

### Dans les revues à comité de lecture en 2002 et 2003

CATHERINE BILLAUD, JEAN ADRIAN (2003). **Louis-Camille Maillard. 1878-1936.** Food Rev. Int., **19 (4)**, 345-374.

**Abstract:** This review summarizes the life and work of Louis-Camille Maillard, the most worldwide renowned French Biochemist of the 20<sup>th</sup> century. It focuses on the main events in Maillard's life and the reaction sugar-amino acids in his work, and offers an overview of the Maillard reaction in vitro and in vivo. **Keywords :** L-C Maillard; Maillard's biography; Maillard reaction in vitro; Maillard reaction in vivo.

FRANCINE EL AMRANI , OLIVIER FAYOL , ROGER DRAPRON, JACQUES POTUS, JACQUES NICOLAS. (2003).

**Simplified method for the determination of lipolytic activity in low moisture media.** *Sci. Aliments*, 23, 209-221.

**Abstract:** A new method for the determination of lipolytic activity (LA) in milled products from cereals is described. This method is based on the use of the pHstat titration of free fatty acids (FFA) released by LA after incubating a mixture of defatted wholemeal or milling wheat fraction and olive oil during 72 h at selected conditions of temperature and activity of water (AW). The results given by this method have been compared systematically to those given by the time-consuming and classic one of the determination of the LA in low moisture media based upon the FFA determination by gas chromatography (GC) after separation by thin layer chromatography. The two methods have been used under various experimental conditions in order to study the effects of temperature, AW and addition of exogenous lipase in different wheat milled products. For the germ, bran, flour and whole meal fractions at 30°C and AW = 0.8, LA determined by the titration pHstat method was correlated to the values obtained by the GC method ( $r = 0.99$ ). By pHstat, LA was found equal to 0.054, 0.75, 0.29 and 0.51  $\mu\text{mol.h}^{-1}.\text{g}^{-1}$  (dm) vs 0.053, 0.79, 0.27 and 0.48  $\mu\text{mol.h}^{-1}.\text{g}^{-1}$  (dm) by GC for the flour, bran, germ and wholemeal fraction resp. When experimental conditions were modified, LA determined by pHstat was correlated with LA obtained by GC either when AW was varied for the bran fraction between 0.17 and 0.87 or temperature between 30 and 40°C ( $r = 0.95$ ) or after addition of exogenous lipase to wheat flour ( $r = 0.97$ ). This less time-consuming method for the determination of LA may be of a great interest to improve the storage conditions of cereal milled products as well as to est. the efficiency of heat treatments on the denaturation of endogenous lipase in these products.

CATHERINE BILLAUD, EMELINE ROUX, SOPHIE BRUN-MERIMEE, CHRISTELLE MARASCHIN, JACQUES NICOLAS. (2003). **INHIBITORY EFFECT OF UNHEATED AND HEATED D-GLUCOSE, D-FRUCTOSE AND L-CYSTEINE SOLUTIONS AND MAILLARD REACTION PRODUCTS MODEL SYSTEMS ON ENZYMATIC BROWNING AND APPLE PPO ACTIVITY, USING SPECTROPHOTOMETRIC AND POLAROGRAPHIC METHODS.**

*Food chemistry*, **81**, 35-50. **Abstract :** To demonstrate whether either caramelization products (CP) and Maillard reaction products (MRP) could inhibit enzymatic browning and / or inactivate apple PPO, L-cysteine, D-glucose, D-fructose aqueous solutions and equimolar mixtures (1 M) of hexose / cysteine were each tested on purified enzyme activity, using both spectrophotometric and polarographic methods. Inhibition was evaluated as a function of temperature (80-110 °C), time (0-48 hr) of heating and concentration of reactants. High (1-2 M) concentrations of hexoses were needed to develop a slight inhibiting effect on PPO activity. Heating at 90 °C for extended time periods, increased their inhibitory effect. Conversely, MRP showed a very strong inhibiting effect. The kinetic study with apple PPO and 4-methylcatechol revealed that both MRP model systems were mixed-type inhibitors, glucose / cysteine solution being the most effective one. Inhibition efficiency increased with heating time and increasing concentrations. The extent of inhibitory effect was positively correlated with absorbance measurements of MRP at 350 nm used as indicator of the Maillard reaction development. Possible mechanisms of inhibition of PPO activity by MRP are discussed, in relation with a chelator effect upon cupric ions. **Keywords :** Maillard reaction products, cysteine, PPO, enzymatic browning, inhibition, copper.

EMELINE ROUX, CATHERINE BILLAUD, CHRISTELLE MARASCHIN, SOPHIE BRUN-MÉRIMEE, JACQUES NICOLAS. (2003). **INHIBITORY EFFECT OF UNHEATED AND HEATED D-GLUCOSE, D-FRUCTOSE AND L-CYSTEINE SOLUTIONS AND MAILLARD REACTION PRODUCTS MODEL SYSTEMS ON POLYPHENOLOXIDASE FROM APPLE. II. KINETIC STUDY AND MECHANISM OF INHIBITION.** *Food chemistry*, **81**,

51-60 **Abstract** : Our previous study showed that Maillard reaction products (MRP) derived from equimolar glucose or fructose and L-cysteine model solutions (1 M) were potent inhibitors of polyphenoloxidase (PPO) from apple. In the present paper, a kinetic study was made of the behaviour of a Michaelis-Menten PPO-catalyzed reaction in the presence of MRP heated at 90 °C for various times (2-39 h), using 4-methylcatechol as the substrate. Results obtained revealed that both MRP systems were mixed-type inhibitors, glucose / cysteine model solution being the most effective one. Activity of preincubated PPO at 0 °C for different times with either heated L-cysteine or MRP was only slightly restored via exhaustive dialysis. Recovery of enzyme activity was more marked when cupric ions were added in the reaction medium. Possible mechanisms of inhibition of PPO activity by MRP are discussed, in relation with a chelation of cupric ions. **Keywords** :Maillard reaction products, cysteine, apple PPO, inhibition kinetic, mixed-type inhibition, copper, chelation.

SAUVAGEOT N., PICHEREAU V., LOUARME L., HARTKE A., AUFRAY Y., LAPLACE J-M., (2002) **Purification, characterization and subunits identification of diol dehydratase of *Lactobacillus collonoides***. *Eur. J. Biochem.*, **269**, 5731-5737. **Abstract**: The three genes *pduCDE* encoding the diol dehydratase of *Lactobacillus collonoides*, have been cloned for overexpression in the pQE30 vector. Although the three subunits of the protein were highly induced, no activity was detected in cell extracts. The enzyme was therefore purified to near homogeneity by ammonium sulfate precipitation and gel filtration chromatography. In fractions showing diol dehydratase activity, three main bands were present after SDS/PAGE with molecular masses of 63, 28 and 22 kDa, respectively. They were identified by mass spectrometry to correspond to the large, medium and small subunits of the dehydratase encoded by the *pduC*, *pduD* and *pduE* genes, respectively. The molecular mass of the native complex was estimated to 207 kDa in accordance with the calculated molecular masses deduced from *pduC*, D, E genes (61, 24.7 and 19.1 kDa, respectively) and a  $\alpha_2\beta_2\gamma_2$  composition. The *Km* for the three main substrates were 1.6 mM for 1,2-propanediol, 5.5 mM for 1,2-ethanediol and 8.3 mM for glycerol. The enzyme required the adenosylcobalamin coenzyme for catalytic activity and the *Km* for the cofactor was 8  $\mu$ M. Inactivation of the enzyme was observed by both glycerol and cyanocobalamin. The optimal reaction conditions of the enzyme were pH 8.75 and 37 °C. Activity was inhibited by sodium and calcium ions and to a lesser extent by magnesium. A fourth band at 59 kDa copurified with the diol dehydratase and was identified as the propionaldehyde dehydrogenase enzyme, another protein involved in the 1,2-propanediol metabolism pathway.

VIGNAUD, C.; KAID, N; RAKOTOZAFY, L.; DAVIDOU, S.; NICOLAS J.,(2002) ,**Partial purification and characterization of sulfhydryl oxidase from *Aspergillus niger***. *Journal of Food Science* , **67(6)**, 2016-2022. **Abstract** : Sulfhydryl oxidase (SOX) was purified after extraction. and the contaminating catalase activity was completely eliminated in the last chromatography. step. A yield of 25% was obtained with a purification. factor higher than 300. The isoelectric. point was 3.7 and the molecular. weight. 110 kDa. SOX exhibited an optimal activity at pH 5.6 and its efficiency ( $V_{mapp}/K_{mapp}$ ) increased from pH 4.5 to 6.5. At pH 5.6, the  $K_{mapp}$  values were 0.5, 2.5, 10.5, 110, and 450 mM for GSH, cysteine, g-glu-cys, dithiothreitol, and homocysteine, respectively., and the  $V_{mapp}$  values represented 2, 34, 24, and 44% of the  $V_{mapp}$  value found for GSH, respectively. Cys-gly was not oxidized by SOX. In the presence of GSH, SOX is able to catalyze the oxidation. of cysteine and cys-gly at a significant rate.

GARCIA R., RAKOTOZAFY L., TELEF N., POTUS J.,NICOLAS J., (2002),**Oxidation of Ferulic Acid or Arabinose-Esterified Ferulic Acid by Wheat Germ Peroxidase**. *Journal of Agricultural and Food Chemistry*, **50(11)**, 3290-3298. **Abstract** : The oxidation of ferulic acid (FA) or 5-O-(*trans*-feruloyl)-L-arabinose (EFA) by a purified wheat germ peroxidase was followed by UV spectrophotometry and high-performance liquid chromatography using an electrochemical detection. Wheat peroxidase (POD) exhibits a ping-pong bireactant mechanism forming phenoxy radicals more rapidly from FA than from EFA in routine assay conditions. When both the free and the esterified forms of FA are present, the reverse was found. This result could be due to a nonenzymic cooxidation of FA by the phenoxy radicals of EFA leading to the formation of phenoxy radicals of FA and the EFA regeneration. Addition of ascorbic acid (AA) provokes a delay of FA consumption. AA reduced very rapidly the phenoxy radicals formed by POD back to initial phenol avoiding the formation of ferulate dimers until it was completely oxidized in dehydroascorbic acid. Conversely, cysteine addition slowed but did not delay the FA consumption. The thiol reduced a fraction of the phenoxy radicals produced by wheat POD and was oxidized into cystine, while the other part of phenoxy radicals formed ferulate dimers. These results could be of interest to understand the POD effect on the wheat dough rheological properties.

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