Effects of Filtration Through Activated Carbons on Peroxide, Thiobarbituric Acid and Carbonyl Values of Autoxidized Soybean Oil

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Effects of filtration bleaching on peroxide value (PV), thiobarbituric acid value (TAV) and carbonyl value (CV) of autoxidized soybean oil were investigated by using twenty-three kinds of activated carbon in order to improve oil quality. From the decreases in PV, TAV and CV and from the physical and chemical properties of activated carbons, it was suggested that hydroperoxides, aldehydes and ketones were adsorbed on the acid sites distributed over the surface or within the pores of the activated carbons while the autoxidized soybean oil flowed through the packed column. The residual tocopherols in autoxidized soybean oil and treated soybean oil were determined during storage. The decrease in oxidative stability of treated soybean oil seemed to be caused by elimination of α-, β- and γ-tocopherols. δ-Tocopherol was chemically more stable than α-, β- and γ-tocopherols in autoxidized soybean oil.

KEY WORDS: Acidity, activated carbon, autoxidized soybean oil, bleaching effect, carbonyl value, peroxide value, specific surface area, storage, thiobarbituric acid value, tocopherol.

Autoxidation is one of the most important reactions occurring in soybean oil. The hydroperoxides produced by reaction with dissolved oxygen split into smaller organic compounds, such as aldehydes, ketones, alcohols and acids, with toxicities that are considerably stronger to animals (1). It is therefore necessary to remove peroxides, ketones and aldehydes from the autoxidized soybean oil. The standard activated clay effectively reduces the peroxide value (PV) (2), thiobarbituric acid value (TAV) and carbonyl value (CV) (3) of autoxidized soybean oil. Boki *et al.* (2,3) indicated that peroxides are decomposed by the strongest acid sites on the clay and that aldehydes and ketones are adsorbed on their active sites.

Adsorption efficiency of activated carbon depends on the area of exposed surface, pore volume or surface acidic oxides. Surface basic oxides of activated carbon as a catalyst are reported to decompose hydrogen peroxide (4). The object of this study is to elucidate the effects of filtration through activated carbons on PV, TAV and CV of autoxidized soybean oil. Residual tocopherols in autoxidized soybean oil and treated soybean oil were determined. The relationships between residual amounts of α-, β-, γ- or δ-tocopherols and PV, TAV or CV of autoxidized soybean oil and treated soybean oil were discussed.

MATERIALS AND METHODS

Materials. Edible soybean oil was obtained from Wako Pure Chemical Ind. Ltd. (Osaka, Japan). The autoxidized soybean oil was prepared by heating the fresh soybean oil in an electric oven at 60°C. Standards of α-, β-, γ- and δ-tocopherols were obtained from Wako Pure Chemical. Filtering media employed to treat the autoxidized soybean oil were: Activated carbon No. 1 (Hana F2 dry; Daisan Ind. Ltd., Tokyo, Japan); activated carbon No. 2 (Hana D dry; Daisan Ind. Ltd.); activated carbon No. 3 (Tokusei Umebachi Shirushi; Taihei Chemical Ind. Ltd., Osaka, Japan); activated carbon No. 4 (Charcoal, Activated, powder; Wako Pure Chemical Ind. Ltd.); activated carbon No. 5 (Silver A dry; Daisan Ind. Ltd.); activated carbon No. 6 (Charcoal, Activated, powder, BA; Hokuetsu Tanso Ind. Ltd., Yokohama, Japan); activated carbon No. 7 (Tokusei Umebachi H-R Shirushi; Taihei Chemical Ind. Ltd.); activated carbon No. 8 (Charcoal, Activated, powder, ZN; Hokuetsu Tanso Ind. Ltd.); activated carbon No. 9 (Charcoal, Activated, granule CL-H; Hokuetsu Tanso Ind. Ltd.); activated carbon No. 10 (Gold S; Daisan Ind. Ltd.); activated carbon No. 11 (Yuki S; Daisan Ind. Ltd.); activated carbon No. 12 (Charcoal, Activated, granule, CL-K; Hokuetsu Tanso); activated carbon No. 13 (4GM; Tsurumi Coal Ind. Ltd., Yokohama, Japan); activated carbon No. 14 (Shirasagi Sx; Takeda Chemical Ind. Ltd., Osaka, Japan) activated carbon No. 15 (Charcoal, Activated; Sigma Chemical Co., St. Louis, MO); activated carbon No. 16 (Charcoal, Activated, powder, F-17; Hokuetsu Tanso); activated carbon No. 17 (G-AC; Hokutan Kasei Chemical Ind. Ltd., Saitama, Japan); activated carbon No. 18 (Charcoal, activated for column chromatography; Wako Pure Chemical); activated carbon No. 19 (Charcoal, activated for measurement of oxidant concentration; Nacalai Tesque Ltd., Kyoto, Japan); activated carbon No. 20 (Activated Carbon, granule; Kanto Chemical Co. Inc., Tokyo, Japan); activated carbon No. 21 (Technicoal; Bamberg Co. Ltd., Germany), activated carbon No. 22 (Shirasagi Sx; Takeda Chemical); and activated carbon No. 23 (Charcoal, Activated, granule, Wako Pure Chemical Ind.). The particle sizes of activated carbons were sieved to be 75 μm or less. Activated carbons were dried at 110°C for 15 hr before use. All the other chemicals used for the measurements of PV, TAV and CV were reagent grade.

Filtration through activated carbon. Filtration through activated carbon was carried out by the method described previously (2). The decreases in PV, TAV and CV were obtained by treating 10 g autoxidized soybean oil (PV, 45.1 meq/kg; TAV, 1.0; CV, 10.5) with 1 g activated carbon.

Peroxide, carbonyl and thiobarbituric values. PV was determined by AOAC methods 28025 and 28026 (5). TAV and CV were determined by Standard Methods of Analysis for Hygienic Chemists (6) and JOCS methods 2•4•22-73 (7), respectively. PV, TAV and CV reported were the average value of three measurements.

Specific surface area. Specific surface area of activated carbon was measured by the method described previously (2).

Pore size distribution. Pore size distribution of activated carbon was determined by the method of Dollimore and

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Heal (8) from the data of nitrogen adsorption isotherm up to a relative pressure of 0.95.

Acidity. Acidic oxides of activated carbon were measured by the method of Akiyoshi and Shirasaki (9). Activated carbon (250 mg) was added to a 30-mL portion of aqueous sodium hydroxide (0.01 N) in a well-stoppered flask of 50 mL capacity. The suspension was allowed to stand in a thermostat maintained at 25°C and shaken at a constant rate for 15 hr. The blank was run simultaneously. Residual sodium hydroxide was estimated by titrating aqueous hydrogen chloride (0.01 N) to the filtrate. Deionized and distilled water was used in all the experiments.

Basicity. Basicity of activated carbon was measured according to the method of Okazaki and Toyoda (10). Activated carbon (250 mg) was added to a 30-mL portion of aqueous hydrogen chloride (0.01 N) and the suspension was shaken for 15 hr. Basicity was determined by titrating aqueous sodium hydroxide (0.01 N) to the filtrate.

Stability test. Autoxidized soybean oil and treated soybean oil were stored in a brown desiccator over silica gel at 30°C. Samples were withdrawn periodically for measurements of PV, TAV and CV.

Determination of tocopherols. Tocopherols were determined by JOCS methods 2•4•31-86 (11). A Hitachi high-performance liquid chromatography (HPLC) model L-6200 (Hitachi Co. Ltd., Tokyo, Japan) equipped with a Hitachi F-1150 fluorescence spectrophotometer was used. The excitation was set at 298 nm and emission at 325 nm. A 25 cm × 4.6 mm column of 5 μm Lichrosorb Si 60 and a mobile phase of hexane/dioxane/ethanol (490:10:1) at a flow rate of 1.50 mL/min were used to provide the separation of α-, β-, γ- and δ-tocopherols. The column temperature was maintained at 20 ± 2°C. A Hitachi chromato-integrator model D-2500 was used with the fluorometer during quantitative analysis. The volume injected was usually 20 μL. The results were calculated from the peak areas by using factors derived from chromatography of standards and internal standard (2,2,5,7,8-pentamethyl-6-hydroxychromane).

RESULTS AND DISCUSSION

Effect of filtration through activated carbons. The decreases in PV, TAV and CV of autoxidized soybean oil after filtering through various activated carbons are shown in Table 1. Activated carbons No. 8 and No. 4 were most effective in reducing PV (88 and 76%), TAV (87 and 74%) and CV (25 and 34%), and other activated carbons reduced PV from 0 to 62%, TAV from 26 to 79% and CV from −8 to 19%. The results indicated that activated carbons No. 8 and No. 4 effectively reduced the amounts of hydroperoxides and aldehydes and that activated carbons did not have a noticeable effect on reducing the amounts of ketones in autoxidized soybean oil.

To determine whether the stability of oil treated with activated carbon No. 4 increased, autoxidized soybean oil and treated soybean oil were stored in a brown desiccator at 30°C. The results of PV, TAV and CV measurements are shown in Figures 1 and 2, respectively. PV, TAV and CV of the treated soybean oil were higher after it was stored for approximately 75 days. The results of storage indicated that the quality of the treated soybean oil is slightly better up to *ca.* 75 days.

TABLE 1

Effects of Filtration Through Various Activated Carbons on Peroxide, Thiobarbituric Acid and Carbonyl Values of Autoxidized Soybean Oil

	Decrease (%)		
Activated carbon no.	PV	TAV	CV
1	47	79	19
2	14	50	9
3	14	42	6
4	76	74	34
5	25	73	8
6	10	74	9
7	14	73	4
8	88	87	25
9	14	48	7
10	17	59	9
11	51	78	21
12	17	70	10
13	4	51	4
14	0	41	1
15	14	52	−8
16	25	67	11
17	57	60	1
18	62	73	11
19	18	53	3
20	12	50	1
21	37	62	10
22	7	36	0
23	3	26	2

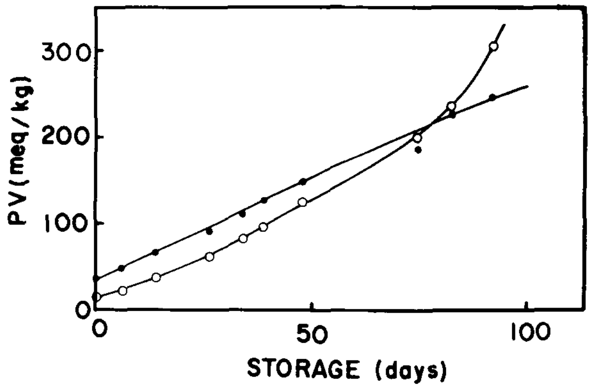

FIG. 1. PV curves of autoxidized soybean oil and treated soybean oil stored at 30°C: PV, peroxide value; -●—●-, autoxidized soybean oil; and -O—O-, treated soybean oil.

Effects of physical and chemical properties of activated carbons on decreases in PV, TAV and CV. The results in Table 1 indicate that the effects on decreases in PV, TAV and CV of autoxidized soybean oil differed with activated carbons. It is possible that differences in physical and chemical properties of activated carbons cause differences in activity for reducing PV, TAV and CV. The specific surface area, acidity and basicity of twenty-three kinds of activated carbons and the pore size distribution curves of typical activated carbons are shown in Table 2 and Figure 3, respectively. Activated carbons Nos. 4, 17, 18 and 21, with greater reduction in PV, TAV and CV (Table 1), have a greater pore volume with radii of 12.5 Å or more. Although activated carbons Nos. 22 and 23 have a greater pore volume with radii of 7.5

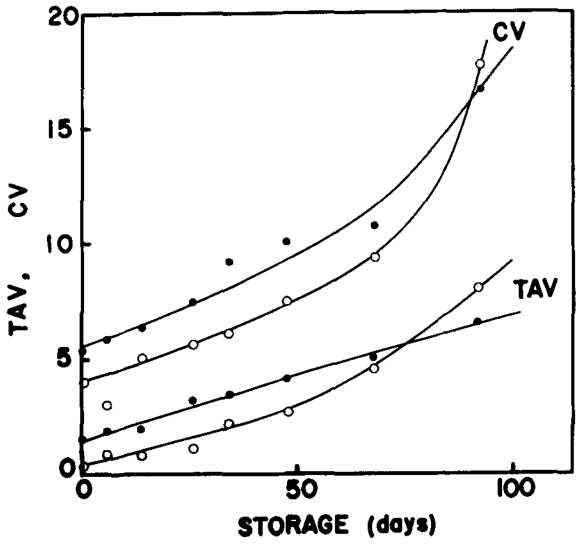

FIG. 2. TAV and CV curves of autoxidized soybean oil and treated soybean oil stored at 30°C: TAV, thiobarbituric acid value; CV, carbonyl value; -●—●-, autoxidized soybean oil; and -O—O-, treated soybean oil.

TABLE 2

Specific Surface Area, Acidity and Basicity of Various Activated Carbons

Activated carbon no.	Specific surface area (m^2/g)	Acidity (meq/g)	Basicity (meq/g)
1	1351.3	0.702	0.190
2	983.1	0.701	0.133
3	1142.8	0.706	0.323
4	1305.0	0.762	0.260
5	1100.4	0.768	0.197
6	1071.2	0.477	0.393
7	1098.3	0.479	0.960
8	1393.2	0.935	0.215
9	997.5	0.458	0.468
10	1036.1	0.614	0.232
11	1160.6	0.506	0.112
12	1419.0	0.327	0.301
13	913.0	0.269	0.725
14	1006.0	0.366	0.315
15	768.5	0.354	1.065
16	998.9	0.800	0.552
17	952.8	0.731	0.052
18	1249.4	0.681	0.116
19	954.8	0.391	0.277
20	1074.0	0.326	0.270
21	1306.8	0.661	0.203
22	894.9	0.429	0.301
23	973.5	0.356	0.396

Å or less, the reduction in PV, TAV and CV were lower (Table 1). Therefore, it seems likely that the restricted porosity in the 12.5–110 Å region is responsible for the adsorption efficiency of activated carbons. The correlation coefficients calculated by using the data of specific surface area, acidity, basicity and pore volume as well as decreases in PV, TAV and CV are shown in Table 3. The relationships between decreases in PV, TAV or CV and specific surface area, basicity or pore volume with pore radii 12.5–110 Å were highly significant at $P<0.05$. From the correlation coefficients, it is suggested that hydroperoxides, aldehydes and ketones are adsorbed on the acid sites distributed over the surface or within the pores of activated carbons while the autoxidized soybean oil flowed through the packed column. The correlation

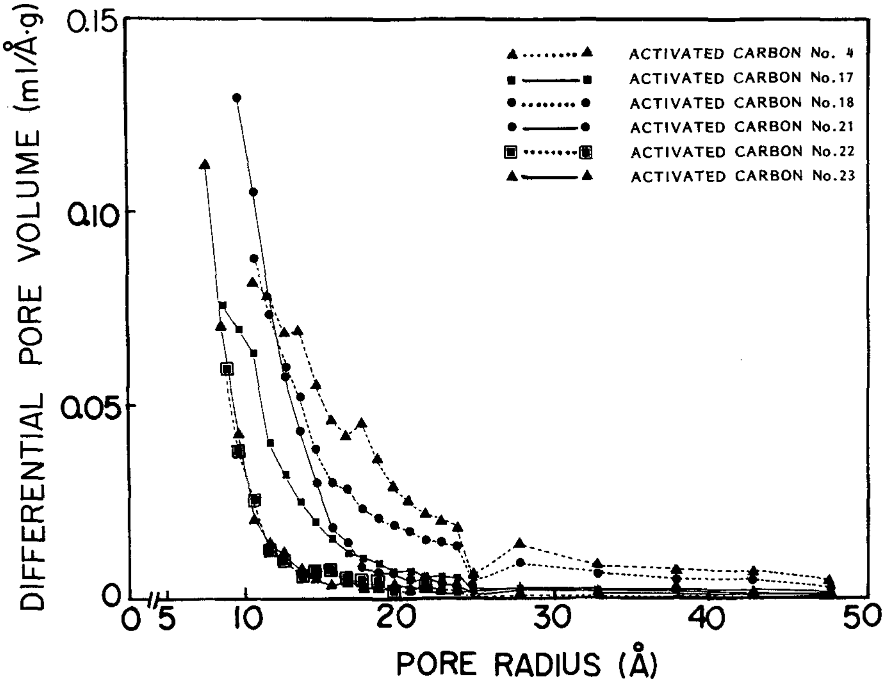

FIG. 3. Pore size distribution curves of activated carbons.

TABLE 3

Coefficient of Determination Value Obtained by Linear Regression Between Decreases of PV, TAV or CV and Specific Surface Area, Acidity, Basicity or Pore Volume

Physicochemical property	Correlation coefficient^{a} PV	TAV	CV
Specific surface area (n=23)	0.620^{b}	0.660^{c}	0.748^{c}
Acidity (n=23)	0.714^{c}	0.535^{d}	0.603^{b}
Basicity (n=23)	−0.438^{d}	−0.160	−0.431^{d}
Pore volume (n=10)			
7.5 ⩽ radius ⩽ 110 Å	0.599	0.848^{b}	0.807^{b}
12.5 ⩽ radius ⩽ 110 Å	0.648^{d}	0.842^{b}	0.845^{b}

[a] Correlation coefficients were calculated by using the data of specific surface area, acidity, basicity and pore volume shown in Table 2 and Figure 3, and decreases of PV, TAV and CV shown in Table 1.

[b] There is significant difference at 1%.

[c] There is significant difference at 0.1%.

[d] There is significant difference at 5%.

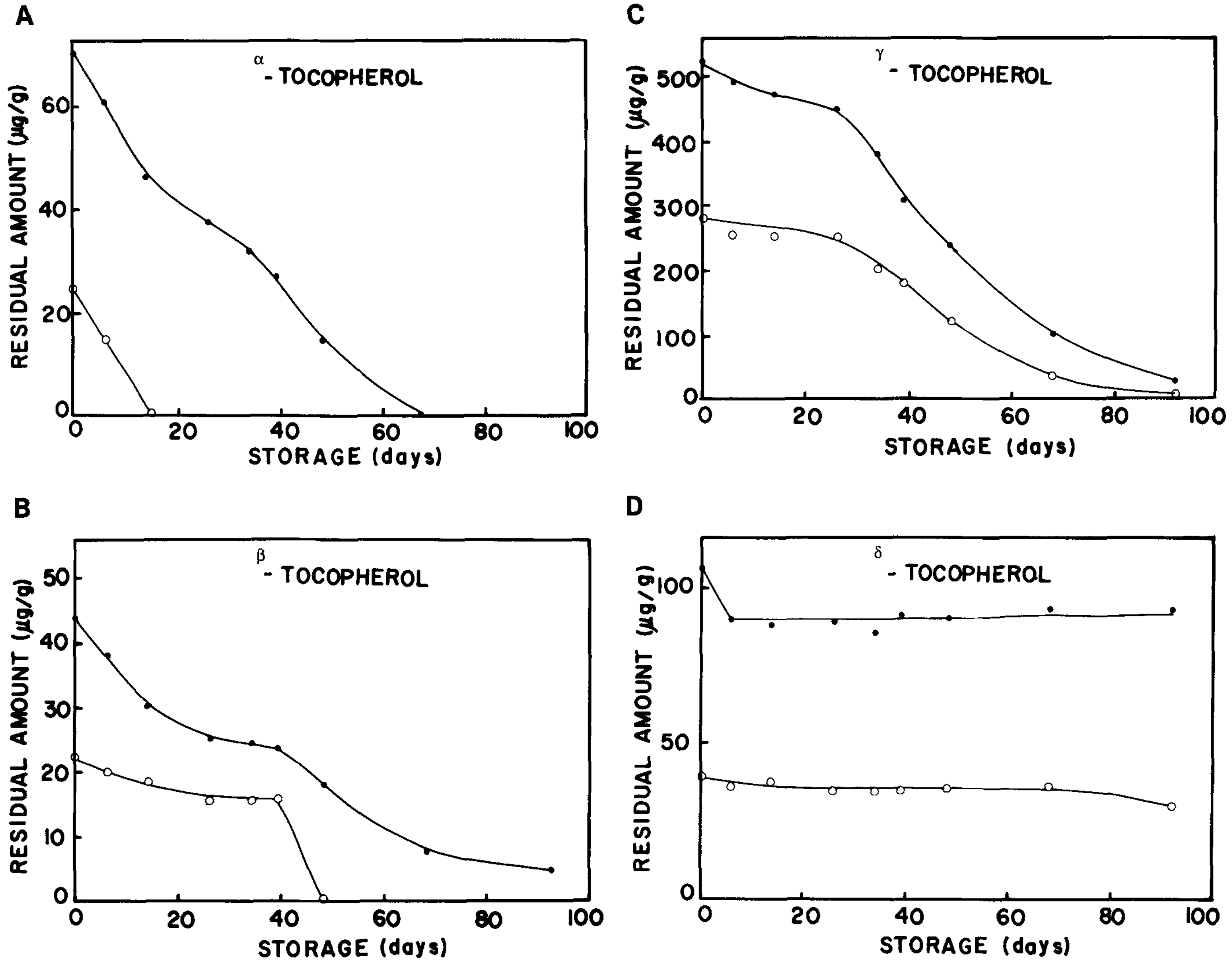

FIG. 4. Residual amounts of A, α; B, β; C, γ; and D, δ-tocopherols in autoxidized soybean oil and treated soybean oil stored at 30°C: -●—●-, autoxidized soybean oil; and -O—O-, treated soybean oil.

coefficient between PV and acidity was larger than those between PV and specific surface area or pore volume. However, the correlation coefficients between TAV or CV and the properties were reversed in numerical order. The results were in agreement with the known property that hydroperoxides are more polar than aldehydes or ketones.

Change in residual amount of tocopherols in autoxidized soybean oil and treated soybean oil stored at 30°C. Residual amounts of α-, β-, γ- and δ-tocopherols in autoxidized soybean oil and treated soybean oil stored at 30°C are shown in Figure 4. The amounts of α-, β-, γ- and δ-tocopherols in autoxidized soybean oil (PV, 36 meq/kg) were 71, 44, 517 and 106 μg/g, respectively. The residual total tocopherol content in treated soybean oil passed through the activated carbon No. 4 was 371 μg/g, that is, *ca.* 50% of tocopherol content was removed. Residual amounts of α-, β- and γ-tocopherols in untreated soybean oil decreased gradually with an increase of storage time; δ-tocopherol remained constant for 3 months. Residual α-, β- and γ-tocopherols in treated soybean oil vanished to nothing at 15, 48 and 92 days, respectively. The treated soybean oil was oxidized faster than the untreated soybean oil after *ca.* 70 storage days (Figs. 1 and 2). Decrease in oxidative stability of treated soybean oil seemed to be caused by removal of α-, β- and γ-tocopherols. The oxidative stability of the tocopherol was α- < γ- < δ-tocopherol (12). Optimum concentrations of α-, γ- and δ-tocopherols to increase oxidative stability of soybean oil was 100, 250 and 500 ppm, respectively (13). The results of residual amounts of tocopherols (Fig. 4) and stability tests (Figs. 1 and 2) suggest that δ-tocopherol at concentrations of less than 100 μg/g had no effect on oxidative stability of soybean oil and that it was chemically more stable than α-, β- and γ-tocopherols.

ACKNOWLEDGMENTS

Appreciation is expressed to Daisan Ind. Ltd., Taihei Chemical Ind. Ltd., Hokuetsu Tanso Ind. Ltd., Tsurumi Coal Ind. Ltd., Hokuetsu Kasei Chemical Ind. Ltd. and Takeda Chemical Ind. Ltd., for their donation of activated carbons.

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[Received December 28, 1990; accepted May 28, 1991]