and IDF were increased in all mushroom types after cooking by 79, 11, 40, and 49%, respectively. CP and SDF concentrations were not affected in a consistent manner by cooking. Cooking resulted in an increase in CP in mature crimini, portabella, and enoki mushrooms, while it resulted in a decrease in CP in white button and immature crimini mushrooms. Likewise, SDF was increased after cooking in immature portabella and enoki mushrooms but decreased after cooking in crimini, white button, and mature portabella mushrooms.

Table 2. Concentrations of TDF, IDF, SDF, β -Glucan, and Chitin in Select Mushroom Varieties

sample	form	TDF (%)	IDF (%)	SDF (%)	β -glucan (%)	chitin (%)
white button	raw	27.4	24.2	3.1	0.1	1.8
(immature)	cooked	41.8	39.9	1.9	0.1	1.3
white button	raw	28.5	25.9	2.6	0.1	3.0
(mature)	cooked	38.0	36.6	1.4	0.0	1.5
crimini	raw	30.4	24.4	6.0	0.1	2.9
(immature)	cooked	36.6	34.6	2.0	0.1	2.0
crimini	raw	23.8	20.8	3.0	0.1	2.7
(mature)	cooked	32.2	31.3	0.8	0.1	2.2
portabella	raw	25.4	24.3	1.1	0.1	6.0
(immature)	cooked	38.6	36.8	1.9	0.0	2.7
portabella	raw	22.9	20.2	1.7	0.2	8.0
(mature)	cooked	33.7	33.6	0.1	0.1	2.7
enoki	raw	29.3	26.4	2.8	0.0	7.7
	cooked	41.6	38.4	3.2	0.0	2.5
maitake (immature)	cooked	52.3	51.6	0.7	0.0	1.4
maitake (mature)	cooked	57.5	56.4	1.0	0.0	1.5
shiitake (immature)	cooked	55.9	53.6	2.4	0.1	2.2
shiitake (mature)	cooked	59.7	57.5	2.3	0.1	3.6

The stage of maturity did not affect proximate constituents of mushrooms in a consistent manner (**Tables 1 and 2**). When harvested at a later stage (mature mushrooms), DM increased in white button and portabella mushrooms but decreased in crimini, maitake, and shiitake mushrooms. OM also decreased for maitake mushrooms; however, OM increased in all other mature mushrooms. Mature portabella and shiitake mushrooms contained higher concentrations of AHF, while lower concentrations of AHF were determined in all other mature mushrooms. As compared with immature mushrooms, starch increased in white button and crimini mushrooms when harvested at a later stage. TDF and IDF were higher in mature maitake and shiitake mushrooms but lower in mature white button, crimini, and portabella mushrooms. SDF decreased in all mature mushrooms except maitake mushrooms.

β -Glucan and Chitin. Concentrations of β -glucan and chitin are presented in **Table 2**. β -Glucan was detected in very low concentrations in all mushroom types except enoki and maitake, which had none. Chitin ranged from 1.3 to 8.0% in mushrooms. The highest concentrations of chitin were detected in portabella (4.9%) and enoki (5.1%) mushrooms, while maitake (1.5%) and

Table 3. Concentrations (DM Basis) of Components of the TDF Residue in Select Mushroom Varieties

sample	form	% TDF residue									$\mu\text{g/g}$ TDF	
		fucose	arabinose	galactose	glucose	xylose	mannose	chitin	β -glucan	resistant starch	uronic acids	
white button (immature)	raw	0.5	0.1	4.0	31.7	0.9	1.8	4.5	0.3	12.3	19.0	
	cooked	0.5	0.1	3.6	37.6	0.6	1.7	1.4	0.4	18.6	25.7	
white button (mature)	raw	0.5	0.1	3.9	34.8	0.8	1.8	6.1	0.3	14.9	19.3	
	cooked	0.5	0.0	3.3	35.0	0.4	1.6	9.0	0.3	20.4	22.3	
crimini (immature)	raw	0.5	0.0	3.2	27.6	1.0	1.9	4.5	0.3	15.7	26.4	
	cooked	0.5	0.0	3.4	29.8	0.7	1.8	4.7	0.3	18.3	31.4	
crimini (mature)	raw	0.5	0.1	3.2	37.9	0.8	1.9	1.3	0.4	19.3	24.7	
	cooked	0.5	0.0	3.0	39.3	0.5	1.8	1.6	0.4	22.4	18.6	
portabella (immature)	raw	0.4	0.1	2.8	39.1	0.6	1.8	18.7	0.4	21.8	13.1	
	cooked	0.4	0.0	2.1	42.5	0.3	1.4	10.9	0.3	26.3	12.9	
portabella (mature)	raw	0.4	0.0	2.3	35.5	0.6	1.9	18.9	0.4	19.1	11.3	
	cooked	0.4	0.0	2.2	35.7	0.4	1.7	14.5	0.4	26.2	12.6	
enoki	raw	1.2	0.0	2.7	57.5	2.8	6.1	9.7	0.2	15.0	1.8	
	cooked	1.3	0.0	3.1	54.0	3.0	5.6	5.1	0.2	14.4	1.8	
maitake (immature)	cooked	1.5	0.0	2.2	48.2	1.7	5.0	16.9	0.2	17.0	9.7	
maitake (mature)	cooked	1.4	0.0	2.2	44.9	1.7	4.6	11.9	0.2	13.0	8.0	
shiitake (immature)	cooked	0.7	0.0	2.7	59.8	0.5	3.1	15.9	0.3	21.9	8.2	
shiitake (mature)	cooked	0.7	0.0	2.6	57.7	0.4	3.6	12.9	0.3	20.5	6.9	

white button (1.9%) contained the lowest concentrations (**Table 2**). Cooking mushrooms decreased the concentration of chitin in all mushroom samples (**Table 2**). Because the β -glucan concentrations were so low, cooking did not appear to have an effect (**Table 2**). Harvesting mushrooms at a later stage of maturity increased the concentration of chitin in all mushroom types; however, there was no difference in chitin concentration in crimini mushrooms harvested at a later stage. Again, because of the low concentration of β -glucan present, the stage of maturity did not appear to affect the concentration of this carbohydrate.

Fiber-Associated Monosaccharides, Chitin, β -Glucan, RS, and Uronic Acids. Fiber-associated monosaccharides and uronic acids were quantified and expressed as a percentage of the TDF residue (**Table 3**). Of the monosaccharides associated with fiber, fucose, arabinose, and xylose, concentrations were low in all samples, ranging from 0.1 to 3%. Mannose and galactose contributed 1.4–6.1% of fiber-associated components. Of the fiber-associated monosaccharides, glucose was detected in the highest concentration, ranging from 27.6 to 59.8%. RS associated with the fiber residue was high and ranged from 12.3 to 26.3%. Portabella mushrooms contained higher concentrations of RS as compared with the other mushroom types, while the lowest concentrations of RS were detected in enoki mushrooms. Fiber-associated chitin was detected in a range of 1.3–18.9% (**Table 3**). Portabella, maitake, and shiitake mushrooms contained higher concentrations of fiber-associated chitin as compared with white button, crimini, and enoki mushrooms. Fiber-associated uronic acids ranged from 1.8 to 31.4 $\mu\text{g/g}$ TDF, with white button and crimini mushrooms containing the highest concentrations (21.6 and 25.3 $\mu\text{g/g}$ TDF) and enoki mushrooms containing the lowest concentrations (1.8 $\mu\text{g/g}$ TDF).

Cooking did not affect the concentrations of fiber-associated fucose or arabinose (**Table 3**). Cooked mushrooms typically contained lower concentrations of fiber-associated galactose, xylose, and mannose, while concentrations of fiber-associated glucose increased by approximately 7% after cooking for all mushroom types except enoki. Cooking did not affect fiber-associated chitin consistently in all mushroom types. Cooking decreased fiber-associated chitin, by approximately 45%, in immature white button, portabella, and enoki mushrooms, while

increasing fiber-associated chitin, by approximately 25%, in mature white button and crimini mushrooms. Additionally, RS increased by approximately 30% in white button, crimini, and portabella mushrooms after cooking but decreased by approximately 11% in enoki, maitake, and shiitake mushrooms (**Table 3**). Uronic acids increased after cooking in immature white button and crimini mushrooms but decreased after cooking in all other mushrooms (**Table 3**).

The stage of maturity did not alter the concentrations of fiber-associated fucose, arabinose, xylose, or mannose in mushrooms (**Table 3**). On average, fiber-associated glucose increased with stage of maturity in white button and crimini mushrooms, while decreasing with age in portabella, maitake, and shiitake mushrooms. In addition, fiber-associated galactose decreased with age for all mushrooms by approximately 6%, except in maitake mushrooms that were not affected. Chitin associated with fiber increased with stage of maturity in white button (60%) and portabella (11%) mushrooms but decreased with maturity in crimini (67%), maitake (30%), and shiitake (19%) mushrooms. RS associated with fiber was not affected by maturity in a consistent manner. Fiber-associated RS increased with maturity in white button (12%) and crimini (19%) mushrooms but decreased with maturity in portabella (6%), maitake (24%), and shiitake (6%) mushrooms. On average, fiber-associated uronic acids ($\mu\text{g/g}$) decreased with stage of maturity by approximately 15% (**Table 3**).

OSs. Total OSs were detected in very low concentrations in mushroom samples, ranging from 80.7 to 5271.7 $\mu\text{g/g}$ DM (**Table 4**). OSs were not detected in enoki, maitake, or shiitake mushrooms. Total galactooligosaccharides (GOSs) (raffinose) were detected in only raw white button mushrooms (87.4 and 100.7 $\mu\text{g/g}$ DM for immature and mature raw white button mushrooms, respectively). Total glucooligosaccharides (Gluco-OSs) (cellotriose, cellotetraose, and cellopentaose) ranged from 86.7 to 5271.7 $\mu\text{g/g}$ DM in mature cooked white button and immature raw portabella mushrooms, respectively. Fructooligosaccharides (FOSs) (nystose and fructofuranosyl-nystose) were detected only in immature cooked white button mushrooms (663 $\mu\text{g/g}$ DM). Cooking affected concentrations of OSs in a variable manner (**Table 4**). Mushrooms that contained detectable concentrations of OSs (white button, crimini, and portabella

Table 4. Concentrations of Total OSs in Select Mushroom Varieties

sample	form	DM basis ($\mu\text{g/g}$)			
		total FOS	total GOS	total Gluco-OS	total OS
white button (immature)	raw	0.0	87.4	0.0	87.4
	cooked	663.0	0.0	0.0	663.0
white button (mature)	raw	0.0	100.7	0.0	100.7
	cooked	0.0	0.0	86.7	86.7
crimini (immature)	raw	0.0	0.0	0.0	0.0
	cooked	0.0	0.0	1154.5	1154.5
crimini (mature)	raw	0.0	0.0	461.0	461.0
	cooked	0.0	0.0	80.7	80.7
portabella (immature)	raw	0.0	0.0	5271.7	5271.7
	cooked	0.0	0.0	0.0	0.0
portabella (mature)	raw	0.0	0.0	1254.5	1254.5
	cooked	0.0	0.0	0.0	0.0
enoki	raw	0.0	0.0	0.0	0.0
	cooked	0.0	0.0	0.0	0.0
maitake (immature)	cooked	0.0	0.0	0.0	0.0
maitake (mature)	cooked	0.0	0.0	0.0	0.0
shiitake (immature)	cooked	0.0	0.0	0.0	0.0
shiitake (mature)	cooked	0.0	0.0	0.0	0.0

mushrooms) appeared to have higher concentrations of total OSs when harvested at an earlier maturity than a later maturity (Table 4).

Monosaccharides, Total Free Monosaccharides, and Sugar Alcohols. Values for sugar alcohols ranged from a low of 5364 $\mu\text{g/g}$ DM for immature raw crimini mushrooms to 28967 $\mu\text{g/g}$ DM for immature raw portabella mushrooms (Table 5). Portabella mushrooms contained the highest concentrations of sugar alcohols (7989–28967 $\mu\text{g/g}$ DM) and white button mushrooms contained the lowest concentrations of sugar alcohols (7032–8012 mg/g DM). On average, cooking increased the concentration of sugar alcohols by approximately 8% in white button mushrooms and by 7% in immature crimini mushrooms. Cooking decreased the concentrations of sugar alcohols by as much as 72% in other mushrooms. Harvesting mushrooms at a later stage of maturity was associated with a slight (6%) decrease in sugar alcohol concentrations found in white button, maitake, and shiitake mushrooms and a 40% increase in sugar alcohol concentration in crimini mushrooms.

Amounts of free fucose, arabinose, rhamnose, glucose, and mannose are presented in Table 5. Arabinose was detected only in enoki mushrooms (12.4 and 4.5 $\mu\text{g/g}$ DM for raw and cooked, respectively). Rhamnose ranged from 46.1 to 95.3 $\mu\text{g/g}$ DM and was not detected in mature white button, immature crimini, enoki, maitake, or shiitake mushrooms. Mannose was detected only in portabella mushrooms at a low concentration of 60.7–94.3 $\mu\text{g/g}$ DM for immature and mature varieties, respectively. Free fucose was detected in all mushrooms except mature white button mushrooms and ranged from 4.2 to 426.9 $\mu\text{g/g}$ DM. The highest concentrations were detected in enoki mushrooms. Total free monosaccharides were predominantly composed of free glucose. Free glucose was not detected in immature cooked portabella mushrooms; however, immature raw portabella mushrooms contained the highest concentration of free glucose (22949 $\mu\text{g/g}$ DM). With the exception of immature crimini mushrooms, cooking decreased the concentrations of free glucose in mushrooms (Table 5).

Portabella mushrooms contained the highest concentrations of total free monosaccharides and sugar alcohols (7.9–52.1 mg/g DM), while white button mushrooms contained the lowest concentrations (7.4–8.7 mg/g DM). With the exception of immature crimini mushrooms, cooking decreased total mono-

saccharides between 3 and 85% (immature white button and immature portabella mushrooms, respectively). In addition, with the exception of crimini mushrooms, mature mushrooms contained 8–21% more total free monosaccharides, on average, as compared with immature mushrooms (Table 5).

Comparison of mushrooms is based on a single serving size of 84 g, measured prior to cooking. Concentrations of CP, AHF, TDF, IDF, and SDF supplied in single servings of select mushrooms are listed in Table 6.

DISCUSSION

Mushrooms exhibited wide variation in concentrations of proximate constituents (Table 1). The ash content ranged from 4 to 15.4%. The higher concentrations of ash found in raw mushrooms may enhance mineral nutrition of humans if consumed on a routine basis, provided the minerals were bioavailable. The DM content of raw mushrooms was higher as compared to cooked mushrooms. Cooking mushrooms resulted in cooking losses and, therefore, concentrated the DM constituents.

CP concentrations were consistently high in mushrooms, ranging from 20 to 43.6% (Table 1). The total nitrogen was analyzed and corrected for the nitrogen associated with chitin; however, some CP found in mushrooms may include free amino acids or nonproteinaceous nitrogenous compounds. Guo et al. (35) reported CP concentrations of 208 and 103 g/kg DM for intact *Lentinus edodes* and *Tremella fuciformis* mushrooms, respectively. In the current study, enoki mushrooms contained similar CP concentrations of 20%. In contrast, Manzi et al. (36) detected concentrations of CP in three different varieties of mushrooms ranging from 1.5 to 6.8% (edible portion). The lower values reported may be a result of using $4.38 \times \%N$ as the CP conversion as compared with the standard $6.25 \times \%N$. A lower N factor was indicated as more appropriate for available protein nitrogen in edible mushrooms (37).

Immature cooked white button and maitake mushrooms contained the highest concentrations of AHF (7.2 and 7%, respectively). Overall, however, mushrooms contained low concentrations of AHF, ranging from 3.3 to 7.2%. In support, Manzi et al. (36) reported low fat concentrations of raw mushrooms of 0.6–1.6% (wet basis), respectively. In the current study, fresh mushrooms contained 0.3–0.6% AHF (wet basis), respectively. None of the mushroom varieties would be viewed as significant sources of fat.

The TDF concentrations of maitake and shiitake mushrooms were much higher as compared with the remaining varieties (Table 2). Manzi et al. (36) reported TDF concentrations of 2.6–10.7 $\text{g}/100$ g (edible weight) for Italian *Boletus* group mushrooms. Expressed on a wet basis, the mushrooms in the current study contained TDF concentrations ranging from 1.5 to 4.9%. IDF constituted the majority of TDF, while SDF was found in low concentrations. Manzi et al. (36) found IDF concentrations in mushrooms ranging from 2.3 to 9.0 $\text{g}/100$ g (edible weight) and SDF values ranging from 0.3 to 2.2 $\text{g}/100$ g (edible weight). Expressed on a wet basis, mushrooms in the current study contained IDF and SDF values ranging from 1.3 to 4.4% and 0.1 to 0.4%, respectively.

β -Glucan was found in low concentrations in mushrooms (Table 2), ranging from 0.1 to 0.2% DM. Likewise, Manzi and Pizzoferrato (38) reported β -glucan concentrations of 0.24 and 0.26 $\text{g}/100$ g DM for *Pleurotus ostreatus* and *Lentinula edodes* mushrooms, respectively. Manzi et al. (36) reported higher concentrations of β -glucans in *Boletus* group mushrooms,

Table 5. Concentrations of Free Monosaccharides and Sugar Alcohols in Select Mushroom Varieties

sample	form	DM basis ($\mu\text{g/g}$)						DM basis (mg/g)
		sugar alcohols	fucose	arabinose	rhamnose	glucose	mannose	total free monosaccharides
white button (immature)	raw	7055.2	114.2	0.0	65.7	1433.2	0.0	8.7
	cooked	8011.9	11.9	0.0	0.0	415.5	0.0	8.4
white button (mature)	raw	7031.9	0.0	0.0	0.0	1229.1	0.0	8.3
	cooked	7370.6	0.0	0.0	0.0	55.8	0.0	7.4
crimini (immature)	raw	5364.3	0.0	0.0	0.0	1021.4	0.0	6.4
	cooked	5751.5	21.2	0.0	0.0	1240.6	0.0	7.0
crimini (mature)	raw	12487.9	0.0	0.0	46.1	9404.4	0.0	21.9
	cooked	6689.5	17.5	0.0	0.0	460.0	0.0	7.2
portabella (immature)	raw	28967.2	17.9	0.0	95.3	22948.6	60.7	52.1
	cooked	7988.5	50.0	0.0	0.0	0.0	0.0	8.0
portabella (mature)	raw	26032.4	176.1	0.0	83.8	13446.3	94.3	39.8
	cooked	7763.7	12.3	0.0	0.0	132.0	0.0	7.9
enoki	raw	12037.9	426.9	12.4	0.0	6118.5	0.0	18.6
	cooked	11186.0	124.1	4.5	0.0	3489.6	0.0	14.8
maitake (immature)	cooked	11027.9	0.0	0.0	0.0	1935.6	0.0	13.0
maitake (mature)	cooked	10621.8	25.5	0.0	0.0	1008.9	0.0	11.7
shiitake (immature)	cooked	10526.6	12.3	0.0	0.0	474.7	0.0	11.0
shiitake (mature)	cooked	9721.8	4.2	0.0	0.0	188.1	0.0	9.9

Table 6. Proximate Components in a Single Serving of Select Mushroom Varieties^a

sample	form	grams					
		CP (chitin-N removed)	AHF	NG-Starch	TDF	IDF	SDF
white button (immature)	raw	1.8	0.3	0.3	1.3	1.1	0.2
	cooked	1.3	0.3	0.5	2.2	2.1	0.1
white button (mature)	raw	1.8	0.3	0.3	1.3	1.2	0.1
	cooked	1.4	0.2	0.5	2.2	2.1	0.1
crimini (immature)	raw	2.4	0.3	0.4	1.7	1.4	0.3
	cooked	1.9	0.3	0.5	2.3	2.2	0.1
crimini (mature)	raw	2.2	0.3	0.4	1.3	1.1	0.2
	cooked	2.0	0.2	0.7	2.1	2.0	0.1
portabella (immature)	raw	2.0	0.3	0.4	1.4	1.3	0.1
	cooked	1.8	0.2	0.8	2.5	2.4	0.1
portabella (mature)	raw	2.3	0.3	0.3	1.3	1.2	0.1
	cooked	1.8	0.2	0.7	2.1	2.1	0.0
enoki	raw	1.9	0.3	1.1	2.8	2.5	0.3
	cooked	0.8	0.2	0.5	1.9	1.7	0.2
maitake (immature)	cooked	1.6	0.4	0.9	3.8	3.7	0.1
maitake (mature)	cooked	1.4	0.3	0.6	3.4	3.3	0.1
shiitake (immature)	cooked	1.6	0.2	1.2	3.7	3.6	0.1
shiitake (mature)	cooked	1.4	0.3	1.1	3.5	3.3	0.2

^a Components expressed in g/84 g serving of raw mushrooms.

ranging from 309.5 to 1110.3 mg/100 g (edible weight). These higher values may be due to the drying of these mushrooms prior to analysis. Additionally, the variation in β -glucan concentrations observed in that study was thought to be a result of mushroom maturity. In the current study, however, no differences were observed among immature and mature mushrooms.

Chitin was detected in all mushrooms ranging from 1.3 to 8% DM. Expressed on a wet basis, the mushrooms in the current study contained 0.1–0.9% chitin. In support, Manzi et al. (36) reported chitin concentrations ranging from 1.1 to 3.3 g/100 g edible weight for dried *Boletus* group mushrooms. In the current study, the chitin concentration increased with stage of maturity. According to Novaes-Ledieu and Mendoza (39), chitin is a major constituent of the cell wall of mushrooms and, therefore, will increase with the stage of maturity as the fungi grows and matures.

Glucose, RS, and chitin accounted for 47.8–97.6% of fiber-associated components of mushrooms (Table 3). Fiber-associ-

ated glucose was detected in concentrations ranging from 27.6 to 59.8% of TDF. Likewise, Cheung and Lee (40) reported glucose as a major constituent of TDF (56%) in *Pleurotus tuberregium* mushrooms. In the current study, neither stage of maturity nor cooking consistently affected the concentrations of these components in TDF. Fiber-associated RSs increased with maturity in white button and crimini mushrooms but decreased in portabella, maitake, and shiitake mushrooms. RS accounted for 12.3–26.3% of fiber-associated carbohydrates. RS is classified into four types: RS I, RS II, RS III, and RS IV. RS I is a starch physically inaccessible to digestive enzymes and, therefore, available for fermentation by microbiota inhabiting the large bowel. RS II is raw starch granules found primarily in raw potatoes and green bananas, while RS III is a starch that represents retrograded (recrystallized) amylose (41). RS IV is chemically modified starch. The RS found in mushrooms is likely to be type I; however, cooking mushrooms, particularly white button and crimini mushrooms, may lead to an increase in RS III concentration. RS has been associated with effects on

intestinal microbiota and metabolism and improvements in gut health, function, and physiology (41).

Fiber-associated mannose and galactose accounted for moderate proportions of the TDF residue and were not affected by mushroom maturity. Likewise, fiber-associated fucose, arabinose, and xylose did not appear to be affected by mushroom maturity and accounted for only small proportions of TDF. Fiber-associated β -glucans and uronic acids were detected in all mushrooms but accounted for a very small proportion of the TDF. In the current study, uronic acids were detected in low concentrations, 31.4 $\mu\text{g/g}$ (0.0031%) TDF, as compared to reported values of 1.2% uronic acids associated with TDF (40). These differences may be due to the variety of mushrooms analyzed and variations in methods used to fractionate nonstarch polysaccharide (40) as compared to the current study.

Several categories of OS (Gluco-OSs, GOSs, and FOSs) were found in low concentrations in some of the mushrooms and were not associated with the stage of maturity or cooking (Table 4). The highest concentration of total OSs was detected in raw portabella mushrooms (5271.7 $\mu\text{g/g DM}$). Many OSs are inaccessible to mammalian enzymes in the small intestine and, therefore, are available as substrates for colonic fermentation. Many OSs serve to promote the growth of more favorable colonic bacterial populations and may optimize stool characteristics (42). The consumption of raw portabella mushrooms would serve as the best source of OSs; however, mushrooms in general do not provide significant concentrations of OSs for humans.

All mushrooms contained detectable concentrations of sugar alcohols and free monosaccharides (Table 5). Total free monosaccharides ranged from 6.4 to 52.1 mg/g DM with sugar alcohols accounting for 56–99% of total free monosaccharides (Table 5). Likewise, Tan and Moore (43) reported mannitol concentrations up to 50% dry weight in *Agaricus bisporus* mushrooms. In the current study, sugar alcohols were detected in higher concentrations in mature mushrooms with the exception of crimini mushrooms. Sugar alcohols, particularly mannitol, function to provide support and expansion of the fruit body, possibly explaining the increase in sugar alcohol concentration with maturity of the fruit as observed in the current study.

Concentrations of CP, AHF, and starch (Table 1), TDF, β -glucan, and chitin (Table 2) were summed to determine the OM concentration accounted for by our chemical analyses. These values then were compared with the analyzed concentrations of OM presented in Table 1. The summation of CP and TDF accounted for the majority of OM in mushrooms. In the case of immature cooked white button, crimini, portabella, and maitake mushrooms, 100% of the OM was accounted for in our analyses. On the other hand, the OM concentration of raw enoki mushrooms was 91.2%, but organic components added to only 71.8%. Obviously, additional compounds such as vitamins, phenolics, and volatile compounds in mushrooms may exist that were not accounted for by our analyses, and these compounds may account for many of the bioactive components of mushrooms. Phenolic compounds may have accounted for a large proportion of the OM not accounted for in our analyses. For example, dried *Boletus* group mushrooms contained approximately 235.9–403.8 mg/100 g edible weight phenolic compounds (36). For the remaining mushrooms, our analyses accounted for 77.9–98.3% of the analyzed OM. In the case of shiitake mushrooms, summed constituents accounted for 112.9 and 115.2% of the OM in immature and mature mushrooms, respectively. Shiitake mushrooms contained very high concen-

trations of TDF (55.9 and 59.7% for immature and mature mushrooms, respectively). Glucose and RS accounted for 81.7 and 78.2% of the TDF in shiitake mushrooms. Because of the complexity of analyzing monosaccharides individually, perhaps some glucose was accounted for in both constituents and, thus, contributed twice to the final value.

Concentrations of fiber-associated components (Table 3) were summed to determine the TDF concentration accounted for by our chemical analyses. The summation of fiber-associated glucose, RS, and chitin accounted for the majority of TDF in mushrooms. In the case of portabella, enoki, maitake, and shiitake mushrooms, 79–100% of TDF was accounted for in our analyses. In contrast, only 55–71% of TDF was accounted for in white button and crimini mushrooms. Additional fiber-associated polysaccharides may exist that were not analyzed in the current study. According to Brauer et al. (44), mushrooms may contain multiple chitin and glucan–protein complexes, in addition to high molecular weight polysaccharides such as lentinan.

Nutrient concentrations in single servings of select mushrooms are listed in Table 6. Serving size is based on weight prior to cooking, although some mushrooms are consumed in the cooked form only, such as maitake and shiitake. CP in a single serving of mushrooms ranged from 0.8 to 2.4 g. Because of cooking losses, cooked mushrooms typically contained less CP and AHF as compared with raw mushrooms. AHF in a single serving was very low in all mushrooms, ranging from 0.2 to 0.4 g. Single servings of crimini and portabella mushrooms provided the highest concentrations of CP (2.1 and 2.0 g, respectively). Starch, TDF, and IDF concentrations in single servings of mushrooms were typically higher following cooking, due to concentration of the nutrients and potential elevations in RS concentration. TDF ranged from 1.3 to 3.8 g per serving, and IDF ranged from 1.1 to 3.7 g per serving. Regardless of maturity, maitake and shiitake mushrooms contained the highest concentrations of TDF and IDF in single servings.

Variation in composition among mushrooms may be due to several factors including mushroom strain/type, composition of growth media, time of harvest, management techniques, handling conditions, and preparation of the substrates (36, 44). Brauer et al. (44) reported a higher concentration of high molecular weight polysaccharides in shiitake mushrooms grown on logs of southern red oak as compared with substrate-grown shiitake mushrooms.

Generally, cooking processes will result in a loss of moisture and a subsequent concentration of nutrients. On the other hand, cooking also may promote a loss of nutrients due to interactions among constituents, chemical reactions, solubility in cooking medium, and (or) degradation (36). Carbohydrates (starch and TDF) and AHF in the current study were typically concentrated in mushrooms following cooking. CP and chitin were typically decreased in mushrooms after cooking.

Results of this study indicated that a large proportion of the chemical composition of select mushroom varieties is carbohydrate and protein. TDF content accounted for a large proportion of mushroom OM (Table 2). With the addition of CP, the percentage of OM accounted for increased to a high of nearly 84%. Mushrooms are healthful foods with many functional and nutritional properties. Quantification of their carbohydrate and proximate components hopefully will be useful to those charged with making greater use of them in food products.

ABBREVIATIONS USED

AHF, acid-hydrolyzed fat; CP, crude protein; DM, dry matter; FOSs, fructooligosaccharides; GOSs, galactooligosaccharides;

GlucO-OSs, glucooligosaccharides; IDF, insoluble dietary fiber; NG-Starch, starch corrected for free glucose; OM, organic matter; OSs, oligosaccharides; SDF, soluble dietary fiber; TDF, total dietary fiber.

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