STUDY OF FUNCTIONAL PROPERTIES OF CHITOSAN-LACTOSE DERIVATIVES OBTAINED BY MAILLARD REACTION

Ana I. Ruiz-Matute[a], Ana B. García-Bermejo[a], Alejandra Cardelle-Cobas[a,b], Agustín Olano[a], Nieves Corzo[a]*

[a]Instituto de Investigación en Ciencias de la Alimentación CIAL (CSIC-UAM), Madrid, Spain, [b]Current address: CBQF - Centro de Biotecnologia e Química Fina, Escola Superior de Biotecnologia, Centro Regional do Porto da Universidade Católica Portuguesa, Porto, Portugal.
*corresponding author: nieves.corzo@csic.es

INTRODUCTION

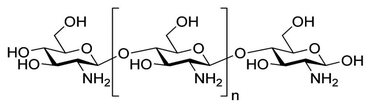
Among the different strategies studied to improve chitosan solubility and extend its applications, one very promising approach is the synthesis of carbohydrate-chitosan derivatives through Maillard Reaction (MR). This reaction has potential industrial application since it is easy to control and may occur readily in the absence of solvent. In a recent work, our group has studied the effect of different drying methods on chitosan reactivity towards MR during storage of dried chitosan-lactose systems and modified chitosans were obtained [1]. MR development was assessed by quantification of a new compound formed during the acid hydrolysis of Amadori compounds resulting from the chitosan-lactose interactions (NFMD).

OBJECTIVE

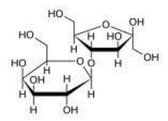
The objective of the present work was to determine the solubility, water and fat-binding capacity and antioxidant activity of native chitosan and compared to those of chitosan-lactose derivatives obtained via Maillard reaction.

MATERIALS AND METHODS

CHITOSAN DERIVATIVE SYNTHESIS



Lactose



Lactose addition

Lyophilization

Storage under vacuum

Conditions:
- Temperature: 60ºC
- Water activity: 0.65
- Time: 48 hours

Dialysis

(Purification of chitosan-lactose derivative)

CHROMATOGRAPHIC ANALYSIS

SAMPLE PREPARATION

Hydrolysis under inert conditions
0.1 g of sample + 8 mL 8N HCl
110ºC/23 hours

→ Filtration through Whatman nº40 →

Purification

0.5 mL of the filtrate Sep-Pack C18

→ Elution with 3 mL 3N HCl →

100 µL evaporated and reconstituted In mobile phase for HPLC analysis

ION PAIR RP-HPLC-UV

- ✓ C_{18} column (250 x 4.6 mm i.d.)
- ✓ Room temperature
- ✓Mobile phase: 20% acetonitrile, 0.2% formic acid and 5mM sodium heptanesulfonic acid solution
- ✓Flow rate: 1.2 mL/min
- ✓Wavelength: 280 nm

ANTIOXIDANT ACTIVITY

ABTS

10 µL sample
+
1 mL ABTS radical aqueous solution (7mM ABTS + 2.45mM potassium persulfate, room temperature, 16h)

Room Temperature (30 min)

734 nm

PowerWaveTM XS Microplate spectrophotometer (BioTek)

517 nm

Chitosan-lactose solution in 1% acetic acid
(0, 0.2, 0.5, 1, 5 and 10 mg/mL)

DPPH

0.4 mL sample
+
3mL of 0.1 mmol/L DPPH radical methanolic solution

Storage: 30 min at room temperature in the dark

Scavenging effect (%) = [(1 − Asample)/Acontrol] × 100%

FUNCTIONAL PROPERTIES

SOLUBILITY

10 mg chitosan + 1 mL distilled water
→ Adjust pH to 7 with NaOH
→ Stirring, 30 min, 20ºC
→ Centrifugation (7000g, 20 min) → Lyophilization → weight

WATER BINDING CAPACITY (WBC)

500 mg chitosan + 10 mL distilled water
→ 20ºC, 30 min (stir 5 s every 10 min)
→ Centrifugation (8000g, 40 min) → weight

WBC (%)= [water bound (g)/sample weight (g)] × 100

FAT BINDING CAPACITY (FBC)

500 mg chitosan + 10 mL soybean oil
→ 20ºC, 30 min (stir 5 s every 10 min)
→ Centrifugation (8000g, 40 min) → weight

FBC (%)= [fat bound (g)/sample weight (g)] × 100

RESULTS

CHITOSAN DERIVATIVE FORMATION

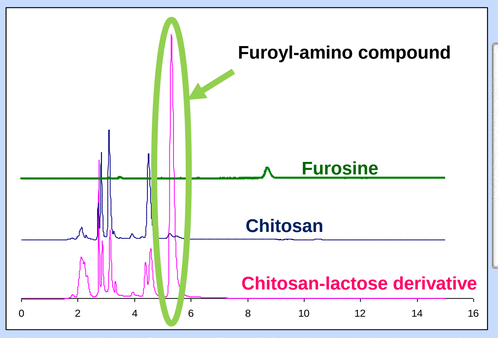


Figure 1. RP-HPLC-UV profiles of furosine standard, and acid hydrolysates of chitosan (control) and chitosan–lactose derivative.

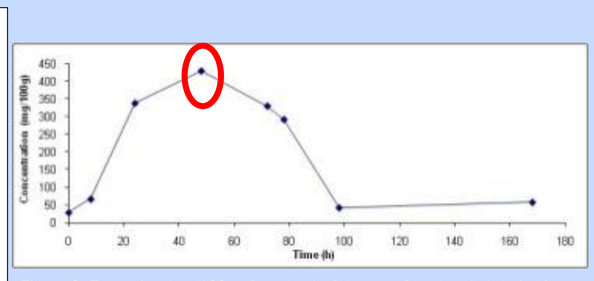


Figure 2. Formation (mg/100g of product) of the new furoylmethyl derivative (NFMD) during storage at 60ºC and a_w 0.65 of chitosan-lactose system

✓ Maillard reaction development was assessed by quantification of a new compound originated from the acid hydrolysis of Amadori compounds (NFMD) resulting from chitosan-lactose interactions and not detected in the acid hydrolysates of freshly prepared chitosan-lactose systems (Figure 1).

✓ Under controlled conditions, the highest level of NFMD formed (428.45 mg/100g) was obtained after 48 h storage (Figure 2).

FUNCTIONAL PROPERTIES

Table 1.- Solubility, water (WBC) and fat binding capacities (FBC) of chitosan and its lactose derivative (obtained after 48h of storage at 60ºC and a_w=0.65).

	FUNCTIONAL PROPERTIES		
	SOLUBILITY (mg/mL) pH 7, 20ºC	WBC (%)	FBC (%)
PURIFIED CHITOSAN	1.5 ± 0.4	1083.5 ± 195.9	2646.6 ± 22.8
CHITOSAN-LACTOSE DERIVATIVE	6.8 ± 0.5	3944.5 ± 1011.4	8124.6 ± 399.7

✓ Chitosan-lactose derivative exhibited an improvement in all of the functional properties studied comparing to those of native chitosan.

✓ Solubility increased in the chitosan-lactose derivative respect to that of the native chitosan from 1.5 to 6.8 mg/mL. WBC and FBC were also higher in the derivatives, varying from 1084 % to 3945% and from 2647 % to 8125 %, respectively.

ANTIOXIDANT ACTIVITY

ABTS

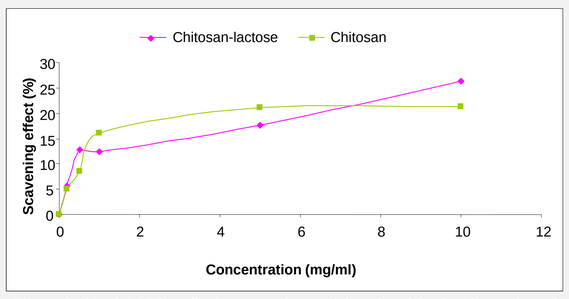


Figure 3. % of ABTS radical scavenging activity after 30 min of reaction of: native purified chitosan and chitosan-lactose derivative (obtained after 48h of storage at 60ºC and a_w 0.65).

✓ Similar results were obtained for % of ABTS (Figure 3) and DPPH (Figure 4) radical scavenging activity of native purified chitosan and chitosan-lactose derivative.

✓Chitosan-lactose derivative showed similar antioxidant activity to that of native chitosan, being slightly higher at concentration of 10 mg/mL..

DPPH

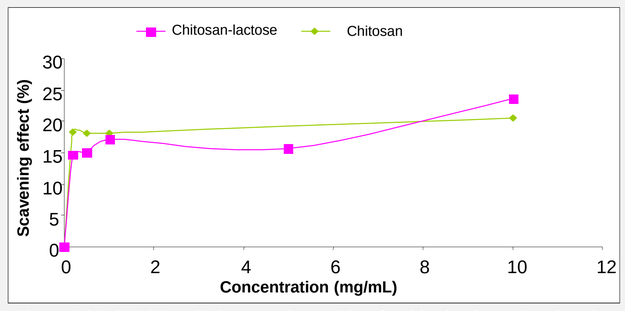


Figure 4. % of DPPH radical scavenging activity after 30 min of reaction of: native purified chitosan and chitosan-lactose derivative (obtained after 48h of storage at 60ºC and a_w 0.65).

CONCLUSIONS

✓ Under assayed conditions, the interaction of lactose with chitosan gives rise to a derivative with improved solubility, and water and fat-binding capacity.

✓ Higher concentrations of chitosan-lactose derivative also enhanced the antioxidant activity.

✓ These chitosan-lactose derivatives with modified properties could be considered as very promising for their future use as additives in the food industry.

REFERENCES

[1] García-Bermejo, A. B., Cardelle-Cobas, A., Ruiz-Mature, A. I., Montanes, F., Olano, A., Corzo, N. (2012). Effect of drying methods on the reactivity of chitosan towards Maillard reaction. *Food Hydrocolloids*, 29: 27-34.

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