

Improved Chemical Methods for Extraction of Fin Rays from Shark Fins

By

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Introduction

Dried shark-fin is a valuable commercial product of export from Sri Lanka. (Ref. Tables 1 and 2.) These shark-fins are exported to Singapore and Hong-Kong where they are further processed for "fin-rays". Shark fins from all species are accepted, but fins of sharks less than five feet (<1.6 m.) in length are too small and are not worth the trouble and expense of processing and exporting. The sharks and skates encountered in Sri Lanka waters which mainly contribute to the shark-fin industry are :

- (1) *Carcharhinus* spp. . . Grey sharks, Mora (S) 5-15 feet in length.
- (2) *Sphyrna* spp. . . Hammer-head sharks, Udalu Mora (S) 5-20 feet in length.
- (3) *Rhynchobatus djiddensis* . . Shovel nose rays, Velawa (S) 5-10 feet in length.

The two dorsal fins and caudal (tail) fins are extracted from saw fish and pectorals are not used as with other ray fishes.

A complete set of fins from a shark consists of the lower (ventral) lobe of tail (caudal) fin, the two pectoral fins and the first dorsal fin. Smaller anal (pelvic), medium ventral and second dorsal fins have no value in the shark-fin industry. The upper lobe of the caudal fin does not contain much rays and has no value. The fins are classified as black fins and white fins. Black fins are mainly obtained from the *Carcharhinus* species and contain a lesser amount of rays. White fins are obtained mainly from *Rhynchobatus djiddensis*. The two dorsal and caudal fins of this Ray are yellowish in colour when fresh and turn white when dried ; these contain more rays than fins of other species, hence fetch a maximum price in the export market.

For the processing of wet fins into dried fins, the fins should be cut off from the body correctly, by removing as little as possible the flesh adhering to the base and trimmed. They are then washed thoroughly in sea-water, using a hard brush to remove foreign materials like sand and mud from the skin. The cleaned fins are sun-dried after spreading on mats or on chicken wire to prevent contact with sand. The drying time is 14 to 20 days or even more till the final moisture level is 10 per cent to 12 per cent. When adequately dried, fins are stiff and hard ; they are packed in water-tight

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containers or polythene-lined gunny bags. The grading is according to the colour, size and position and variety of fins. According to Indian standard specifications for dried shark fins, I. S. 5471, 1969 (Ramachandran Nair, K. G. & Madhavan, P. 1974), the grading of dried shark fins is as follows :—

<i>Position of fins</i>	<i>Grade</i>	<i>Size* (cm)</i>
I. Dorsal	.. A	.. <10
	.. B	.. 10-20
	.. C	.. 20-30
	.. D	.. >30
II. Caudal (tail)	.. A	.. <20
	.. B	.. 20-30
	.. C	.. 30-40
	.. D	.. >40

* Size—the length of the anterior margin of the fin.

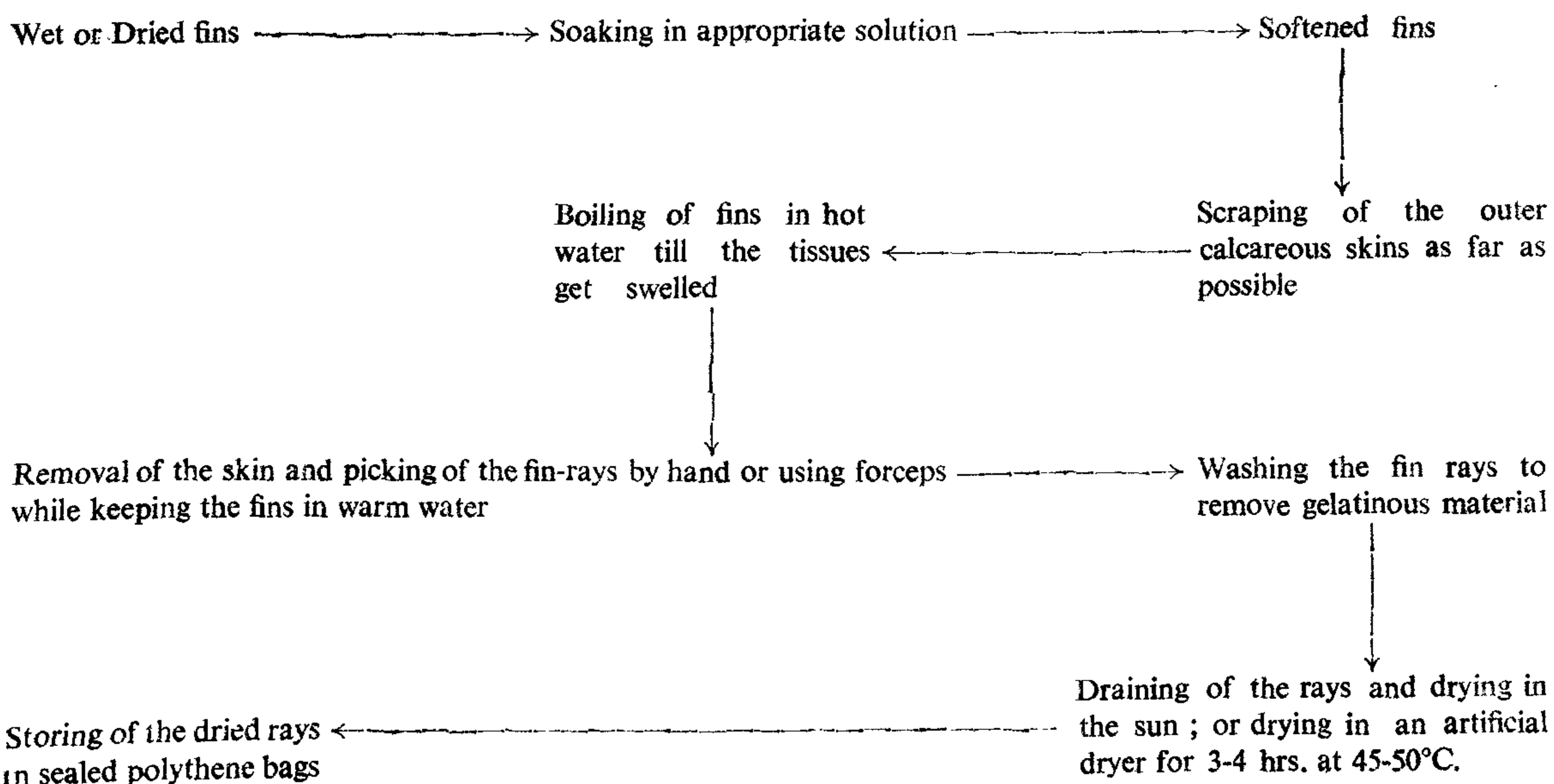
The extracted good quality dried fin rays should be light, yellowish-white in colour, odourless, and have no gelatinous substances on the surface of the strands. These fin rays are used with other ingredients in the preparation of soups in Chinese cuisine.

When hygienically processed fin-rays can be exported instead of the entire fins ; they may fetch a better price in the export market while reducing the freight charges from lesser bulk of the shipped material. More-over, such processing will provide more local employment.

A survey of the available methods of extraction of fin rays from the shark-fins and the development of new, quicker and easier methods of processing are presented in this paper.

Materials and Methods

The extraction of fin-rays was carried out using black and white fins in wet and dried forms. The type of fins and the solutions used, for the processing is given in table 3. The procedure followed is given below :—



The following analyses were carried out in duplicate :—

(1) *Moisture Content* :

2 g. of the fin-ray sample was heated in a drying oven at 100°–105° C for 24 hrs.

(2) *Ash Content* :

2 g. of the sample was washed at 600° C. for 24 hrs. in a muffle furnace.

(3) *Crude Protein Content* :

Determined by Microkjeldhal method. The total nitrogen content was multiplied by 5.55 (nitrogen to protein conversion factor for collagen).

(4) *Oil Content* :

Soxhlet method followed using Petroleum ether (B. P. 40°—60° C).

(5) *Yield Comparisons of the dried Fin-rays on the Basis of—*

(a) Wet weight of fin-rays,

(b) Wet weight of fins, and

(c) Dry weight of fins.

Results and Discussion

Appearance of the Fin Rays

Colourless to light yellowish colour, long, thick but flexible and slightly hard fin-rays were obtained in wet form from most of the samples. The wet rays obtained from the samples (5) and (6) using 10 per cent vinegar were dark yellowish-coloured, very short and thick.

The dried fin-rays obtained from the sample of white caudal fins (both lower and upper lobes) using 1 per cent HCl was of very poor quality, very thin, short and shrunk. The dried fin-rays extracted from black dorsal fin using 10 per cent vinegar were dark yellow, thick (stumpy) and opaque. The dried fin-rays obtained from all the other samples were light yellow to white in colour, transparent, brittle, thin, glass-like, long and slightly shrunken. No odour was detected from any of the dried samples.

Table 4 shows the yield of the dried fin-rays and the moisture contents.

The proximate analysis of the dried fin-rays is as follows :—

Moisture content	..	10.00 %
Ash content	..	0.23 %
Total nitrogen content	..	14.8 %
Crude protein content	..	82.0 %
Oil content	..	Negligible.

The extraction of fin-rays by soaking in water was a time-consuming, slow process. It was observed that the fins were soaked in freshwater, the bacterial break-down of adhering muscle tissues occurred even though the water was changed daily and it gave a putrid odour to the fins and also to the extracted rays. It was possible to remove the putrid smell from the rays by washing them in water several times. There was no putrid odour on the dried rays, but it was observed again in the solution when the rays were resoaked before consumption. This problem did not arise when using the other solutions. The rays obtained from soaking in water for a few days (traditional method) were rather stiff and long, needle-like in wet form ; and the rays obtained with use of chemicals were softer than in all other samples. This softening could be due to the greater hydrolysing effect of the collagenous threads into gelatin. This effect could also be seen from the percentage yield of dry rays on wet rays basis, where the percentage yield in 1 per cent HCl samples was very much lower than in other products.

This softening property is useful when the fin-rays are soaked again before consumption. It was possible to extract the rays from the dried fins more quickly and easily using 1 per cent HCl, than with any other fluid. It also made the extraction process less tedious, as the rays could be extracted from the dried fins by soaking the fins in 1 per cent HCl for 1-2 days after boiling in freshwater for 10 minutes only. By thorough washing, the excess acid could be removed. However, with 1 per cent HCl the excessive hydrolysing effect of HCl on fin-rays will disintegrate the whole fin and picking out rays intact would be difficult. Some control could be gained by reducing the acid concentration and increasing the boiling time. It was also observed that, for smaller shark-fins, about 18 hours soaking in 1 per cent HCl was sufficient to extract the fin-rays. The boiling process will facilitate removal of the unwanted flesh, cartilagenous and the gelatinous and calcareous materials from the fin. As technical grade HCl (10.2 N, 34.5 per cent, (w/w)) is of local manufacture and free of health hazards when diluted, it could be possible to use HCl acid safely for the quicker and easier extraction of fin-rays from both dried and wet shark fins on a commercial scale.

Vinegar or Acetic acid may also be used. Acetic acid is not produced locally ; vinegar is available as a by-product of the coconut industry. But the processing takes a longer time than with HCl though there was no difference observed in the appearance, reabsorption of water or odour of the dried fin-rays obtained in each of these experiments.

The extraction of fin-rays using 0.1 per cent (w/v) NaOH was tested. The extracted rays got soapy to touch and hence required neutralization with dilute acid (HCl or Acetic acid). The NaOH solution dissolved other fin tissues so well that picking out fin-rays was an easy operation.

The fin-rays obtained from fresh fins were dried (a) in an oven, and (b) in the sun ; no difference was observed in them by appearance or rehydration capacity.

The content of the rays in the different fins is variable and the extraction methods do not influence the yield. The reduction of length was observed with the fin-rays obtained from 19 per cent Acetic acid, but these fin-rays were thicker in diameter in dried form.

The reabsorption of water by the dried fin-rays of each sample was tested by heating the dried fin-rays in hot water (80°C.) for two hours and soaking them for a further 2-3 hours in warm water. Only the resoaked fin-rays of HCl acid process were softer, and flexible than all the samples. No adhering materials (flesh parts, cartilagenous tissues) were observed. The rehydrated fin-rays gave a bland, tasteless, gelatinous substance when tasted by itself. There was no fishy odour or taste with dried and rehydrated strands.

The approximate chemical composition of fin-rays showed a very high crude protein content (82 per cent) and hence a very low ash content (0.23 per cent); and the balance may be moisture and carbohydrate. The oil content is negligible. The main constituent in shark fin-rays is a collagenous protein substance (Proteinoid). Collagen-like substances are connective tissue proteins and not soluble either in water, in salt, alkaline or dilute acid solutions as shown in the experiment. When boiled in water, proteinoids turn into glue or gelatin; but collagen is less hydrolysed for edible gelatine than for glue. With bony fish collagen usually contains 2-4 per cent of the total protein in flesh; with cartilagenous fishes (sharks, skates and Rays) the collagen-like proteinoids is larger in content (8-10 per cent). These substances are different in chemical structure from many other proteins in having high total nitrogen content, averaging 18 per cent. Hence the factor for converting collagen nitrogen to protein is 5.55 (100 : 18). Collagen-like substances are low grade proteins, due to lack of essential amino acids like Tryptophane, cystine, cysteine and very little Methionine and Tyrosine and also does not readily react with the digestive enzymes. (Zaitsev *et al.*, 1969). Hence, shark fin-rays has not any food value.

Conclusion

1. A dilute HCl solution (1 per cent) could be safely used for quicker and easier extraction of shark fin-rays from the fins.
2. 10 per cent (v/v) Acetic acid or Vinegar; 0.1 per cent NaOH solution could also be used safely for the extraction but the process is slower than with HCl. With NaOH solution, the wet fin-rays should neutralize with a dilute acid like HCl or acetic acid.
3. There were no observed differences between the samples obtained from chemical methods and the traditional method using water concerning the appearance and yield of fin-rays.
4. The extracted and dried fin-rays were very light and easy to handle and pack in polyethylene bags. Hence, it requires less space and freight charges and may fetch a better price at the export market.

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TABLE 1
TOTAL FRESH FISH PRODUCTION, PRODUCTION OF SHARKS AND SKATES
AND EXPORTS AND VALUE

Year	Total local Production of fresh fish (tons)	Production of Sharks and Skates (tons)	Export of shark fins and fish maws (cwt.)	Value of exported fins and maws (Rs.)
1970	96,608	11,465	2,816	1,313,981
1971	83,897	9,954	1,380	1,130,454
1972	100,110	9,778	1,067	1,179,991
1973	99,116	16,978	1,151	2,532,675
1974	108,952	14,901	1,225	1,975,778
1975	127,106	12,648	1,076	1,320,228
1976	133,731	15,366	1,209	2,689,845
1977	126,581	11,135	1,194	3,900,000

TABLE 2
CURRENT PRICES (1979) FOR SHARK FINS IN THE C. F. C.

<i>Fin Grade</i>	<i>Buying Price (Rs. per lb.)</i>	<i>Selling Price (US\$ per kg.)</i>
1. Wet, black fin ..	70 -80 ..	—
2. Dried, black fin ..	100	
> 12 inches ..	—	12.18
< 12 inches ..	—	10.51
< 8 inches ..	—	8.59
< 4 inches ..	—	
3. Dried, white fin ..	150	
4. Dried, white fin ..		
> 12 inches ..	—	18.07
< 12 inches ..	—	14.23

TABLE 3
TABLE (3) — PROCESSING OF WET AND DRIED SHARK FINS FOR FIN-RAYS

<i>Type of fins</i>	<i>Position of fins</i>	<i>Soaking Solution, time period and pH</i>	<i>Boiling time after Soaking (in minutes)</i>
1. Dried/white ..	dorsal ..	fresh water, 5 days ..	30 minutes in fresh-water (80-90°C)
2. Dried/white ..	dorsal ..	1% Hydrochloric acid, 2 N, 34.4% w/w (Technical grade) 1-2 days, pH 1.5 ..	10 minutes in fresh-water (80°C)
3. Dried/white ..	caudal—upper lobe ..	1% Hydrochloric acid 18 hrs., Soaking, pH 1.5 ..	10 minutes boiling in fresh water
4. Dried/white ..	caudal—lower lobe ..	do. ..	do.
5. Dried/black ..	pectoral and dorsal ..	1% Hydrochloric acid, 2 days, pH 1.5 ..	10 minutes boiling in fresh- water
6. Dried/black ..	caudal ..	1% Hydrochloric acid, 18 hrs. pH 1.5 ..	30 minutes boiling in fresh- water
7. Dried/black ..	dorsal ..	10% (v/v) Vinegar, 5 days, pH 3.5 ..	60 minutes in 10% (v/v) Vinegar
8. Dried/white ..	dorsal ..	do. ..	do.
9. Dried/white ..	dorsal ..	0.1% (w/v) Sodium hydroxide. 5 days, pH 11.5 ..	30 minutes in fresh-water (80-90°C)
10. Dried/black ..	pectoral and dorsal ..	do. ..	do.
11. Wet/black ..	pectoral and dorsal ..	Fresh water, 5 days ..	30 minutes in fresh-water (90°C)
12. Wet/black ..	do. ..	— ..	Direct boiling for 2½ hrs. in 10% (v/v) acetic acid at 60°C, pH 4.0

TABLE 4
TABLE (4) — PERCENTAGE OF YIELDS AND MOISTURE CONTENT OF THE
DRIED SHARK FIN-RAYS

Type of fins and Extraction Solvent	Position of fins	Length of the fins (CM)	Weight of the fins (g)	% Moisture of the dried rays	% Yield (dried rays to wet or dried fins)	% Yield (dried rays to wet rays)
1. Dried/white fin in water	.. Dorsal ..	25.0 10-20.0	.. 105.6 8.46-36.3 10.5 10.1 16.2 22.0 28.5 27.4 ..
2. Dried/white fin in 1% HCl	.. Dorsal Dorsal ..	24.0 10.0	.. 89.0 6.89 10.0 10.3 22.1 32.2 11.4 9.9 ..
3. Dried/white fin in 1% HCl	.. Caudal—upper lobe ..	15.0	.. 9.9 10.2 21.0 7.1 ..
	.. Caudal—lower lobe ..	9.5	.. 9.7 10.3 18.1 5.0 ..
4. Dried/black fin in 1% HCl	.. Pectoral Dorsal Caudal ..	31.0 15.0 19.0	.. 128.36 42.5 64.4 10.4 10.5 10.3 11.9 23.8 47.2 8.3 9.6 24.6 ..
5. Dried/white fin in 10% Vinegar	.. Dorsal ..	11.0	.. 9.22 8.7 21.3 30.7 ..
6. Dried/black fin in 10% Vinegar	.. Dorsal ..	22.0	.. 75.84 9.5 18.1 34.6 ..
7. Dried/white fin in 0.1% NaOH	.. Dorsal ..	22.0	.. 39.94 9.8 31.4 30.8 ..
8. Dried/black fin in 0.1% NaOH	.. Pectoral ..	40.0	.. 100.56 10.2 3.0 33.4 ..
9. Dried/black fin in 0.1% NaOH	.. Dorsal ..	15.0-25.0	43.55-29.10	10.4	.. 21.3 21.3 ..
10. Wet/black fin in water	.. Pectoral and Dorsal ..	20.0-35.0	1086.43	.. 10.0 6.0 32.7 ..
11. Wet/black fin in 10% Acetic acid	.. Pectoral ..	20.0-35.0	853.0	.. 10.0 8.2 18.0 ..

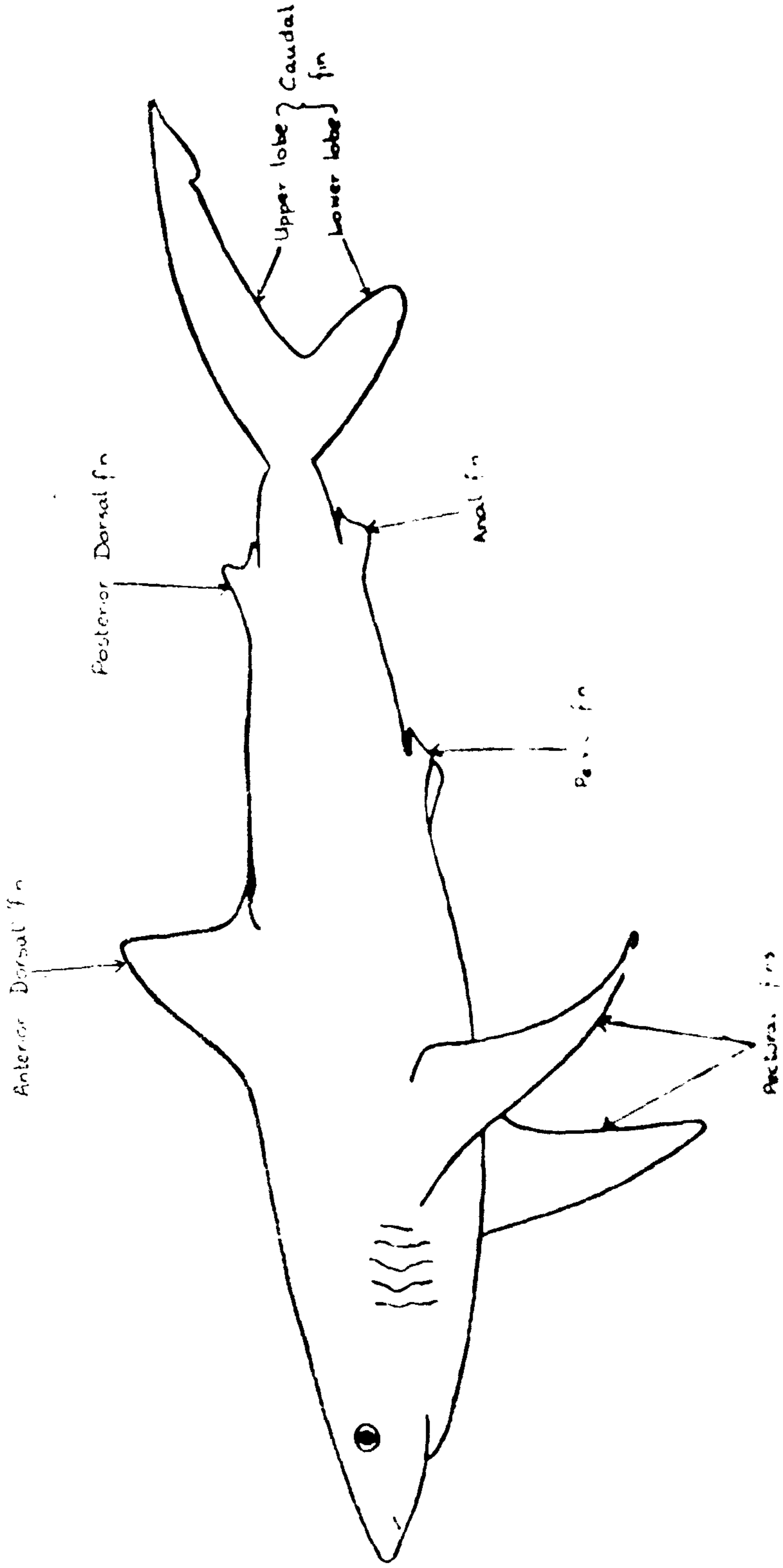


Fig 1 - *Carcharhinus* spp. (Shark).

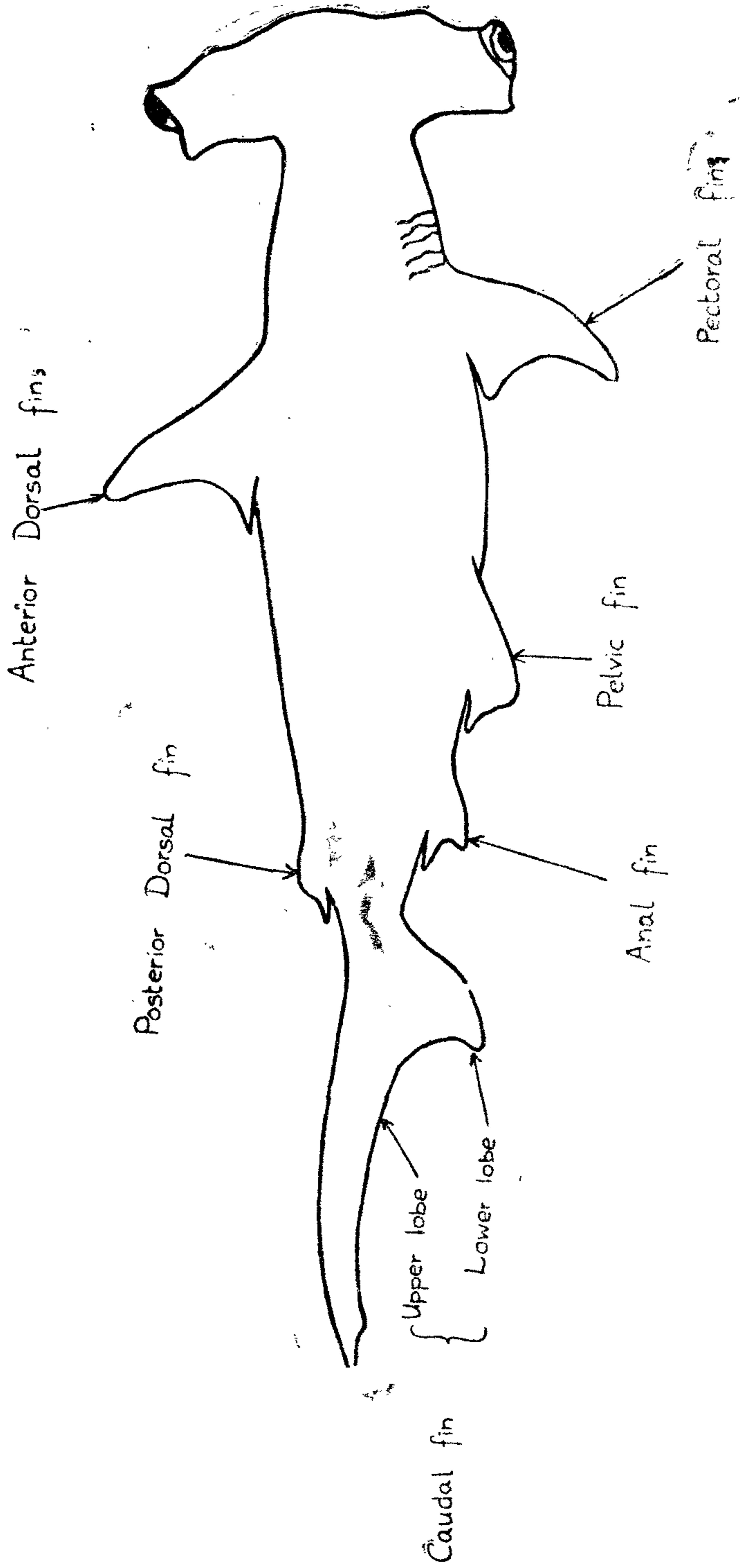


Fig. 2 - *Sphyrna* spp. (Hammer-head shark)

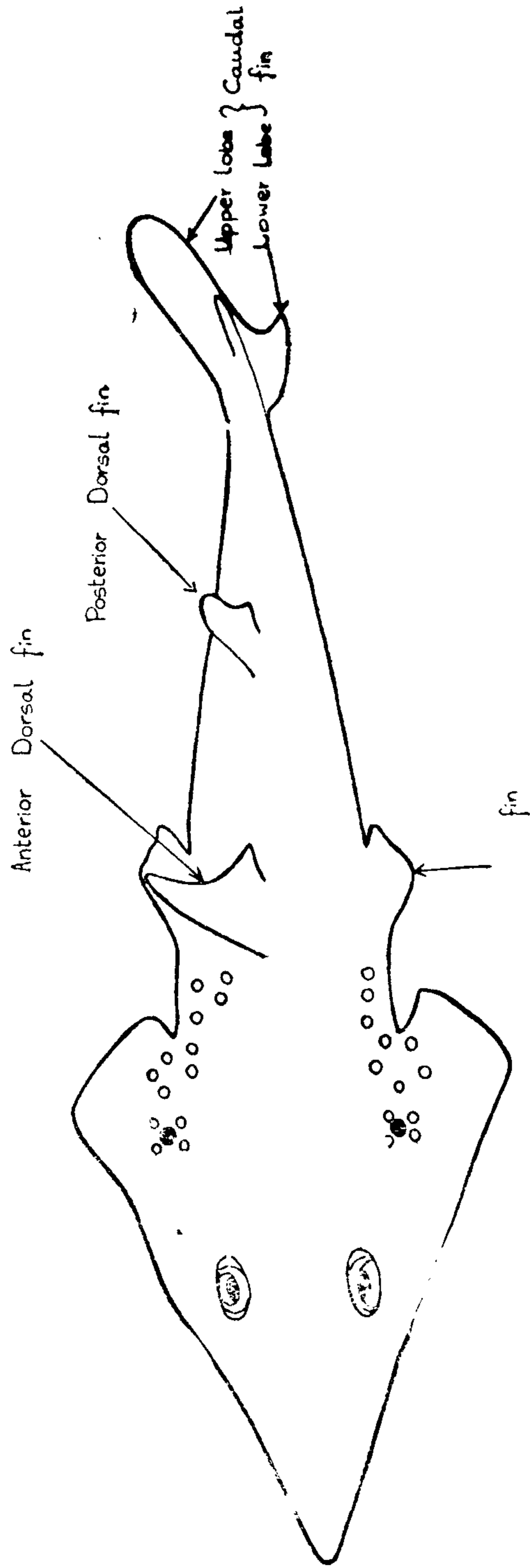


Fig. 3 - *Rhynchobatus djiddensis* (White spotted shovel nose ray)