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Thermal Degradation Pattern of Tocopherols on Heating without Oxygen in a Model Food System

Hae-Young Chung

Dept. of Home Economics, Kyungwon College, Sungnam 461-702, Korea

모델식품계에서 무산소 가열시 토코페롤의 열분해 패턴

정 혜 영

경원전문대학 가정과

Abstract

The thermal degradation pattern of α-, γ- and δ-tocopherols in glycerol was investigated during heating at 100~250℃ for 5-60 min in the absence of oxygen. The tocopherols and their thermally decomposed products were separated by HPLC with a reversed phase μ-Bondapak C_{18}-column. The degradation pattern of α-tocopherol during the heating in the absence of oxygen was different from those of γ- and δ-tocopherols. But the degradation patterns of γ- and δ-tocopherols were similar to each other. The residual content of α-tocopherol during the heating in the absence of oxygen decreased to the range 12~65% and those of γ- and δ-tocopherols decreased to the range 4~96%. The thermal degradation of tocopherols in the absence of oxygen was less than that in the presence of oxygen.

Key words : α-, γ- δ-tocopherols, thermal degradation pattern, without oxygen.

INTRODUCTION

Oxidation is common in biological systems and foods. Although some oxidations are beneficial in foods, most of oxidation reactions can lead to detrimental effects, including degradation of vitamins and pigments, loss of nutritional value, and development of off-flavors[1]. Lipid oxidation at high temperature in the presence of oxygen produces various decomposed compounds which exert both desirable and undesirable effects on food quality[2].

In order to maintain the high quality of food product, control of undesirable oxidation reactions in foods is usually achieved by adding antioxidants, such as BHA and tocopherols, or by replacing oxygen with nitrogen[3, 4]. Nowadays, many companies manufacture packed products with nitrogen filled to prevent the oxidation of oils and fats. Many studies have been done on the antioxidant effects of tocopherols in foods[5~9]. In the previous work[10~12], the thermal degradation pattern of tocopherols in the presence of oxygen and their kinetics were studied. However, the thermal degradation of tocopherols in the absence of oxygen has never been reported. Thus, the objective of this research was to study the thermal degradation of tocopherols in the absence of oxygen during heating at 100~250℃ for 5~60 min.

MATERIALS AND METHODS

1. Materials

Tocopherols, α-, γ- and δ-tocopherols, were

Corresponding author : Hae-Young Chung

purchased from Sigma Chemical Co. (St. Louis, MO, U.S.A.). Glycerol was obtained from Junsei Chemical Co. (Tokyo, Japan) and membrane filter from Acrodisc Gelman (Gelman LC13, 0.45 μm, Ann Arbor, MI, U.S.A.). All solvents (hexane, acetonitrile, methanol, 2-propanol, chloroform, methylene chloride) were of HPLC grade.

2. Experimental System

To study the thermal degradation pattern of tocopherols during heating in the absence of oxygen, a model food system was designed as follows : 50 mg α-tocopherol was added to 10 ml glycerol which was used as a heating medium. A mixture of tocopherol and glycerol was placed at a crucible in a furnace and heated at 100, 150, 200 and 250℃ for 5, 15, 30 and 60min. The same method was applied for γ- and δ-tocopherol except that 2mg of γ-tocopherol and 4mg of δ-tocopherol were added. A continuous stream of nitrogen was flushed through the furnace to remove oxygen during heating.

3. Extraction and Separation of Thermal Degradation Products

Extraction and separation of the thermal degradation products of tocopherols without oxygen were performed with the described method in the previous study[10~12]. The thermal degradation products of tocopherols were analyzed by HPLC with the same analytical conditions as described in the previous study[10~12].

RESULTS AND DISCUSSION

The residual content of each tocopherol and quantities of those thermal degradation products during heating in the absence of oxygen were studied. Fig. 1 shows the changes in the content of α-tocopherol during heating at 100, 150, 200 and 250℃ for 5, 15, 30 and 60min. The residual content of α-tocopherol decreased gradually during heating at 100, 150 and 200℃. But it decreased steeply at 250℃. The residual content of α-tocopherol decreased to the range 12~28% at 100, 150 and 200℃. About 65% of α-tocopherol was degraded after 60min at 250℃. The thermal degradation of α-tocopherol in the absence of oxygen (Fig. 1) was less than that in the presence of oxygen[10~12] which was stu-

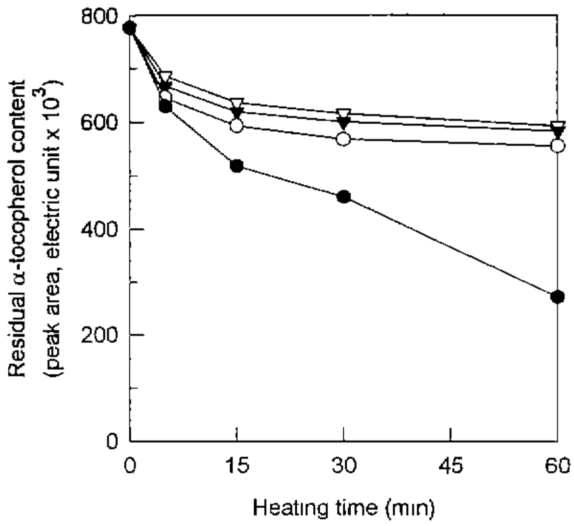

Fig. 1. Residual α-tocopherol content during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

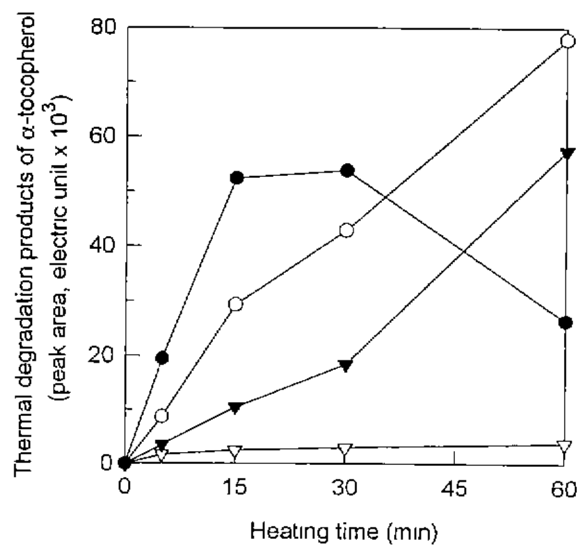

Fig. 2. Thermal degradation products of α-tocopherol during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

died under the same experimental condition. These data indicated that oxygen accelerated the degradation of α-tocopherol. This result is consistent with the data of Widicus and Kirk[13], in that oxygen is required for lipid oxidation-dependent α-tocopherol degradation, and that the rate of α-tocopherol degradation is significantly decreased by limiting oxygen available for reaction.

The changes in content of the major thermal degradation products of α-tocopherol during heating in the absence of oxygen are illustrated in Fig. 2. The content of the major thermal degradation products of α-tocopherol increased slightly at 100℃, but increased greatly during heating at 150, 200 and 250℃. At 250℃, the thermal degradation products are not easily extracted from glycerol with hexane, because tocopherols were oxidized to form insoluble products. The thermal degradation products of α-tocopherol in the absence of oxygen are produced less than that in the presence of oxygen[10~12]. The content of the major thermal degradation products of α-tocopherol was affected by heating time, temperature and oxygen.

The changes in γ-tocopherol content heated at 100, 150, 200 and 250℃ for 5, 15, 30 and 60 min in the absence of oxygen are shown in Fig. 3. The residual content of γ-tocopherol decreased gradually at low temperatures such as 100 and 150℃, and decreased greatly at high temperatures such as 200 and 250℃. The residual content of γ-tocopherol decreased to the range 4~96% during heating at 100~250℃ for 5-60 min. In the absence of oxygen, γ-tocopherol is less degraded too. The residual content of γ-tocopherol was about 4% after 30 min at 250℃ in the absence of oxygen, while the residual γ-tocopherol in presence of oxygen was in trace amount[11,12]. As in the case of α-tocopherol, the thermal degradation of γ-tocopherol was accelerated by oxygen.

Fig. 4 also shows the changes in the thermal degradation product content of γ-tocopherol without oxygen. The content for the thermal degradation products of γ-tocopherol increased slightly at 100℃, but increased greatly at 150 and 200℃. At 250℃, it increased steeply until 15 min, thereafter it decreased.

In the absence of oxygen, γ- and δ-tocopherols degraded with a similar pattern (Fig. 3 and Fig. 5). However, the thermal degra-

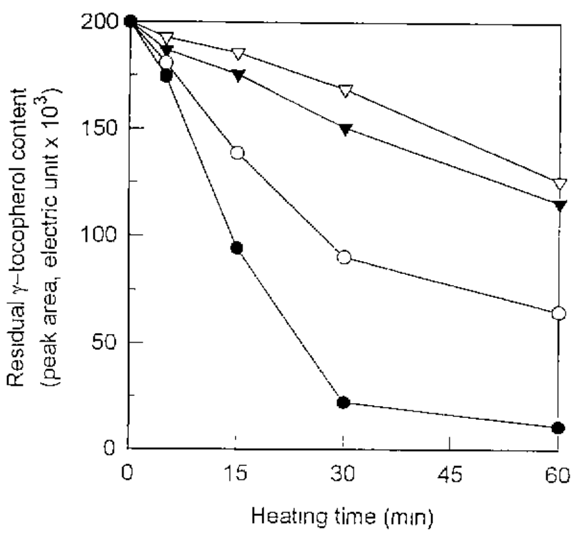

Fig. 3. Residual γ-tocopherol content during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

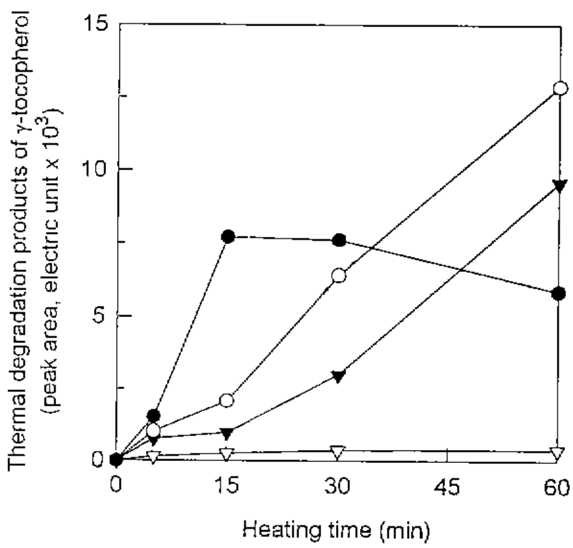

Fig. 4. Thermal degradation products of γ-tocopherol during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

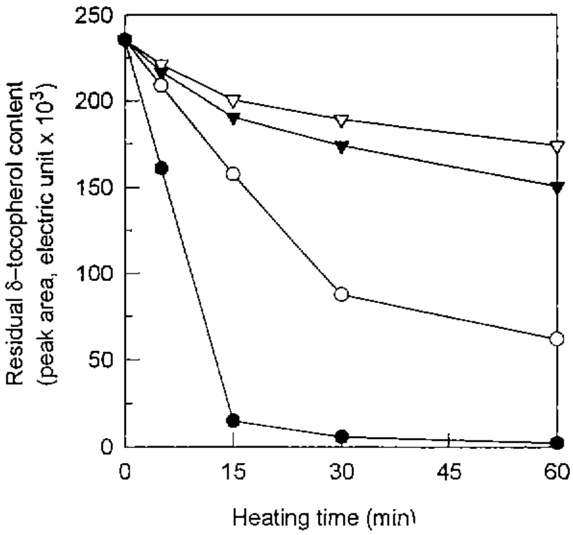

Fig. 5. Residual δ-tocopherol content during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

dation products of γ- and δ-tocopherols were produced with different pattern (Fig. 4 and Fig. 6). At 200℃, the content for the thermal degradation products of δ-tocopherol increased until 30min, after which the increase slow down. At 250℃, the content for the thermal degradation products of δ-tocopherol increased

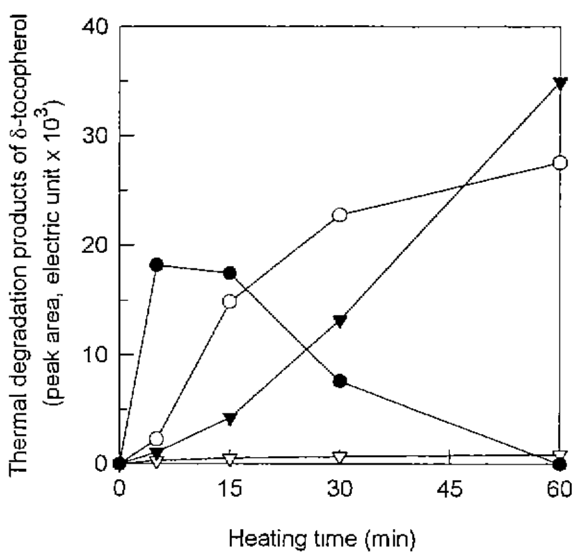

Fig. 6. Thermal degradation products of δ-tocopherol during heating at various temperatures without oxygen. —▽— 100℃ —▼— 150℃, —○— 200℃, —●— 250℃.

steeply until 5 min, thereafter it decreased. The decreasing rate after 15 min was greater for the δ-tocopherol than γ-tocopherol.

요 약

토코페롤은 식품 내에서 항산화제 역할뿐 아니라 비타민 E 활성을 나타낸다. 본 연구에서는 알파-, 감마-, 델타-토코페롤을 글리세롤에 첨가하고, 도가니를 사용하여 회화로에서 100~250℃로 5분 내지 60분 동안 무산소 조건을 만들기 위하여 질소 존재하에 가열한 다음 헥산으로 토코페롤의 열분해 생성물을 추출하였다. 추출한 생성물은 두 종류의 용출 용매와 역상 μ-Bondapak C_{18}-컬럼을 사용한 HPLC로 분리하였다. 가열 온도가 높을수록, 그리고 가열 시간이 길수록 토코페롤의 분해량이 많아져 잔존량이 감소하였고 토코페롤 열분해 생성물의 양과 종류는 증가하였다. 또한 무산소 가열의 경우, 산소가 있을 때보다 분해율이 낮았다. 알파-토코페롤은 12~65%, 감마와 델타-토코페롤은 4~96%가 분해되었다.

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