

VOLATILE SUBSTANCES FORMED BY DECOMPOSITION OF THE PEROXIDES OF METHYL ESTERS OF HIGHLY UNSATURATED ACIDS

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In a previous study,¹⁾ a highly unsaturated methyl ester fraction prepared from sardine oil was oxidized with a current of air at 45°-55° C, and volatile oxidation products carried off with the air were collected and examined with the results that several saturated acids and aldehydes were identified. Although unsaturated carbonyl compounds appeared to be present in the volatile oxidation products, none of these unsaturated carbonyl compounds could be identified. The lack of any decisive evidence for unsaturated carbonyl compounds was considered to be attributable to the condition of experiments in the previous study; unsaturated carbonyl compounds, even if they had been once formed, would have mostly undergone a secondary change due to a prolonged contact with the air current. In the present study, therefore, highly unsaturated methyl ester fractions prepared from sardine oil were subjected to oxidation with molecular oxygen until oxidized methyl ester fractions with high peroxide values were obtained. The oxidized ester fractions were then heated while a current of nitrogen was being passed through them, and volatile decomposition products were collected and examined.

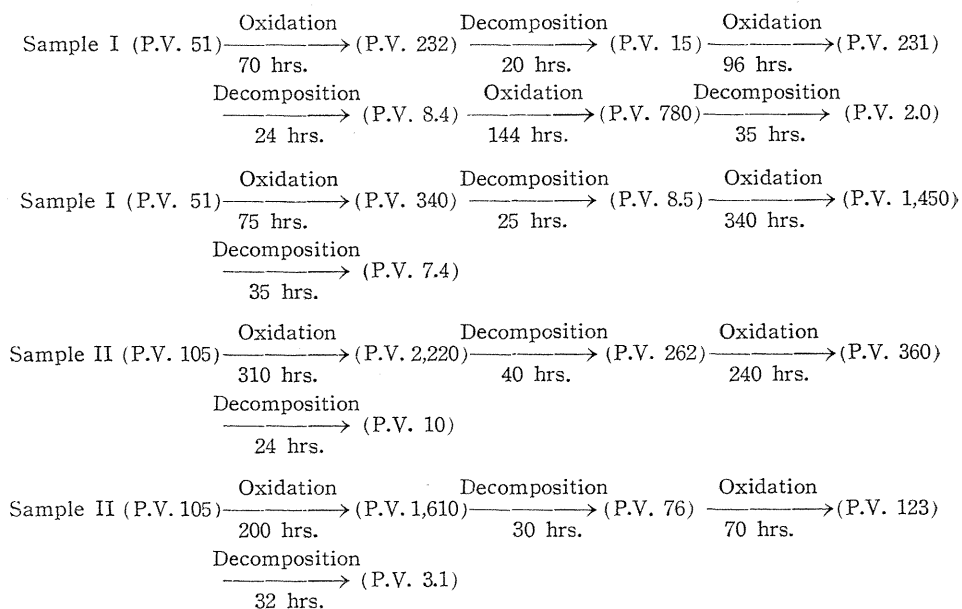
1. Highly Unsaturated Methyl Ester Fractions

Two samples of highly unsaturated methyl ester fractions were used in these experiments: sample I of S.V. 193.6, I.V. (Wijs) 279.2 and P.V. (milli equivalent per kg) 51; sample II of S.V. 185.6, I.V. 330.9 and P.V. 105. Both samples had been obtained by fractionation of methyl esters of highly unsaturated acid concentrate prepared from sardine oil by means of the sodium salt acetone method. The sample I, according to its iodine value, was contaminated with less unsaturated methyl ester to a considerable proportion. Relatively high peroxide values of both samples indicated that they must have already undergone oxidation to some extent during the storage from their preparation to the commencement of the present experiments.

2. Oxidation of Highly Unsaturated Methyl Ester Fractions and Decomposition of Peroxides

One hundred g of each sample was placed in a flask, the air in the flask was replaced with oxygen, and the flask was shaken under atmosphere of oxygen at room temperature, 0°-15° C for the sample I and 15°-25° C for the sample II, until an oxidized methyl ester fraction of high peroxide value was obtained. The flask

containing the oxidized methyl ester fraction was then placed on a water bath and heated gradually to 90°–100° C in the course of about one hour and kept at that temperature thereafter while a current of nitrogen was being passed through the flask. Volatile substances formed by decomposition of the peroxide were carried off by the nitrogen current, and passed successively through a trap *A* containing a 5% solution of sodium carbonate, a trap *B* containing a 0.2% solution of 2, 4-dinitrophenylhydrazine in 2 *N*-hydrochloric acid, and finally a trap *C* containing a 10% solution of sodium bisulfite. Carbonyl compounds were almost completely caught by the trap *B*, and there was found no detectable amount of carbonyl compounds in the trap *C*. The nitrogen current coming out of the trap *C* had scarcely any pungent odor. After completion of oxidation-decomposition procedure, the same sample was repeatedly subjected to the same procedure. In total, 200 g of each sample was treated in this manner. Some data on the oxidation-decomposition procedure are given below.



The decomposition of oxidized samples proceeded gently, giving rise to fine foams. However, when the decomposition was performed at an elevated temperature from the start, it proceeded violently; at an initial temperature of 120° C, the greater part of oxidized samples decomposed instantly.

3. Examination of Volatile Substances

a) Volatile acids. The solution (about 300 cc) obtained in the trap *A* was concentrated to about 30 cc, acidified with a slight excess of hydrochloric acid, and extracted with relatively large amount of ether. After washing the ether solution with small amounts of a saturated solution of sodium chloride followed by dehydration and distillation of ether, there remained a light yellow liquid having a pungent odor resembling acetic acid. The yield was 1 g from the sample I (200

g) and 0.8 g from the sample II (200 g). This material was considered to consist of saturated compounds since it did not react with iodine monochloride in acetic acid. The material from the sample I was converted into hydroxamic acid, and the latter was analyzed by paper chromatography in ethanol with the results shown in Table 1, which indicate the presence of formic, acetic and propionic acids.

TABLE 1

| Hydroxamic acid from | R _f value (Descending method) | | Coloration |
|----------------------|------------------------------------------|--------------------------|------------|
| | Pure sample | Sample under examination | |
| Formic acid | 0.31 | 0.31 | Purple |
| Acetic acid | 0.63 | 0.64 | " |
| Propionic acid | 0.73 | 0.73 | " |

Filter paper: "Toyo Filter Paper" No. 50; temperature: 10°-16° C; developer: butanol saturated with water; chromogenic reagent: 10% solution of ferric chloride in ethanol.

b) Carbonyl compounds. Reddish orange precipitates of 2,4-dinitrophenylhydrazones were formed in the trap *B*. The yields of precipitates were 0.5 g, both from the samples I and II. The precipitates from the sample I were recrystallized from 100 cc of methanol, giving the crop *A*₁. Concentration of the filtrate from the crop *A*₁ gave the crops *A*₂, *A*₃ and *A*₄. The precipitates from the sample II were recrystallized from 30 cc of 95% ethanol yielding the crop *B*₁. The filtrate was added with water until the second crop *B*₂ separated. By repeating the addition of a further quantity of water to the filtrate, the crops *B*₃ and *B*₄ were obtained. Melting points and N-contents of each crop together with those of 2,4-dinitrophenylhydrazones of some known aldehydes are given in Table 2.

From the melting points and N-contents, the crops *A*₁, *A*₂, *A*₃ and *A*₄ from the sample I are regarded as 2,4-dinitrophenylhydrazones of crotonaldehyde, 2-pentenal, 2-hexenal and *n*-butanal, respectively. The crops *B*₃ and *B*₄ from the sample II

TABLE 2

| Crop | M.P. (°C) | N (%) | Yield (mg) |
|-----------------------------|---------------------------|-------|------------|
| <i>A</i> ₁ | 185 -187 | 21.9 | 120 |
| <i>A</i> ₂ | 162 -163 | 21.0 | 80 |
| <i>A</i> ₃ | 143 -145 | 20.4 | 43 |
| <i>A</i> ₄ | 118 -120 | 22.1 | 170 |
| <i>B</i> ₁ | 138 -140 | 25.2 | 70 |
| <i>B</i> ₂ | 133.5-135 | 23.8 | 82 |
| <i>B</i> ₃ | 123 -125 | 22.4 | 150 |
| <i>B</i> ₄ | 103 -105 | 20.4 | 135 |
| Formaldehyde | 164.8-165.3 ²⁾ | 26.66 | |
| Acetaldehyde | 168.5 ³⁾ | 24.99 | |
| Propionaldehyde | 155 ⁴⁾ | 23.52 | |
| <i>n</i> -Butanal | 122 ⁴⁾ | 22.21 | |
| <i>n</i> -Pentanal | 98 ⁴⁾ | 21.04 | |
| <i>n</i> -Hexanal | 104 ⁴⁾ | 19.99 | |
| Crotonaldehyde | 187 -188 ²⁾ | 22.39 | |
| 2-Pentenal | 163 ⁵⁾ | 21.20 | |
| 2-Hexenal | 145.0-145.4 ⁶⁾ | 20.14 | |

are considered to be 2,4-dinitrophenylhydrazones of *n*-butanal and *n*-hexanal, respectively. The crops B_1 and B_2 have relatively low melting points in contrast to higher N-contents, and are possibly mixtures of 2,4-dinitrophenylhydrazones of lower aldehydes, such as acetaldehyde and formaldehyde. Spectrophotometric examination afforded a further evidence for the fact that the crops A_1 , A_2 and A_3 are 2,4-dinitrophenylhydrazones of α , β -unsaturated aldehydes, while the crops B_1 , B_2 , B_3 and B_4 are those of saturated aldehydes. It has been reported by previous authors⁷⁾ that 2,4-dinitrophenylhydrazones of saturated aldehydes exhibit a maximum absorption at 356-358 $m\mu$ and a minimum absorption at 292.5 $m\mu$, while 2,4-dinitrophenylhydrazones of α , β -unsaturated aldehydes exhibit a maximum absorption at 375-378 $m\mu$ and a minimum absorption at 313 $m\mu$. As is seen from the absorption curves (in methanol) shown in Fig. 1, a mixture of the crops A_1 and A_2 and the crop A_3 exhibit a maximum absorption at 375 $m\mu$ and a minimum absorption at 312-313 $m\mu$, while the crops B_1 , B_2 and B_4 exhibit a maximum absorption at 354-358 $m\mu$ and a minimum absorption at 294-296 $m\mu$.

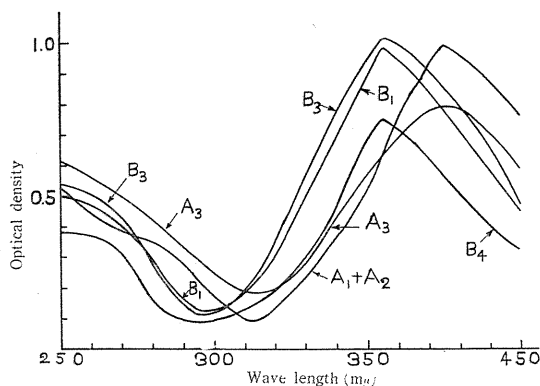


FIG. 1

4. Discussion

The foregoing results indicate that volatile substances formed by the decomposition of the peroxides of highly unsaturated methyl ester fractions contain unsaturated aldehydes such as crotonaldehyde, 2-pentenal and 2-hexenal in addition to several lower fatty acids and saturated aldehydes. However, these unsaturated aldehydes have been found among volatile substances formed by the oxidation of some vegetable oils and the esters of their component fatty acids such as linolic and linolenic acids, and can not be regarded as the essential components of odoriferous substances formed on standing highly unsaturated esters in the air. If substances responsible to the odor characteristic to highly unsaturated esters are formed by the decomposition of peroxides of highly unsaturated esters, they are possibly carbonyl compounds which are either more highly unsaturated or of longer carbon chain than those identified in the present study. The marked difference in components between the aldehydes from the samples I and II, that the former contain predominantly unsaturated aldehydes while the latter consist mainly of saturated aldehydes, may possibly be attributable to the fact that the oxidized esters from the sample II had higher peroxide values than the oxidized

esters from the sample I on the whole, although the possibility is not excluded that it is caused by the difference in components between the original samples I and II.

Summary

Two samples of highly unsaturated methyl ester fraction prepared from sardine oil were oxidized with molecular oxygen at 0°-25° C, and the oxidized esters of high peroxide values were obtained. The oxidized esters were then decomposed at 90°-100° C while passing a current of nitrogen, and the volatile decomposition products were collected and examined. Among the volatile acids, the presence of formic, acetic and propionic acids was indicated. Among the volatile aldehydes, unsaturated aldehydes such as crotonaldehyde, 2-pentenal and 2-hexenal in addition to saturated aldehydes consisting of *n*-hexanal, *n*-butanal and some lower members were found.

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