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## LABORATORY METHOD OF OBTAINING UNSATURATED FATTY ALCOHOLS FROM FISH OILS

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### PREFATORY ABSTRACT

A laboratory method of obtaining unsaturated fatty alcohols without the disadvantages of the conventional sodium-reduction process was worked out for fish-oil fatty acids. This method involves the use of lithium aluminum hydride. A combination of low-temperature crystallization and urea-complexing provides the best practical means of obtaining these highly unsaturated fractions, with a minimum of molecular change. These techniques are needed in the development of new industrial products from fish oils.

### BACKGROUND

Research is being conducted on fish oils at the Service's Seattle Technological Laboratory for the purpose of developing new industrial products. In the past there has been very little work on the development of such products from fish oils. About three years ago, need for more research of this nature became evident because of a downward trend in fish-oil consumption.

Fish oils contain fatty-acid constituents that are different from those in animal and vegetable oils in two respects. First, the fatty acids of fish oils have, on the average, molecules of longer chain lengths than have the other common commercial oils. Second and more important, the fish-oil fatty-acid molecules have a greater concentration of highly unsaturated constituents than have the other common oils. This high unsaturation is unique in that it constitutes 4 to 6 carbon-atom-to-carbon-atom double bonds, as compared to 2 to 3 double bonds in other oils.

In the development of new products, the question is: what aspect of these unique compounds can best be utilized? In other words, (1) should the high degree of unsaturation of the oils be used to obtain products that cannot be prepared from other commercial oils or (2) should

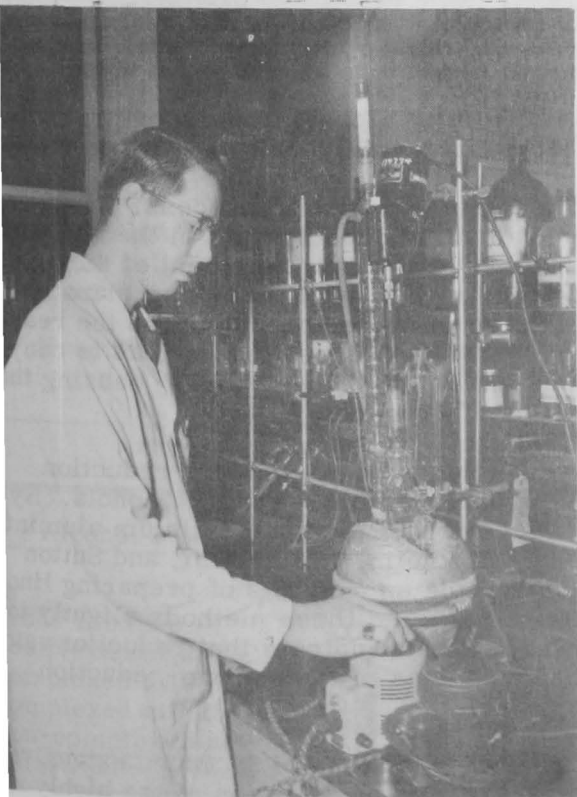


Fig. 1 - Apparatus for carrying out sodium-reduction of triglycerides of fish oils, Seattle Technological Laboratory, Seattle, Wash.

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products be developed that possess the available high degree of unsaturation of the oils? Epoxy fatty acids, which contain no unsaturation, are an example of a product that results from using the unsaturation to produce it. Polyunsaturated fatty alcohols are an example of the other type of product in which the unsaturation is maintained.

Much of the research carried on at the Seattle laboratory has been of this latter type, the thinking being that products from fish oils that maintain the high degree of unsaturation will help add to a technology based on polyunsaturation. Many of our paints and lacquers rely on polymerization through unsaturation of this kind for their film-forming properties. It is quite possible that desirable properties can be obtained through the presence of carbon-to-carbon unsaturation as well as of other functional chemical groups.

#### NATURE OF EXPERIMENTAL WORK

POLYUNSATURATED FATTY ALCOHOLS: Polyunsaturated fatty alcohols have been given considerable attention in this laboratory. The fatty alcohols are intended to serve as a link or an intermediate to the production of many possible derivatives. Initial work in this study was reported by Gruger (1957). A method that was developed by Pryde (1951) for the sodium reduction of menhaden oil was carried out on methyl esters of pure fatty acids to produce the corresponding fatty alcohols. This method was subsequently applied at this laboratory to the natural triglycerides of sardine oil.



Fig. 2 - Simultaneous hydrolysis and steam distillation of sodium-reduction products of triglycerides, Seattle Technological Laboratory, Seattle, Wash.

Several disadvantages were noted in the sodium-reduction process. The reaction required high temperatures in order to maintain the sodium in the required molten state. This high temperature was conducive to rearrangement of the double bonds in the resulting fatty alcohols, besides aiding oxidation and polymerization. Furthermore, the presence of a strongly alkaline mixture contributed to the rearrangement of the double bonds. This rearrangement, in most cases, led to conjugated double bonds, which in turn produced an unstable system, thereby causing the products to polymerize readily in the presence of oxygen.

We are attempting to overcome the disadvantages of the sodium-reduction process by using another method of producing polyunsaturated fatty alcohols. Nyström and Brown (1947) were among the first to report the use of lithium aluminum hydride for the reduction of carboxylic acids. Lighthelm, von Rudloff, and Sutton (1950) reported the use of lithium aluminum hydride as a means of preparing linolenyl alcohol from methyl linolenate. We have modified these methods slightly to apply to fish-oil fatty acids and esters. Initial results indicate that reduction using lithium aluminum hydride overcomes the disadvantages of the sodium-reduction process.

SEPARATION METHODS APPLIED TO FATTY ALCOHOLS: More extensive, however, has been the work relating to separation and purification of the highly unsaturated fatty alcohols derived from fish oil. These separations were studied for the purpose of finding the best means for concentrating the highly unsaturated fatty

alcohols that possess tetraene, pentaene, and hexaene structures. Much attention was given to low-temperature fractional crystallization, fractionation of urea-inclusion compounds, and fractional distillations at reduced pressures.

The low-temperature fractional crystallization of the fatty alcohols was carried out at room temperature, 0° C., and -25° C., employing acetone as the solvent. A ratio of 10:1 (volume to weight) of acetone to fatty alcohols was used. An addi-

Table 1 - Analytical Results of Some Low-Temperature-Fractionated Sardine-Oil Fatty Alcohols <sup>1/</sup>

| Fraction   | Weight              | Yield          | Iodine Value<br>(Wijs)   | Refractive<br>Index          | Acid<br>Value       |
|--|---------------------|----------------|--|------------------------------|---------------------|
|  | <u>Grams</u>        | <u>Percent</u> |  | <u><math>n_D^{30}</math></u> |                     |
| Destearinated sardine<br>oil . . . . .                               | 300.0               | -              | 197.7  | 1.4782                       | 175.4 <sup>2/</sup> |
| Crude fatty alcohols . . .   | 243.7               | 100.0          | 191.6  | 1.4738                       | 19.2                |
| Fatty alcohols from<br>-5° C. precipitate . . . .                    | 44.4 <sup>4/</sup>  | 18.2           | 137.1  | 1.4511 <sup>3/</sup>         | 13.5                |
| Fatty alcohols from<br>-25° C. precipitate . . .                     | 61.5 <sup>4/</sup>  | 25.3           | 119.6  | 1.4485                       | 12.8                |
| Fatty alcohols from<br>-25° C. filtrate . . . . .                    | 137.6 <sup>4/</sup> | -              | 235.2  | 1.4803                       | 22.8                |
| Fatty alcohols from<br>-70° C. precipitate . . .                     | 77.2 <sup>4/</sup>  | 31.7           | 197.6  | 1.4748                       | -                   |
| Fatty alcohols from<br>-70° C. filtrate . . . . .                    | 43.4 <sup>4/</sup>  | 17.8           | 300.8  | 1.4930                       | -                   |
| <sup>1/</sup> Fatty alcohols prepared by a sodium reduction process. |                     |                | <sup>3/</sup> Measured at 70° C.   |                              |                     |
| <sup>2/</sup> Saponification value.                                  |                     |                | <sup>4/</sup> Weights based on 243.7 grams crude alcohols. (The actual weight of crude alcohols fractionated was 200 grams.) |                              |                     |

itional fractionation was studied at -70° C. (dry ice in acetone) using a 5:1 (volume to weight) ratio of methanol to fatty alcohols. The data shown in table 1 were obtained using this method for fractionating the unsaturated fatty alcohols.

Fractionation of urea-inclusion compounds, a relatively new technique, was investigated in our laboratory by Domart, Miyauchi, and Sumerwell (1955). By ap-

Table 2 - Analytical Results of Fatty Alcohols Fractionated as Urea-Inclusion Compounds

| Alcohol Fraction                 | Weight       | Yield <sup>1/</sup> | Iodine Value<br>(Wijs) | Refractive<br>Index          |
|----------------------------------|--------------|---------------------|------------------------|------------------------------|
|                                  | <u>Grams</u> | <u>Percent</u>      |                        | <u><math>n_D^{30}</math></u> |
| Crude mixture                    | 150.0        | 100.0               | 190.1                  | 1.4722                       |
| Complexed at 20° C. . . . .      | 36.4         | 24.3                | 25.8                   | (solid)                      |
| Complexed at 0° C. . . . .       | 33.2         | 22.8                | 91.4                   | 1.4569                       |
| Complexed at -25° C. . . . .     | 7.7          | 5.1                 | 211.8                  | 1.4735                       |
| Non-complexed at -25° C. . . . . | 58.5         | 39.0                | 286.1                  | 1.4969                       |

<sup>1/</sup> Lower yields than expected--should be quantitative.

Applying the findings of Domart and his coworkers to fatty-alcohol mixtures, we were provided with an additional tool for performing the necessary separations.

The best method thus far developed for separating the fatty alcohols by this technique is as follows: The fatty alcohols are dissolved in a solution of methanol containing 16.6 grams of urea per 100 milliliters of methanol. A 14:1 mole ratio of urea to fatty alcohols is used. The mixture is heated and stirred until it forms a clear solution. The solution is allowed to stand at room temperature until precipitation of the urea-inclusion compounds (urea-complexes) is complete. (This usually required 8 to 16 hours.) The solid complexes are removed by filtration, and the remaining filtrate then is cooled to the next lower temperature, in this case 0° C. The process of cooling and filtering is repeated at 0° C. and at -25° C. The precipitated complex fractions are extracted with petroleum ether (b.p. 30° to 60° C.) to remove the fatty alcohols. The filtrate from the precipitation at -25° C. is evaporated nearly to dryness and then is extracted with petroleum ether. Table 2 shows some analytical results of fatty alcohols separated by this method.

A separation study was carried out using a combination of low-temperature crystallization and fractionation of urea-complexes. Table 3 shows analytical re-

Table 3 - Analytical Results of Fatty Alcohols Separated by Low-Temperature Crystallization Followed by Urea-Inclusion Compound Formation

| Fraction   | Weight | Yield   | Iodine Value<br>(Wijs) | Refractive<br>Index |
|--|--------|---------|------------------------|---------------------|
|  | Grams  | Percent |                        |                     |
| Alcohol mixture <sup>1/</sup> . . . . .                    | 31.5   | 100.0   | 300.8                  | 1.4930              |
| Alcohols from combined<br>precipitated complexes . . . . . | 10.2   | 32.4    | 233.9                  | 1.4822              |
| Alcohols from final 0° C.<br>filtrate . . . . .            | 18.2   | 57.8    | 345.7                  | 1.5009              |

<sup>1/</sup> See table 1 for fraction from -70° C. filtrate.

sults of a urea-complex separation applied to fatty alcohols soluble in methanol at -70° C. (the final fraction shown in table 1). The urea-complexing was terminated at 0° C., and the precipitated urea-complex fractions were combined. Using this combination of methods of separation, we obtained polyunsaturated fatty alcohols having a preponderance of four to six double bonds.

Some work has been carried out in fractionally distilling polyunsaturated fatty alcohols at reduced pressures. These pressures have ranged from 0.8 to 1.0 millimeters of mercury, which are about the lowest pressures for operating conventional distillation apparatus for good fractionation. In spite of performing the distilla-

Table 4 - Analytical Results of Fractions of Polyunsaturated Fatty Alcohols Separated by Fractional Distillation at Reduced Pressures

| Fraction   | Boiling Point | Pressure | Volume | Refractive Index | Wijs Iodine Value <sup>1/</sup> |
|------------|---------------|----------|--------|------------------|---------------------------------|
|            | Degrees C.    |          |        |                  |                                 |
| Pot charge | -             | -        | 15.0   | 1.4921           | 294                             |
| A          | 119°-125°     | 1.0      | 1.02   | 1.4593           | 150                             |
| B          | 125°-138°     | 1.0      | 0.52   | 1.4631           | 180                             |
| C          | 138°-145°     | 1.5      | 1.14   | 1.4681           | 204                             |
| D          | 145°-149°     | 1.2      | 1.60   | 1.4798           | 265                             |
| E          | 149°-159°     | 1.2      | 0.62   | 1.4924           | 303                             |
| F          | 159°-162°     | 1.2      | 0.74   | 1.4969           | 323                             |
| G          | 162°          | 1.0      | 0.87   | 1.4972           | 253                             |

<sup>1/</sup> Approximate iodine values, owing to too small a sample to permit more than one determination.

tions in an inert atmosphere of pure nitrogen, we obtained yields of the order of 40 percent. Much polymerization occurs, with ultimate destruction of the highly unsaturated species, as is shown in table 4 by the poor yield.

If distillation techniques are to be used for separating and purifying polyunsaturated fatty alcohols, a multiple molecular distillation, performed at about 0.01 to 0.00001 mm. Hg., would have to be used in conjunction with one or both of the other two separation methods mentioned above. The low pressures are needed to prevent undue losses caused by polymerization from heating.

**OTHER WORK:** In addition to this work on fatty alcohols, similar work is being carried out on unsaturated fatty aldehydes, sulfur-containing fatty acids, fatty amines, and quaternary ammonium salts. A recent article (Gruger 1957) describes some of these preliminary studies. In the near future, chemical reactions will be studied involving the addition of various substituents to the unsaturation. This type of reaction, mentioned earlier, will give products free of unsaturation and, accordingly, will not have the unstable character found in derivatives possessing a high degree of unsaturation.

### SUMMARY

The sodium reduction process of preparing highly unsaturated fatty alcohols from fish oils has several disadvantages that appear to be overcome by the lithium aluminum hydride reduction process. A means of obtaining highly unsaturated fatty alcohols in concentrated form has best been effected by using low-temperature fractional crystallization followed by fractionation of urea-inclusion compounds. Fractional distillations, performed at about 1.0 millimeter mercury pressure, are not successful for collecting higher unsaturated fatty alcohols. The low yields caused by polymerization indicate that in order to distill polyunsaturated fatty alcohols, one must distill at pressures nearer to those for molecular distillations. Other derivatives are being studied in a similar manner as for the fatty alcohols.

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