80°C. Accelerated storage tests at 25°C. were also made. Wheeler peroxide numbers and spectrophotometric vitamin A were determined at intervals. Use of NDGA at 0.1 to 0.5% level without added synergist did not give effective protection at 97.7°C. but did at the lower temperature. NDGA was more effective at all temperatures if a synergist as citric or ortho-phosphoric acid was added; however, the relative effectiveness appeared to increase markedly with the lowering of the oxidation temperature. At lower temperatures the increased efficiency of NDGA with synergists permitted concentrations of less than 0.1% NDGA for effective stabilization. A loss of 50% vitamin A was associated with a peroxide value from 40 to 55. Undesirable effects in the oil, due to the addition of the antioxidant, were at a minimum below concentrations of 0.3%.

With 0.1% added NDGA to the oil by weight plus 0.1% citric acid as a synergist the protection factor at 25°C. was greater than 28.

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The Catalytic Isomerization of Cod Liver Oil With Sulphur Dioxide

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Introduction

AN extensive study in this laboratory of the catalytic properties of sulphur dioxide with regard to fatty oils, showed that different reactions may take place, dependent on the reaction conditions. At about 100-120°C. liquid sulphur dioxide performs a cis-trans isomerization in unsaturated fatty acids and their glycerides. When starting with low melting isomers, this reaction brings about a considerable increase in the melting point of the oil. By crystallization a still higher melting fraction may be obtained (1). If a semidrying oil is treated in the same way and the less unsaturated solid fraction thus obtained is separated, a more unsaturated liquid fraction is left, which shows very good drying properties.

A second process catalyzed by SO_2 is the "activation" of oils containing linolic or linoleic esters (2). This process is characterized by a large increase of the diene number of the oil, and this generally takes place at about 60 atm. pressure and 180-200°C.

At still higher temperatures it is found that a considerable polymerization also occurs (3), and this process has been further developed after the war (4).

The present paper will describe an application of the above mentioned research work to a new raw material, a Norwegian cod liver oil.

Experimental

The cod liver oil was freed from peroxides by heating at 180°C. for one hour while a stream of nitrogen was passed through. Its behavior towards sulphur dioxide was investigated at different temperatures by placing a sample of the oil in an autoclave of Hastalloy (58% Ni, 20% Mo, 20% Fe, 2% Mn, volume ± 120 ml.) with about the same volume of liquid SO_2, which was added afterwards.

The autoclave was then heated to the desired reaction temperature for some time. The reaction conditions for each experiment are given in Table I. After the reaction the reaction-mixture was cooled to about 90°C. and the SO_2 was blown off. The last traces of SO_2 were removed by heating the oil at 90°C. in a vacuum of about 5 mm. Hg with nitrogen ebullition. The products obtained were then analyzed by determining n^{20}_{D}, d^{20}_{4}, iodine number, viscosity, acid value, saponification value, and diene number (D.N.), which values are given in Table I. Furthermore, the ultraviolet absorption spectra of the oil and its reaction products were determined. These spectra are given in Figures 1 and 2.

Discussion of the Results

From the relatively high iodine value of the original oil it can be expected, depending on the reaction

TABLE 1

Product	Grams of oil		Grams of SO_2	p atm.	T°C.	Time, hours	n^{20}_{D}	d^{20}_{4}	r^{20}_{D}	I.V.*	Acid V	Sap V	y_{20}** poises	D.N.***
	Before experiment	After experiment												
Original oil	......	......	......	......	......	......	1.4788	0.9227	0.3072	166	1	......	0.53	2-3
Exp. 2	nitrogen	nitrogen	......	1	180	1	1.4789	0.9227	0.3073	165	1	201	0.53	2-3
Exp. 3	42	39	37	25	100	3	1.4780	0.9219	0.3071	165	2	......	0.94	2-3
Exp. 3a	28	26	42	?	100	5	1.4782	0.9223	0.3070	165	4	203	0.99	......
Exp. 4	30	27	37	25	125	3	1.4778	0.9211	0.3072	162	6	......	0.91	2-3
Exp. 5	30	26	42	60	150	3	1.4831	0.9269	0.3082	146	15	......	1.46	10
Exp. 6	27	23	41	80	180	3	1.4865	0.9464	0.3036	96	18	199	3.62	6

*According to Wijs. ** Determined with an Ostwald-type viscometer. *** Method of Ellis and Jones, Analyst *61*, 1812 (1936).

conditions, that all of the processes mentioned in the introduction may be found. The reaction products obtained after treatment at 100° and 125°C. (Experiments 3, 3a, and 4) show a small decrease in the refractive index and the density whereas the specific refraction and the iodine value hardly change. By a crystallization from acetone it is possible to separate these reaction products into a solid and a liquid fraction. The constants of these fractions are mentioned in Table II. The solid fraction, which contains the isomerized mono-olefinic acids and the saturated fatty acids, should have a lower iodine value than the original oil, which is found. The liquid fraction contains the more unsaturated fatty acids and hence shows an increase in iodine value. As the diene number of the reaction product is hardly altered, only cis-trans isomerization has taken place. Some polymerization may have occurred as there is a slight increase in the viscosity of the oil.

The above results are confirmed by the study of the ultraviolet absorption spectra of these reaction products. Curves 2 and 3 of Figure 1 show only a slight altering of the absorption. The indication to the presence of some conjugated double bonds (230 mμ.) (5) in the starting material vanishes by treatment at 100°C., which supports the above suggestion that some polymer formation had occurred. Although the diene number of the product treated at 125°C. did not increase, the absorption shows small peaks at 230, 270, and 310 mμ. (5) showing that some conjugation already takes place at this temperature (Curve 4, Figure 1). In Figure 2 a comparison is made between the absorption curves of the solid and the liquid fraction obtained from Experiment 3a (see also Table II). The less unsaturated, solid fraction (Figure 2, Curve 3a solid fraction) shows that no conjugated double bonds are present in this fraction whereas the liquid part shows a slight activation (Curve 3a, liquid fraction).

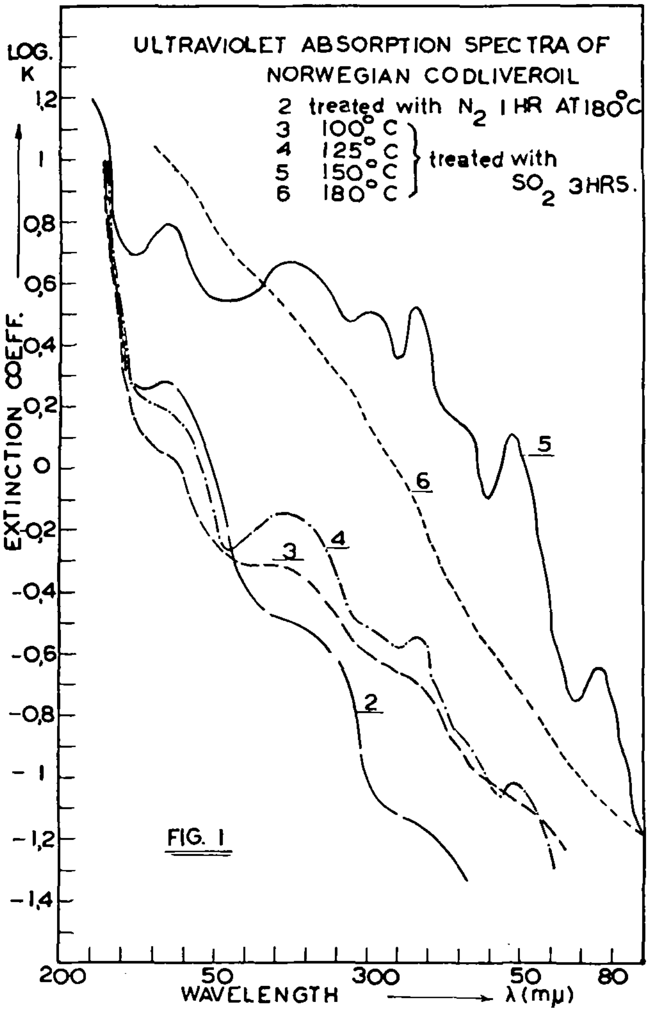

FIG. 1

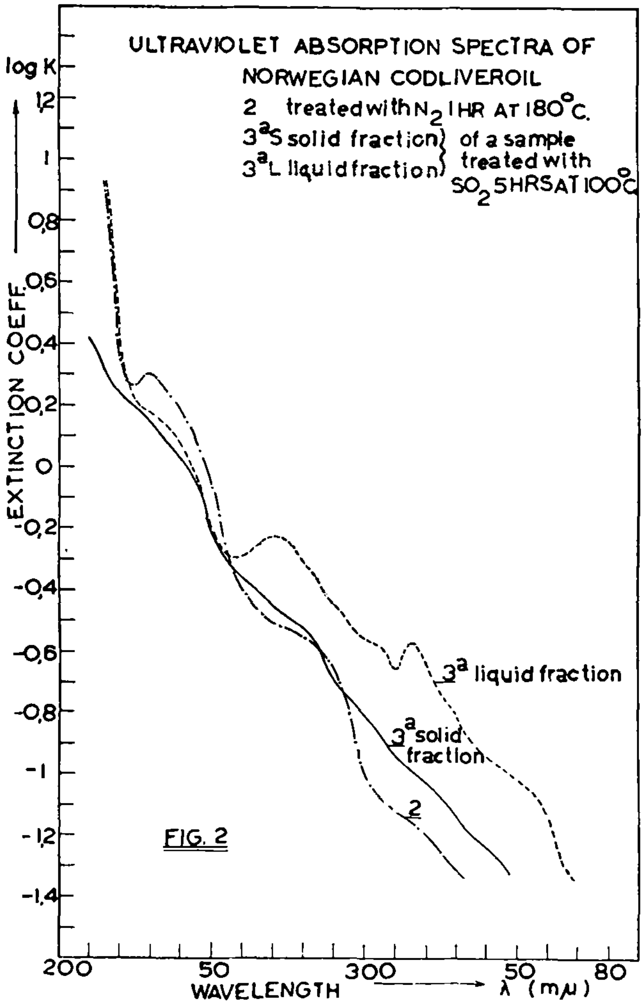

FIG. 2

A treatment of the cod liver oil at 150°C. (Experiment 5) results in an increase of n_D^{20}, d_4^{20}, and the specific refraction and a decrease of the iodine value. The notable rise in diene number leads to the conclusion that the change in the constants mentioned is largely due to conjugation. As the viscosity in this experiment also slightly increases, some polymerization accompanies this conjugation. The ultraviolet absorption is quite in agreement with these conclusions as is shown by the increase of the maxima of Curve 5, (Figure 1), which are much more pronounced than those of Curve 4 (Figure 1).

If the reaction temperature is still increased to 180°C. the viscosity of the oil increases more than before and the diene number decreases again. Hence the conjugated systems are partly converted into polymers, which also follows from the ultraviolet absorption spectra. This is represented by the gradually sloping curve of Experiment 6 (Figure 1). This polymerization is also represented by the changes in n_D^{20} and d_4^{20}, which show a considerable increase, whereas

TABLE II

Product	n_D^{20}	d_4^{20}	r_D^{20}	I.V.	Sap V	n_{20} poises	Technical m.p.*	% total product
Reaction product 3a	1.4782	0.9223	0.3070	165	203	0.99	......	......
Solid fraction	1.4720	0.9147**	0.3061	91	212	......	27.0	28
Liquid fraction	1.4808	0.9255	0.3074	182	200	1.00	......	72

* Compare C. v. Vlodrop, Thesis Delft 1938, p. 109. ** Calculated from the d_4^{20} of the reaction product and the liquid fraction, using the ratios of the amounts of solid and liquid fractions.

at the same time the specific refraction sharply decreases. The acid values show that some saponification takes place, notably in the experiments at temperatures higher than 150°C.

Summary

A Norwegian cod liver oil upon treatment with sulphur dioxide under pressure shows cis-trans isomerization, conjugation (activation), and polymerization dependent on the reaction temperature. After a cis-trans isomerization the reaction product can be separated into a higher melting part with a decreased iodine value and a liquid part with an increased degree of unsaturation.

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The Effect of Baking Powder Residues on Rancidity

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RESEARCH on the control of oxidative deterioration in the fat of bakery products has been reviewed by Triebold (13) and later by Lundberg (7). Several of the best known primary antioxidants, which are very effective in stabilizing edible oils and shortenings, do not protect the baked products made from these fats, either because the antioxidants are destroyed during the baking or because they become relatively more soluble in the aqueous than in the fat phase at the high pH of many baked products (8). This is true of the naturally occurring tocopherols and of propyl gallate. On the other hand, the antioxidant activity of nordihydroguaiaretic acid (NDGA), gum guaiac, and higher fatty acid esters of gallic acid (11) have been reported to carry over at least to some extent in baked products.

A number of compounds are known which enhance the effectiveness of primary antioxidants in fats. Various di- and polybasic inorganic and organic acids are the best known of such synergists, but many other compounds may show synergistic activity if coupled with a suitable primary inhibitor (10). Practically no work has been reported on the effectiveness of these synergists in baked products. In fact, very little information is at present available concerning their activity in any complex food containing an aqueous phase.

In the course of an investigation of frozen batter and dough products off odors and flavors were noted after varying periods of freezing storage which seemed to be associated with the type of baking powder employed. No tests were run at the time to determine whether the off odors were caused by oxidative deterioration of the fat. However since baking powders contain ingredients which are known to exert an antioxidant effect on dry fats containing primary inhibitors, it seemed worthwhile to investigate their effect on rancidity in a system more characteristic of baked products, i.e., where the fat is in contact with aqueous solutions usually having an alkaline reaction.

Commercially available baking powders belong to one of the following types, depending upon the nature of the acid ingredient (1):

1. Tartrate (cream of tartar and tartaric acid).
2. Calcium acid phosphate.
3. Combination (sodium aluminum sulfate and calcium acid phosphate).
4. Sodium acid pyrophosphate.

The residues from the heated powders consist of the salts of these acids.

Kaufman (4) mentions a catalytic effect of baking powders containing sodium aluminum sulfate on rancidity in products like prepared flour mixes. There is considerable evidence that aluminum itself has no effect on rancidity (2). Sulfuric, tartaric, and phosphoric acids all act as synergistic antioxidants, but there seems to be no published information of the effect of their anions on rancidity in alkaline solutions. The effectiveness of pyrophosphates in neutral as well as acid solutions was pointed out by Lea (6).

Experiments on Artificial Aqueous Fat Systems

Method. Rate of rancidification was followed in several experiments in which heated solutions of the four commercial types of baking powders were brought in contact with several different fats. Four grams of each powder were added to 100 ml. of water (a concentration within the range normally used in baking). Since it was desired to investigate the end products of baking powder reactions, the solutions were heated in a boiling water bath for a period of 20 minutes.

The pH of each solution was measured with a glass electrode. The pH for the same baking powder solution tended to increase with increased heating and with time elapsing after heating. The values recorded were those obtained at the beginning of an experi-