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by I. Reichwald

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[Chemistry of fish lipids]

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ABSTRACT

The muscle ('meat') of freshwater fishes and marine fishes contains 1–25 % lipids which are predominantly triglycerides; phospholipids are generally present in rather small proportions. The lipids in the muscle of typical freshwater fishes contain considerable proportions of oleic and linoleic acids, whereas the lipids of most marine fishes contain relatively large amounts of highly unsaturated fatty acids having 20 and 22 carbon atoms. The fatty acid patterns of lipids in the muscle of freshwater predatory fishes resembles to a greater extent that of marine fishes than herbivorous freshwater fishes. In the meat of sharks, alkyldiacylglycerols occur in addition to small amounts of alk-1-enyldiacylglycerols (neutral plasmalogens). In the muscle lipids of marine fishes from depths of more than 1000 m, wax esters predominate. As a rule, the liver of marine fishes, especially of sharks, is rich in alkoxylipids, wax esters, steryl esters, vitamin A esters and hydrocarbons.

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INTRODUCTION

Fish are rich in high quality biological proteins. In view of this they are of great importance in nutritional physiology. Their taste as well as their stability are affected by the lipids contained in their meat. The lipid content of the fish muscle is between 1 and 25% (1-3). As a rule the lipid content of freshwater fish is lower than that of marine fish. Lipid concentrations also vary considerably within various fish species (4). The major portion of the lipids in the 'meat' or muscle of fish consists of triglycerides, whereas phospholipid proportions are usually low. Uncommon lipids, such as alkoxylipids (5), wax esters (6) and hydrocarbons (7), have been detected in relatively large amounts in liver oils and - to a considerably lesser extent - also in the muscle fat of marine fish, while freshwater fish only carry traces of such lipids. Additional secondary components of fish lipids are sterols, sterol esters, carotinoids and fat soluble vitamins. Fluctuations in lipid concentrations and in lipid composition are governed by sexual maturity, spawning time, living space and the particular time at which the fish are caught. But the food on which the fish feed plays the major role in the composition of their lipids (8). In this context, the marine food chain assumes great importance (9,10).

MARINE FOOD CHAIN

The phytoplankton, predominantly composed of algae living close to the surface of the sea, is the primary producer of organic material. These algae form proteins, carbohydrates and fats through photosynthesis. The herbivorous representatives of the zooplankton - mostly oar-footed animals, the copepods , feed on these algae. These animals are capable of converting a certain part of the lipids they have taken up into wax esters, in other words, fatty acids from dietary lipids are reduced to the corresponding alcohols and esterified with long-chain fatty acids. The fatty acid composition of the reserve lipids of oar-footed animals - wax esters and triglycerides - strongly resembles that of phytoplankton; it is characterized by high concentrations in C_{16} and C_{22} fatty acids and comparatively low concentrations of C_{18} fatty acids. The zooplankton, in turn, forms the food supply for numerous fish, such as herrings, sardines, anchovies, which are then eaten by larger fish, such as tunny fish and salmon as we progress further up the food chain; the latter again are eaten by sharks (9,10). In the deep strata of the sea the food chain differs from the scheme outlined above inasmuch as the copepods living there are all exclusively carnivorous. These copepods are capable of synthesizing wax esters along with triglycerides, and they store considerably larger quantities of the former than the herbivorous copepods. In some species wax esters may account for up to 70% of dry mass. Deep sea fish, such as BORSTENMÄULER* (Gonostomatidae) and lantern fish (Myctophidae) which feed on zooplankton also contain large quantities of wax esters, as do some shark species. As a rule, all marine creatures which live below a depth of 1000 meters are capable of synthesizing and storing wax esters. Yet, within the food chain, the copepods are the major producers of wax esters (9,10).

Fish, such as herrings, sardines and anchovies, whose food consists in the main of zooplankton rich in wax esters, are equipped with a specific, highly active wax 329 ester lipase which enables them to cleave not only triglycerides, but wax esters as well. Thus, no wax esters, nor any alcohols, have been detected in their blood. This means that the alcohols liberated from wax esters are obviously oxidized to the corresponding fatty acids. These fatty acids are then used as energy sources and drawn upon for the de novo synthesis of lipids (10). As a result of multiple environmental influences to which fish are exposed, and their specific metabolism, the fatty acid patterns of fish lipids, as well as the occurrence and composition of individual lipid classes, exhibit some characteristic properties.

FATTY ACIDS AND TRIGLYCERIDES

The broad spectrum of the lengths of chains, ranging from 12 to 26 carbon atoms, and the relatively high concentration of highly unsaturated long chain fatty acids (11) are characteristic for the composition of fatty acids in fish lipids by comparison with the fatty acid pattern in evidence in terrestrial animals. This abundant variety in fatty acids is primarily attributable to the fish's eminently developed ability to alter fatty acids by elongation and desaturation. In this manner arise - inter alia -

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* Translator's Note: The German term "Borstenmäuler" not found in any dictionary available to translator. Literal translation: bristle mouth. The Latin term given in brackets in the German text (Gonostomatidae)

the C_{20} and C_{22} fatty acids characteristic for fish lipids, which may contain up to six double bonds. However, there are also tetraethenoid C_{16} and C_{18} acids, for example, in the lipids of herring (12,13).

Fatty acids have strikingly regular structures. Unbranched, even-numbered carbon chains predominate; in the case of unsaturated fatty acids, these exhibit cis-double bonds. In polyunsaturated acids the double bonds are always separated by methylene groups (14). Fig. 1 shows that - depending on the position of the double bonds - the overwhelming number of unsaturated fatty acids can be divided into three families:

1. ω9-fatty acids, evolving from oleic acid.
2. ω6-fatty acids formed from linoleic acid; arachidonic acid also numbers among this fatty acid family.
3. ω3-fatty acids, which arise from alpha-linoleic acid. Among this family number the polyenoic acids characteristic for fish lipids, such as eicosatetraenoic acid, eicosapentaenoic acid and docosahexaenoic acid.

The ω6-fatty acids preponderate in the lipids of man and of terrestrial animals, whereas a high percentage of ω3-fatty acids is most characteristic for fish lipids.

Table 1 lists the fatty acid composition in the lipids of freshwater and marine fish muscles (15). In the lipids of both types of fish, palmitic acid is the dominant component of the saturated fatty acid group; the concentrations of myristic acid and stearic acid are noticeably lower, while usually only traces of lauric acid and arachidic acid are in evidence. A further dictum that applies to the lipids of both types of fish is that monoethenoid acids account for the major portion of unsaturated fatty acids, with oleic acid quantitatively predominant. While the lipids of marine fish are relatively rich in eicosenoic acid and docosenoic acid, those of freshwater fish contain relatively large amounts of palmitoleic acid. As a rule, there are no major differences between the lipids of freshwater fish and those of marine fish with respect to the composition of saturated as well as monounsaturated fatty acids (15). But, in their concentrations in highly unsaturated fatty acids the two types of fish exhibit distinct differences in their fatty acid patterns. The lipids of marine fish

Fig. 1

The three most important families of cis-unsaturated fatty acids.

1 = fatty acids
2 = oleic acid type
3 = linoleic acid type
4 = linolenic acid type

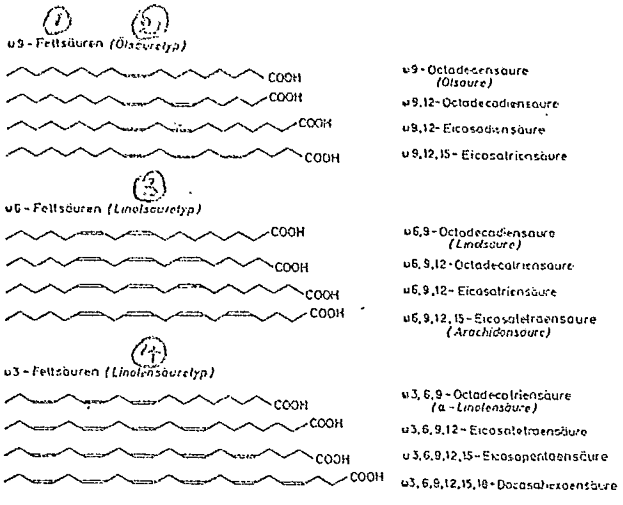


Table 1

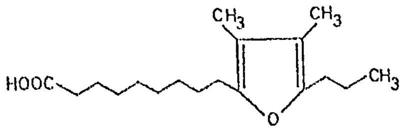
Average composition of major fatty acids in the lipids of freshwater fish and marine fish (in weight percent)

1 = fatty acids
2 = freshwater fish
3 = marine fish

① Fettsäuren	② Süßwasserfische	③ Seefische
$C_{14:0}$	6.4	5.0
$C_{16:0}$	17.0	16.1
$C_{18:0}$	3.0	3.0
$C_{16:1}$	15.5	9.4
$C_{18:1}$	19.6	21.0
$C_{20:1}$	1.3	7.0
$C_{22:1}$	1.9	5.5
$C_{18:2}$	3.0	1.3
$C_{18:3}$	4.2	0.7
$C_{20:4}$	3.1	2.0
$C_{20:5}$	5.8	9.8
$C_{22:5}$	1.5	1.9
$C_{22:6}$	3.9	8.5

Fig. 2

Furanoid C_{18}-fatty acids



are characterized by higher concentrations in polyethenoid acids, especially fatty acids of the C_{20} and C_{22} series with the five and six double bonds. On the other hand, the lipids of freshwater fish contain relatively more linoleic acid, linolenic acid and arachidonic acid (15-17). The fatty acid pattern of the lipids of freshwater predatory fish such as pike, eel-pout, and perchpike, tends to resemble that 330 of marine fish rather than that of herbivorous freshwater fish (18). Along with the highly unsaturated fatty acids listed above, polyenoid C_{24} acids with four, five and six double bonds have also been demonstrated in the liver oils of some marine fish species. Like those of the C_{20} and C_{22} series, the principal isomers of these fatty acids exhibit a ω3-structure (19).

Some uncommon, exceptional fatty acids are also found in the lipids of a few freshwater and marine fish. Thus, in the triglycerides of the lipids of the mullet, *Mugil cephalus*, more than 25% of the unbranched fatty acids are esterified with 13, 15, 17 and 19 carbon atoms (20). Two further rather uncommon fatty acids have been discovered in the lipids of the ocean sunfish, *Mola mola*, 7-Methyl-7-*cis*-hexadecenoic acid and *trans*-6-hexadecenoic acid have been isolated from the lipids found in the liver as well as several other tissues of this fish species (21,22). These fatty acids account for 1 to 3% of total fatty acids. An analysis of the composition of the food on which this fish feeds has revealed that the lipids of jelly fish, which form the major component in the fish's diet, contain the same fatty acids (23). Recently, American authors have discovered a group of eight homologous fatty acids of uncommon structure in the lipids of the pike, *Esox lucius*: these are fatty acids which contain a furane ring (Fig. 2)(24). They are only esterified in triglycerides and cholesterol esters, but not in phospholipids (25). In the lipids of the pike's testes and liver these fatty acids account for 25% of total fatty acids, and in the liver lipids of the remaining species investigated they may even represent up to 50% of all fatty acids. On the other hand, muscle, heart and blood lipids only contain low concentrations of these fatty acids, which have, moreover, so far only been demonstrated in male animals (25).

Polyethenoid acids with chain lengths of 20, 22 or 26 carbon atoms, whose double bonds are not separated by a methylene group - "non-methylene interrupted fatty acids" - have so far not been found in the lipids of fish, but have been demonstrated in those of invertebrate animals, such as oysters and molluscs (26-28) and in some marine algae (29). It should further also be mentioned that a high proportion of isovalerianic acid has been found to form a component of triglycerides and wax esters in the lipids of the acoustic organ of some marine mammals (30,31).

Fatty acids absorbed from the food are primarily incorporated into the glycerolipids of fish, i.e. triglycerides, phospholipids and in some instances alkoxylipids. As a rule, triglycerides form the major portion of depot lipids in fish. An analysis of fatty acids esterified in triglycerides has shown that certain fatty acids tend to be esterified in certain positions of the glycerol. The polyethenoid acids characteristic for fish lipids are mostly found at the C-2 position of glycerol (8), in some instances a certain degree of preference for palmitic acid in the 2-position can also be discerned. On the other hand, the 1- and 3-positions are occupied by saturated, long-chain fatty acids. Long-chain acids, such as, for example, docosenoic acid, are primarily found in 3-position (8).

PHOSPHOLIPIDS

In fish - as in man and in terrestrial animals - phospholipids seem to function as structural elements in membranes and enzymes (32). Their principal representatives are phosphatidylcholine and phosphatidylethanolamine (Fig.3). Cardiolipin, phosphatidylinositol, cerebroside, the sphingomyelins and lysolecithin are found at concentrations lower than in the lipids of mammals. Plasmalogens have been found in the lipids of sea anemones (32) among others. As a rule, phospholipids contain higher concentrations of the characteristic polyethenoid C_{20} and C_{22} acids than do 331 the triglycerides of the same oil. As in the triglycerides, they tend to be esterified preferably in the 2-position of the glycerol.

ALKOXYLIPIDS

Some species in the group of marine fish are equipped with enzymes which enable them to reduce fatty acids to the corresponding alcohols, and to utilize these for the synthesis of alkoxylipids. Primarily cartilagenous fish and sharks are endowed with this capacity. Alkyldiacylglycerols and alk-1-enyldiacylglycerols have been found in their lipids (34). It is clearly evident from Fig.4 that the structure of these alkoxylipids greatly resembles that of the triglycerides. They merely differ from the latter by the ether bond at C-1 of the glycerol molecule. No derivatives with an ether bond at C-2 of the glycerol molecule have been detected in the lipids of fish or the lipids of other animals. Like all natural alkoxylipids found to date, the 1-0-alkyl and 1-0-alk-1-enylglycerol derivatives of fish lipids also belong to the optically active compounds of the d-series. The double bond of the alk-1-enyl moiety always has a cis-configuration (35,36). In some shark species, alkyldiacylglycerols can partly replace the triacylglycerols. Larger quantities of these alkyldiacylglycerols are found in the liver lipids of sharks. Their proportion in the unsaponifiable of the liver lipids of some shark species may range from 1%, as in the giant shark, Cetorhinus maximus, to 85% as in the dogfish, Squalus acanthias. Their proportion in the total amount of liver lipids varies from one shark species to the next: it ranges from 0.4% to about 11% (37). Rather high proportions of alkyldiacylglycerols have also been found in the muscle lipids of the dogfish, Squalus acanthias. The 'meat' of this shark contains 35% of this lipid class, compared to 45% in the liver lipids (38). Most recently, 2-hydroxyalkyl (39) and 2-methoxyalkyl moieties (40) have also been found in neutral alkoxylipids of various shark species.

So far, alk-1-enyldiacylglycerols have only been demonstrated and analyzed in the liver lipids of the ratfish, Chimaera monstrosa and Hydrolagus colliei, where they account for approximately 5% (35,41,42). Usually the alkyl and alk-1-enyl moieties in the alkoxylipids of sharks are saturated or monounsaturated but chain length distribution varies (42). The quantitatively most important alkyldiacylglycerols have 16:0, 18:0 and 18:1 alkyl residues which account for 64% of the alkyldiacylglycerols found in the liver lipids of the dogfish, and for up to 71% of those found in the Greenland shark, Somnius microcephalus (43). Smaller amounts of tetradecyl-, hexadecenyl-, eicosenyl- and docosenyldiacylglycerols, and up to 3.3% of octadecadienyldiacyl glycerols have been identified in the liver lipids of various sharks (37,43). Low concentrations of glycerol ethers, whose alkyl moieties have unbranched chains or an odd number of carbon atoms, have also been found in sharks (37,42-44).

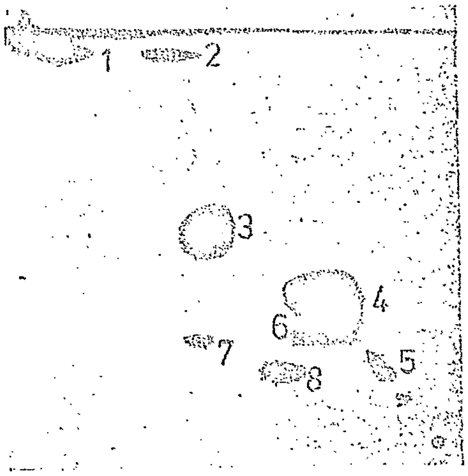
The alkyl glycerols in the liver and muscle lipids of the dogfish are of the same qualitative composition, but the concentrations of 16:0 alkylglycerols in the 'meat' (muscle), which amount to 61%, are distinctly higher than those in the liver where they amount to 47%; on the other hand 18:1 alkylglycerols are preponderant in the liver lipids where they amount to 60% (38). The distribution of chain lengths in the alk-1-enyl moieties of neutral plasmalogens have been studied primarily in the lipids of the ratfish (42,45). A comparison with the alkyl moieties of the corresponding derivatives in the lipids of this fish reveals the following facts: whereas the alkyl moieties predominantly exhibit chain lengths of 16 and 18 C-atoms, the spectrum of the alk-1-enyl moieties lies between C_{18} and C_{22}, with a clearcut preference for 18:0 and 20:1 alk-1-enyl moieties (35). Neutral plasmalogens with monounasaturated alk-1-enyl moieties account for approximately 46% of total plasmalogens in the liver lipids of the ratfish, while the alkyldiacylglycerols present 72% monounsaturated alkyl moieties (45). The alkyl- and alk-1-enyl residues in the neutral alkoxylipids of the ratfish differ with respect to branched chains: while 332
5% of branched alkyl moieties are found, there are 16.7% of branched alk-1-enyl moieties (42)

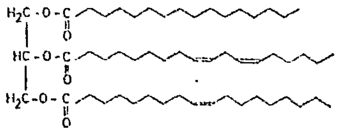
In the glycerol ethers of the liver lipids of Squalus acanthias and Galeorhinus zyopterus the major isomer of the monounsaturated C_{18}-alkylglycerols is Δ^9-octadecenyl glycerol, followed by the Δ^7-isomer; the Δ^6, Δ^8, Δ^{10} and Δ^{11} isomers are also found in smaller amounts (46). The predominant isomer in the liver lipids of the ratfish is likewise Δ^9-octadecenyl glycerol, whereas the Δ^7-isomer is dominant in the hexadecenyl and eicosenyl glycerols (45). Δ^9 - 18:1 alk-1-enyl moieties are

Fig. 3

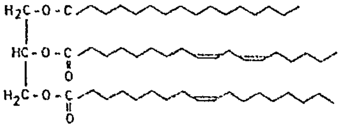
Two-dimensional thin layer chromatogram of lipids found in the 'meat' of <u>Hariotta raleighana</u>

1 = triglycerides and cholesterol
2 = fatty acids
3 = phosphatidyl ethanolamine
4 = phosphatidyl choline
5 = sphingomyelin
6 = lysophosphatidyl ethanolamine
7 = phosphatidyl inositol
8 = phosphatidyl serine

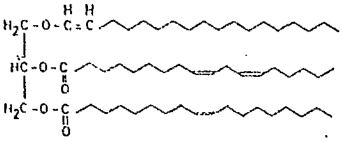




Triacylglycerin
(Triglycerid, "Fett")



Alkyldiacylglycerin
(Glycerinatherdiester)



Alk-1-enyldiacylglycerin
(Neutrales Plasmalogen)

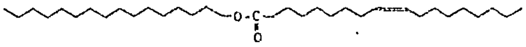
Fig 4

Neutral glycerolipids

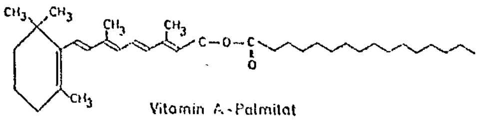
...glycerin = ...glycerol
neutrales = neutral

Fig. 5

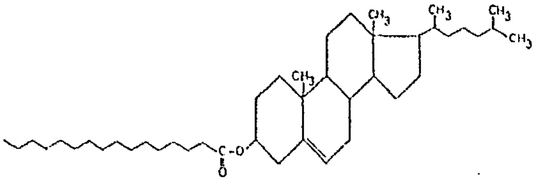
Wax esters and related compounds



Hexadecyloleat



Vitamin A-Palmitat



Cholesterylpalmitat

also predominant in the neutral plasmalogens of the ratfish, whereas Δ^7 isomers preponderate in the 20:1 and 22:1 alk-1-enyl moieties (45).

An analysis of the acyl residues in the alkyl and alk-1-enyldiacylglycerols of the liver lipids of the ratfish reveals that oleic acid is preferably esterified in both lipid types. On the other hand, a broad spectrum of unbranched and branched acyl moieties is found at the C-3 position of glycerol; moreover this spectrum differs considerably in these two derivatives (42). The similar composition of the 2-acyl residues in the alkyl- and alk-1-enyldiacylglycerols of the ratfish suggests that the 2-acylglycerol forms the ground structure for these two classes of lipids and may possibly originate from lipids in the food chain (42).

DIOL LIPIDS

The lipids of animals, plants and microorganisms often contain small quantities of liophilic acyl- and alk-1-enyl derivatives of ethylene glycol and other diols. So far no such compounds have been detected in fish lipids. However, in the marine milieu, in surface lipids of the Crustacea *Ligia oceanica* (47) and in the lipids of the acoustic organ of the porpoise, *Phocoena phocoena* dialkyl ethers of diols, or dialkoxyalkanes, have been identified and isolated (54,48).

WAXES

As we have mentioned above, creatures living at a depth of more than 1000 meters are capable of synthesizing wax esters by reducing fatty acids to the corresponding alcohols and esterifying the latter with long-chain fatty acids (10,49). Wax esters (Fig. 5) have been demonstrated in the lipids of sea anemones, corals, molluscs, in zooplankton, in bonefish, cartilagenous fish, as well as in the "acoustic" lipids of marine mammals (10,30,49,50). Apparently, apart from their function as energy reserves, they are also required for heat isolation and for the animals' ability to swim. Accordingly, larger quantities of wax esters are found in the depot lipids of some marine fish, while structural lipids contain only very low proportions of these compounds (10,49). More than 90% of wax esters are found in the muscle lipids of the crossopterygian *Latimeria chalumnae* from the family of Acinaceidae, while the liver lipids of these animals contain less than 10% of this lipid class (51). The liver lipids of the dogfish, as well as those of two other shark species, *Galeorhinus zyopterus* and *Carcharhinus falciformis*, even contain less than 1% of wax esters (46); the livers of some deep sea sharks, however, contain rather high levels of wax esters (8). With some 70-85%, the body lipids of the white Baracudina, *Paralepsis rissoi*, from the lantern fish family, are also very richly endowed with wax esters (52).

In general, wax esters with 21 to 44 carbon atoms are found in fish lipids and in the lipids of zooplankton, especially some Calanus species. The greatest proportion of these is accounted for by monoethenoid and diethenoid compounds with 30 to 42 carbon atoms (6,49). Roe lipids of the mullet, *Mugil cephalus* and the labyrinth fish *Trichogaster cosby*, which contain more than 80% of wax esters, contain more than two thirds in triethenoid and polyethenoid homologues (53,54). Like those of the alkyl glycerols, the alkyl moieties of the wax esters are - as a rule - saturated or monounsaturated. The major components are hexadecyl- and octadecenyl residues; only traces of polyunsaturated alkyl residues are present (8,49,53-55). A total of about 3.3% of polyunsaturated alkyl residues with 18, 20 and 22 carbon atoms is found in the wax esters of the roe lipids of *Mugil cephalus* (53). The lipids of various developmental stages of *Euchaeta japonica*, a remiped, contain very high proportions of saturated alcohol components; most surprising is a rather high level of tetradecanol amounting to 24 to 42%, and hexadecanol amounting to 25 to 65% (56).

Chain lengths and position of the double bonds in the alkyl- and acyl moieties of the wax esters are very similar although the composition of the acyl moieties exhibits much greater variety (49,57,58). As a rule, oleic acid is the dominant 333 fatty acid component in wax esters, but quite frequently hexadecenoic acid and eicosenoic acid may form the major component of the acyl moiety (49). Polyunsaturated fatty acid residues account for about 1 to 12% of the acyl moieties in wax esters of fish lipids (49). Their relatively lower proportion in the muscle lipids appears to be a characteristic of wax esters in marine creatures. On the other hand, in roe lipids they may reach levels of up to 45% (49). Another remarkable fact is that the alkyl- and acyl moieties of roe lipid wax esters in the mullet and hake have a noticeable amount of chains with odd numbers of carbon atoms, e.g. 15,17,19 and 21 carbon atoms (54,57,58). The major part is accounted for by saturated C_{15}-alkyl moieties of which as much as up to 18.6% were found in the wax esters of Mugil cephalus roe (54,57,58). Very short-chain alkyl residues from 8 carbon atoms on, have been found esterified in the wax esters of Lepidocybium flavobrunneum, which - like Ruvettus pretiosus - hails from the Acidaceidae family (59). Such short chains are also found in the acyl moieties of the triglycerides of this species, but not in the acyl moieties of their wax esters (59).

The fact that the alkyl- and acyl moieties of wax esters are usually rather similar argues for the assumption that the alcohols arise from the fatty acids by reduction, but due to a specific enzyme system only traces of polyunsaturated fatty acids are reduced to the corresponding alcohols (53,60).

The tissues of bony fishes, such as mackerels, anchovies, sardines and herrings, which feed mostly on zooplankton rich in wax esters, contain almost no wax esters. As we have mentioned before, these fish species are capable of cleaving wax esters. On the other hand, the "HAGFISCH"* and some sharks seem to absorb wax esters uncleaved from food lipids (10). Wax esters have been demonstrated in the lipoproteins of their serum (10). Conceivably they may also have assumed a transport function for fatty acids in the blood (10).

By comparison with the meat of terrestrial animals, the 'meat' of fish has considerably lower concentrations of cholesterol and cholesterol esters; on the average levels are between 30 and 50 mg/100 g fish 'meat' (61,62).

HYDROCARBONS

Up to 90% of squalene has been found in the liver lipids of some deep sea sharks (8,63). In some species squalene accounts for 5 to 15% of total body weight. It has been found that the squalene content of the liver does not depend on the size of the liver nor on the sex of the animal analyzed (7). Other shark species, and many other fish species contain only low levels of hydrocarbons, in some instances as

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* Translator's Note: "Hagfisch" is in QUOTATION marks in the GERMAN text, presumably indicating that this is not a commonly used term. The term was not found in any dictionary or German reference book available to

little as 0.1% (7,64). Table 2 lists hydrocarbon and sterol concentrations in the liver oils of six sharks (7). The three species Centroscyllium, Centrophorus and Cethorhinus which live at considerable depths possess distinctly higher concentrations of hydrocarbons in their liver oil than do the remaining species analyzed. At the same time, one is struck by the fact that - by comparison with the liver oils of Triakis, Squalus and Apristurus - they have low levels of sterols. In all sharks examined, quantitatively squalene is the preponderant hydrocarbon in the liver oils, amounting to 66 to 99.9% of total hydrocarbons (7). Apparently squalene is the major representative of hydrocarbon in the marine biosphere. Usually smaller amounts of pristane, also called norphytane, which is the tetramethylpentadecane, are found along with squalene, as well as norphytene, the unsaturated analogue (Fig. 6) 8,65).

In herring oil, which contains only 0.05% of hydrocarbons, eight branched chain hydrocarbons and 21 straight chain hydrocarbons have been demonstrated by thin layer and gas chromatography (8). Among the compounds with branched chains pristane and squalene predominate, with the pristane content considerably higher. In the unbranched hydrocarbons, compounds with uneven chain length are dominant. They may conceivably have arisen from the corresponding fatty acids by enzymatic decarboxylation, perhaps through the interaction of intestinal bacteria. Almost no isoprenoid hydrocarbons could be demonstrated in the lipids of four freshwater fish (60). The oils of the marine species codfish, herrings and sand eel, which 334
feed mostly on herbivorous Crustaceae, were analyzed for comparison: pristane levels were found to be higher than in the freshwater fish analyzed. The analysis further revealed that among the unbranched alkanes present, heptadecane predominates in the oils of freshwater fish, whereas octadecane is dominant in those of marine species (66).

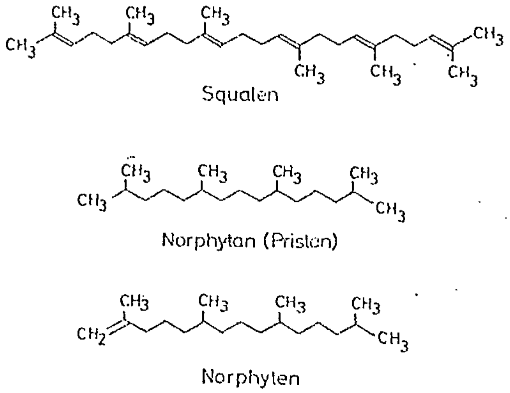
Obviously the isoprenoid hydrocarbon pristane originates in phytoplankton. Herbivorous Crustaceae seem to be capable of forming pristane from phytol, a component of chlorophyll. These animals are probably the most improtant source for

Table 2:

Hydrocarbons and sterols in shark liver oils (7)

Leberlipide = liver lipids
Kohlenwasserstoffe = hydrocarbons
gesamt = total
Sterine = sterols

Spezies	Leberlipide		
	Kohlenwasserstoffe		Sterine
	gesamt [%]	(Squalen : Pristan)	[%]
Triakis scyllia	0.4	(93.5 : 6.1)	4.1
Squalus acanthias	0.4	(65.5 : 34.5)	1.0
Apristurus macrorhinus	2.1	(70.5 : 29.5)	1.2
Centroscyllium ritteri	35.5	(96.8 : 3.2)	1.7
Centrophorus Spp.	64.1	(99.9 : 0.1)	0.7
Cetorhinus maximus	34.3	(98.0 : 2.0)	0.9



Squalen

Norphytan (Pristan)

Norphyten

Fig. 6:

Isoprenoid hydrocarbons

pristane although so far it is not known whether they possess their own enzyme system for its synthesis or intestinal bacteria are responsible for the conversion (8). However, once formed, pristane appears to be very stable and to traverse the food chain quite unaltered (8). Direct conversion of phytol to pristane by freshwater invertebrates - if it occurs at all - would appear to yield only low quantities. The very low concentrations of pristane in freshwater fish argue in favor of this hypothesis (8).

The occurrence of larger amounts of squalene in the liver oil of deep sea sharks would also seem to be attributable to their nutritional intake: an oil containing up to 45% of squalene has been demonstrated in the intestinal content of these animals, especially in Dalathias licha (64); however, the source of this oil is obscure. One possible reason for the accumulation of squalene, an intermediary product in cholesterol biosynthesis in the liver lipids of deep sea sharks, would seem to be inadequate supply of oxygen or of other factors, e.g. deficiency in the coenzymes required for cyclization (7).

BIOLOGICAL SIGNIFICANCE OF LIPIDS IN FISH

The sometimes rather large quantities of uncommon lipids, such as alkoxy lipids, wax esters and hydrocarbons which appear - along with triglycerides - in the 'meat' and in the liver of fish - especially in the liver of deep sea sharks - apparently not only serve as energy reserves or structural elements (34,36,64). These compounds differ from triglycerides with respect to their specific weight (46,64). It has been found that external factors, such as pressure, temperature and oxygen concentrations may affect the metabolism, and thus the composition of lipids in fish (8). Therefore, alternating ratio of alkoxylipids or wax esters or hydrocarbons to triglycerides in the liver, for example, may conceivably regulate the hydrostatic properties of the fish in the course of vertical migrations (34,67).

OUTLOOK

In view of the expansion of fishing limits and the marked decline in catches, high sea fishery is attempting to find new catch grounds and to discover new fish that may be utilized. Krill, crustaceans from antarctic waters, are now also considered as a possible source for the feeding of animals, and for human consumption. Apart from the eminent significance of fish as a supplier of protein, the low fat content of fish 'meat', with its insignificant cholesterol concentrations and high levels of polyunsaturated fatty acids, is a further advantage in human nutrition. Freshwater fish, especially those which - like carp and sheat fish - can be produced by intensive cultivation, contain relatively high proportions of fatty acids of the linoleic acid family. These properties of fish lipids are very important, especially in the diet of persons with vascular and circulatory disease. In this context, it is very important that the fatty acid composition of lipids and the nutrition physiological properties of uncommon lipids in various fish, especially in new utility fish, and fish grown in intensive cultures, should undergo systematic investigation.

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Translation of foreign Reference titles (list on p.18):

3. Marine fish as food.
4. The composition of foodstuffs.

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