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International Fishmeal and Oil Manufacturers Association

DETERMINATION OF ETHOXYQUIN AND TWO OF ITS OXIDATION PRODUCTS IN FISH MEAL BY GAS CHROMATOGRAPHY PART 2

RESEARCH REPORT NUMBER: 1993-9

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EXECUTIVE SUMMARY

In IFOMA Research Report 1993-2 it was reported that a standard method for measuring ethoxyquin produced incorrect values as a result of the poor separation of ethoxyquin from the dimer, as well as other unidentified yellow substances in the meal. A revised analytical method was proposed.

It was noted that this research work was still continuing with two antioxidant-treated fish meals under commercial conditions being analysed over a period of time for ethoxyquin and its breakdown products.

This Report summarises the results of this continued study. Meals 1 and 2 listed in this Report are the same as meals 4 and 5 listed in Research Report 1993-2.

The results again confirm that the proposed new method (gas chromatography) should replace the previous standard method (chromatography over alumina).

In addition the fatty acid composition of the lipids in the fish meal were analysed. Over the period of two years the ethoxyquin in both fish meals clearly protected the polyunsaturated fatty acids against oxidation, whereas considerable oxidation took place in the non-antioxidant-treated fish meals.

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PROJECT FOR THE INTERNATIONAL FISHMEAL AND OIL MANUFACTURERS ASSOCIATION

Evaluation of the interference by two oxidation products of ethoxyquin in the determination of ethoxyquin in fish meal

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In August 1992 I wrote the fifth progress report of the abovementioned project. This report recorded, amongst other things, the decrease in EQ content of two reactive meals stored at 25°C for one year, together with their quinolone and EQ-dimer contents.

In October 1992 I suggested that the two meals be stored for another year so as to establish the fate of EQ, quinolone and EQ-dimer during lengthy storage. The extension to the project was approved by IFOMA (22 January 1993).

The present report records the outcome of this further work.

The results are shown in Table 1. It is interesting to note that after two years' storage at 25°C both meals still contain detectable amounts of EQ, meal 1: 52 mg/kg and meal 2: 8 mg/kg. This presumably means that the polyunsaturated fatty acids of the meal lipids are still being protected from oxidation (see below).

The chromatography over alumina procedure for EQ determination yielded substantially higher values in the aged meals than the gas chromatographic method. This confirms what has already been said in the fifth progress report namely: "for these meals the gas chromatographic method should be used". The EQ-dimer content of both meals had dropped rather sharply from around 90 mg/kg to about 20 mg/kg on prolonged storage. This suggests that EQ-dimer acts as an antioxidant and at this stage of storage its consumption exceeded its generation.

Although it is not part of the original proposal it was decided to determine the fatty acid compositions of the meal lipids together with those of two corresponding control meals untreated with EQ and compare them with the fatty acid compositions of the meal lipids at the outset of storage. The results are shown in Table II.

In pair 1 the polyunsaturated fatty acid content had decreased from 35.5% to 21.8% in the untreated meal while in the EQ-treated meal it had only decreased to 34.6%, clearly demonstrating the protective action of EQ. In pair 2, which is the more reactive meal, the effect was greater: the polyunsaturated fatty acid content had dropped from 31.6% to 14.8% in the control meal while in the EQ-treated meal it had remained constant at 32.0%.

This pattern of total protection of the polyunsaturated fatty acids is not always observed. In a test carried out some years ago I found that the polyunsaturated fatty acid content of an untreated anchovy meal had decreased from 41.3 to 4.2% in 670 days, while in the meal treated with 400 mg/kg it had decreased to 20.0%.[1] Clearly that meal was even more reactive than the present meal 2. It was considered to be more reactive because its polyunsaturated fatty acid content was much higher at 41.3% compared with 31.6% in meal 2. However, this cannot be the only criterion since meal 1 with 35.5% polyunsaturated fatty acids was less reactive than meal 2 with 31.6% polyunsaturated fatty acids. Another criterion is the amount of natural antioxidants, such as vitamin E, present in a meal. It might well be possible to assess the reactivity of a meal by determining the amount of polyunsaturated fatty acids and vitamin E in the residual lipids of a meal.

Reference

1. DE KONING A J & MOL Theodora H. 1989. Lipid determination in fish meal: An investigation of three standard methods applied to stabilised and non-stabilised anchovy meals at increasing stages of maturity. *J. Sci. Food Agric*, 46 : 259-266.

TABLE 1

Ethoxyquin, quinolone and EQ-dimer in fish meal during storage at 25°C

Meal history	Storage time (days)	EQ (mg/kg) Chromatography over alumina	EQ (mg/kg) Gas chromatography	Quinolone (mg/kg)	Dimer (mg/kg)	"total EQ equivalents"
1. Anchovy factory	0	-	400	-	-	
meal	59	164	185	21	111	238
400 mg/kg EQ added	133	105	150	13	64	181
in the laboratory	186	134	134	3	98	169
	259	117	100	5	78	130
1 year	347	79	87	22	96	136
	588	78	56	4	21	66
2 years	730	74	52	7	35	69
2. Anchovy factory	0	-	400	-	-	-
meal	68	68	87	17	104	134
400 mg/kg EQ added	181	62	30	9	124	78
in the laboratory	248	44	25	7	93	61
	321	62	20	4	70	46
1 year	365	51	20	2	76	47
	562	38	11	0	18	17
2 years	730	9	8	7	20	20

TABLE II

Fatty acid composition of the Bligh and Dyer lipids from two pairs of anchovy meal untreated or treated with 400 mg/kg ethoxyquin on storage for two years at 25°C

	PAIR 1			PAIR 2		
		Day 730			Day 730	
	Day 0	No EQ	400 mg/kg EQ	Day 0	No EQ	400 mg/kg EQ
C14:0	6.7	7.2	5.8	7.1	8.4	6.7
C15:0	0.3	0.4	0.4	0.3	0.4	0.3
C16:0	20.1	24.2	20.2	24.4	26.9	21.0
C17:0	0.3	0.5	0.4	0.3	0.3	0.3
C18:0	4.0	5.1	4.3	4.5	5.7	4.3
TOTAL SATURATED	31.4	37.4	31.1	36.6	41.7	32.6
C16:1	11.2	12.7	11.0	11.4	14.0	11.3
C18:1n-9	9.7	10.6	9.2	10.5	14.8	12.0
C18:1n-7	2.9	4.5	3.7	7.3	5.1	3.3
C20:1	2.4	2.9	2.4	0.7	2.0	1.4
C22:1n-11	2.4	4.2	3.3	1.3	2.8	1.8
C24:1	2.9	0.7	0.6	0.2	0.7	0.4
TOTAL MONOENES	31.5	35.6	30.2	31.4	39.4	30.2
C16:4	1.8	1.3	1.7	1.6	1.3	2.0
C16:3	0.9	0.7	1.1	0.8	0.7	1.2
C18:4	1.1	1.0	1.3	1.5	0.7	1.4
C18:2	1.0	1.2	1.4	1.0	0.5	0.9
C20:5n-3	18.3	11.3	17.5	18.0	8.3	17.5
C20:4n-3	0.7	0.3	0.5	0.3	0.1	0.4
C21:5	0.5	0.3	0.5	0.3	0.2	0.5
C22:6n-3	9.9	4.9	9.3	7.3	2.3	7.3
C22:5n-3	1.3	0.8	1.3	0.8	0.7	0.8
TOTAL POLY-UNSATURATED	35.5	21.8	34.6	31.6	14.8	32.0