Behavior of Tocopherol and Vitamin K₁ in the Hydrogenation of Edible Oil

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Abstract: Determination was made of α- and γ-tocopherol, vitamin K₁ and 2′, 3′-dihydrovitamin K₁ in vegetable oil during the course of hydrogenation under various conditions. Iodine value (IV) was found to decrease from 80 to 60 with hydrogenation, with consequently considerable reduction in vitamin K₁. At IV 50 or less, vitamin K₁ was virtually essentially absent (0.1 mg/kg or less). 2′, 3′-dihydrovitamin K₁ increased with decrease in vitamin K₁. 2′, 3′-dihydrovitamin K₁ peaked at 2.9 mg/kg at IV 50, and then decreased. α- and γ-Tocopherol content remained basically the same under all conditions. Subsequent to oil hydrogenation and then deodorization at 260°C for 120 minutes, α-tocopherol showed the highest residual ratio (80%) of all the vitamins, followed by 2′, 3′-dihydrovitamin K₁ (66%) and vitamin K₁ (60%).


Key words: hydrogenation, deodorization, edible oil, tocopherol, vitamin K₁, 2′, 3′-dihydrovitamin K₁

1 Introduction

Vitamins E and K are fat-soluble vitamins. Vitamin E, regarded as an antisterile vitamin, has major involvement in the lipid in vivo and anemia (1). Vitamin K is required for blood coagulation subsequent to following hemorrhage and has been found essential to bone formation, thus warranting attention to its content in food (2). Vegetable fats and oils are important major sources of these vitamins. Vegetable fats and oils as fat and oil products contain these vitamins in large amounts. These products are obtained through hydrogenation, fractionation, and interesterification (3). In this study, examination was made to determine the behavior of vitamins E and K in the hydrogenation of vegetable oil on a pilot plant scale. Change in content of α-tocopherol, vitamin K₁, and 2′, 3′-dihydrovitamin K₁ formed by hydrogenation of vitamin K₁ was determined based on deodorization assessment.

2 Experimental

2.1 Hydrogenation

Refined soybean oil was used, with no change in γ-tocopherol or vitamin K₁ content. 500 mg/kg dl-α-tocopherol were added to d-α-tocopherol naturally present in soybean oil for comparison with γ-tocopherol. After the start of hydrogenation, sampling was made every 30 minutes and α-tocopherol, γ-tocopherol, vitamin K₁ and 2′, 3′-dihydrovitamin K₁ and iodine value (IV) were determined. The conditions for hydrogenation are listed in Table 1, as follows: 0.3% and 0.5% of catalyst by weight of the oil, reaction temperature, 150°C to 210°C, hydrogen flow rate, 0.9 mL/min to 1.8 mL/min and stirring at 600 rpm and 800 rpm.
### Table 1  Conditions for Hydrogenation.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Catalyst (%)</th>
<th>Temperature (°C)</th>
<th>Hydrogen flow rate (ml/min.)</th>
<th>Stirring (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>150</td>
<td>1.35</td>
<td>600</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>180</td>
<td>1.35</td>
<td>600</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>210</td>
<td>1.35</td>
<td>600</td>
</tr>
<tr>
<td>D</td>
<td>0.5</td>
<td>180</td>
<td>0.9</td>
<td>600</td>
</tr>
<tr>
<td>E</td>
<td>0.5</td>
<td>180</td>
<td>1.8</td>
<td>600</td>
</tr>
<tr>
<td>F</td>
<td>0.3</td>
<td>180</td>
<td>1.35</td>
<td>600</td>
</tr>
</tbody>
</table>

### 2.2 Deodorization

To determine change in vitamin content during deodorization, hydrogenated oil (IV 63) was used. 2 mg/kg vitamin K₁ were added to the oil so as to make its concentration essentially the same as that of 2′,3′-dihydrovitamin K₁. Deodorization was conducted at 260°C for 120 minutes while blowing steam into 1 kg hydrogenated oil in vacuo. Samples were obtained every 30 minutes for vitamin content determination.

### 2.3 Analytical Methods

Tocopherol and IV were found by Standard methods (4) and, vitamin K₁ and 2′,3′-dihydrovitamin K₁, by refining 0.5g oil by silica gel column chromatography followed by HPLC (5) under the following conditions:

- Analytical column: Finepak SIL C18 (4.6 × 250 mm) (Nippon Bunko).
- Mobile phase: methanol (reagent grade, Wako).
- Reduction column: platinum black column (4 × 10 mm) (Eicom).
- Fluorescent detector: measurement wavelength Ex. 244 mm, Ex. 418 nm.

### 3 Results and Discussion

#### 3.1 Change in Tocopherol Content Due to Hydrogenation

**Figure 1** shows the relationship between α- and γ-tocopherol content and IV. α-Tocopherol content showed no change throughout the experiment, as neither did γ-tocopherol. It thus follows that α- and γ-Tocopherol are highly stable toward hydrogenation. In view of the nutritional value and oxidation stability of fats and oils, it is a merit of hydrogenation that it causes no reduction in α-Tocopherol and γ-Tocopherol.

#### 3.2 Vitamin K₁ and 2′,3′-dihydrovitamin K₁

**Content Change Due to Hydrogenation**

Vitamin K₁ is converted to 2′,3′-Dihydrovitamin K₁ during the hydrogenation of vegetable fats and oils(6), but its physiological activity has been shown less com-
Fig. 2  Relationships of Vitamin K, to 2',3'-dihydrovitamin K, and IV.

Fig. 3  Relationship between Deodorization Time and Vitamin Residual Ratios.
pared to the parent compound vitamin K₃(2). Fig. 2 shows the relation of vitamin K₁ to 2',3'-dihydrovitamin K₁ and IV in hydrogenation. IV was noted in this study to decrease from 80 to 60 with hydrogenation. Vitamin K₁ underwent considerable conversion to 2',3'-dihydrovitamin K₁. At IV of 50 or less, vitamin K₁ decreased to 0.1 mg/kg or less. 2',3'-dihydrovitamin K₁ peaked at 2.9 mg/kg at IV 50 and then decreased. At IV 2 or less, virtually no vitamin K could be detected though 0.3 to 1.1 mg/kg 2',3'-dihydrovitamin K₁ were present. Davidson, K.W. et al. have indicated heavily hydrogenated soybean oil to contain 0.01 mg/kg vitamin K₁ and 0.52 mg/kg 2',3'-dihydrovitamin K₁ (6), these values being essentially the same as the present data. Total vitamin K content (sum of vitamin K₁ and 2',3'-dihydrovitamin K₁) remained basically the same up to IV 50 but rapidly decreased at IV 50 or less. Therefore heavily hydrogenated oils are not important sources of vitamin K₁. Highly hydrogenated fats and oils are generally used for coating candies or adjusting the consistency of shortenings and margarines in minute amounts(7). Highly hydrogenated fats and oils are thus not an important sources of vitamin K. Hydrogenated oils, frequently used for producing shortening and margarine, generally melt at 30 to 40°C owing to their property of plasticity. Soybean oil in this study corresponded to IV 65 to 75 and contained 0.12 to 1.4 mg/kg vitamin K₁ and 1.3 to 2.9 mg/kg 2',3'-dihydrovitamin K₁.

3.3 Relationship of Deodorization Time to Vitamin Residual Ratios

This relationship is presented in Fig. 3. α-Tocopherol, vitamin K₁ and 2',3'-dihydrovitamin K₁ in the oil all decreased with deodorization time. At 120 minutes deodorization, the highest residual ratio (80%) was noted for α-tocopherol, followed by 2',3'-dihydrovitamin K₁ (66%) and vitamin K₁ (60%). In Japan, tasteless, odorless and colorless oils are held in preference(8), and thus deodorization as conducted in this study is generally performed. The results presented here indicate tocopherol and vitamin K present in fats and oils to be lost with increase in deodorization time. The effective use of minor components should thus be considered in deodorization.

References