Influence of UV Exposure on Phenolic Acid Content, Mechanical Properties of Bran, and Milling Behavior of Durum Wheat (*Triticum Durum* Desf.)

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Cereal Chem. 79(5):726–731

ABSTRACT

Durum wheat bran was exposed to UV radiation up to 48 hr and the changes in ferulic acid (FA) content in the peripheral parts of grain were measured. The treatment resulted in a 25% decrease in FA monomer and a 44% decrease in dehydrodiferulic acid (DHD) ester-linked to the cell-wall arabinoxylans. This reduction was partly explained by a significant increase of FA (30%) and DHD (36%) engaged in hot alkali-labile linkages. The results suggest that UV irradiation induced the formation of new cross-links between feruloylated arabinoxylan and lignin in the pericarp. The effects of UV treatment on bran mechanical properties and wheat milling behavior were investigated. UV irradiation for 15 hr increased the stress to rupture by 30% and decreased the extensibility of bran tissues by 54%. This stiffening was associated with an increase in bran friability during grinding. Although this effect was due in part to the hydrothermal history of the grain, chemical modification induced by UV significantly influenced the size reduction of bran particles, which can be explained by the modification of the mechanical properties of bran. Relationships between the organization of cell-wall polymers, the mechanical properties of tissues, and the behavior of wheat grain during milling were investigated.

Ferulic acid (FA) is an ubiquitous cereal constituent (Fincher 1976; Smart and O'Brien 1979; Wetzel et al 1988) bound by an ester linkage to some α-L-arabinose units of cell wall arabinoxylans (AX) (Smith and Hartley 1983). Two ester-linked FA monomers may undergo an oxidative coupling to induce AX cross-linking. This dimerization can be realized in various ways. Chemical agents (ferric chloride, ammonium persulfate) and various enzymatic systems such as peroxidase/H_2O_2 and laccase have been used to catalyze ferulate dehydrodimer formation (Crowe and Rasper 1988; Izydorczyk et al 1990; Figueroa-Espinoza and Rouau 1998). In addition, ultra violet (UV) irradiation is also known to induce phenolic acid dimerization. Due to the high degree of unsaturation, FA and *p*-coumaric acid constitute strong UV absorbers. Irradiation initiates phenoxy radical formation leading to *Z-E* isomerization (Graf 1992) and photodimerization (Morrison et al 1992; Turner et al 1993). The dimerization results from opening and subsequent cyclization of the double bond of the propenoyl side chain. The cyclodimers generated by this mechanism are called truxillic acid (head-to-tail) and truxinic acid (head-to-head). Their structure and molecular weight are thus different from dehydrodiferulic acid formed by oxidative coupling (Ford and Hartley 1989; Hanley et al 1993).

Considerable interest has been shown in the involvement of these compounds in the mechanical properties of plant cell wall. Many studies have shown the inhibitory effect of light on elongation growth. In cereal coleoptiles, white fluorescent light stimulates ferulate dimerization in cell walls and thereby increases the cell wall rigidity, resulting in limited cell extension (Tan et al 1992; Miyamoto et al 1994; Parvez et al 1996).

In the wheat grain, if different ferulic acid dehydrodimers have been already identified in the constituent tissues of bran (aleurone layer, testa and pericarp), no cyclodimers have been isolated (Lempereur et al 1998). Considering their involvement in the mechanical properties of some tissues, the FA dimer concentration in the external parts of the grain could constitute a determining factor in wheat milling behavior. Actually, the separation between semolina and bran during milling is based on difference of elasticity between endosperm and peripheral layers of grain (Chaurand et al 1999). The production of large bran particles allowed an easier separation based on sieving and decreased the ash content of both flour and semolina (Willm 1995). Consequently, modifications of bran mechanical properties could optimize the milling (Mabille and Abecassis 2001). The induction of ferulate cross-linking in bran layers by enzymatic oxidative treatments increased tissue resistance (Peyron et al 2001). Arabinoxylan cross-linking by UV irradiation could then be an alternative way to modify the mechanical properties of wheat bran.

The objective of this work was to modify the mechanical properties of the peripheral layers of wheat grain by inducing AX cross-linking. To induce such reticulation UV irradiation was used. The effects of UV toward cell-wall FA was studied in relation to the mechanical characteristics of irradiated tissues. In a second step, the influence of this treatment on wheat milling behavior (bran particle size and specific milling energy) was measured to advance the understanding of the involvement of bran mechanical properties in milling.

MATERIALS AND METHODS

Durum wheat (*Triticum durum* Desf.) used in this study was cv. Ardente grown in 1999 (Sud Céréales, Arles, France). Bran fractions were produced from conventional milling in a semi-industrial semolina production mill (150 kg/hr) at the Cereal Technology and Agropolymer Unit (INRA-Montpellier; France).

Germ, dorsal, and ventral parts of the grain were sandpapered to a plane form. After 10 hr of immersion in distilled water, the disk was divided in two parts by incising the crease. Each part was soaked again in water for 2 hr and the endosperm was removed using a scalpel. Two strips were isolated on each lateral face of the grain. After rinsing, the two strips were dried between two slides to impose a plane shape. The strips obtained were ≈6 mm length and 2–3 mm width.

Bran milling fractions, bran strips, and wheat grains were exposed to UV light (HPK 125W, Philips) in an air-conditioned room (20°C, 65% rh). Samples were arranged in a monolayer and exposed to 1,739 J/cm^2 total energy and 772 J/cm^2 UV energy (<420 nm). The change in FA concentration was measured during 48 hr of exposure (5 min, 30 min, 1 hr, 6 hr, 24 hr, and 48 hr).

To produce a control sample with a drying effect similar to UV irradiation, a wheat grain sample was dried by exposure to infrared (IR) light (Sartorius, MA 30) for 80 min at 50°C to decrease the sample moisture content to 8.5% (moisture content of grains after 15 hr of UV irradiation).

Bran samples were immersed for 15 min in distilled water. After centrifugation (10 min, 700 × *g*) the supernatant was collected, and the WEAX concentration was determined according to the method of Rouau and Surget (1994).

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Publication no. C-2002-0806-03R.

Analysis of Esterified Phenolic Acids

Wheat bran fractions were ground (freezer-mill 6570, Avantec, France) and freeze-dried before FA extraction. Ground samples (80 mg) were saponified for 2 hr in the dark with 2*M* NaOH (10 mL) at 35°C. Internal standard, 3-(3,4,5 trimethoxy)phenyl-2-propenoic acid (TMCA) was added (50 µg), and the solution was adjusted to pH 2 with 4*M* HCl. Phenolic acids were extracted twice with diethyl ether (5 mL). Ether phases were evaporated in the presence of argon. The dry extract was dissolved in methanol (MeOH) and water (50:50, v/v), filtered (0.45 µm), and analyzed by RP-HPLC using a 5-µm C_{18} column (Alltech, Deerfield, MI) (250 × 4.6 mm). Linear gradient elution was performed by acetonitrile and sodium acetate buffer 0.05*M* (pH 4.0) at 1 mL/min at 35°C, from 15/85 to 35/65 in 30 min, from 35/65 to 60/40 in 0.5 min, from 60/40 to 15/85 in 4.5 min, and maintained at 15/85 for 5 min. UV detection was made at 280 and 320 nm using a photodiode array detector (996, Waters, Milford, MA). Standard *(E)*-FA, *(E)*-*p*-coumaric acid, and *(E)*-sinapic acid were purchased from Sigma Chemical Co. Standard *(Z)*-FA was issued from a solution of *(E)*-FA exposed to UV light for 30 min. Standard dehydrodimers (DHD) were kindly supplied by J. Ralph from U.S. Dairy Forage Research Center USDA-ARS and Department of Forestry, University of Wisconsin, Madison (Ralph et al 1995). Abbreviations: 8,5'-diFA = *(E,E)*-4,4'-dihydroxy- 3,5'-dimethoxy-β,3' -bicinnamic acid; 8,5'-benzofuran = *trans*-5- [(E)-2-carboxyvinyl)]-2-(4-hydroxy-3-methoxy -phenyl)-7-methoxy- 2,3-dihydrobenzofuran- 3-carboxylic acid; 8-O-4'-diFA = *(Z)-β-* {4-[*(E)*-2 carboxyvinyl]- 2-methoxy-phenoxy}-4-hydroxy-3-methoxycinnamic acid; 5-5'-diFA = *(E,E)*-4,4' – dihydroxy- 5,5'-dimethoxy-3,3'-bicinammic acid; TMCA = 3-(3,4,5 trimethoxy) phenyl-2-propenoic acid. Response factors relative to TMCA at 320 nm were *(E)*-FA, 0.57; *(Z)*-FA, 1.61; *(E)*-*p*-coumaric acid, 0.59, *(E)*-sinapic acid, 1.48; 5,5'-diFA, 0.60; 8,5'-diFA, 1.07, 8,5'-benzofuran diFA, 1.28; 8-O-4'-diFA, 1.23 (Saulnier et al 1999). Standard photodimers were prepared from a mixture dissolved in MeOH then evaporated under argon. The dried residues were exposed to UV light for 12 hr. The products were dissolved in MeOH and water (50:50, v/v) before analysis by HPLC and identified according to UV absorption spectra (Waldron et al 1996).

Analysis of Ether-Linked Phenolic Acids

Ground samples (50 mg) were digested for 2 hr with 4*M* NaOH (5 mL) at 170°C. After addition of TMCA, released phenolic acids were extracted and quantified as described above. Ether-linked phenolic concentration was obtained by subtracting the amounts of phenolic acids released by alkali at 35°C from the amounts at 170°C.

Mechanical Properties Measurements

Mechanical tests were performed using dynamic mechanical thermal analysis equipment (DMTA Mk III E, Rheometrics Inc., Piscataway, NJ). The strip moisture content was stabilized at ≈17% db (a moisture content generally used in wheat milling) by setting the relative humidity at 78% and the temperature at 30°C. Humidity control was achieved according to the principle of water vapor saturation at different temperatures (Redl et al 2000). The furnace was flushed with air that was bubbled through water at 25.2°C. The furnace temperature was set at 30°C to establish desired humidity:

$$\%\mathrm{HR} = \frac{p_{H_2O}(30°C)}{p_{H_2O}(25.2°C)} \times 100 = 78$$

Sample equilibration was measured by a time sweep test at imposed strain (0.01%) (total time = 10 min; frequency = 1.59 Hz). The stability of elastic modulus (E') was used as an indicator of the sample equilibration.

Uniaxial tension tests were performed at a rate of 0.05 mm/sec until disruption of the sample. Stress-strain curves were used to determine mechanical parameters of maximum tensile strain (ε_{max}), stress of rupture (σ_{max}), elastic modulus (E'), and energy of rupture (W_{max}). Tension tests were performed on at least 10 bran strips. Test where failure did not occur in the center of strip were discarded.

Milling Tests

Milling tests were made on 100 g of wheat grains using a micromill equipped with a torque transducer allowing online measurements of mechanical energy consumption (Pujol et al 2000). The initial moisture content of wheat samples was measured and grains were tempered 24 hr (including 1 hr agitation) to reach 17% (db) by adding water before milling.

Tests were performed by three successive grinding stages (B1, B2, B3) as indicated in the milling diagram (Fig. 1). The corrugated roll configuration was dull-to-dull with a fast roll speed of 500 rpm, a roll differential speed of 2.5, a roll gap of 0.70, 0.15, and 0.04 mm for successive grinding stages (B1, B2, B3), and a linear mass feed rate of 290 kg/hr/m.

According to the roll gap, the functions of the three grinding stages were different. The first grinding (B1) was a break system to open the grain. The second grinding (B2) corresponded roughly to a detaching operation to scrape semolina particles free of bran. The third roller milling (B3) reduced the large endosperm particles to a uniform smaller size. Particle size distribution was established using a series of seven square-meshed sieves (4, 3.15, 2, 1, 0.71, 0.45, and 0.2 mm) under rotary agitation (rotex, Tripette & Renaud,

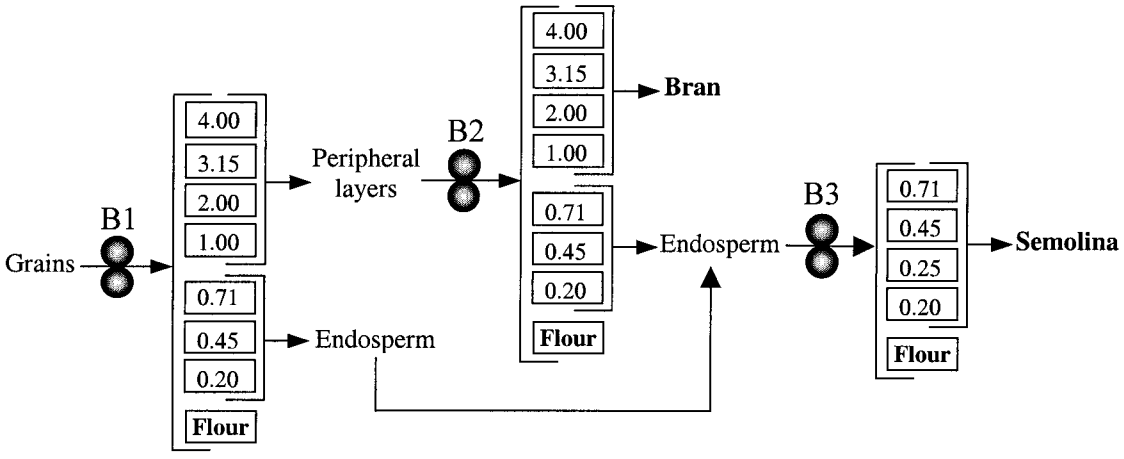

Fig. 1. Diagram of milling test process.

Paris). Each oversized fraction was then weighed to establish the particle size distribution expressed by the D_{50} value (median particle diameter).

RESULTS AND DISCUSSION

Phenolic Acid Composition of Wheat Bran

Alkali treatment of wheat bran released a large array of phenolic compounds under monomer or dimer form. The total concentration of phenolic acids present in wheat bran was 4.9 mg/g of dry matter (DM) after saponification at 35°C and 6.1 mg/g DM after 170°C alkali treatment. These values were noticeably higher than the quantity reported wheat bran studies (*Triticum aestivum* L.) (Pussayanawin et al 1988; Sanchez et al 1991). *Trans*-ferulic acid (*(E)*-FA) was the major component and accounted for 65% of the detected phenolic acids. *(E)*-ferulic, *(E)*-sinapic and *(E)-p*-coumaric acids were detected in low amounts (0.23, 0.30, and 0.16 mg/g of bran, respectively). Various forms of ferulic acid dimers were extracted. 8,5'- Benzofuran and 8-O-4'-diFA, were the major forms of ferulate dehydrodimers (1.15 and 0.92 mg/g of bran, respectively) but 5,5-' and 8,5'-diFA forms also occurred in low amounts (0.49 and 0.30 mg/g of bran). No cyclodimer was observed on the elution profile, demonstrating that natural photodimerization of FA or *p*-coumaric acid did not occur in wheat bran layer.

Saponification of Phenolics in UV-Irradiated Wheat Bran

The changes in FA composition of wheat bran were measured during 48 hr of irradiation. As described earlier (Towers and Yamamoto 1985; Graf 1992), UV irradiation induced *E-Z* isomerization of FA (Fig. 2A). After only 1 hr of reaction, 22.5% of *(E)*-FA was converted into *(E)*-FA. Beyond 1 hr of reaction, the rate of isomerization slowed down progressively until a threshold was reached at 6 hr. The final equilibrium ratio was 67% *(E)*-FA and 33% *(Z)*-FA. This ratio was similar to that reported by Fenton et al (1978) after two weeks of light exposition of a FA solution.

Concurrently, a decrease in measurable FA monomer occurred without production of dimers. During the irradiation, the total content of FA decreased by 25% without any formation of cyclodimers, showing that no photochemical coupling occurred. In addition, the whole dehydrodimer concentration underwent a decrease that paralleled that of *(E)*-FA (Fig. 2B). The four major ferulate dehydrodimers were partly consumed during the UV treatment and their mean total content decreased by 44% after 48 hr of irradiation.

A possible explanation for this loss of measurable FA and DHD after cold alkali extraction was their binding to other cell-wall constituents, and the most probable hypothesis is that the FA was chemically incorporated into the lignin. Such linkages have already been identified in wheat straw and internode (Scalbert et al 1985; Iiyama et al 1990). Evidence of heteroxylan-lignin association has been also established in the cell wall of maize bran (Lapierre et al 2001). In wheat grain, the lignin is particularly concentrated in the inner pericarp and the seed coat at concentrations of 2.8–7.2% DM, depending on the analytical method (Ring and Selvendran 1980; Schwarz et al 1988). It is possible that UV irradiation induced the formation of ferulate-lignin covalent linkage by nonenzymatic radical coupling. According to Iiyama et al (1994), this linkage implies the FA etherification at the C-8 position of the propanoid side of the lignin units (coniferyl and sinapyl alcohols). In addition, although DHD coupled at C-8 (8,8'-; 8,5'- and 8-0-4'-diFA) the propensity to copolymerize with lignin units was lower than 5,5'-diFA, but it has been demonstrated that ferulate monomer and all forms of dimers are able to form ether linkages with lignin (Grabber et al 2000).

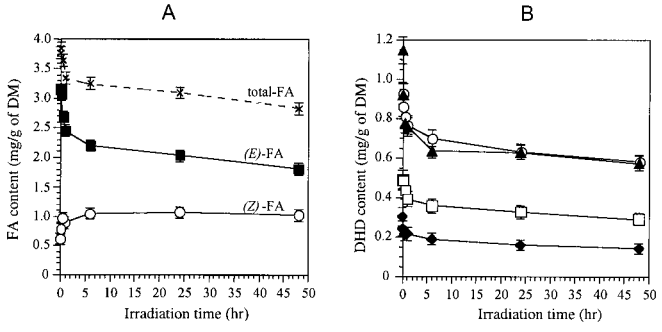

Fig. 2. Changes in ferulic acid (**A**) and dehydrodiferulic acid (**B**) content of wheat bran during UV irradiation. (◆) 8,5'-diFA = *(E,E)*-4,4'-dihydroxy-3,5'-dimethoxy-β,3'-bicinnamic acid; (○) 8-O-4'-diFA = *(Z)*-β- {4-[*(E)*- 2 carboxyvinyl]-2-methoxy-phenoxy}-4-hydroxy-3-methoxy-cinnamic acid; (▲) 8,5'-benzofuran = *trans*-5-[*(E)*-2-carboxyvinyl)]-2-(4-hydroxy-3-methoxy -phenyl)-7- methoxy- 2,3-dihydrobenzofuran-3-carboxylic acid; (□) 5-5'-diFA = *(E,E)*-4,4' –dihydroxy- 5,5'-dimethoxy-3,3'-bicinammic acid; TMCA = 3-(3,4,5 trimethoxy)phenyl-2-propenoic acid.

High Temperature Alkali Liberation of Phenolics in UV-Irradiated Wheat Bran

An alkali treatment at 170°C allowed to release ester-linked and ether-linked phenolic acids but released also some other unknown compounds. The bran content in ether-linked phenolic acids was determined as the difference between saponified and high-temperature-extracted phenolics (Fig. 3).

After 15 hr of UV irradiation, the content of ether-linked *(E)*-FA was 30% higher than in the control with a total concentration of FA (*(E)+(Z)*) similar in the two bran samples. This result may explain the decrease in saponifiable FA along the UV irradiation.

On the other hand, the content of measured ether-linked DHD did not compensate for the loss of saponified DHD during the irradiation. 8,5'-diFA was the only DHD form significantly more released from the irradiated bran than from the control (+37%). It should be noted that the high-temperature alkali treatment damaged some dehydrodimers with an ether linkage in their structure. The hydrolysis of 8-O-4' dehydrodimer form led to the release of monomer FA and the 8,5'-benzofuran form was converted into the noncyclic 8,5'-form. This led to an underestimation of the DHD involved in UV-induced linkages.

In addition, it has been established that such a reaction may occur only with mono-lignols and not with preformed lignin polymers (Ralph et al 1995). This suggests that ferulate (monomers and

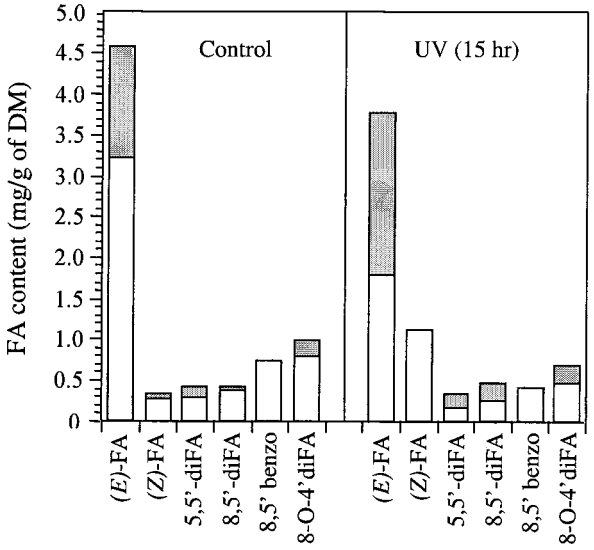

Fig. 3. Content of ester-linked (open) and ether-linked phenolic acids (shaded) in control and 15 hr-irradiated wheat bran.

dimers) esterified to AX may constitute an initiation site for lignification. Consequently, if UV irradiation initiated new covalent cross-links between lignin and AX in the cell wall of a mature tissue, the FA-monolignol bonds were distinct from those naturally established during cell-wall lignification.

Effect of UV Irradiation on AX Solubility

The degree of AX cross-linking in wheat bran is much higher than in the endosperm, which can explain the low bran WEAX content (1.38% DM). WEAX content of bran samples was measured during 48 hr of UV irradiation (Fig. 4). A significant decrease (50%) in AX solubility during the first hour of UV exposure suggested the establishment of new AX cross-linking. Beyond the first hour, AX solubility increased slowly until reaching a higher value than the initial solubility. This result suggests a depolymerization of AX chains. UV radiation can induce a photolysis of water molecule leading to the release of hydroxyl radical ($OH^{\cdot}$). This radicals are extremely reactive molecules able to degrade polysaccharides by cleavage of covalent linkages (Halliwell and Gutteridge 1989; Schweikert et al 2000). Cleavage of glycosidic bonds must occur randomly in the chains so as to induce a constant increase in the AX solubility. Alternatively, further oxidation of ferulate moieties could result in partial cross-linking breakdown leading to increased AX chain extractability.

Mechanical Properties of UV-Irradiated Bran

The experiments were performed on samples irradiated during 15 hr compared with untreated controls. With this exposure time, the FA cross-linking was maximum and the AX degradation remained low.

Traction tests were made until the bran strips ruptured. The influence of UV irradiation was determined from rupture characteristics elastic modulus (*E'*), maximum stress of rupture (σ_{max}), maximum tensile strain (ε_{max}), and rupture energy (W_{max}).

Results for the two sets of samples (Table I) showed UV-irradiated samples presented elastic modulus values (*E'*) 4× higher than control samples, indicating an increase in the material stiffness. Maximum tensile strain (ε_{max}) underwent a 54% decrease in the UV-treated sample, pointing out a reduction in extensibility. The material became more elastic and fragile which constitutes a loss of plasticity. Thus, the UV irradiation produced a transition from elastoplastic to elastic behavior of material. Therefore, it is possible that the connections between polymers induced by the UV irradiation prevent their sliding and reorientation during the material deformation. This reduction of polymer mobility in the cell wall network could then explain the loss of plasticity.

TABLE I
Effect of UV Irradiation (15 hr) on Mechanical Properties of Wheat Bran Strips[a]

	Control	UV Irradiated
Strain to rupture (ε_{max}, %)	16.60 ± 0.55	7.56 ± 0.94***
Stress to rupture (σ_{max}, $\times 10^7$ Pa)	1.61 ± 0.23	2.30 ± 0.41*
Elastic modulus (*E'*, $\times 10^7$ Pa)	1.01 ± 0.14	4.43 ± 0.15**
Rupture energy (W_{max}, kJ/mm^3)	2.49 ± 0.36	2.31 ± 0.32 ns

[a] *, **, *** significant at $P < 0.05$, $P < 0.01$, $P < 0.001$, respectively; ns, nonsignificant.

In addition, a slight increase of stress of rupture value (σ_{max}) was observed on irradiated sample. This increase indicates that the force exerted per unit of volume, necessary to disrupt the material, was significantly higher for irradiated tissues. However, due to simultaneous increase in σ_{max} value and decrease in ε_{max} value, UV treatments did not significantly modify the energy of rupture (*W)* of the bran.

These modifications of mechanical properties support the formation of new cross-links between hemicellulose and lignins during the UV irradiation. The covalent linkages involving cell-wall polymers appeared to participate both to the extensibility and the strength of tissues. These support the existence of a relationship between bran friability and cell-wall polymer organization. Considering the implications of mechanical properties of bran in milling, this may be a relevant factor for the determination of wheat milling ability.

Milling Tests

The moisture content and the hydration history of the grain are determining factors in wheat milling behavior. To determine the effect of the UV irradiation on milling performance, it was necessary to take into account the drying effect of the UV exposure. Irradiation for 15 hr induced a 30% loss of the water content of the grain (final moisture content 8.5%, db). Such a drying could weaken tissues (developing cracks during drying), resulting in a decrease in the mean particle size after milling. To distinguish between the effect of AX cross-linking and the influence of grain drying from UV irradiation, results of milling tests performed on UV-irradiated grains were compared with an untreated control (12.4%, db) and with an IR-dried sample (80 min, 50°C), whose the moisture content was also reduced to 8.5%. After the treatments, the three grain samples were stabilized at 16%, db, for the milling.

At the B1 grinding stage, the particle-size distribution and the specific milling energy revealed significant statistical differences according to grain pretreatment (Table II). The UV irradiation and

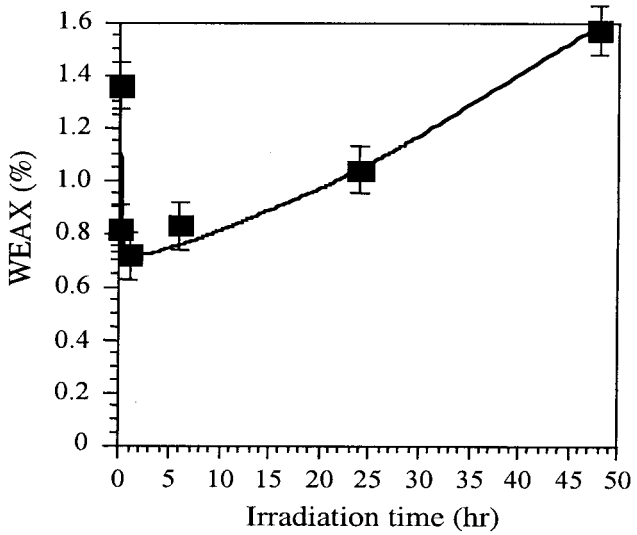

Fig. 4. Changes in AX solubility during UV irradiation.

TABLE II
IR Drying (80 min at 50°C) and UV Irradiation (15 hr) on Bran Particle Size and Specific Milling Energy (Et) at Three Grinding Stages

	B1			B2			B3	
	D_{50} (mm)[a]	% Particles > 1 mm	Et (kJ/kg)	D_{50} (mm)	% Particles > 1 mm	Et (kJ/kg)	D_{50} (mm)	Et (kJ/kg)
Control	0.90	71.20 ± 0.60	22.37 ± 0.16	0.41	44.10 ± 0.40	29.36 ± 0.08	0.16	11.15 ± 0.16
IR	0.86	67.30 ± 0.10	19.52 ± 0.09	0.38	37.20 ± 0.20	25.53 ± 0.12	0.17	11.43 ± 0.16
UV	0.81	62.70 ± 0.7	18.06 ± 0.04	0.34	32.50 ± 0.20	22.19 ± 0.10	0.16	11.80 ± 0.16

[a] Median particle diameter.

IR drying were responsible for a 10.0 and 4.4% decrease, respectively, in the D_{50} values leading to a reduction (11.9 and 5.4%, respectively) in the proportion of large particles (>1 mm). In addition, significant decreases in milling energy requirements were measured on UV-irradiated and IR-dried samples (19.2 and 12.7%, respectively).

Similar results were observed at the B2 grinding stage. UV irradiation and IR drying resulted in decreases of 27.2 and 15.9%, respectively, of the large particle, and 24.0 and 13.0% reduction of milling energy requirements. Considering that these two grinding stages affected the bran fraction, the concomitant reduction of particle size and decrease of milling energy confirm the increase in bran friability induced by the UV irradiation. However, this UV effect can also be assigned to a combination of drying and chemical action. Results obtained from an IR-dried sample showed that the decrease in particle size and milling energy from the UV treatment was partly (≈45%) due to a drying effect.

On the other hand, no significant modification of the particle size and specific milling energy was observed after the B3 stage. As previously explained, this stage constituted a reduction of large endosperm fragments into flour and semolina particles. Considering the absence of bran particles in this fraction, this result showed that the effect of UV treatment was probably limited to the external layers of grain, where phenolic compounds constituted the preferential targets of the treatment.

The mechanical properties study indicates that UV irradiation produces an increase of tissue rigidity (elastic modulus) and a decrease of extensibility without significant modification of rupture energy. It is difficult to establish a unique relationship between the traction force exerted on isolated bran layers and the action of mill crushing-rollers applied on whole grains. However, due to the inertia of the crushing rollers, the force exerted on the grain exceeded the rupture stress of bran layer and the grinding operation would be then equivalent to a fixed force stress. Consequently, the size of bran particles produced by the grinding would be more related to the extensibility than to the strength of grain envelopes. The size reduction of bran particles observed in the UV-irradiated sample would be more in agreement with the decrease in bran extensibility measured during the traction tests than with the increase of elastic modulus.

In addition, if a slight decrease in the rupture energy of bran was measured during micro-mechanical tests only, a significant reduction in the milling energy with UV-irradiated sample was noted. The absorption of water by bran layers during the grain conditioning could be different for both samples. The formation of UV-induced cross-linking between cell-wall polymers could produce variations in the water distribution within the cell wall that led to a modification of tissue toughness and a reduction of grain milling energy. Moreover, the high strain rate applied on the bran layer by the crushing roller during the grinding could modify rheological behavior of a plastic material, leading to increase in both stress and energy to rupture. Indeed, whereas an elastic material is insensitive to the variation of strain rate, the increase of strain rate increased stress to rupture of a plastic material (Ferry 1980). Consequently, during the grinding, the rupture energy of untreated bran layer could be higher than the irradiated layer whose the behavior became elastic during the treatment.

The results suggest the occurrence of a close relationship between cell-wall architecture of external layer of the grain and the milling behavior of durum wheat. The influence of UV irradiation on the mechanical properties of bran layers is to decrease tissue extensibility and increase bran friability during milling through induction of new interactions between polysaccharides into the cell wall.

CONCLUSIONS

UV irradiation induces either an isomerization or a photodimerization of ferulic acid. This study demonstrated that other reactions could occur in lignified cell walls. UV treatment of wheat bran layers produced new alkali-labile linkages, implying FA esterified to arabinoxylan chains. However, UV-catalyzed linkages between FA and lignin units have not been formally identified. The modifications of bran mechanical properties induced by the irradiation support the possibility that such connections were formed. The rigidification of irradiated tissues measured by micro-mechanical tests argues for a strengthening of the cell-wall polysaccharides network.

In addition, milling tests performed with a micromill demonstrated the effects of this modification of the cell-wall architecture during wheat milling. Strengthening of peripheral layers of the grain produced by UV-radiation resulted in an increase in bran friability and bran reduction to smaller particles during milling. This implies the influence of polymer organization in pericarp and aleurone cell walls on wheat milling properties. Consequently, our results suggest that the content of covalent phenolics cross-links involving hemicelluloses and lignins may constitute a new basis for assessing durum wheat milling quality.

ACKNOWLEDGMENTS

This study was carried out in the framework of the "Aliments Qualité Sécurité" program focusing on the semolina value of durum wheat with the financial support of ONIC (Office National Interprofessionnel des Céréales) and with the assistance of CFSI (Comité Français de la Semoulerie Industrielle). We thank A. Surget for her technical assistance.

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[Received August 6, 2001. Accepted April 25, 2002.]