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Antioxidant Activity of Ethanol-Extracts from a Maillard Browning Mixture and Some Antioxidants in Soybean Oil and Soybean Oil-Water Emulsion Systems

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콩기름 및 콩기름-물 에멀젼基質에서의 마이얄型 褐色化反應生成物과 一部 酸化防止劑의 酸化抑制效果

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Abstract

The antioxidant activity of ethanol-extracts (M-2 and M-30), which had been obtained from a Maillard-type browning mixture after 2 and 30 hr browning, and BHA, BHT, TBHQ, and ascorbyl palmitate was investigated in soybean oil and soybean oil-water emulsion systems. The activity of the extracts and antioxidants was estimated by comparing the POV and TBA value development of the corresponding substrates with that of controls. The substrates and controls were stored at 45.0±0.5°C for 25 days.

The activity of the extracts (10 *ml* each) and antioxidants (0.02%) based mainly on the POV development of the corresponding anhydrous substrates was, in decreasing order, as follows :

As. palmitate, TBHQ > M-30, M-2 > BHT, BHA

The activity of the extracts and antioxidants in the oil-water emulsion substrates was, in decreasing order, as follows :

As. palmitate > M-30, M-2 > BHT, TBHQ, BHA

The activity of the extracts appeared to be more effective in the oil-water emulsion system than in the anhydrous system, and it was greater than that of the phenolic antioxidants such as BHA, BHT, and TBHQ in the oil-water emulsion system.

Introduction

Fats and oils in food occur in a variety of physical forms: liquid forms such as vegetable oils, plastic forms such as lard, tallows, or shortening, or emulsion forms such as margarine, butter, mayonnaise, meat, and meat products. Behaviors

of antioxidants in complex food systems will certainly be different from those in pure fats and oils.

Both butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) have been widely used because of their effectiveness[1,2], low cost, and ready availability despite the fact that their toxicity in higher doses in experimental animals has been well-known[3]. Tertiarybutylhydroquinone (TBHQ) has been reported by many workers[4~6] effective in crude oils and fatty foods. Feeding tests and comparative biochemical studies appear to indicate TBHQ safe for food use[7]. Ascorbyl palmitate has also been used as food antioxidant[8].

Effectiveness of propyl gallate, lauryl gallate, alpha-tocopherol, BHA, and NDGA (0.005% by weight) on beta-carotene oxidation was tested by Lehman[9] in pure dry lard and the same lard in contact with an aqueous solution. The effectiveness in the dry lard was, in decreasing order, NDGA, BHA, PG, lauryl gallate, and alpha-tocopherol. In the lard in contact with the aqueous solution, NDGA was less active and BHA was most effective among the antioxidants tested.

It is well-known that Maillard browning reaction products possess significant activity in various fats and oils, or fatty food products[10~15]. The activity of Maillard browning reaction products in an anhydrous oil system has been compared with that in an oil-water emulsion system[16]. However, there has not been much work on the comparison of the activity of the browining reaction products with that of some representative commercial antioxidants in anhydrous oil and oil-water emulsion systems.

Therefore, in the present study, an attempt was made to compare the antioxidant activity of ethanol-extracts of a Maillard browning reaction mixture with that of commerial antioxidant BHT, BHT, TBH, TBHQ, and ascorbyl palmitate in anhydrous oil and oil-water emulsion systems.

Materials and Methods

Materials

The results of some chemical analyses of the commercial edible soybean oil which had been used as the anhydrous substrate and as the oil ingredient of the emulsion substrate are as follows :

Peroxide value	0.3±0.1
Thiobarbituric acid value	0.03±0.01
Free fatty acid value	0.23±0.04
Iodine value	123.0±1.1
Saponification vaue	189.0
Refractive index	1.4725 (at 25°C)

The peroxide value was determined by the A.O.C.S. method[16] and expressed as *meq* peroxides/*kg* oil. The thiobaraituric acid and free fatty acid values were determined by the methods described by Sidwell *et al*[17] and by Triebold and Aurand[18] respectively. The iodine value and saponification values were estimated by the A.O.A.C.-Wijs method[19] and the method described by Pearson[20]. The refractive index was measured with an Abbe refractometer (No.16093 Model, Erma Optical Co., Japan).

The synthetic antioxidants used in this study were butylated hydroxyanisole (BHA, Ueno Pharmaceutical Co., Japan), butylated hydroxytoluene (BHT, Ueno Pharmaceutical Co.), tertiary-butyl hydroquinone (TBHQ, Eastman Chemical Products, Inc., USA), and ascorbyl palmitate (Hoffman La Roche Co., Ltd., Switzerland).

The emulsifiers used were Tween 80 and Span 80 (Wako Pure Chemical Co., Japan).

Preparation of ethanol-extracts of a Maillard browning mixture

A 0.2 equimolar mixture of glucose and glycine was introduced into a 1000 *ml* flask fitted with a reflux condenser, and heated at 100°C. A 10 *ml* portion of the browning mixture was withdrawn respectively at 2 and 30 hr after the heating had started. Each portion was transfered into a small flask and extracted several times with abs. ethanol. The extracts were combined and the combined extracts for each portion were dehydrated with

anhydrous Na_2SO_4, filtered, cooled at 4°C, and then filtered again. The filtrates were concentrated and the concentrated extracts were made respectively to 10 *ml* with abs. ethanol.

Preparation of anhydrous soybean oil substrates

A small amount of each antioxidant was dissolved in 10 *ml* of abs. etanol and the ethanol solution was added to a 210 *g* soybean oil. The solvent was removed from the oil on a water bath. The soybean oil substrate was then equally divided into three parts in Petri dishes and stored in an incubator kept at 45.0±0.5°C for 25 days. The final concentration of each antioxidant in the soybean oil sustrate was 0.02 percent by weight. The substrates with the antioxidants and ethanol-extracts were termed respectively BHA, BHT,TBHQ, As. palmitate, M-2, and M-30. The substrate without any added antioxidant or extract was used as a control.

Preparation of soybean oil-water emulsion substrate

A stable oil-water emulsion (oil: water=50 : 45 by weight) with a small amount of an emulsifier mixture (5% by weight, Span 80: Tween 80=30 : 70). was prepared. The emulsion was prepared first by blending the oil with Span 80, and then by adding this mixture to the water mixed previously with Tween 80[21]. The emulsion contained 0.2 percent sodium dehydroacetate as preservative[22]. The emulsification was carried out in a cell homogenizer (8000 rpm for 3 min). Ten *ml* ethanol solutions of each antioxidant and ethanol-extract were added respectively to 500 *ml* of the emulsion and the solvent was removed. Each 500 *ml* emulsion was divided equally into two parts in 250 *ml* Erlenmeyer flasks. The final concentration of each antioxidant was 0.02 percent by weight. The emulsion substrate without any antioxidant or extract was used as a control. These substrates were also termed respectively BHA, BHT, TBHQ, As. palmitate, M-2, and M-30. The emulsion substrates including the control were stored in an incubator kept at 45.0±0.5°C. for 25 days.

Emulsion stability test

Stability of emulsions with various composition was evaluated by the procedure reported by Acton and Saffle[23,24], which was a modification the method of Titus[25]. Stability rating for an emulsion sample can be determined from the variation of percent moisture contents of the sample utilizing the following equation.

$$\text{Stability rating (SR)} = \frac{100 - M_{test}}{100 - M_{initial}} \times 100$$

where

M_{test} = the percent moisture content of the sample after 24 hr

$M_{initial}$ = the initial moisture content of the sample

Determinatin of antioxidant activity

The activity of each antioxidant and extract was estimated by comparing the POV and TBA value development of the corresponding substrates with that of the control The POV and TBA values were determined respectively by the A.O.C.S. method[16] and the method of Sidwell et al[18].

In case of the soybean oil-water emulsion substrates, 50 *ml* of each substrate was taken into a 250 ml flask, and the oil in the substrate was extracted with petroloeum ether (B.P. 35~45°C). A small amount of anhydrous Na_2SO_4 was added to the extract and the extract was filtered. The solvent was removed from the filtrate and the resulting oil was used for the determination of POV and TBA values.

Relative effectiveness of the antioxidants and extracts

To facilitate the comparison of the effectiveness of the antioxidants and extracts with one another, arbitrary induction periods were determined for the anhydrous oil and oil-water emulsion substrates of each antioxidant and extract. Since the POVs of the substrates containing As. palmitate and TBHQ did not increase appreciably during the storage period, the induction period was taken arbitrarily as the time in hour required for a substrate to reach a POV of 20 *meq/kg* oil.

The relative antioxidant effectiveness of the antioxidants and extracts in the anhydrous oil and oilwater emulsion substrates was calculated by the following equation.

Relative antioxidant effectiveness (RAE)

$$= \frac{\text{Induction period of antioxidant or extract in the anhydrous or emulsion substrate}}{\text{Induction period of control in the same type of substrate}} \times 100$$

Results and Discussion

Emulsion stability

The results of the emulsion stability test are shown in Table 1. The emulsion which had consisted of 50% oil, 45% water, and 5% emulsifier mixture was very stable, as can be expected from the Table. It was also found that the emulsion stability seemed to have no direct relationship to the HLB values of the emulsion systems tested. Titus et al[25] and Acton and Saffle[23] have reported that the fat contents of emulsion systems have greater effects on the emulsion stability than the percent contents of the emulsifiers used or the HLB values of the systems. In the present study, an emulsion system (oil content: 50%) with an HLB value of 11.8 (emusifier content: 5%) was used because an oil-in-water type emulsion was desired.

Antioxidant activity of the antioxidants and extracts in the anhydrous substrates

The results of the POV determination of anhydrous substrates and the control are shown in Fig. 1 and 2. The POVs of all the substrates increased continuously during the storage period, but they were significantly lower than those of the control throughout the storage period.

The POVs of the anhydrous soybean oil substrates. i.e., BHA, BHT, TBHQ, As. palmitate, M-2, M-30, and the control after 10 day storage were respectively 1.9±0.1, 2.2±0.1, 1.3±0.1, 0.9±0.2, 1.7±0.2, 1.6±0.1, and 5.1±0.1. Those after 25 day storage were 22.9±0.3, 17.3± 0.1, 4.5±0.1, 4.0±0.2, 14.9±0.3, 12.4±1.0, and 75.0±0.4,

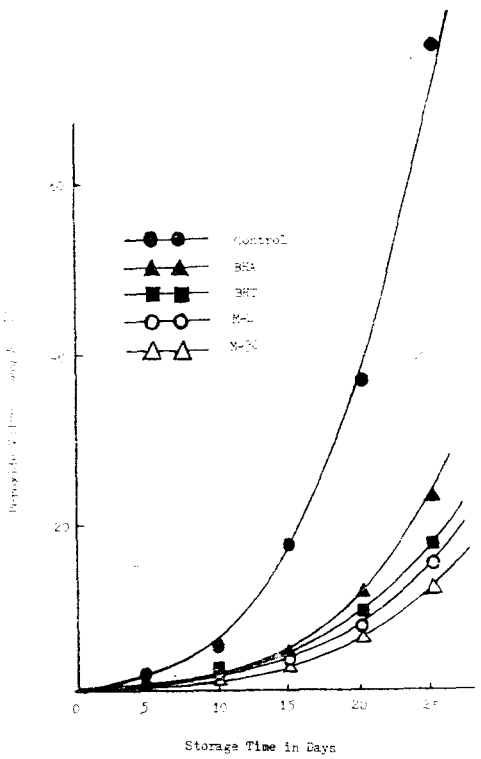

Fig. 1. Variations of peroxide values of anhydrous soybean oil substrates with storage time in days

Table 1. Stability rating[1] of soybean oil-water emulsion systems with different compositions and HLB values

Emulsifier mixture (5% by weight) Tween 80/Span 80	HLB[2]	Percent soybean oil (by weight)					
		30	45	50	60	75	90
10/90	5.4	—	99	100	101	101	99
30/70	7.6	—	100	100	100	101	99
50/50	9.7	—	99	100	99	—	102
70/30	11.8	97	100	100	100	100	—
90/10	13.9	—	99	100	100	—	—

(1) Stability rating was determined by the method described by Acton and Saffle[23,24].

(2) $HLB_{\text{mixture AB}} = (\%A)(HLB_A) + (\%B)(HLB_B)$[25]

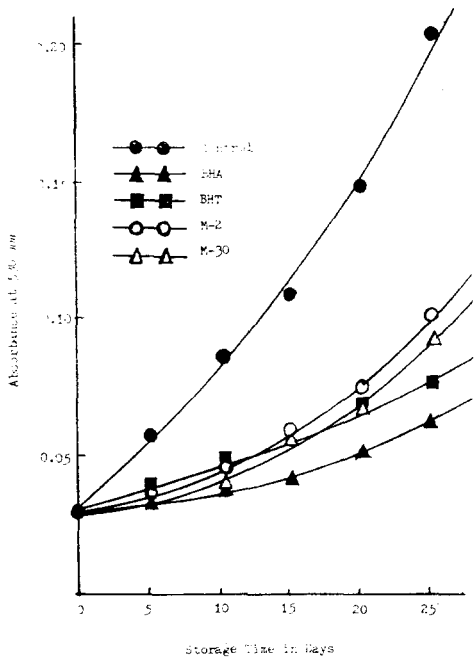

Fig. 2. Variations of peroxide values of anhydrous soybean oil substrates with storage time in days

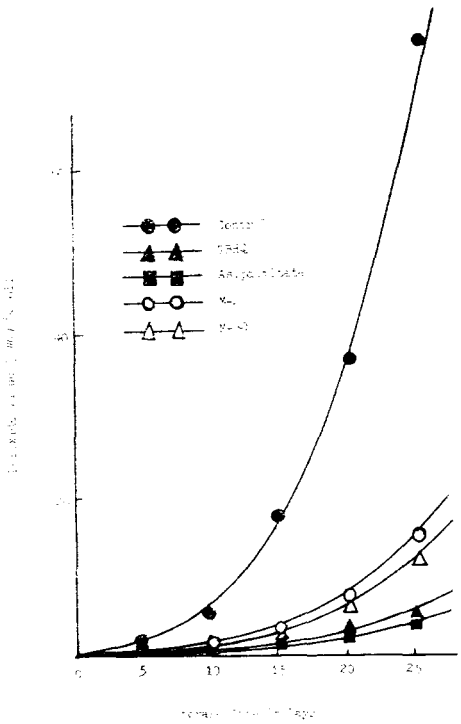

Fig. 3. Variationsof TBA values of anhydrous soybean oil substrates with storage time in days

The antioxdant activity of BHT, based on the POV development of the substrates, was initially similar to that of BHA, but it became slightly greater than that of BHA at the end of storage period. Both TBHQ and ascorbyl palmitate showed the strongest activity among the antioxidants and extracts tested. Both ethanol-extracts of the Maillard reaction mixture demonstrated stronger activity than BHA or BHT, but weaker activity than TBHQ or As. palmitate.

Variations of the TBA values of the substrates and control during the storage period are shown in Fig. 3 and 4. The TBA value development of the substrates were generally in good agreement with the POV development.

The TBA values of the anhydrous soybean oil substrates, i.e., BHA, BHT, TBHQ, As. palmitate, M-2, M-30, and the control after 10 day storage were respectively 0.062±0.0001, 0.057±0.001, 0.037±0.001, 0.051±0.001, 0.052±0.001, 0.039±0.001, and 0.088±0.0001. Those after 20 day storage were 0.098±0.001, 0.074±0.001, 0.051±

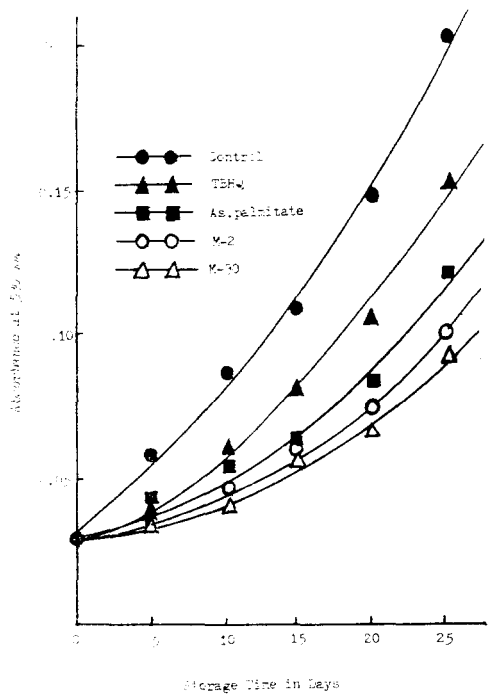

Fig. 4. Variations of TBA values of anhydrous soybean oil substrates with storage time in days

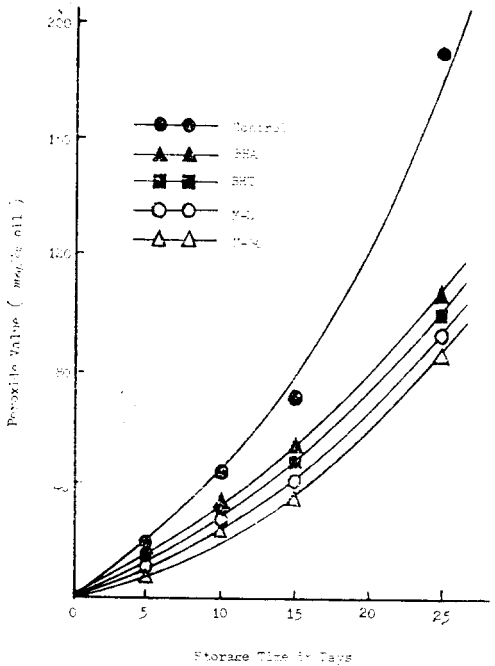

Fig. 5. Variations of peroxide values of soybean oil-water emulsion substrates with storage time in days

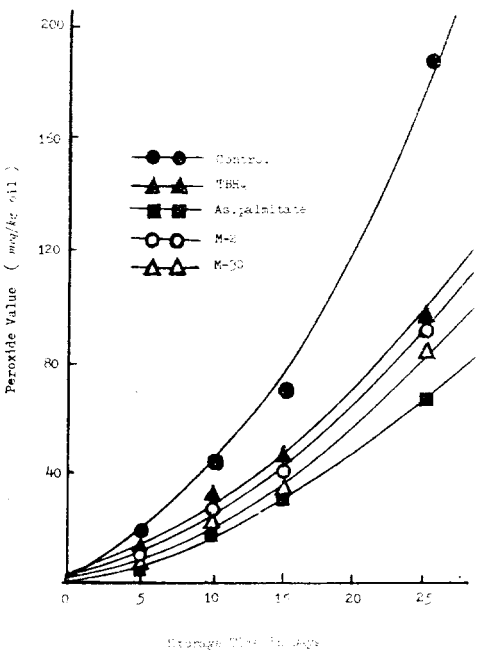

Fig. 6. Variations of peroxide values of soybean oil-water emulsion substrates with storage time in days

0.0001, 0.070±0.0001, 0.073±0.001, 0.066±0.001, and 0.148±0.001. The antioxidant activity of both ethanol-extracts, based on the TBA development of the substates, was slightly stronger than that of TBHQ or As. palmitate, and far stronger than that of BHA or BHT.

Antioxidant activity of the antioxidants and extracts in the emulsion substrates

The results of POV determination of the emulsion substrates and the control are shown in Fig. 5 and 6.

The POVs of the soybean oil-water emulsion substrates, i.e., BHA, BHT, TBHQ, As. palmitate, M-2, M-30, and the control after 10 day storage were respectively 35.0±0.8, 33.6±0.8, 33.6±0.4, 17.4±0.1, 28.5±1.1, 25.9±0.3, and 44.2±0.5. Those after 25 day storage were respectively 100.3 ±0.6, 98.8±0.5, 93.8±0.6, 64.5±1.9, 91.2±0.5, 85.8±0.1, and 187.9±0.1.

When the POV development of the emulsion substrates was compared with that of the anhydrous sustrates, the activity of the antioxidants and ethanol-extrats in the oil-water emulsion substrates did not seem strong. As. palmitate showed the strongest activity, whereas BHA and BHT exhibited the weakest activity among the antioxidants and extracts tested. TBHQ and both ethanol-exracts showed intermediate activity.

The variations of the TBA values of the emulsion substrates and the control are shown in Fig. 7 and 8. The TBA values of the emulsion substrates, i.e.. BHA, BHT, TBHQ, As. palmitate, M-2, M-30, and the control after 10 day storage were respectively 0.41±0.01, 0.40±0.10, 0.35±0.01, 0.22± 0.01, 0.31±0.01, 0.29±0.06, and 0.49±0.01. Those values after 20 day storage were respectively 0.59±0.05, 0.58±0.05, 0.54±0.03, 0.43±0.06, 0.37±0.07, 0.32±0.11, and 1.80± 0.01. As. palmitate showed the strongest activity among the antioxidants and extracts tested in the initial stages of the storage period, but the activity became greater than that of As. palmitate in the later stages of the storage period. BHA and BHT demonstrated definite antioxidant activity in the oil-water emulsion substrates, but the activity was far weaker than that of the ethanol extracts, The

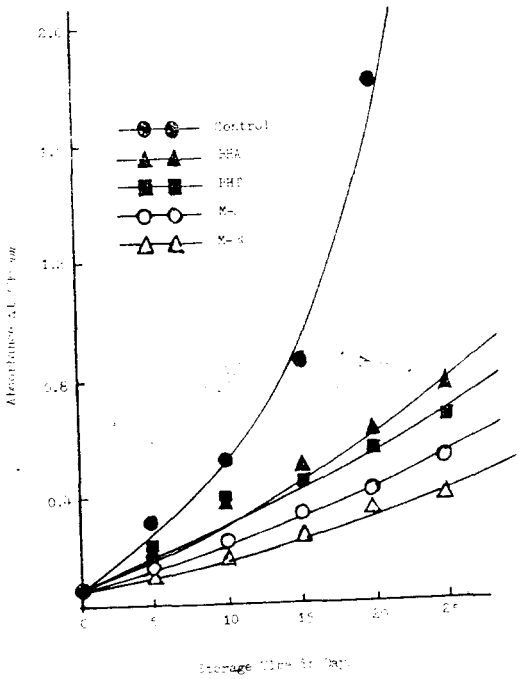

Fig. 7. Variations of TBA values of soybean oil-water emulsion substrates with storage time in days

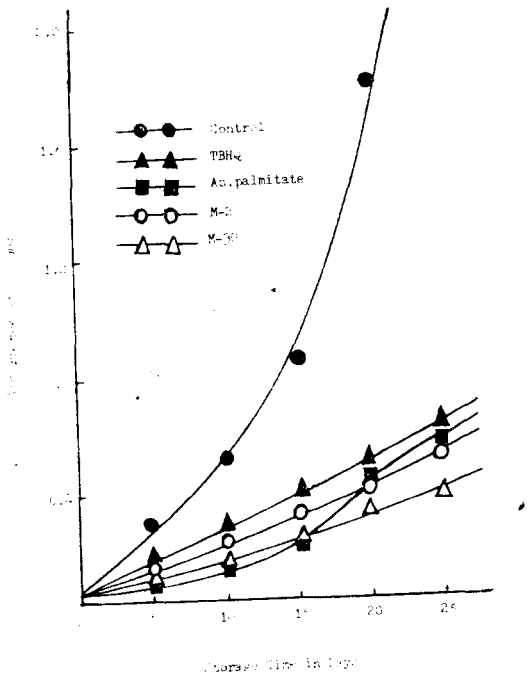

Fig. 8. Variations of TBA values of soybean oil-water emulsion substrates with storage time in days

Table 2. The induction periods[1] and relative antioxidant effectiveness[2] of the antioxidants, ethanol-extracts, and control both in the anhydrous soybean oil and oil-water emulsion substrates

Antioxidants extracts and control	Anhydrous oil substrates		Oil-water emulsion substrates	
	Induction periods (hr)	Relative effectiveness (%)	Induction periods (hr)	Relative effectiveness (%)
Control	383	100	117	100
BHA	572	149	143	122
BHT	638	167	158	135
M-2	679	177	178	152
M-30	715	187	204	174
TBHQ	1,185	309	153	131
As. palmitate	1,256	328	271	232

(1) The time in hour required for a substrate to reach a POV of 20 *meq/kg* oil

(2) Relative antioxidant effectiveness

$$= \frac{\text{Induction period of antioxidant or extract in the anhydrous or emulsion substrate}}{\text{Induction period of control in the same substrate}} \times 100$$

activity of TBHQ in the oil-water emulsion substrates, based on the TBA development, was similar to that of BHA and BHT.

Induction periods and relative antioxidant effectiveness of the antioxidants and ethanol-extracts

The induction period, which had been arbitrarily taken as the time in hour required for a substrate to reach a POV of 20 *meq/kg* oil, was estimated graphically from POV-storage time curves. The induction periods of the antioxidants, extracts, and the control are shown in Table 2. The relative antioxidant effectiveness, which is the percent ratio of the length of an induction period of a substrate containing one of the antioxidants or extracts to that of the control, was calculated for each antioxidant and extract and included in the Table.

The autoxidation of the soybean oil proceeded with far greater speed in the soybean oil-water emulsion system than in the anhydrous system. The induction period of the control in the anhydrous oil substrate was 383 hr, whereas that in the oil-water emulsion substrate was 117 hr.

The greater rate of autoxidation in the oil-water emulsion substrates can be attributed mainly to the intrinsic nature of the emulsion substrates, although contribution of other factors such as the presence of a small amount of the emulsifier mixture (Tween 80+Span 80) to the rate of the autoxidation cannot be disregarded. In oil-water emulsion systems autoxidation of the oil can take place not only by initiators residing within the oil phase, but also by oxidation reactions at the interface because the oil phase is surrounded by water, an oxygen-rich environment. Sims *et al*[27] have reported that the diffusion rate of oxygen at the interface of an oil-water emulsion decreases as the viscosity of the water-phase increases.

It has also been suggested by Sims *et al*[27] that the diffusion of oxygen through the oil-water interface is the determining step in the oxidation of the oil in an oil-water emulsion. The diffusion rate of oxygen through the oil-water interface of an emulsion is related to the total interface area, which in turn depends on the particle sizes of oil-droplets in the water-phase and hence on the general stability of the emulsion. Berner *et al*[28] have reported that the rate of oxygenuptake through the oil-water interface of an oil-water emulsion decreases as the emulsion starts to separate into water and oil phases. The emulsion system used in the present study maintained its stability well for more than 25 days at a temperature of 45.0±0.5°C. The greater rate of autoxidation in the oil-water emulsion in the present study can be attributed partly to the active oxygen-uptake through the oil-water interface of the emulsion substrates during the storage period.

The relative antioxidant effectiveness of the antioxidants and extracts both in the anhydrous oil and oil-water emulsion systems is included in Table 2. In the anhydrous system, As. palmitate and TBHQ seemed to possess the strongest activity among the antioxidants and extracts tested. Both extracts showed stronger activity than BHT or BHA, but the activity of the extracts was weaker than that of As. palmitate and TBHQ. The antioxidant activity of the antioxidants and extracts in the anhydrous system was, in decreasing order, as follows :

As. palmitate, TBHQ > M-30, M-2 > BHT, BHA

The sequence of the antioxidant effectiveness of the antioxidants and extracts in the anhydrous system based on the TBA value develoment of the substrates was in good agreement with that based on the POV development of the substrates.

The sequence of the antioxidant effectiveness of the antioxidants and extracts in the oil-water emulsion system was similar to that in the anhydrous oil system except for the fact that TBHQ was less effective than the extracts in the oil-water emulsion system. The activity of the antioxidants and extracts in the emulsion system was, in decreasing order, as follows :

As. palmitate > M-30, M-2 > BHT, TBHQ, BHA

It was surprising that ascorbyl palmitate exhibited the strongest activity among the antioxidants and extracts tested both in the anhydrous oil and oil-water emulsion systems The storage time in the present study was relatively short (25 days). Whether or not ascorbyl palmitate can maintain its strong antioxidant activity for longer storage

period is not certain. In the oil-water emulsion system the activity of the extracts based on the TBA development of the substrates appeared to be stronger than As. palmitate.

The strong activity of the ethanol-extracts of the Maillard browning mixture both in the anhydrous soybean oil and oil-water emulsion systems was very remarkable. Hong and Rhee[29] have recently published the results of their study that the ethanol-extracts of a Maillard browning reaction mixture (0.5 M glucose+0.5 M glycine) demonstrated strong antioxidant activity in a commercial soybean oil subjected to active oxygen test (heating at 97.8±0.2°C., aeration at a rate of 2.23 *ml* air/sec). They have also reported[29] that the ethanolextracts showed strong synergistic effects on antioxidant BHT or BHA in the same substrate.

要 約

콩기름基質과 콩기름-물 에멀전基質에서 反應 2 및 30時間 後의 Maillard型 褐色化反應液에서 얻은 에탄올 抽出物(M-2와 M-30, 각각 10 m*l*)과 BHA, BHT, TBHQ와 ascorbyl palmitate (각각 0.02%, w/w)의 酸化防止效果를 比較하고저 하였다. Control 및 各 基質은 45.0±0.5°C에서 貯藏되었으며, 5日마다 過酸化物값과 TBA값을 測定하였다. 그 結果는 다음과 같다.

주로 POV 測定結果에 의거한 無水基質에서의 酸化防止效果의 順序는 As. palmitate, TBHQ ≫ M-30, M-2 > BHT, BHA 였으며, 에멀전基質에서의 順序는 As. palmitate ≫ M-30, M-2 > BHT, TBHQ, BHA 였었다.

한편, Maillard型 褐色化反應 抽出物들은 無水基質에서 보다는 에멀전基質에서 더 效果的이였으며, 에멀전基質에서는 그 效果는 phenol系 酸化防止劑인 BHA, BHT, TBHQ 보다 더 컸었다.

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