J Am Oil Chem Soc (2009) 86:553–559
DOI 10.1007/s11746-009-1383-6

ORIGINAL PAPER

Lipid Components of North American Wild Rice (*Zizania palustris*)

R. Przybylski · D. Klensporf-Pawlik · F. Anwar · M. Rudzinska

Received: 7 January 2009 / Revised: 2 April 2009 / Accepted: 4 April 2009 / Published online: 24 April 2009

Abstract The content and composition of fatty acids, sterols, tocopherols, and γ-oryzanol in wild rice (*Zizania palustris*) grown in North America were compared with those in regular brown rice (*Oryza sativa* L.). The lipid content of wild rice ranged from 0.7 to 1.1%, compared with 2.7% in regular brown rice. The lipids of wild rice comprised mainly linoleic (35–37%) and linolenic (20–31%) acids. Other fatty acids included palmitic (14.1–18.4%), stearic (1.1–1.3%), and oleic (12.8–16.2%). Wild rice lipids contained very large amounts of sterols, ranging from 70 g/kg for a Saskatchewan sample to 145 g/kg for Minnesota Naturally Grown Lake and River Rice. The main sterols found in an unsaponified fraction were: campesterol (14–52%), β-sitosterol (19–33%), Δ^5-avenasterol (5–12%), and cycloartenol (5–12%). Some of sterols, γ-oryzanols, were present as the phenolic acid esters; the amount ranged from 459 to 730 mg/kg in wild rice lipids. The largest amounts of tocopherols and tocotrienols, 3682 and 9378 mg/kg, were observed in North Western Ontario wild rice samples, whereas the lowest were 251 mg/kg in an Athabasca Alberta sample and 224 mg/kg in regular long-grain brown rice. The α isomer was the most abundant among tocopherols and tocotrienols. The results of this study showed that wild rice lipids contain large amounts of nutraceuticals with proven positive health effects.

Keywords Wild rice lipids · Linolenic acid · Tocopherols · α-Tocopherol · Phytosterols · β-Sitosterol · γ-Oryzanol

R. Przybylski (✉)
Department of Chemistry and Biochemistry,
University of Lethbridge, Lethbridge,
AB T1K 3M4, Canada
e-mail: roman.przybylski@uleth.ca

F. Anwar
Department of Chemistry,
University of Agriculture,
Faisalabad 38040, Pakistan

D. Klensporf-Pawlik · M. Rudzinska
Institute of Food Technology of Plant Origin,
Poznan University of Life Sciences, Poznan, Poland

Introduction

Wild rice, known also as Canadian rice, Indian rice, and water oats, which belongs to the genus *Zizania*, is grown as an aquatic cereal grain. It consists of four species: *Zizania palustris* L., *Zizania aquatica* L., *Zizania texana* H., and *Zizania latifolia* G. The first three species are native to the North America and the fourth to Asia. *Zizania palustris* L. and *Zizania aquatica* L. are annuals whereas the others are perennials [1–3]. Wild rice varieties *Zizania palustris* L. and *Zizania aquatica* L. are predominantly grown naturally in lakes, rivers, and streams in the Great Lakes region and the Northern part of the Canadian prairies, and they are harvested from an air boat [1, 4, 5].

The wild rice kernel has a long and narrow cylindrical shape, with a length from 7.5 to 18.0 mm and a width from 1.5 to 4.0 mm, and is usually used dehulled but non-polished [4]. Like other cereals, wild rice grain is a food commodity containing 74% starch and 14% protein as the main constituents. In addition, it also contains dietary fiber (6.8%), lipids (1.7%), and ash (1.8%) [4]. The relatively high level of ash suggests that wild rice grain may serve as a good source of minerals such as potassium and phosphorus [1, 6].

Wild rice has been consumed as a staple food by the native North Americans, especially the Ojibway, Menomini, and Cree tribes, since prehistoric time [7, 8].

Recently, the utilization of wild rice is gaining popularity among consumers, and is commonly available in supermarkets and restaurants. It is also used as ingredient in a variety of foods such as soups, meat dishes, stuffings, breakfast cereals, pancakes, muffins, cookies, and others [1, 3].

To the best of our knowledge, no data are available about the lipid components of North American wild rice; the main objective of this study was, therefore, to assess the content and composition of fatty acids, tocopherols, sterols, and γ-oryzanol in commercial brands of wild rice.

Materials and Methods

Materials

Samples of commercial wild rice were obtained from the following suppliers; the abbreviation in the brackets following the name of the rice is used in this paper: Minnesota Natural Lake (MNL; C & G Enterprises, Minnesota, USA), North Western Ontario (NOW; Shoal Lake Wild Rice, Winnipeg, Manitoba, Canada), Saskatchewan (S; Points North Wild Rice Company, Yorkton, Saskatchewan, Canada), Athabasca Alberta (AA; Alice Ptolemy Lakeland Wild Rice, Athabasca, Alberta, Canada), Manitoba Far North (FNM; Far North Wild Rice, Manitoba, Canada), Minnesota Naturally Grown Lake & River (MNGLR; Moose Lake Wild Rice Company, Minnesota, USA), Minnesota Cultivated Wild Rice (MC; Moose Lake Wild Rice Company, Minnesota, USA). Regular long (LGR) and medium grain (MGR) brown rice were obtained from Riceland Foods (Arkansas, USA) and used as references.

Reagents, solvents, and sterol standards were purchased from Sigma–Aldrich (St Louis, MO, USA). Standards of tocopherols were obtained from Calbiochem–Novabiochem (San Diego, CA, USA). Fatty acid methyl ester standards were purchased from Nu-Chek-Prep (Elysian, MN, USA). Gamma-oryzanol was a kind gift from Oryza Oil and Fat Chemical (Japan). BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide), TMCS (trimethylchlorosilane), and pyridine were obtained from Supelco (Bellefonte, PA, USA).

Lipid Extraction

The wild rice kernels were ground in a coffee mill before lipid extraction. Ground seeds (40 g) were homogenized with 400 mL chloroform–methanol (2:1, *v*/*v*) following the Folch procedure [9]. Extraction was repeated thrice. Distilled water (100 mL) was added to the combined extracts. The lipid extract was concentrated under vacuum in a rotary evaporator (Büchi Labortechnik, Switzerland) at 35 °C. Solventless lipids were transferred to brown glass vials with 10 mL *iso*-octane, flushed with nitrogen, and stored at −20 °C until analyzed.

Fatty Acid Composition

The fatty acid composition of wild rice lipids was analyzed by following AOCS Official Method Ce 1-62 [10]. The FAMEs were separated on a TR-FAME capillary column (100 m × 0.25 mm × 0.25 μm; ThermoFisher Scientific, Waltham, USA) installed in a Trace GC Ultra gas chromatograph (Thermo Electron, Rodano, Italy). The FAME sample, 1 μL, was injected with an AS 3000 autosampler (Thermo Electron, Rodano, Italy) into a temperature-programmed injector (PTV). Hydrogen was used as carrier gas at a flow rate of 1.5 mL min^{-1}. Column temperature was programmed from 70 °C to 160 °C at 25 ° min^{-1}, held for 30 min, then further programmed to 210 °C at 3 ° min^{-1}. Initial and final temperatures were held for 5 and 30 min, respectively. Detector temperature was set at 250 °C. Fatty acids were identified by comparison of the retention times with those of authentic standards and the results are reported as a weight percentage of the lipid.

Sterol Analysis

Sterols content and composition in rice samples were assessed by gas chromatography following the procedure described by Rudzińska et al. [11]. Briefly, lipids were saponified with 1 M KOH in methanol overnight at room temperature, then water was added and unsaponifiables extracted with diethyl ether. Dry residues were silylated with BSTFA containing 1% TMCS. Derivatives of the sterols were separated on a Hewlett-Packard 6890 gas chromatograph with an HP-5 capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, Folsom, CA, USA). Split injection with split ratio 1:25 was used. Temperatures were set as follows: column isothermal at 290 °C, injector and detector at 310 °C. Helium was used as the carrier gas at a flow of 1.6 mL/min. An internal standard, 5α-cholestane, was used for quantification. Phytosterols were identified by comparison of retention data and by GC–MS using a Finnigan Trace 2000 gas chromatograph coupled to a Finnigan Polaris Q quadrupole ion-trap mass spectrometer after separation on a DB-5 capillary column (50 m × 0,2 mm × 0.32μm; J&W). Helium was used as carrier gas at a flow rate of 0.6 mL/min. All mass spectra were recorded using electron-impact ionization mode at 70 eV and scanning mass in the range of 100–650 D. Ion source was held at 200 °C and injector at 300 °C. A combination of the NIST Mass Spectra Library and collected spectra of sterols were used to identify the sterols.

Tocopherol Analysis

Tocopherols were analyzed as previously described [12]. Briefly, 50 mg oil was weighed directly into a 1.5-mL vial and mixed with 1 mL hexane. Separation was done using a Finnigan Surveyor Plus HPLC System (Thermo Electron, Waltham, MA, USA) with a Finnigan Surveyor model FL Plus fluorescence detector set for excitation at 292 nm and emission at 394 nm. A 20-μL sample was injected on to a diol column (250 × 4.6 mm, 5 μm; Monochrom, Varian, Palo Alto, CA, USA). The mobile phase was 7% *tert*-butyl methyl ether in hexane at a flow rate of 0.6 mL/min. Standards of tocopherol isomers were used for identification by comparing retention data. Quantification was based on external calibration for each isomer separately and all results are expressed as mg tocopherols per kg lipids.

Gamma-Oryzanol

Gamma-oryzanol standard and wild rice oil samples (50 mg/mL) were analyzed by HPLC using a Finnigan Surveyor Plus HPLC system (Thermo Electron, Waltham, MA, USA). A 20-μL sample was injected on to a C_{18} column (300 × 3.9 mm; 4 μm, NovaPak, Waters) held at 30 °C. Separation was achieved by using acetonitrile–methanol (65:35, *v*/*v*) as mobile phase at a flow rate of 0.85 mL/min. Detection was at 325 nm using a Finnigan Surveyor photodiode-array detector (PDA). Total amounts of gamma-oryzanols is expressed as a group of esters and quantified by using the external calibration method.

Statistical Analysis

Data are presented as means ± SD from experiments in triplicate in which each analysis was also performed in triplicate. Statistical analysis of the data was performed by analysis of variance (ANOVA) using Minitab 2000 Version 13.2 statistical software (Minitab, PA, USA). Statistically significant differences were determined at $P < 0.05$.

Results and Discussion

Lipid Content

The lipid content of the rice samples analyzed ranged from 0.7 to 1.1% (Table 1). The NOW wild rice contained the largest amount of lipids whereas the lowest content was found in FNM rice (Table 1). Conversely, the lipid content of LGR and MGR regular rice samples, used in this study as the controls, were 2.6 and 2.8%, respectively. The lipid content of analyzed wild rice samples were in agreement with data reported for North American wild rice (*Zizania aquatica* L. and *Zizania palustris* L.) [1, 4]. Zhai et al. [3] and Aizawa et al. [13] reported lipid contents of Chinese and Japanese wild rice (*Zizania latifolia*) at levels of 1.1% and 1.4%, respectively.

Fatty Acid Composition

Substantial differences were observed in the amounts of saturated, monounsaturated, and polyunsaturated fatty acids among wild and regular rice samples (Table 1). Among saturated fatty acids, amounts of palmitic acid were similar in both types of rice whereas the amount of stearic acid in regular brown rice was almost twice that in wild rice (Table 1). Oleic acid was the most abundant monounsaturated fatty acid in wild rice. Values ranged from 12.8% in NOW to 16.2% in AA rice samples, whereas in regular rice the level was found to average 40% (Table 1). Among polyunsaturated fatty acids, linoleic and linolenic were predominant. The linoleic acid content ranged from 35% in NOW to 37.8% in MC wild rice, comparable to levels of 35.2–37.5% observed in regular rice. The amount of linolenic acid in wild rice was 11 to 18 times higher than observed in regular rice (Table 1). In agreement with our observations, Oelke [1] reported that wild rice lipid usually contains a larger proportion of linoleic and linolenic acids, with a collective contribution of 68%, which is higher than that observed in standard cereals [14]. Aizawa et al. [13] found that Japanese wild rice (*Zizania latifolia*) was a rich source of linoleic (41%) and linolenic (22%) acids. The ratios of omega-6 to omega-3 in wild rice samples were from 1.1 for NOW to 1.8 for AA, whereas those in standard rice were from 20.2 to 22.4 (Table 1). Low ratios of n-6/n-3; determined in wild rice lipids may have beneficial effect on human blood lipids [15].

Sterols Composition and Contents

Wild rice lipids contained very large amounts of total sterol, varying from 70 g/kg in S to 145 g/kg in MNGLR, whereas regular rice contained 27 g/kg (Fig. 1). The phytosterols content of wild rice lipids was 3.5 times higher than reported for cereal by-products such as rice bran, wheat bran, and wheat germ [16]. The phytosterols composition was different among the wild rice samples analyzed, as shown in Table 2. Campesterol, β-sitosterol, and cycloartenol were the main phytosterols found in the wild rice lipids. These compounds contributed 54% of the total sterol content in NOW and 75% in MNGLR wild rice samples. In the latter sample, an unusually high campesterol content, 52%, was observed (Table 2). Substantial amounts of the major phytosterols were found among the phytosterols of wild and regular rice. In the wild rice lipids, amounts of 24-methylenecycloartenol and stigmasterol (3.2–7.8% and 3.7–6.5%, respectively)

Table 1 Lipid content and fatty acid composition of wild and regular rice[a]

Parameters	Wild rice							Standard brown rice	
Fatty acids[b]	MNL	NOW	S	AA	FNM	MNGLR	MC	LGR	MGR
C16:0	14.25 ± 0.16	14.13 ± 0.16	14.23 ± 0.16	18.39 ± 0.21	16.05 ± 0.18	15.89 ± 0.18	14.96 ± 0.17	15.17 ± 0.17	15.42 ± 0.18
C18:0	1.31 ± 0.06	1.03 ± 0.05	1.01 ± 0.05	1.26 ± 0.06	1.31 ± 0.06	1.1 ± 0.05	1.3 ± 0.06	2.04 ± 0.09	1.89 ± 0.09
C18:1 cis 9	13.84 ± 0.07	12.88 ± 0.07	14.37 ± 0.08	16.23 ± 0.09	16.01 ± 0.08	14.62 ± 0.08	13.9 ± 0.07	41.56 ± 0.22	39.16 ± 0.21
C18:1 cis 7	1.85 ± 0.05	1.77 ± 0.05	ND	2.72 ± 0.08	2.45 ± 0.07	2.3 ± 0.06	1.96 ± 0.05	0.94 ± 0.03	1.08 ± 0.03
C18:2	36.21 ± 0.23	35.02 ± 0.22	36.8 ± 0.24	36.37 ± 0.23	37.74 ± 0.24	36.99 ± 0.24	37.79 ± 0.24	35.15 ± 0.22	37.45 ± 0.24
C18:3	27.57 ± 0.45	31.45 ± 0.51	27.6 ± 0.45	20.07 ± 0.33	24.66 ± 0.40	24.28 ± 0.40	26.51 ± 0.51	1.74 ± 0.03	1.67 ± 0.03
C20:0	0.53 ± 0.01	0.33 ± 0.01	0.55 ± 0.02	0.45 ± 0.01	0.16 ± 0.01	0.43 ± 0.01	0.35 ± 0.01	0.75 ± 0.02	0.72 ± 0.03
C20:1	0.51 ± 0.01	0.49 ± 0.01	0.56 ± 0.01	0.59 ± 0.01	0.20 ± 0.01	0.55 ± 0.02	0.41 ± 0.01	0.54 ± 0.02	0.52 ± 0.02
C22:0	1.04 ± 0.03	0.31 ± 0.01	0.79 ± 0.02	0.61 ± 0.01	0.22 ± 0.01	0.59 ± 0.02	0.44 ± 0.01	0.33 ± 0.01	0.36 ± 0.01
C22:2	1.08 ± 0.05	1.27 ± 0.06	1.52 ± 0.05	1.39 ± 0.05	0.47 ± 0.01	1.51 ± 0.05	0.88 ± 0.02	0.23 ± 0.01	0.27 ± 0.01
C24:0	0.83 ± 0.04	0.63 ± 0.02	1.67 ± 0.06	0.77 ± 0.02	0.26 ± 0.01	0.78 ± 0.02	0.76 ± 0.02	0.87 ± 0.03	0.70 ± 0.02
Others[c]	0.98 ± 0.05	0.69 ± 0.03	0.89 ± 0.04	1.17 ± 0.05	0.47 ± 0.01	0.97 ± 0.04	0.74 ± 0.04	0.67 ± 0.03	0.77 ± 0.03
Groups and ratio of fatty acids									
SFA	18.17 ± 0.80	16.65 ± 0.74	18.42 ± 0.82	21.82 ± 0.98	18.07 ± 0.81	18.99 ± 0.89	18.03 ± 0.81	19.53 ± 0.88	19.51 ± 0.85
MUFA	15.12 ± 0.48	13.84 ± 0.44	15.65 ± 0.51	17.65 ± 0.56	16.61 ± 0.53	15.94 ± 0.51	14.83 ± 0.47	42.4 ± 0.45	40.03 ± 0.42
PUFA	64.86 ± 0.97	67.74 ± 1.01	65.92 ± 0.98	57.83 ± 0.86	62.87 ± 0.94	62.78 ± 1.02	65.18 ± 0.78	37.12 ± 0.56	39.39 ± 0.59
n-6/n-3	1.3	1.1	1.3	1.8	1.5	1.5	1.4	20.2	22.4
Lipids[b]	0.82 ± 0.10	1.10 ± 0.08	1.00 ± 0.10	1.07 ± 0.15	0.74 ± 0.12	0.89 ± 0.07	1.05 ± 0.12	2.60 ± 0.20	2.80 ± 0.15

MNL, Minnesota Natural Lake; NOW, North Western Ontario; S, Saskatchewan; AA, Athabasca Alberta; FNM, Manitoba Far North; MNGLR, Minnesota Naturally Grown Lake & River; MC, Minnesota Cultivated Wild Rice; LGR, standard brown long grain; MGR, standard brown medium grain

[a] Values are reported as mean ± SD from triplicate determination ($n = 3$)

[b] Fatty acids in %, lipids content g/100 g rice

[c] C14:0, C16:1, C22:1

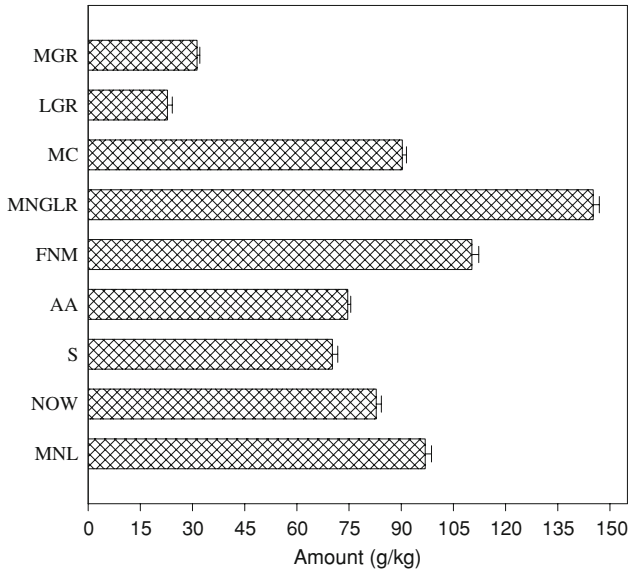

Fig. 1 Total amounts of phytosterols in wild and regular rice lipids. For sample abbreviations see Table 1

were lower than observed in LGR and MGR brown rice (13–14% and 10.1–10.4%, respectively). Amounts of Δ^5-avenasterol in the wild rice samples were larger than in regular rice (Table 2). Other minor sterols, namely, clerosterol (1.9–5.5%), Δ^7-avenasterol (1.7–5.0%), citrostadienol (1.0–5.0%), 23-dehydrositosterol (1.1–3.4%), and gramisterol (1.8–3.3%) were identified in the wild rice lipids. Phytosterols play a positive role in reducing absorption of cholesterol and reducing the level of negative lipoproteins in human blood, thus potentially reducing the development of heart diseases [15].

Tocochromanols

We found substantial amounts of tocopherols and tocotrienols in the wild rice samples analyzed (Fig. 2). The lipids of NOW wild rice contained the highest amounts of tocopherols and tocotrienols, 3682 and 9378 mg/kg lipids, whereas the lowest amount was found in AA wild rice, 251 and 540 mg/kg of lipids, respectively. Brown rice samples differ in the amount of tocopherols; MGR contained 2565 mg/kg lipids, seven times the amount found in LGR. Additionally, the total amount of 4478 mg/kg tocotrienols in MGR was 20 times higher than that found in LGR (Fig. 2). The amounts of total tocopherols in the wild rice samples were higher than observed in standard refined rice bran oil 16–452 mg/kg [17], deodorized rice bran oil 297 mg/kg [18], and high-oryzanol rice bran oil 123 mg/kg [19]. Alpha tocopherol was the main isomer found in the wild rice lipids analyzed, with amounts ranging from 142 to 2537 mg/kg lipids. We also observed smaller amounts of β, γ, and δ-tocopherol isomers—224, 386, and 608 mg/kg lipids, respectively (Table 3). In the North American wild rice samples and in regular rice samples over 80% of total tocopherols were the α and δ isomers (Table 3). The total tocotrienols content of the wild rice samples were much higher than in rice bran (155–163 mg/kg) and brown rice powder (38–53 mg/kg) [20], and in a methanolic rice bran extract (220–460 mg/kg) [21]. Similarly to tocopherols, alpha-tocotrienol was the main isomer found in the wild rice samples; amounts in AA and NOW ranged from 370 to 9169 mg/kg lipids (Table 3). Other tocotrienol isomers, β, γ, and δ, were found at 92, 294, and 462 mg/kg lipids, respectively. However, the level of γ-tocotrienol was twice the level of the α isomer in LGR. MGR rice contained

Table 2 Sterol composition of wild and regular rice lipids (% of total sterols)[a]

Sterols	Wild rice							Standard brown rice	
	MNL	NOW	S	AA	FNM	MNGLR	MC	LGR	MGR
Campesterol	16.6 ± 0.2^{b}	14.9 ± 0.4^{a}	14.3 ± 0.2^{a}	16.4 ± 0.3^{b}	15.6 ± 0.2^{b}	51.7 ± 0.6^{d}	17.1 ± 0.5^{c}	14.2 ± 0.3^{a}	16.8 ± 0.2^{c}
Stigmasterol	5.5 ± 0.2^{b}	5.3 ± 0.2^{b}	5.8 ± 0.1^{b}	6.5 ± 0.3^{c}	6.5 ± 0.3^{c}	3.7 ± 0.1^{a}	5.8 ± 0.1^{b}	10.1 ± 0.2^{d}	10.4 ± 0.4^{d}
Clerosterol	1.9 ± 0.2^{a}	2.8 ± 0.1^{c}	4.6 ± 0.3^{d}	5.5 ± 0.2^{e}	4.4 ± 0.2^{d}	2.4 ± 0.1^{b}	1.9 ± 0.2^{a}	1.9 ± 0.1^{a}	2.9 ± 0.2^{c}
23-Dehydrositosterol	2.9 ± 0.2^{e}	2.1 ± 0.1^{c}	1.9 ± 0.2^{bc}	3.3 ± 0.2^{f}	1.4 ± 0.1^{ab}	1.1 ± 0.1^{a}	3.4 ± 0.1^{f}	2.4 ± 0.2^{d}	1.6 ± 0.1^{b}
β-Sitosterol	26.6 ± 0.5^{c}	29.7 ± 0.4^{e}	31.0 ± 0.5^{f}	32.5 ± 0. 6^{g}	32.5 ± 0.3^{g}	19.1 ± 0.4^{a}	26.7 ± 0.4^{c}	25.2 ± 0.4^{b}	28.8 ± 0.3^{d}
Δ^5-Avenasterol	9.0 ± 0.3^{e}	6.2 ± 0.2^{c}	8.5 ± 0.3^{d}	9.0 ± 0.2^{e}	11.7 ± 0.5^{f}	5.1 ± 0.2^{b}	9.5 ± 0.2^{e}	6.2 ± 0.1^{c}	4.1 ± 0.2^{a}
Gramisterol	3.1 ± 0.1^{c}	3.3 ± 0.1^{c}	3.2 ± 0.2^{c}	2.7 ± 0.3^{bc}	3.2 ± 0.1^{c}	1.8 ± 0.2^{a}	3.0 ± 0.2^{c}	2.4 ± 0.2^{b}	1.7 ± 0.1^{a}
Cycloartenol	12.2 ± 0.3^{g}	9.9 ± 0.3^{e}	10.1 ± 0.5^{e}	8.2 ± 0.4^{c}	7.2 ± 0.2^{b}	4.7 ± 0.2^{a}	11.3 ± 0.3^{f}	11.7 ± 0.3^{f}	9.0 ± 0.2^{d}
Δ^7-Avenasterol	3.5 ± 0. 2^{c}	3.7 ± 0.1^{c}	4.4 ± 0.1^{d}	3.5 ± 0.2^{c}	5.0 ± 0.1^{e}	1.7 ± 0.1^{a}	3.6 ± 0.1^{c}	3.7 ± 0.2^{c}	3.1 ± 0.2^{b}
24-Methylenecycloartanol	6.9 ± 0.3^{d}	6.5 ± 0.1^{d}	5.0 ± 0.2^{c}	4.0 ± 0.1^{b}	3.2 ± 0.2^{a}	3.6 ± 0.2^{a}	7.8 ± 0.3^{e}	14.0 ± 0.2^{g}	13.0 ± 0.4^{f}
Citrostadienol	3.8 ± 0.1^{e}	5.0 ± 0.2^{f}	3.3 ± 0.1^{d}	1.9 ± 0.2^{b}	1.6 ± 0.1^{b}	1.0 ± 0.1^{a}	3.3 ± 0.1^{d}	3.1 ± 0.2^{c}	4.9 ± 0.2^{f}
Others[b]	7.9 ± 0.3^{f}	10.5 ± 0.3^{g}	8.0 ± 0.3^{f}	6.4 ± 0.2^{d}	7.5 ± 0.3^{e}	4.2 ± 0.2^{b}	6.6 ± 0.3^{d}	5.2 ± 0.2^{c}	3.7 ± 0.3^{a}

Means in the same row followed by different superscript letters are significantly different ($p < 0.05$)

For sample abbreviations see Table 1

[a] Values are reported as mean ± SD from triplicate determination ($n = 3$)

[b] Total unidentified sterols as group

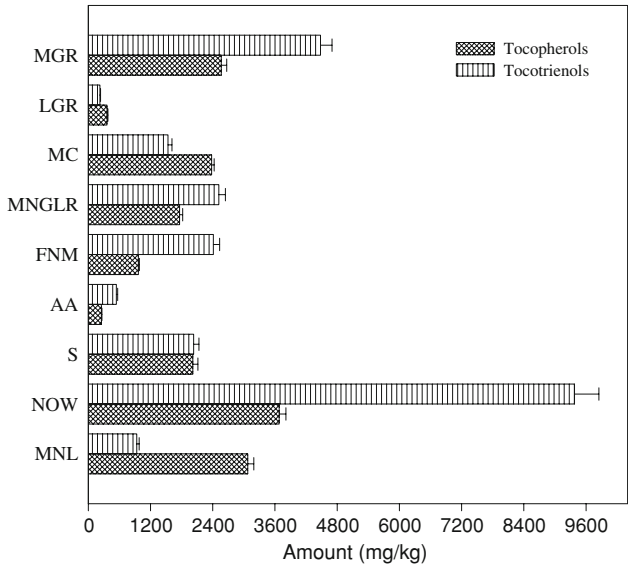

Fig. 2 Amounts of tocopherol and tocotrienol in wild and regular rice lipids. For sample abbreviations see Table 1

mainly α-tocotrienol, 93%, with very small amounts of γ-tocotrienol (Table 3). Published data related to the tocopherol, tocotrienols, and sterols content of wild rice lipids is lacking and comparison is not possible.

γ-Oryzanol

Gamma-oryzanol is a complex mixture of ferulic acid esters with sterols and triterpenic alcohols [22]. Total amounts of γ-oryzanols in analyzed lipids of the rice samples varied from 459 to 730 mg/kg in the North American wild rice and from 459 to 613 mg/kg in regular brown rice. The largest amount was observed in MNL and the lowest in NOW wild rice sample. S, MNGLR, and MC samples contained 524, 534, and 535 mg/kg, respectively (Fig 3). The amount of γ-oryzanols in wild rice lipids was higher than in regular rice bran oil (RBO), which is regarded as a rich source of oryzanol [20]. Rogers et al. [17] reported that the total amount of γ-oryzanol in three refined RBO from different manufacturers ranged from 510 to 787 mg/kg, whereas in two other samples the amounts found were below 150 mg/kg. The North American wild rice contains 1.5 times more γ-oryzanol than Brazilian rice bran oil, which contained 290 mg/kg oil [18]. Abidi and Rennick [19] reported lower amounts of oryzanol in a RBO (359 mg/kg), but much higher levels in high-oryzanol RBO (7435 mg/kg). In these RBO oils, cycloartanyl ferulate was identified as the main ester of γ-oryzanol. Results for the North American wild rice, and previously published data [17–19], suggest that γ-oryzanol content depends on rice origin, variety, and growing conditions. Gamma-oryzanol is known to have antioxidant and cholesterol-lowering properties, and wild rice could be recognized as potential health-promoting food containing nutraceuticals [23, 24]. Not only were differences between the concentrations of γ-oryzanols in the North American rice samples observed; disparity in the composition of sterol esters was also found. HPLC analysis led to separation of 6–10 different esters which were analyzed as a total γ-oryzanols.

Conclusion

The results of our study reveal that the lipids of the North American wild rice are an excellent source of linoleic and linolenic essential fatty acids; the latter, in particular, is present in unusually large amounts. These oils also contain large amounts of nutraceuticals such as phytosterols, tocopherols, and γ-oryzanol. The lipid composition suggests that the wild rice could be a good source of nutraceuticals with positive health benefits. Wild rice may well be

Table 3 Tocopherols and tocotrienols composition of wild and regular rice lipids (% within chromanol group)[a]

Chromanol	Wild rice							Standard brown rice	
	MNL	NOW	S	AA	FNM	MNGLR	MC	LGR	MGR
α-Tocopherol	69.5 ± 3.5	68.9 ± 3.4	81.1 ± 4.1	56.6 ± 2.8	52.8 ± 2.6	65.6 ± 3.3	70.7 ± 3.5	81.8 ± 4.1	72.1 ± 3.6
β-Tocopherol	6.5 ± 0.2	5.9 ± 0.3	7.6 ± 0.3	ND[b]	7.9 ± 0.4	8.3 ± 0.4	9.4 ± 0.5	0.2 ± 0.01	2.3 ± 0.1
γ-Tocopherol	4.3 ± 0.2	10.5 ± 0.5	1.9 ± 0.1	ND	10.8 ± 0.5	10.2 ± 0.5	7.0 ± 0.3	18.0 ± 0.9	11.5 ± 0.6
δ-Tocopherol	19.8 ± 1.0	14.7 ± 0.7	9.4 ± 0.5	43.4 ± 2.2	28.6 ± 1.4	15.9 ± 0.8	12.9 ± 0.6	ND	14.1 ± 0.7
α-Tocotrienol	76.9 ± 3.8	97.8 ± 4.9	77.3 ± 3.8	68.4 ± 3.4	91.4 ± 4.6	80.2 ± 4.0	85.6 ± 4.3	32.4 ± 1.6	93.4 ± 4.7
β-Tocotrienol	9.4 ± 0.4	0.7 ± 0.1	ND	ND	ND	1.7 ± 0.1	6.0 ± 0.2	ND	ND
γ-Tocotrienol	ND	ND	ND	ND	ND	ND	ND	67.6 ± 3.4	6.6 ± 0.3
δ-Tocotrienol	13.7 ± 0.7	1.5 ± 0.1	22.7 ± 1.1	31.6 ± 1.6	8.6 ± 0.4	18.1 ± 0.9	8.4 ± 0.4	ND	ND

For sample abbreviations see Table 1

[a] Values are reported as mean ± SD from triplicate determination ($n = 3$)

[b] Not detected

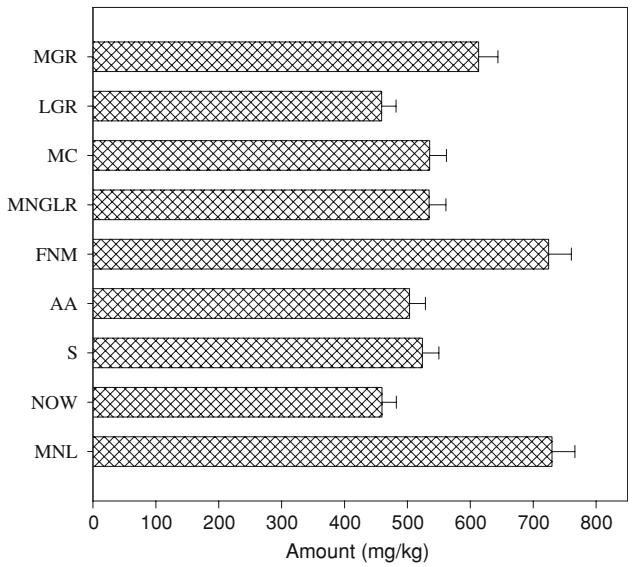

Fig. 3 Amounts of γ-oryzanol in wild and regular rice lipids. For sample abbreviations see Table 1

incorporated into our daily diet to improve nutritional value of our Western diet.

Acknowledgement We thank wild rice producers and distributors for facilitating the provision of the samples used for this study. This work was financially supported by a Alberta Value Added Corporation grant.

References

1. Oelke EA (1993) Wild rice: domestication of native North American genus. In: Janick J, Simon JE (eds) New crops. Wiley, New York, pp 235–243
2. Aiken SG, Lee PF, Punter D, Stewart JM (1998) Wild rice in Canada. New Canada Publication, Toronto
3. Zhai CK, Lu CM, Zhang XQ, Sun GJ, Lorenz KJ (2001) Comparative study on nutritional value of Chinese and North American wild rice. J Food Comp Anal 14:371–382
4. Hoover R, Sailaja Y, Sosulski FW (1996) Characterization of starches from wild and long grain brown rice. Food Res Int 29:99–107
5. Stevenson S (1988) Wild rice report 1987 – Northwestern Region of Ontario. Ontario Min Nat Res, Kenora
6. Oelke EA (1976) Amino acid content in wild rice (*Zizania aquatica* L.) grain. Agron J 68:146–148
7. Jenks AE (1901) The wild rice gatherers of the Upper Lakes. U.S. Department of Interior, Bur Amer Ethnol 9th Rpt 1899: 1015–1160
8. Johnson E (1969) Archaeological evidence for utilization of wild rice. Science 163:273–277
9. Folch J, Lees M, Stanley GHS (1957) A simple method for the isolation and purification of total lipids from animal tissues. J Biol Chem 266:497–509
10. American Oil Chemist's Society (AOCS) (1997) Official and recommended practices of the American Oil Chemist's Society, 5th edn. AOCS, Champaign
11. Rudzińska M, Kazuś T, Wąsowicz E (2001) Sterols and their oxidized derivatives in refined and cold pressed seed oils. Rośliny Oleiste 22:477–494
12. Anwar F, Przybylski R, Rudzinska M, Gruczynska E, Bain J (2008) Fatty acid, tocopherol and sterol compositions of Canadian Prairie fruit seed lipids. J Am Oil Chem Soc 85:953–959
13. Aizawa O, Saito Y, Nishi S, Koaze H (2007) Properties of the lipids and polyphenols in wild rice (*Zizania palustris* L.,) seeds. Res Bull Obihiro University 28:28–34
14. Przybylski R (2006) Cereal grain lipids. In: Shahidi F (ed) Nutraceutical and specialty lipids and their co-products. CRC Taylor & Francis, Boca Raton, pp 57–71
15. Schaefer EJ (2002) Lipoproteins, nutrition, and heart disease. Am J Clin Nutr 75:191–212
16. Jiang Y, Wang T (2005) Phytosterols in cereal by-products. J Am Oil Chem Soc 82:439–444
17. Rogers EJ, Rice SM, Nicolosi RJ, Carpenter DR, McClelland, Romanczyk LJ (1993) Identification and quantitation of γ-oryzanol components and simultaneous assessment of tocols in rice bran oil. J Am Oil Chem Soc 70:301–307
18. Ribeiro Pestana V, Zambiazi RC, Mendonca CRB, Bruscatto MH, Lerma-Garcia MJ, Ramis-Ramos G (2008) Quality changes and tocopherols and γ-oryzanol concentration in rice bran oil during the refining process. J Am Oil Chem Soc 85:1013–1019
19. Abidi SL, Rennick KA (2003) Determination of nonvolatile components in polar fractions of rice bran oils. J Am Oil Chem Soc 80:1057–1062
20. Aguilar-Garcia C, Gavino G, Baragano-Mosqueda M, Hevia P, Gavino VC (2007) Correlation of tocopherol, tocotrienol, γ-oryzanol and total polyphenol content in rice bran with different antioxidant capacity assays. Food Chem 102:1228–1232
21. Chotimarkorn C, Benjakul S, Silalai N (2008) Antioxidant components and properties of five long-grained rice bran extracts from commercial available cultivars in Thailand. Food Chem 111:636–641
22. Chen M-H, Bergman CJ (2005) A rapid procedure for analyzing rice bran tocopherol, tocotrienol and γ-oryzanol contents. J Food Anal 18:139–151
23. Graf E (1992) Antioxidant potential of ferulic acid esters. Free Radic Biol Med 13:435–448
24. Kim JS, Suh MH, Yang CB, Lee HG (2003) Effect of γ-oryzanol on the flavor and oxidative stability of refrigerated cooked beef. J Food Sci 68:2423–2429