Nippon Suisan Gakkaishi 59(9), 1539–1544 (1993)

Prospects for the Utilization of Ray as a Canned Product

Laura Pastoriza* and Gabriel Sampedro*

(Received May 5, 1993)

Using frozen ray as a raw material and utilizing the muscle of this species as a principal component, three types of canned ray wing products with different packing liquids (garlic, pickle, and mustard sauces) have been developed as well as different canned patés similar to liver or salmon paté, and patés with pork meat and ray liver as ingredients. In the raw material, yield during processing, proximate analysis, and nitrogenous compounds were determined. In the final products, quality assessments were carried out during the storage period.

When the fish was cut up it was seen that the yield from the skinned wings corresponded to approximately 38% and that of the liver to 3% of the total fish weight. The proximate analysis of the muscle showed 2.07% protein nitrogen, 78% moisture content, and a fat content lower than 1%. The urea content reached the level of 2%. In the canned ray wing products it was observed that the intermuscular cartilage fraction was gelatinised after thermal treatment and subsequent storage, which increased the yield of the product and also avoided the necessity of filleting prior to canning. All the canned patés proved to have excellent textural, spreading, and sensory characteristics.

Ray *Raja radiata* is an abundant fish resource, but is perhaps undervalued from a technological point of view as far as its industrial transformation in creating new products is concerned. This work deals with research to improve the exploitation of undervalued or insufficiently commercialised species caught by the Spanish frozen-storage fleet in the North Atlantic. The main interest of this study has been to develop new methods of utilization of this species in order to increase its commercial value as well as the volume of catch, since only the wings, either fresh or in a frozen state, are commercialised at the moment. This would favour profitable exploitation and would also lead to obtaining new products of possible interest in the canning industry. Therefore, this research has been based on a study of the following topics:

–Yield calculation of the different parts into which the fish are cut up.
–Determination of proximate analysis in ray muscle (edible part).
–Determination of the nitrogenous compounds present in the ray.
–Obtaining the ideal processing parameters in the stages prior to the manufacture of the canned product: thawing, immersion in brine, cooking, dehydration, and sterilization.
–Preparation of canned products by utilizing ray wings and using different packing liquids.
–Production of canned ray paté.
–Preparation of canned products from ray liver.

Materials and Methods

The ray *Raja radiata* was caught by the Spanish frozen-storage fleets in the Terranova area. The fish was frozen on board immediately after being caught. In the Pilot Plant, 100 kg of ray were used, which were skinned by hand after the removal of the wings (Fig. 1). The sampling on land was carried out on the muscle of the species once thawed in a refrigerator (8–10°C). Ray liver and pork meat were also used as ingredients. The fish was cooked in a direct steam and forced circulation utensil at 95°C. For the paté preparation, the muscle tissue was homogenized in a mincer (MOBBA 3CV) with 8 mm diameter orifices and a mixer with OSTERIZER type blades. The containers used for the preparation of the canned products were of 120 ml capacity for the patés and liver and 360 ml for the ray wing products. The sterilization was carried out in a reduced prototype overpressure autoclave at 110°C for 90 min in the case of canned ray paté and for 75 min in that of canned ray wing and liver.

* Instituto Investigaciones Marinas (CSIC), Eduardo Cabello, 6, 36208 Vigo, Spain.

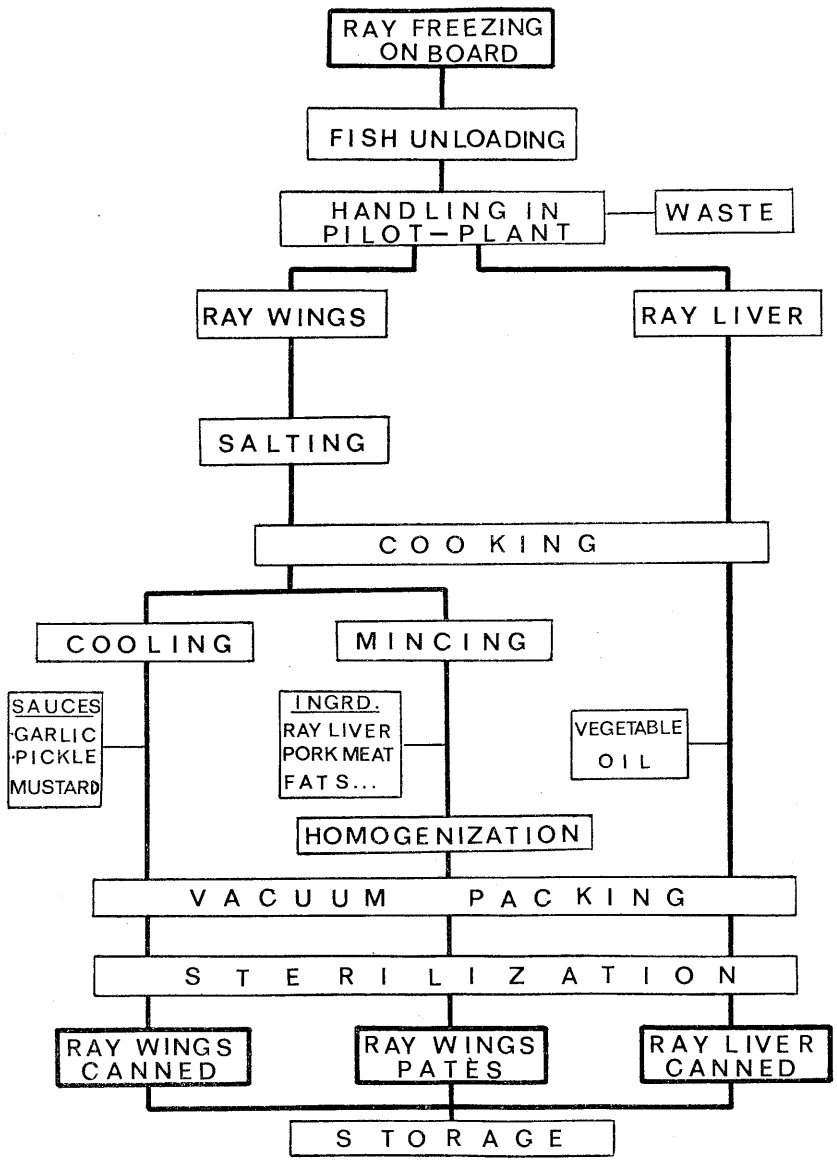

Fig. 1. Steps in the processing of canned ray products.

The total nitrogen was determined by the Kjeldahl technique,[1] the determination of protein nitrogen and non-protein nitrogen was carried out according to the Kjeldahl technique after precipitation of the protein with 10% trichloroacetic acid. The urea levels were determined by colorimetric reaction according to the AOAC method.[2] Lipids were extracted following the method of Bligh and Dyer.[3] Ash[4] and moisture[5] were determined by the AOAC method. The sensory evaluations were based on preference-acceptability, discriminatory and descriptive methods, and were

Table 1. Typical hedonic assessment sheet

1.	Dislike extremely
2.	Dislike very much
3.	Dislike moderately
4.	Dislike slightly
5.	Neither like nor dislike
6.	Like slightly
7.	Like moderately
8.	Like very much
9.	Like extremely

evaluated according to the criteria of a test panel consisting of five specialists. For the acceptability qualification, a 9-point hedonic scale was used (Table 1) which described a complete intensity range (Peryam and Pilgrim[6]). The significance between the treatments applied to the canned products of wings, patés, and ray liver was studied using Scheffé's test ($P<0.05$).

Preparation of Canned Ray Wings

For the preparation of canned products, the whole fish was thawed in the way shown previously. Later, the wings were removed from the ray and immersed in 10% brine for 1 h before cooking. Cooking was done in direct steam for 5 min. After cooking, the wings were skinned manually and were then kept at room temperature for 2 h before sterilization.

As packing liquid, different formulas were used, *i.e.* garlic sauce, pickle sauce, and mustard sauce (Table 2). All these preparations, used previously by the authors, were specially adapted for the preparation of the canned ray products after tests carried out by a panel consisting of five specialists.

The cans were closed after adding hot packing liquid by using 360 m*l* format containers with an average drained wieght of approximately 230 g of ray.

Manufacture of Canned Ray Paté

For the preparation of the canned paté the raw material used was either ray muscle or ray muscle mixed with pork meat and ray liver. The raw material, previously steam cooked, was homogenized with ingredients and flavourings resulting in different kinds of canned patés—similar to liver paté or to salmon paté, as well as patés with pork meat and with ray liver as ingredients by using 120 m*l* format containers. The formulas of the patés which were most appropriate are shown in Table 3.

Table 2. Composition (%) of the packing liquid used in the preparation of canned ray wings: pickle sauce (P), mustard sauce (M) and garlic sauce (G)

Ingredients	Content in weight		
	P	M	G
Vegetable oil	86.0	71.0	69.0
Pickle	8.5	14.0	28.0
Garlic	2.6	—	1.5
Mustard	—	7.0	—
Paprika	2.6	—	2.0
Tomato sauce	—	7.0	—
Flavouring	—	2.0	—

Table 3. Ray muscle patés (Composition (%))

Ingredients	Content in weight			
	a	b	c	d
Ray muscle	63.12	63.65	55.30	56.49
Ray liver	—	—	8.48	—
Animal fat	13.74	16.61	12.21	15.54
Vegetable fat	3.46	0.83	3.28	3.11
Natural colouring	8.19	8.08	2.17	6.95
Flavouring	6.80	5.34	5.84	4.77
Thickener	4.72	5.47	4.07	1.05
Pork meat	—	—	8.48	12.05

a: Paté of muscle ray similar to liver paté, b: Paté of muscle ray similar to salmon paté, c: paté of muscle and liver ray and pork meat, and d: paté of muscle ray and pork meat.

Manufacture of Canned Ray Liver

For the preparation of canned liver products, the raw material was subjected to different treatments before being packed. Thus, liver was packed as a raw material, *i.e.* with no treatment, or after being scalded in boiling water for 3 s, or after being cooked in salt water (2% NaCl) for either 2 or 5 minutes. Hot vegetable oil was added as a packing liquid in 120 m*l* format containers. Sterilization procedures were similar to those used for canned ray wings.

Results and Discussion

In the study of yields (in relation to the weight of the whole ray) it can be seen that the wing yield corresponded to approximately 35% and that of the liver to 3% (Table 4).

The proximate analyses showed that the ray

Table 4. Yield of ray separation in relation to the whole fish

Sample	Yield (%)
Gutted ray	91
Wings with skin	49
Skinned wings	38
Skinned wings without fin	36
Wing muscle	25
Waste (head, gut, tail)	49
Liver	3
Guts	9

The proportion of liver in relation to the total weight of guts was 34%.

Table 5. Proximate analysis of frozen ray wing muscle (% wet weight basis)

Humidity	Lipids	Ashes	Total-N	Protein-N	Non-protein-N	Urea
77.98	0.23	2.20	3.20	2.07	1.09	2.01
(0.25)	(0.01)	(0.20)	(0.05)	(0.03)	(0.02)	(0.03)

s.d. in parenthesis, n=3.

Table 6. Sensory assessment of canned ray wing in pickle sauce (P), mustard sauce (M), and garlic sauce (G)

	P	M	G	P-M	M-G	P-G
Visual Appearance	8.1 (0.42)	8.2 (0.45)	8.5 (0.79)	NS	NS	NS
Colour	7.2 (0.27)	8.2 (0.57)	8.6 (0.42)	S	NS	S
Flavour Quality	7.4 (0.42)	8.4 (0.22)	8.6 (0.65)	S	NS	S
Texture	7.6 (0.55)	8.6 (0.89)	8.8 (0.45)	S	NS	S
Smell Quality	7.5 (0.79)	8.3 (0.44)	8.5 (0.79)	NS	NS	

S: Significant (Scheffe's test, $P<0.05$).
NS: Not significant.
Standard deviations in brackets, n=5.

contained very little fat and had a protein content of 20%. The protein and non-protein nitrogenous compounds were also analysed, the latter being characteristic in the species. In the ray muscle there was a total and protein nitrogen content of 3.20 and 2.07%, respectively (Table 5). The difference which appears between the values of total and protein nitrogen is significant to all elasmobranch fish as a consequence of the high non-protein nitrogen content. In this work, quantities of 1.09% non-protein nitrogen were found. The urea content reached 2.01%, a quantity similar to those observed in other elasmobranch fish (Lisac,[7] Stansby and Olcott,[8] Suyama and Tokuhiro.[9])

As a consequence of the high urea content, unpleasant smells can originate during the handling of the fish and subsequent processing which cause a decrease in the quality of the products formed. In an earlier work, when the ray was subjected to thermal treatment during manufacture by cooking in steam or brine followed by sterilization, a considerable decrease in this compound was detected, such that a urea reduction of 73–80% could be noted in the stored product (Pastoriza and Sampedro[10]), which noticably improved its sensory characteristics. These results motivated an interest in developing the preparations investigated in this work.

In the tests carried out in the pilot plant to obtain a good quality canned ray wing product, it was found that the most suitable conditions for processing the raw material before sterilization, with reference to the immersion in brine, cooking the product, and dehydration before canning were: 10% brine bath, immersion time 1 h, steam cooking at a temperature of 90–100°C for 5 min, and dehydration of the cooked wing at room temperature for 2 h (after skinning the wing when hot). The sterilization was carried out at 110°C for 75 minutes (the F_0 value was 3.5 min).

The canned products prepared with ray wings were qualified after a year of storage. The sensory quality was assessed as visual appearance, colour, flavour quality, texture, and smell quality, and these parameters were evaluated according to the criteria of a panel consisting of five specialists (Table 6). In general, the qualification of the quality of canned wing products in pickle (P), mustard (M), or garlic (G) sauce was excellent. Significant differences were found ($p<0.05$) in the sensory evaluations of colour, flavour quality, and texture between samples P and samples M and G. The products in pickle sauce showed a less firm texture, a stronger taste, and a slightly darker colour. Two samples (M and G) were not significant ($p<0.05$). These were the canned products of ray wings in garlic sauce and in mustard sauce, which were those of the highest acceptability.

It is also to be emphasised that no darkening was observed on the surface of the canned product, a usual effect in other species of white fish which limits their utilization. Another outstanding advantage was the gelatinization of the intermuscular cartilaginous fraction during the thermal treat-

Table 7. Sensory assessment of canned ray paté

	a	b	c	d	a-b	a-c	a-d	b-c	b-d	c-d
Visual Appearance	8.0 (0.35)	8.3 (0.45)	7.9 (0.22)	8.2 (0.57)	NS	NS	NS	NS	NS	NS
Colour	8.3 (0.27)	8.9 (0.42)	8.5 (0.35)	8.4 (0.22)	S	NS	NS	NS	NS	NS
Flavour Quality	6.9 (0.42)	7.8 (0.27)	8.7 (0.44)	8.6 (0.55)	NS	S	S	NS	NS	NS
Spreading	8.2 (0.57)	8.4 (0.42)	8.6 (0.55)	8.5 (0.79)	NS	NS	NS	NS	NS	NS
Smell Quality	7.4 (0.42)	8.0 (0.35)	8.6 (0.42)	8.5 (0.79)	NS	S	NS	NS	NS	NS

a: Paté of muscle ray similar to liver paté, b: paté of muscle ray similar to salmon paté, c: pate of muscle and liver ray and pork meat, and d: paté of muscle ray and pork meat.
S: Significant (Scheffé's test, $P<0.05$).
NS: Not significant.
Standard deviations in brackets, n=5.

Table 8. Sensory assessment of canned ray liver

	e	f	g	h	e-f	e-g	e-h	f-g	f-h	g-h
Visual Appearance	5.4 (0.42)	6.9 (0.42)	8.5 (0.79)	7.9 (0.22)	S	S	S	S	NS	NS
Colour	4.7 (0.44)	5.4 (0.42)	8.0 (0.70)	7.5 (0.35)	NS	S	S	S	S	NS
Flavour Quality	4.4 (0·42)	5.4 (0.42)	8.7 (0.45)	8.3 (0.45)	S	S	S	S	S	NS
Texture	4.9 (0.65)	5.9 (0.65)	8.0 (0.70)	7.4 (0.42)	S	S	S	S	S	NS
Smell Quality	6.9 (0.42)	7.8 (0.27)	8.6 (0.42)	8.2 (0.57)	S	S	S	NS	NS	NS

e: Liver packed raw, f: liver (scalded), g: liver cooked in brine 2 min, and h: liver cooked in brine 5 min.
S: Significant (Scheffe's test, $P<0.05$).
NS: Not significant.
Standard deviations in brackets, n=5.

ment and subsequent storage. This gelatinization makes the cartilage unnoticable to the taste, which means that it is possible not only to avoid the difficult preliminary operation of boning and later filleting of the wing but also to increase the weight yield of the raw material.

This commercially undervalued fish showed ideal qualities for the manufacture of patés. A fish paté was prepared with very acceptable texture, spreading capacity, and sensory characteristics. For different types of formula were tested to achieve distinct aspects of the finished product, *i.e.* similar to liver paté (a), similar to salmon paté (b), and a third (c) and a fourth (d) in which, in addition to ray muscle, liver of the species studied and pork meat were included (Table 7). The sensory qualifications (visual appearance, colour, flavour quality, spreading, and smell quality) of the sterilized products indicated that all the preparations showed high acceptability.

No significant difference ($p<0.05$) was found in the samples in spreading (Table 7), as all the patés spread easily. There was significant variation in flavour ($p<0.05$) between samples consisting of ray muscle (sample a) and those that also had meat pork or ray liver and meat pork as ingredients (samples d and c, respectively). The samples with ray liver or pork meat gave a stronger taste. Only ray muscle patés, *i.e.* samples a and b, showed a significant difference in colour ($p<0.05$). These were the canned products with ray muscle in which greater differences in colour were observed as a consequence of the different formulation. The thermal treatment for the sterilization of canned ray patés was carried out at 110°C and 90 minutes (the F_0 value was 6 min).

As far as canned liver products in oil are concerned, the organoleptic tests gave an acceptable product (Table 8). It can be seen that only the samples which were cooked in water either for 2 min (sample g) or 5 min (sample h) before sterilization were not significant ($p<0.05$). These samples also showed the best characteristics of visual appearance, colour, flavour quality, texture, and smell quality. There was a significant variation ($p<0.05$) between the raw packed samples (sample e) and the samples scalded in water (sample f) with respect to samples g and h. Raw packed ray liver and scalded samples gave a bitter taste, a softer texture, and a darker colour. It was also observed that this product presented good spreading properties.

All the products were original and brought about an important reassessment of the species with a view to a better commercialisation and consumption.

Acknowledgements

The authors are grateful to the General Maritime Fishing Secretary and the Interministerial Commission of Science and Technology (CICYT) in Research Project ALI89–0555 for their financial support in carrying out this research.

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