

Bleaching of Alkali-Refined Vegetable Oils with Clay Minerals

Keito Boki^{a,*}, Moriaki Kubo^a, Tetsuyuki Wada^a and Takamichi Tamura^b

^aFaculty of Pharmaceutical Sciences, Kinki University, Higashi-Osaka, Osaka 577, Japan and ^bDepartment of Public Health, School of Medicine, The University of Tokushima, Tokushima 770, Japan

Bleaching efficiencies of bentonites, montmorillonites and sepiolites for alkali-refined rapeseed, soybean, wheatgerm, safflower, corn, cottonseed and sunflower oils were investigated by a batch method at 110°C. The sepiolites with more acid sites at $-5.6 > H_0 \geq -3.0$ were the most effective in bleaching of each alkali-refined oil. Surface area and acidity at $-5.6 > H_0 \geq -3.0$ were highly significant with bleaching efficiency. The sepiolites (numbers 2 and 3) were more suitable than standard activated clay because they were more effective both in retaining tocopherols and in reducing free fatty acids after bleaching.

KEY WORDS: Adsorption, alkali-refined oil, bleaching, free fatty acids, sepiolite, tocopherols.

Crude oil is processed by degumming, alkali refining, bleaching and deodorizing. Bleaching reduces chlorophylls, carotenoids and peroxides (1) by adsorbing coloring matters onto the bleaching medium (2). Residual free fatty acids in oil decrease the stability towards autoxidation (3), thermal oxidation (4) and flavor (5). Bleaching with acid-activated clay increases the content of free fatty acids in soybean oil (1). Since tocopherols possess antioxidant properties and vitamin E activity, it is desirable to retain as many as possible in bleached oil.

The present study was conducted to identify the optimal bleaching medium for reducing the amounts of pigments and free fatty acids, while retaining tocopherols in bleached oils. The residual amounts of pigments, tocopherols and free fatty acids in rapeseed, soybean, wheatgerm, safflower, corn, cottonseed and sunflower oils after bleaching with bentonite, montmorillonite and sepiolite were investigated. Standard activated clay was used for comparison.

MATERIALS AND METHODS

Materials. Alkali-refined rapeseed oil was donated by Ajinomoto Co., Inc. (Tokyo, Japan). Alkali-refined soybean, corn and sunflower oils were donated by Honen Oil Co., Ltd. (Shimizu, Shizuoka Prefecture, Japan). Alkali-refined wheatgerm, safflower and cottonseed oils were donated by Summit Oil Mill Co., Ltd. (Chiba Prefecture, Japan). The oils were stored in a dark cooler at 4°C until use. Acid value, iodine absorption number, saponification number and peroxide value were measured by the Japan Oil Chemists' Society (JOCS) method (6). Bleaching media employed to remove pigment from alkali-refined oils were: Bentonite No. 1 (powder; Wako Pure Chemical Ind., Ltd., Osaka, Japan), particle diameter (PD) < 75 µm; bentonite No. 2 (powder; Fuji Talc Ind., Ltd., Osaka, Japan), PD < 75 µm; montmorillonite No. 1 (powder; Nacalai Tesque Ltd., Kyoto, Japan), PD < 75 µm; montmorillonite No. 2 (powder; Kunimine Ind. Co., Ltd., Tokyo, Japan), PD < 75 µm; sepiolite No. 1 (coarse powder, American origin), PD

< 75 µm; sepiolite No. 2 (powder, Turkish origin), PD < 75 µm; sepiolite No. 3 (spherule, Turkish origin), PD < 75 µm; sepiolite No. 4 (fiber, Chinese origin), size, 1000 × 1 µm; sepiolite No. 5 (fiber, Chinese origin), size, 5000 × 1 µm; sepiolite No. 6 (fine powder, American origin), PD < 75 µm; sepiolite No. 7 (powder, American origin), PD < 75 µm. All the sepiolites were donated by Fuji Talc Ind. Ltd.; standard activated clay (powder, certificated by The Japan Oil Chemists' Society, Wako Pure Chemical Ind., Ltd.) PD < 75 µm. Bleaching media were dried at 110°C for 15 hr before use. Hammet indicators (neutral red, methyl red, dimethyl yellow and benzene-azo-diphenylamine, Wako Pure Chemical Ind., Ltd.; 1-phenylazo-2-naphthyl-amine, dicinnamalacetone and benzalacetophenone, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan; anthraquinone, Kishida Chemical Co., Ltd., Osaka, Japan) were reagent grade. All other chemicals used were reagent grade.

Procedure for bleaching. Bleaching efficiency was determined by the JOCS method 2·2·7-71 (7). Alkali-refined oil (10.0 g) was stirred and heated to 110 ± 2°C within 5 min under a vacuum of 18 mmHg in a suction bottle of 50-mL capacity. The clay material (0.4 g) was then added to the heated oil, and the mixture was agitated with a magnetic stirrer for 15 min under vacuum at 110°C. The mixture was allowed to cool to 25°C under vacuum before being filtered through a glass funnel (TOP, 3G4) covered with glass-fiber paper (Whatman, GF/F). The filtered oil (approximately 2.0 mL) was added to benzene (8 mL) in a measuring flask to a total volume of exactly 10 mL. Residual β-carotene content was measured at maximum wavelength of 457 nm in a Shimadzu spectrophotometer UV-120-02 (Shimadzu Corporation, Kyoto, Japan).

Determination of tocopherols. Residual tocopherols in unbleached and bleached alkali-refined oils were determined by the method described previously (8).

Determination of free fatty acids. Free fatty acids in unbleached and bleached alkali-refined oils were determined by programmed-temperature gas chromatography (9). Methyl esters of palmitic, stearic, oleic, linoleic, and linolenic acids were prepared from the oil by the boron trifluoride-methanol method (10). Oil (approximately 0.5 g) was weighed accurately in a 50-mL Erlenmeyer stoppered flask, and then 1 mL of internal standard solution (lauric acid with a purity of 98.0%, Tokyo Kasei Kogyo Co., Ltd.) and 7 mL of boron trifluoride-methanol complex solution (reagent for gas chromatography, Wako Pure Chemical Ind., Ltd.) were added. After the mixture was boiled for 2 min in a stoppered flask connected to a Liebig reflux condenser, 5 mL of hexane was added and the mixture was then boiled for 1 min. Water saturated with sodium chloride was added until the hexane solution reached the neck of the flask to completely precipitate the boron trifluoride. Approximately 1 mL of hexane solution, dried with anhydrous sodium sulfate in a test tube, was used for quantitative analysis. Methyl esters of free fatty acids were measured in a Hitachi G-3000 gas chromatograph equipped with a Hitachi flame ionization detector and a Hitachi D-2500 chromatointegrator (Hitachi Ltd., Tokyo, Japan). The operating conditions

*To whom correspondence should be addressed at Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan.

BLEACHING OF ALKALI-REFINED VEGETABLE OILS

were: glass column, 300 cm \times 1.5 mm packed with 15% EGS Chromosorb WAW DMCS 60:80 mesh (GL Sciences Inc., Tokyo, Japan); carrier gas, nitrogen; column oven, 100–200°C; program rate, 4°C/min; injection volume, 2 μ L. The calibration curve for each methyl ester of free fatty acid was found to be linear in the range of 0.043 to 9.800 mg/mL hexane.

Acid strength and acidity. Acid strength and acidity of medium were measured by the Benesis' buthylamine titration method described previously (11).

Specific surface area. Specific surface area of medium was measured by the method described previously (11).

RESULTS AND DISCUSSION

Bleaching effects of clay minerals. Table 1 shows the fundamental properties of alkali-refined oils used and the relative content of pigment. Rapeseed oil had the highest pigment content and was approximately twice that of soybean and wheatgerm oils. Pigment contents of safflower, corn, cottonseed and sunflower oils were 14% or less of that in rapeseed oil.

Table 2 shows the bleaching efficiencies of clay minerals for pigment in alkali-refined oils. Exposure of β -carotene to tonsil bleaching earth resulted in the removal of the β -carotene spectrum (12). When soybean oil was allowed to come into contact with acid-activated clay, the lutein spectrum was removed (13). Because there was no shift

in the absorbance maximum of pigment in each alkali-refined oil at continuous absorbance of 400 to 700 nm when mixed with clay minerals, the bleaching efficiency was determined by the decrease in absorbance at maximum wavelength 457 nm. Generally, the results demonstrated that the bleaching efficiencies of various media can be ranked in the order of sepiolites (32–93%) > montmorillonites (1–37%) > bentonites (2–33%). Sepiolite No. 3 was the most effective (72–93%) in bleaching of all alkali-refined oils, and the bleaching efficiency of standard activated clay used as comparison was 89% or more. The differences in bleaching efficiency appeared to be due to differences in physical and chemical properties of the bleaching media.

Table 3 shows acid strength, acidity and specific surface area of the bleaching media. The acid strength of sepiolite No. 3 with the most effective bleaching was $H_0 = -5.6$, and sepiolite No. 3 was found to retain the strongest acid sites among the bentonites, montmorillonites and sepiolites. Acidity is a measure of the number of acid sites (in mmol/g) having an H_0 equal to or lower than the pK_a value of the indicator used. Acidity of sepiolite No. 3 was the greatest (0.629 mmol/g) at $-5.6 > H_0 \geq -3.0$ (the larger the negative value, the stronger the acid strength). The relationships between acidity at $-5.6 > H_0 \geq -3.0$ (Table 3) and bleaching efficiency for each alkali-refined oil (Table 2) were highly significant with coefficients of 0.705 (rapeseed), 0.790 (soybean), 0.744

TABLE 1

Acid Value, Iodine Absorption Number, Saponification Number, Peroxide Value and Relative Content of Pigments of Alkali-Refined Oils

Alkali-refined oil	Acid value	Iodine absorption number	Saponification number	Peroxide value (meq/kg)	Relative content (%)
Rapeseed	0.09	117.8	182.2	11.5	100
Soybean	0.11	133.6	189.3	1.8	48
Wheatgerm	0.06	136.0	180.9	19.3	46
Safflower	0.06	145.9	187.0	16.6	14
Corn	0.06	121.5	187.1	11.7	12
Cottonseed	0.04	110.0	189.1	7.2	11
Sunflower	0.16	139.0	186.5	19.2	9

TABLE 2

Effect of Bleaching Media for Pigments in Alkali-Refined Oils

Medium	No.	Fractional degree of bleaching (%) ^a						
		Rapeseed	Soybean	Wheatgerm	Safflower	Corn	Cottonseed	Sunflower
Bentonite	1	13	12	13	33	23	31	25
	2	12	2	4	10	14	8	10
Montmorillonite	1	19	16	20	37	23	33	24
	2	9	6	1	1	6	9	12
Sepiolite	1	70	55	64	79	59	69	74
	2	80	68	66	89	67	74	82
	3	85	72	86	93	81	82	86
	4	45	35	32	55	35	45	49
	5	52	42	41	66	39	57	58
	6	84	65	63	89	65	73	84
	7	68	61	71	82	62	71	82
Standard activated clay		99	98	96	98	89	95	97

^aFractional degree of bleaching (%) = $(A_{\text{unbleached}} - A_{\text{bleached}}) / A_{\text{unbleached}} \times 100$. $A_{\text{unbleached}}$ and A_{bleached} are absorbances of unbleached oil and bleached oil, respectively, at 457 nm.

TABLE 3

Acid Strength, Acidity and Specific Surface Area of Bleaching Media

Medium	No.	Acid strength	Acidity (mmol/g) in H_0 range		Specific surface area (m^2/g)
			$-8.2 > H_0 \geq -5.6$	$-5.6 > H_0 \geq -3.0$	
Bentonite	1	$H_0 \leq +1.5$	0.000	0.000	40.9
	2	$H_0 \leq +1.5$	0.000	0.000	38.5
Montmorillonite	1	$H_0 \leq -3.0$	0.000	0.041	53.7
	2	$H_0 \leq +1.5$	0.000	0.000	12.7
Sepiolite	1	$H_0 \leq -3.0$	0.000	0.411	225.7
	2	$H_0 \leq -3.0$	0.000	0.404	281.1
	3	$H_0 \leq -5.6$	0.217	0.629	157.9
	4	$H_0 \leq -3.0$	0.000	0.087	107.8
	5	$H_0 \leq -3.0$	0.000	0.121	83.0
	6	$H_0 \leq -3.0$	0.000	0.498	257.2
	7	$H_0 \leq -3.0$	0.000	0.481	206.5
Standard activated clay		$H_0 \leq -5.6$	0.453	2.416	286.9

(wheatgerm), 0.615 (safflower), 0.747 (corn), 0.705 (cottonseed) and 0.667 (sunflower). The values of the correlation coefficients indicate that the acid sites at $H_0 = -3.0$ were responsible for pigment adsorption from alkali-refined oils. Taylor *et al.* (14) reported that both carotene and chlorophyll adsorption could be described by a simple model that employed the surface acidity at $H_0 = -3.0$ and the pore volume in the 50–200 Å pore diameter region. The relationships between surface area (Table 3) and bleaching efficiency (Table 2) were more highly significant, with coefficients of 0.929 (rapeseed), 0.916 (soybean), 0.888 (wheatgerm), 0.896 (safflower), 0.902 (corn), 0.892 (cottonseed) and 0.921 (sunflower). The deodorized palm oil color, measured with the Lovibond Tintometer, was best for acid-activated montmorillonite clay of the greatest surface area, and reached a peak at approximately 260 m^2/g within the range from 140 to 320 m^2/g (15). The relationship between carotene adsorption from refined soybean oil and surface area of alternative layered minerals did not indicate a significant correlation (14). The fact that sepiolite No. 3, with lower surface area (157.9 m^2/g), had higher bleaching efficiency can be explained by its high acidity. The above results indicate that bleaching efficiency of clay mineral is related to a combination of acidity and surface area (14).

Residual content of tocopherols in bleached alkali-refined oil. Tocopherols are important components of oils because of their antioxidant properties and vitamin E activity. It is, therefore, desirable to preserve as much as possible the content of natural tocopherols during bleaching of alkali-refined oils. Table 4 shows the residual contents of α -, β -, γ - and δ -tocopherols in unbleached and bleached alkali-refined oils and the decrease in total tocopherols. Bleaching with sepiolites No. 2 and No. 3 reduced tocopherols in alkali-refined oils by 0–10.4% (mean, 2.9%) and 0.7–13.4% (mean, 4.9%), respectively. In comparison, bleaching with standard activated clay reduced tocopherols by 2.9–43.5% (mean, 21.6%). Among the seven alkali-refined oils, the decrease in tocopherols after bleaching with standard activated clay were the smallest (2.9%) for soybean oil. The decrease was similar to the result of Jung *et al.* (1), which indicated that 5.1% of the tocopherols in alkali-refined soybean oil was removed during oil bleaching. α -Tocopherol, with its higher vitamin E activity, and γ - and δ -tocopherols, with their higher an-

tioxidant effects, were considerably reduced by using standard activated clay. The above results indicate that sepiolites No. 2 and No. 3 were more suitable than standard activated clay for bleaching alkali-refined oils. The results shown in Tables 3 and 4 suggest that the relatively large decrease in tocopherols after bleaching with standard activated clay by comparison with sepiolites No. 2 and No. 3 seemed to be more attributable to the strong acid sites with $H_0 = -3.0$ rather than to surface area. The relative compositions of α -, β -, γ - and δ -tocopherols in unbleached and bleached alkali-refined oils are given in parentheses after each residual content in Table 4. Although the decrease in total tocopherol content differed greatly among bleaching media, the relative compositions of α -, β -, γ - and δ -tocopherols in unbleached and bleached alkali-refined oils were roughly constant. However, the relative content of α -tocopherol in oils bleached with standard activated clay was distinctly larger than that in unbleached oils and oils bleached with sepiolites No. 2 and No. 3. These results indicate that α -tocopherol was less susceptible to removal than β -, γ - and δ -tocopherols during bleaching with standard activated clay and that sepiolites No. 2 and No. 3 did not selectively adsorb α -, β -, γ - or δ -tocopherols in oils.

Removal of free fatty acids by bleaching. Table 5 shows the residual contents of palmitic, stearic, oleic, linoleic and linolenic acids, and the decrease or increase of free fatty acids after bleaching. Bleaching with standard activated clay increased the content of free fatty acids in rapeseed, wheatgerm and sunflower oils, whereas bleaching with sepiolites No. 2 and No. 3 decreased the content of free fatty acids in rapeseed, soybean, safflower, corn, cottonseed and sunflower oils. Since the residual free fatty acids decrease the oxidation stability of oil, sepiolites No. 2 and No. 3 were more suitable than standard activated clay for bleaching of alkali-refined rapeseed, soybean, safflower, corn, cottonseed and sunflower oils. Jung *et al.* (1) reported that bleaching with clay increased the contents of free fatty acids in soybean oil. The increase in free fatty acids has been attributed to the hydrolysis of triglycerides resulting from the use of acid-activated clay (16). Proctor and Palaniappan (17) reported that free fatty acids were more greatly adsorbed on alkaline rice hull ash than on acid rice hull ash and suggested that the adsorption behavior might be more fully understood with

BLEACHING OF ALKALI-REFINED VEGETABLE OILS

TABLE 4

Residual Contents of Tocopherols in Unbleached and Bleached Alkali-Refined Oils and Decrease of Total Tocopherols After Bleaching

Alkali-refined oil	Medium	Contents of tocopherols ($\mu\text{g/g}$)				Decrease of total tocopherols (%)
		α	β	γ	δ	
Rapeseed	None	146(25.6)	nd ^a	424(74.4)	nd	
	Sepiolite No. 2	146(27.8)	nd	380(72.2)	nd	7.7
	Sepiolite No. 3	146(27.6)	nd	383(72.4)	nd	7.2
	Stand. acti. clay ^b	105(32.6)	nd	217(67.4)	nd	43.5
Soybean	None	84(6.3)	21(1.6)	383(63.1)	385(29.0)	
	Sepiolite No. 2	82(6.3)	22(1.7)	842(64.4)	362(27.6)	1.5
	Sepiolite No. 3	81(6.3)	23(1.8)	832(64.2)	359(27.7)	2.5
	Stand. acti. clay	89(6.9)	19(1.5)	804(62.4)	377(29.2)	2.9
Wheatgerm	None	2153(63.7)	1087(32.2)	37(1.1)	101(3.0)	
	Sepiolite No. 2	2158(64.0)	1085(32.2)	39(1.1)	91(2.7)	0.1
	Sepiolite No. 3	2052(63.2)	1056(32.5)	37(1.1)	103(3.2)	3.8
	Stand. acti. clay	1552(65.2)	731(30.7)	31(1.3)	67(2.8)	29.5
Safflower	None	437(96.9)	nd	14(3.1)	nd	
	Sepiolite No. 2	441(96.9)	nd	14(3.1)	nd	0.0
	Sepiolite No. 3	433(96.7)	nd	15(3.3)	nd	0.7
	Stand. acti. clay	361(100.0)	nd	nd	nd	20.0
Corn	None	121(13.5)	94(10.5)	638(71.3)	42(4.7)	
	Sepiolite No. 2	107(13.3)	46(5.7)	608(75.8)	41(5.2)	10.4
	Sepiolite No. 3	101(13.1)	47(6.1)	580(75.2)	43(5.6)	13.4
	Stand. acti. clay	129(18.9)	nd	516(75.7)	37(5.4)	23.8
Cottonseed	None	351(45.3)	nd	424(54.7)	nd	
	Sepiolite No. 2	357(46.1)	nd	418(53.9)	nd	0.0
	Sepiolite No. 3	333(44.2)	nd	421(55.8)	nd	2.7
	Stand. acti. clay	319(48.6)	nd	338(51.4)	nd	15.2
Sunflower	None	637(93.4)	27(4.0)	18(2.6)	nd	
	Sepiolite No. 2	634(93.4)	29(4.3)	16(2.3)	nd	0.4
	Sepiolite No. 3	611(93.3)	28(4.3)	16(2.4)	nd	4.0
	Stand. acti. clay	538(93.9)	23(4.0)	12(2.1)	nd	16.0

^and, Not detected.^bStand. acti. clay, standard activated clay.

The relative compositions (%) are shown in parentheses.

TABLE 5

Residual Contents of Free Fatty Acids in Unbleached and Bleached Alkali-Refined Oils and Decrease or Increase in Contents of Free Fatty Acids After Bleaching

Alkali-refined oil	Medium	Content of free fatty acids (mg/g)					Decrease or increase (%) ^c
		16:0	18:0	18:1	18:2	18:3	
Rapeseed	None	0.227(4.8)	nd ^a	2.426(51.8)	1.553(33.1)	0.480(10.3)	
	Sepiolite No. 2	0.151(3.5)	nd	2.270(53.2)	1.407(33.0)	0.440(10.3)	-8.9
	Sepiolite No. 3	0.128(4.0)	nd	1.683(52.8)	1.061(33.3)	0.318(9.9)	-31.9
	Stand. acti. clay ^b	0.256(4.9)	nd	2.747(52.3)	1.733(33.0)	0.513(9.8)	+12.0
Soybean	None	0.490(12.3)	nd	0.515(13.0)	2.677(67.3)	0.294(7.4)	
	Sepiolite No. 2	0.383(11.5)	nd	0.436(13.1)	2.267(68.0)	0.246(7.4)	-16.2
	Sepiolite No. 3	0.432(12.1)	nd	0.461(13.0)	2.402(67.5)	0.263(7.4)	-10.5
	Stand. acti. clay	0.535(13.4)	nd	0.651(16.3)	2.552(64.1)	0.244(6.2)	+0.2
Wheatgerm	None	1.492(13.9)	nd	0.915 (8.5)	7.469(69.6)	0.848(8.0)	
	Sepiolite No. 2	1.782(15.1)	nd	1.135(9.6)	7.989(67.9)	0.865(7.4)	+9.8
	Sepiolite No. 3	1.578(15.3)	nd	1.003(9.7)	7.006(68.0)	0.713(7.0)	-4.0
	Stand. acti. clay	1.761(16.0)	nd	1.179(10.7)	7.380(67.2)	0.666(6.1)	+2.4
Safflower	None	0.526(6.3)	nd	0.603(7.2)	7.243(86.5)	nd	
	Sepiolite No. 2	0.423(6.3)	nd	0.450(6.7)	5.826(87.0)	nd	-20.0
	Sepiolite No. 3	0.437(6.2)	nd	0.468(6.8)	6.161(87.2)	nd	-15.6
	Stand. acti. clay	0.379(6.8)	nd	0.399(7.2)	4.769(86.0)	nd	-33.7
Corn	None	0.923(13.3)	nd	1.552(22.4)	4.454(64.3)	nd	
	Sepiolite No. 2	0.789(12.7)	nd	1.399(22.6)	4.005(64.7)	nd	-10.6
	Sepiolite No. 3	0.871(12.1)	nd	1.656(23.0)	4.671(64.9)	nd	+3.9
	Stand. acti. clay	0.871(14.1)	nd	1.431(23.2)	3.868(62.7)	nd	-11.0
Cottonseed	None	2.054(23.4)	nd	2.075(23.7)	4.631(52.9)	nd	
	Sepiolite No. 2	1.787(23.3)	nd	1.781(23.2)	4.095(53.5)	nd	-12.5
	Sepiolite No. 3	1.933(23.4)	nd	1.907(23.1)	4.413(53.5)	nd	-5.8
	Stand. acti. clay	2.082(24.6)	nd	1.916(22.6)	4.462(52.8)	nd	-3.4
Sunflower	None	0.429(5.7)	nd	0.869(11.6)	6.167(82.7)	nd	
	Sepiolite No. 2	0.269(5.3)	nd	0.578(11.5)	4.201(83.2)	nd	-32.4
	Sepiolite No. 3	0.329(5.1)	nd	0.751(11.6)	5.401(83.3)	nd	-13.2
	Stand. acti. clay	0.505(6.5)	nd	1.008(13.0)	6.249(80.5)	nd	+4.0

^and, Not detected.^bStand. acti. clay, standard activated clay.^cDecrease or increase in contents of free fatty acids are shown as - or +, respectively. The relative compositions (%) of free fatty acids are shown in parentheses. 16:0, Palmitic acid; 18:0, stearic acid; 18:1, oleic acid; 18:2, linoleic acid; 18:3, linolenic acid.

a better knowledge of adsorbent structure. Hau and Nawar (18) reported that stearic or linoleic acid molecules were adsorbed on surface silanol groups of silica gel. Taylor *et al.* (19) reported that the adsorption of heptanoic and oleic acids is governed by the molecular sieving properties of the zeolites involved, as well as by the electrostatic field strengths of the exchange cations. Neutral or only slightly acidic clays often reduce fatty acid content to some extent through preferential adsorption (19). An increase or decrease in free fatty acid content after bleaching (Table 5) indicates that strong acid sites of bleaching media seem to contribute to the hydrolysis of the glyceride ester linkage or that all the acid sites are involved in the adsorption of free fatty acids. The relative compositions of free fatty acids are also shown in parentheses after each residual content in Table 5. The relative content of palmitic and oleic acids in bleached alkali-refined oils was distinctly increased by standard activated clay, which can be explained by assuming that these fatty acids (double bond, 0 or 1) were more susceptible to hydrolysis or less adsorbed by standard activated clay.

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