Dans les revues à comités de lecture en 1998 et 1999

CASTELLO P., POTUS J., BARET J.L., NICOLAS J. (1999). **Effect of mixing conditions and wheat flour composition on the lipid hydrolysis and oxidation levels in the presence of exogenous lipase**. *Cereal Chem.*, **76 (4)**, 476-482. **Abstract** : The lipid profiles of wheat flour doughs containing exogenous lipase were studied under different mixing conditions using a microscale mixer. An experimental design comparing the effects of dough water content (52-68%), the speed of mixing (50-100 rpm), and the mixer temperature (18-32°) showed that the hydrolysis levels were poitively influenced by temperature and speed of mixing and negatively influenced by water content. The position effect of temperature was enhanced both by high speed mixing and low water content. The lipid oxidation levels were positively influenced by the speed of mixing and negatively influenced by the water content. The positive effect of temperature on the oxidnation levels was less important. A series of experiments conducted with different types of industrial and semi-industrial mixers with equal concentrations of lipase added to the dough showed large differences among the rates of lipid hydrolysis and oxidation. However, the mixing conditions proposed by bakers to obtain doughs with similar handling properties led to similar dough lipid profiles. Sodium chloride did not change the lipid profile when added to dough. Conversely, calcium chloride promoted a large increase of lipid hydrolysis and oxidation due to its activation of lipase activity. Addition of yeast increased the lipid hydrolysis and slightly decreased lipid oxidation.

RAKOTOZAFY L., MACKOVA B., DELCROS J.F., BOUSSARD A., DAVIDOU S., POTUS J., NICOLAS J. (1999). **Effect of adding exogenous enzymes on the activity of three endogenous oxidoreductases during mixing of wheat flour dough**. *Cereal Chem.*, **76**, 213-218. **Abstract** : The behavior of different exogenous enzymes (soybean lipoxygenase [SLOX], horseradish peroxidase [HPOD], catalase from bovine liver [BCAT], and glucose oxidase [GOX] from *Aspergillus niger*) added to dough was studied during mixing. The effect of adding these exogenous oxidoreductases on the activity of three oxidative enzymes present in wheat flour (lipoxygenase [WLOX], peroxidase [WPOD], and catalase [WCAT]) was examinated . Proper assay conditions were established to differentiate between added WLOX, WPOD, and WCAT and the corresponding activities present in wheat flour. For doughs with added SLOX, an immediate loss of extractable SLOX (»40%) was observed which remained constant during further mixing. When compared with the control dough, addition of SLOX decreased the losses in WLOX and WCAT activities, whereas WPOD activity was unaffected. With doughs supplemented by HPOD, an immediate loss of 20% in the HPOD activity was observed which did not change after 20 min of mixing. Compared with control dough, addition of HPOD did not affect the behavior of WLOX and WPOD, whereas a slight decrease in the WCAT losses was observed. Addition of BCAT to the dough did not change the behavior of WLOX and WPOD, whereas the losses in WCAT were less rapid. Half of the extractable activity of BCAT was lost at the beginning of mixing with no change during further mixing. For doughs supplemented with GOX, 25% of the GOX activity was lost in the first 5 min of mixing and an additional loss of 20% was observed after 20 min of mixing. Compared with dough without GOX, addition of GOX decreased the losses in WLOX, whereas losses in WCAT and WPOD increased. Glucose and ferulic acid were also added to doughs supplemented with GOX. Added glucose decreased the losses in GOX and WLOX and did not change the behavior of WPOD and WCAT during mixing. Addition of ferulic acid promoted a slight increase of the losses in WLOX and WCAT and almost no change for GOX and WPOD.

BILLAUD C., KàHLER B., BOIVIN P., NICOLAS J. (1999).**Polyphenolic substrates of cationic and neutral / anionic peroxidases from barley and malt using a chronometric method for the determination of POD activity.** *J. Food Biochem.*, **23**(5), 519-545. **Abstract**: 4-Methylcatechol, phenolic acids from the benzoic and cinnamic series, flavan 3-ols and L-tyrosine were tested to determinate the catalytic behavior of barley peroxidases (POD) at the expense of hydrogen peroxide. A chronometric assay using L-ascorbic acid was described for determining. the peroxidatic activity of basic and neutral/anionic enzymic fractions. The effects of hydrogen donors, H_2O_2, and Ca^{++} concentrations. and pH were studied to set maximal conditions for POD measurement. The sensitivity to endogenous phenolic compounds [ferulic and p-coumaric acids, (+) catechin] along with caffeic acid for POD fractions was investigated and compared with their response versus guaiacol. Under the conditions tested, syringic and sinapinic acids as well as L-tyrosine were very weakly oxidized by POD from barley, whereas ferulic and caffeic acids were rapidly transformed. Levels of POD activity extracted from barley, green malt and kilned malt crude extracts were thereafter compared.

BILLAUD C., LOUARME L., NICOLAS J. (1999). **Comparison of peroxidases from barley kernel (*Hordeum vulgare* L.) and wheat germ (*Triticum aestivum* L.) : Isolation and preliminary characterization**. *J. Food Biochem.*, **23**(2), 145-172. **Abstract**: Peroxidases (PXDs) of crude extracts from barley and wheat germ were separated, partially purified using salt fractionation, ion-exchange and hydrophobic interaction chromatographys, and their properties examinated. Barley and wheat germ PXDs contained basic, neutral, and anionic isoforms as confirmed by isoelectric focusing. Toyopearl-Bu 650 M chromatography resolved PXDs into 4 cationic fractions. Chromatography of wheat germ extract on CM-Sepharose isolated an anionic and a neutral fraction. Following chromatography on Con A-Sepharose, enzymes from both cereals showed differences in their elution properties. Optimum pH ranges were 4.0-5.5 (barley) and 5.3 to > 6.3 (wheat germ) and PXDs reacted differently under acidic or basic conditions. Their catalytic behavior in the presence of Ca^{2+} also differed. The reaction kinetics of PXDs were of Michaelian type with a ping-pong mechanism and the Km values for guaiacol oxidation in the presence of H_2O_2 varied from one enzymic group to another.

RICHARD-FORGET F., AMIOT M.J., DE RIGAL D., NICOLAS J. (1999). **High-performance liquid chromatography analysis of oxidative degradation of phenolic compounds in model solutions.** *Seminars Food Anal.*, **4 (1)**, 3-12. **Abstract** : The oxidation of phenolic compounds into their corresponding o-quinones catalyzed by polyphenol oxidase (PPO) is now well documented. However, in spite of their considerable significance with regard to browning, few reports of non-enzymic secondary reactions involving o-quinones are available. Also, few papers have been devoted to the possible involvement of peroxidase (POD) in enzymic browning. Based on studies performed in model solutions, this paper describes (i) 2 main evolution pathways of o-quinones, i.e. hydroxylation by addition of water and polymerization, (ii) the occurrence of coupled oxidations involving two phenols and the nature of some copolymers, and (iii) the occurrence of secondary reactions between o-quinones and trans-**b**-carotene, leading to phenol regeneration and carotene isomerization. In addition, studies in model solutions revealed 2 mechanisms consistent with an effective implication of POD in enzymic browning: (i) the generation of H_2O_2 during PPO oxidation and its further use by POD and (ii) the use of quinonic forms by POD as peroxide substrate.

RICHARD-FORGET F., CERNY M., FAYAD N., SAUNIER T., VAROQUAUX P. (1998).**Isolation and characterization of a " quinone-trapping " substance from a crude *Carica papaya* protein preparation.** *Int. J. Food Sci. Technol*., **33** , (3), 285-296. **Abstract** : The oxidation. of different phenols [4-methylcatechol, chlorogenic acid, (-)-epicatechin and (+)-catechin] by endive polyphenol oxidase (PPO) was investigated in the presence of an extract from *Carica papaya*. The occurrence of cysteine and another 'quinone-trapping' substance in the extract was demonstrated. The unknown substance was purified, as a 4-methylcatechol conjugate form, by a combination of Bio-gel P2 chromatography and semipreparative high-performance liquid chromatography (HPLC). Use of liquid chromatog./tandem mass spectroscopy (LC-MS/MS) equipment and an amino acid analyzer allowed the authors to identify this agent as a dipeptide cysteine-glutamic acid, com. available as **g**-Glu-Cys. **g**-Glu-Cys formed one adduct compound with 4-methylcatechol and chlorogenic acid, and two with the flavan-3-ols. The thiol adducts were not substrates for endive PPO but, in the case of the 4-methylcatechol conjugate, they acted as competitive PPO inhibitors.

CASTELLO P., JOLLET S., POTUS J., BARET J.L., NICOLAS J. (1998). **Effect of exogenous lipase on dough lipids during mixing of wheat flours**. *Cereal Chem.*, **75 (5)**, 595-601. **Abstract** : In control dough, endogenous wheat lipase was inactive, because the triacylglycerol (TAG), 1,2-diacylglycerol (DAG1,2), and 1,3-diacylglycerol (DAG1,3) fractions of nonpolar lipids were not affected by mixing. Conversely, the free fatty acid (FFA) and monoacylglycerol (MAG) fractions decreased, mainly due to the oxidation of polyunsaturated fatty acids (PUFA) catalyzed by wheat lipoxygenase. Addition of exogenous lipase to flour (15 lipase units [LU] per g of dry matter) resulted in substantial modification of nonpolar lipids during dough mixing. Due to the 1,3 specificity of the lipase used in this experiment, the TAG and DAG1,3 fractions decreased, whereas the MAG and FFA fractions increased. The DAG1,2 fraction increased at the beginning of mixing and decreased after 40 min of mixing. Moreover, part of the PUFA released by lipase activity was oxidized by wheat lipoxygenase, resulting in major losses of PUFA. Conversely, the net content of the saturated and monounsaturated fatty acids (SMUFA) remained constant, because the free SMUFA content increased primarily at the expense of the esterified forms. For a constant mixing time of 20 min, increasing the amount of lipase added to dough (from 2.5 to 25 LU/g of dry matter) resulted in a linear decrease in the TAG fraction and a linear increase in the SMUFA content in the FFA fraction. At the same time, the PUFA content of the FFA fraction increased only for additions of lipase to flour of >5 LU/g of dry matter, due to partial oxidation by wheat lipoxygenase.

DELCROS J.F., RAKOTOZAFY L., BOUSSARD A., DAVIDOU S., PORTE C., POTUS J., NICOLAS J. (1998).**Effect of mixing conditions on the behaviour of lipoxygenase, peroxidase and catalase in wheat flour doughs.** *Cereal Chem.*, **75 (1)**, 85-93. **Abstract** : The effect of mixing was tested on the extractable activities of lipoxygenase, peroxidase, and catalase from dough after 2, 5, and 20 min of mixing, and 30 min of rest period after 20 min of mixing. Different mixing conditions were studied including temperature, atmosphere, speed, amount of water added to the dough, buffer solutions between pH 3.6 and 7.5 added to the dough, and different additives (linoleic acid, guaiacol, hydrogen peroxide, ascorbic acid, cysteine, yeast, and sodium chloride). In all the mixing conditions tested, the dough peroxidase activity remains equivalent to the initial flour activity, whereas losses in lipoxygenase and catalase activities largely varied according to mixing conditions. The results show that a self-destruction mechanism as well as

physico-chemical denaturation are responsible for these losses. Lipoxygenase losses seem mainly associated with the former mechanism, whereas catalase losses are highly increased in acidic conditions (physicochemical denaturation). Therefore, the relative impact of the three oxidoreducing enzymes may be largely modulated by mixing conditions.