

The compound was studied in different solvents and at both 40 Mcps and 60 Mcps to vary  $\nu_0\delta$  and thus check the fit of the assignment of couplings for different spectra. The spectrum shown was recorded in an 11.7 % solution in acetone at 60 Mcps giving  $\nu_0\delta = 10.80$  cps.

The method of analysing  $A_2B_2$  spectra presented here is thus applicable when the spectrum can be regarded as a perturbed AB case and should then be useful. A more extensive discussion with applications to other compounds will be published later.

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## Partial Characterization of the Hydrocarbons of Herring Oil

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Shark liver oils are known to contain high concentrations of hydrocarbons, and squalene is present in as high as 80 % of the oil of the basking shark. Other well characterized hydrocarbons in fish oils are pristane and zamene, belonging to the  $C_{19}$  aliphatic terpenoids <sup>1,2</sup>. Others have been named, but their structures are uncertain <sup>3</sup>.

A preliminary gas chromatographic study of several vegetable oils and fish oils revealed the presence of complicated mixtures of hydrocarbons in many of them. In general the vegetable oils contained fewer hydrocarbons than did the fish oils. Rape seed oil contained several major hydrocarbon constituents, whereas squalene was the principal hydrocarbon in olive oil.

Herring oil was studied in most detail. This oil contained 0.05 % hydrocarbons, about 5 % of the unsaponifiable matter. 500 g of herring oil were saponified <sup>4</sup> using hydroquinone and ascorbic acid as antioxidants. The unsaponifiable fraction was extracted quickly with ethyl ether and resaponified. The unsaponifiable fraction was chromatographed on alumina with hexane and the eluate was concentrated and rechromatographed in the same way on a smaller column. Upon evaporation of the solvent, the fraction gave a near-infrared spectrum corresponding to a pure hydrocarbon.

Table 1. Hydrocarbons occurring in herring oil as determined by gas chromatography.

| Straight chain components |         | Branched chain components |        |
|---------------------------|---------|---------------------------|--------|
| Carbon Number             | % area  | Carbon Number             | % area |
| 14.0                      | 0.3     | 15.4                      | 3.5    |
| 15.0                      | 7.5     |                           |        |
| 16.0                      | 0.6     | 16.8 (pristane)           | 70.0   |
| 17.0                      | 9.0     |                           |        |
| 17.6                      | 2.2     | 17.9                      | 5.0    |
| 18.0                      | 1.7     |                           |        |
| 19.0                      | 10.5    | 19.0                      | 0.5    |
| 20.0                      | 0.3     |                           |        |
| 21.0                      | 6.0     | 19.9                      | 1.0    |
| 22.0                      | 0.3     |                           |        |
| 23.0                      | 0.8     | ~21*                      | 3.5    |
| 24.0                      | 0.3     |                           |        |
| 25.0                      | 9.5     | 22.2                      | 3.5    |
| 26.0                      | trace   |                           |        |
| 27.0                      | 33.0    | 26.3 (squalane)           | 13.0   |
| 28.0                      | trace   |                           |        |
| 29.0                      | 9.0     |                           |        |
| 30.0                      | trace   |                           |        |
| 31.0                      | ~7      |                           |        |
| 32.0                      | (trace) |                           |        |
| 33.0                      | ~1      |                           |        |

\* Flat and broad peak.

Thin layer chromatography on Silica Gel G (Merck) in light petroleum, b.p. 30–60°, revealed at least six components, and charring with sulfuric acid yielded brown to black coloration, suggesting the absence of conjugation. After complete hydrogenation, thin-layer chromatography yielded only one spot, suggesting that the six or more original components were unsaturated.

To achieve partial identification of some of the hydrocarbons, the mixture was completely hydrogenated and the straight-chain and branched components were separated by urea fractionation in isopropanol. The non-complex fraction had a near-infrared spectrum similar to pristane<sup>1</sup> and the complexed fraction had a spectrum similar to eicosane. Gas chromatographic analysis was performed on each fraction using a Barber Coleman Model 20 instrument, with a 1.25 meter  $\times$  6 mm column containing 15 % Apiezon L on celite. Chromatograms were run at 180° and 230° for short and long chain components, respectively. The results of these analyses are given in Table 1.

All straight-chain paraffins from  $C_{14}$  through  $C_{33}$  were observed in the urea-complexed fraction. These were identified by semilog plots using a few normal paraffins as standards. No other components were observed except one unknown substance having a carbon number of 17.6. Odd numbered paraffins were dominant. The 15, 17, 19, and 21 carbon hydrocarbons, probably originally unsaturated, might correspond to decarboxylation pro-

ducts of the principal fatty acids of herring oil. The 25, 27, and 29 carbon members of the series correspond in chain length to the principal wax hydrocarbons of plants. It should be noted that the most prominent plant wax hydrocarbons are saturated and have 29 and 31 carbons<sup>4</sup>, whereas the hydrocarbons of these chain lengths in herring oil are probably unsaturated.

The branched chain hydrocarbons were dominated by pristane, and squalane (carbon number 26.3) was of next importance. The structures of the minor constituents remain unknown.

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