Bleaching of Vegetable Oils: I. Conversions in Soybean Oil, Triolein and Trilinolein

G. VAN DEN BOSCH,[1] Technological University, Eindhoven, The Netherlands

ABSTRACT

Soybean oil, triolein and trilinolein were treated with acid-activated earth (2-15%) at 25-120 C. With low initial peroxides and in the absence of air, little additional conjugation was found. With high initial peroxides or in the presence of air, conjugated dienes and trienes were formed particularly with high amounts of earth. At higher temperatures and longer bleaching times the amount of conjugated compounds also increased. It can be concluded from the bleaching experiments with triolein and trilinolein that conjugated dienes, trienes and tetraenes are formed much more easily with linoleate than with oleate.

INTRODUCTION

During the bleaching of vegetable oils the color pigments are removed (1), some hydrolysis occurs and, in oils containing polyunsaturated fatty acids, conjugated dienes, trienes and even tetraenes are formed (2-6). The formation of the conjugated compounds is explained through a shift of the double bonds from isolated to conjugated positions. Also, oxidation of the unsaturated fatty acids takes place via hydroperoxides to fatty acids with a hydroxyl or carbonyl group. The hydroxy compounds are then possibly dehydrated through the bleaching earth (3,7).

Bleaching takes place usually after neutralization with oils through stirring with a few per cent of earth between 90-120 C under exclusion of air for a period of 20 min to some hours. Earth is usually an acid-activated clay with a montmorillonite structure (8). It contains 8-12% water and absorbs oxygen from the air. Before or during bleaching the oxygen is partly removed, but the exact amount is not known. This publication gives the results of research into the conversions of the unsaturated fatty acids in oils that occur during bleaching under the influence of bleaching earth with or without oxygen.

EXPERIMENTAL PROCEDURES

Materials

Soybean oil (peroxide value = 57 and 1-2, respectively), alkali refined and dried, triolein (peroxide value = 1.5) and trilinolein (peroxide value = 4.0) were used. The low peroxide values were obtained through treatment of the oils (soybean oil, triolein and trilinolein) with Aluminiumoxid Aktiv Neutral (Merck, Aktivitätsstufe I). According to gas liquid chromatography, the fatty acids of triolein consisted of 99.5% oleic acid and 0.5% linoleic acid; in trilinolein these percentages were 97.5% linoleic acid and 2.3% oleic acid.

Bleaching earth was an acid-activated clay (Tonsil Standard FF) of Südchemie (Munich, W. Germany).

The soybean oil was obtained from Verenigde Oliefabrieken Zwijndrecht (The Netherlands), and the triolein and trilinolein from J.B.A. Stroink of the Unilever Research Laboratory (Vlaardingen, The Netherlands).

Bleaching Experiments (Fig. 1)

Bleaching experiments were done in cylindrical, double-walled glass reaction vessels of 500 ml and 100 ml, which were maintained at the desired temperature by pumping heated oil through the double-walled vessels. The soybean oil, triolein or trilinolein in the vessels was mixed with the earth by a magnetic stirrer. In the experiments with

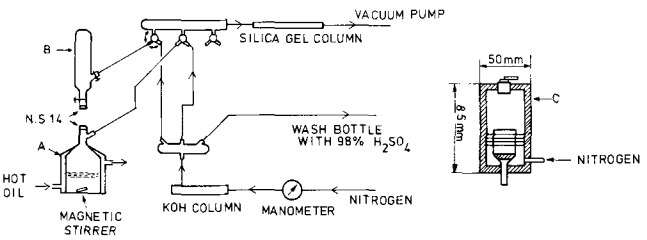

FIG. 1. Reaction and filtration apparatus (A = bleaching vessel, B = barrel from which the bleaching earth is added and C = cylindrical plexiglass enclosure for filtration).

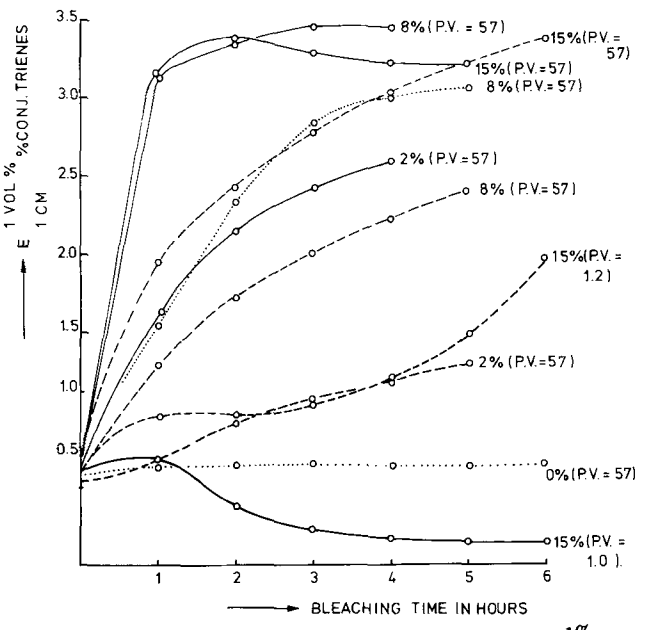

FIG. 2. UV absorption maxima at λ = 268 nm ($E^{1\%}_{1cm}$ of trienes) during bleaching of soybean oil (peroxide value = 57 or 1) with or without admission of air at different percentages bleaching earth (0, 2, 8 and 15%) at 50 C. ---- with air admission; ——— without air admission; • • • • air bubbling through oil.

[1] Present address: Ghave NV, Veghel, The Netherlands.

TABLE I

UV Absorption at Different Maxima of Soybean Oil (Peroxide Value = 57) with Air Admission with 2% Bleaching Earth at 50 C

Bleach time, hr	$E^{1\%}_{1cm}$ at different wavelengths (nm)					
	230	258	268	278	300	316
0	7.50	—	0.55	0.48	0.25	0.12
1	6.15	—	0.67	0.57	0.27	0.15
2	5.63	—	0.92	0.77	0.32	0.20
3	—	—	1.07	0.89	0.34	0.22
4	5.10	1.06	1.18	0.98	0.36	0.24
5	—	1.13	1.28	1.06	0.37	0.25
7	5.10	1.29	1.48	1.22	0.40	0.27
24	5.75	1.61	1.83	1.45	0.41	0.29
30	6.23	1.59	1.80	1.46	0.43	0.30

TABLE II

Peroxide Values (PV) and UV Absorption Maxima of Soybean Oil Bleached with 15% Earth and with Admission of Air

Bleach time, hr	Bleach temperature, 50 C			Bleach temperature, 90 C		
	PV, me/kg	230 mm, $E^{1\%}_{1\ cm}$	268 mm, $E^{1\%}_{1\ cm}$	PV, me/kg	230 mm, $E^{1\%}_{1\ cm}$	268 mm, $E^{1\%}_{1\ cm}$
0	1.2	0.51	0.62	0.8	0.80	1.00
1	0.67	0.74	0.95	0.5	0.99	1.26
2	0	0.77	0.97	0.4	0.74	0.89
3	0.75	0.85	1.05	0	0.44	0.43
4	1.0	0.97	1.19	0	0.58	0.54
6	1.2	1.58	1.96	1.5	1.59	1.74
24	20	4.85	5.13	20	7.55	9.60

oxygen, it originates from the air above the reaction mixture as well as from the bleaching earth. Without oxygen, the oil and the earth were evacuated a few times, alternated with nitrogen admission before the earth was added to the oil in a nitrogen atmosphere. Then the mixture was evacuated before the experiment started. Throughout the experiment a nitrogen atmosphere was kept above the reaction mixture.

During the experiments, which were carried out in duplicate, samples for filtration were taken with a pipette or injection syringe. Filtration was done with a glass filter (Jena 3G3) in a cylindrical plexiglass enclosure under nitrogen pressure (2-5 atm). After filtration the oil was maintained under nitrogen at 0 C before it was examined.

Soybean oil (300 g, peroxide value = 57) was treated with 2, 8 and 15 wt% earth at 25 and 50 C with or without admission of air, and at 120 C with only 8 wt% earth with air admission.

Soybean oil (330 g, peroxide value = 1-2) was treated with 2, 8 and 15 wt% earth at 50 and 90 C with or without admission of air.

Triolein (25 g) and trilinolein (25 g) were treated at 90 C with 15 wt% earth with or without admission of air.

Identification Methods

UV spectra in hexane (Uvasol, Merck) as solvent were recorded by means of a self-registering Cary-Model 14 spectrometer. Absorption maxima were recorded of 1 volume % solutions and measured at 225-235 nm (dienes), 258-268 nm (trienes) and 300-316 nm (tetraenes).

Peroxide values were determined by modified AOCS Method Cd 8-53 (9).

TABLE III

UV Absorption Maxima of Soybean Oil Bleached with 8% Earth

Time, hr	Bleaching temperatures		
	25 C	90 C	120 C
	$E^{1\%}_{1\ cm}$ at 268 mm		
0	2.50	2.50	2.50
1	3.35	4.04	8.90
3	3.48	6.31	7.80
5	3.89	—	8.01
24	4.73	8.00	8.20

RESULTS AND DISCUSSION

The effect of different percentages of bleaching earth (2, 8 and 15%) was studied when soybean oil had low or high peroxide value and with or without admission of air. The formation of the conjugated compounds was followed by UV spectrophotometry (Table I). In Figure 2 the formation of the trienes (λ = 268 nm) is given against the time.

The absorption curves show that without bleaching earth no new conjugated compounds are formed; the higher the

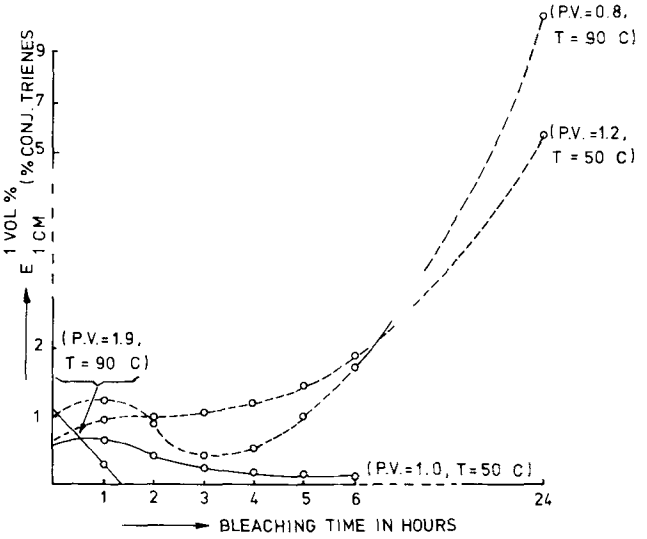

FIG. 3. UV absorption maxima at λ = 268 nm ($E^{1\%}_{1\ cm}$ of trienes) during bleaching of soybean oil (peroxide value = 0.8-1.9) with 15% bleaching earth with or without admission of air at 50 and 90 C. - - - - with air admission; ——— without air admission.

TABLE IV

UV Absorption Maxima of Triolein and Trilinolein Bleached with 15% Earth at 90 C with or without Air Admission

Bleach time, hr	Triolein (peroxide value = 2)				Trilinolein (peroxide value = 5)			
	With air		Without air		With air		Without air	
	230 mm	268 mm	230 mm	268 mm	230 mm	268 mm	230 mm	268 mm
	$E^{1\%}_{1\ cm}$				$E^{1\%}_{1\ cm}$			
0	1.00	0.13	1.38	0.18	24.0	17.0	22.0	16.7
1	1.25	0.10	0.30	—	17.3	25.3	14.9	21.9
2	1.25	0.09	0.32	—	18.8	25.4	14.6	21.5
3	2.05	0.13	0.36	—	20.3	25.5	14.7	21.5
4	3.05	0.20	0.40	—	21.8	16.0	15.2	21.0
6	4.50	0.30	0.44	—	30.7	23.1	16.0	21.0
24	8.50	1.18	0.47	—	Polymerized mixture		16.2	20.2

percentage of bleaching earth, the higher the absorption maxima obtained. In the experiments with exclusion of air the maxima of conjugated compounds were reached rapidly, especially at high percentages of bleaching earth (Fig. 2). These maxima are higher during the first few hours than in the experiments with admission of air, least when the peroxide value of the oil is not too low. This can be explained through the reaction of the conjugated compounds formed with the oxygen present in the experiments with admission of air, so that only after a longer time is the total amount of conjugated compounds greater. These reactions probably take place via newly formed hydroperoxides.

The bleaching experiments of soybean oil (peroxide value = 0.8 and 1.2) with 15% earth with admission of air at 50 and 90 C also give indications for the formation of conjugated compounds via hydroperoxides (Table II). The peroxide values go through a minimum and increase after longer time, and the percentages of dienes and trienes increase gradually at 50 C and go through a minimum at 90 C. The experiments with 8% bleaching earth with admission of air and with air bubbling through the oil (Fig. 2) revealed that more of the conjugated compounds are formed with more admission of air.

From the bleaching experiments at 25, 50, 90 and 120 C with or without exclusion of air, some conclusions can be made regarding the influence of the temperature by means of the absorption maxima of the UV spectra (Tables II and III); the higher the temperature, the more conjugated compounds formed. At 25 C there is a slight formation of conjugated compounds with little difference between the treatments with or without admission of air. At 90 C the reactions take place faster than at 25 and 50 C, and without admission of air the maxima absorption is reached in a short time. For the special case that the oil has a low peroxide value through treatment with Al_2O_3, the formation of trienes is given in Figure 3. At 120 C the reactions again occur more quickly, but only during the first few hours is the conjugation reached different from (higher than) that at 90 C.

To study more accurately the influence of the number of double bonds in the fatty acids, experiments with triolein and trilinolein with bleaching earth were conducted. The absorption maxima of the UV spectra are given in Table IV. It can be concluded that conjugated dienes and trienes are formed much more readily with linoleate than with oleate. This agrees with the mechanism proposed for the formation of conjugated compounds via hydroperoxides (3,7,10,11), because the initial reactions take place more readily (formation of conjugated allyl radical). Further, during bleaching, the absorption maxima of triolein and trilinolein undergo the same changes as soybean oil.

ACKNOWLEDGMENTS

H.A. Boekenoogen (deceased October 26, 1971) gave valuable advice. Assistance during experiments and analyses was offered by J.A.M. Lukkenaer, H.A.J. Hodes and F. Smits.

REFERENCES

1. Rich, A.D., JAOCS 47:564A (1970).
2. Mitchell, J.H., and H.R. Kraybill, J. Amer. Chem. Soc. 64:988 (1942).
3. Hadorn, H., and K. Zürcher, Travaux de Chimie Alimentaire et d'Hygiëne 57:189 (1966).
4. Mayase, O., and B. Mezeik, Technika (Belgrado) 25:953 (1970).
5. Pardun, H., E. Kroll and O. Weber, Fette Seifen Anstrichm. 70:643 (1968).
6. Kaufman, H.P., J.G. Thieme and F. Volbert, Ibid. 58:505 (1956).
7. Guillamin, R., Abstracts of Papers—IXth Congress of the International Society for Fat Research, Rotterdam, 1968.
8. Kögler, H.P., Fette Seifen Anstrichm. 65:834, 940 (1963).
9. "Official and Tentative Methods of the American Oil Chemists' Society, Vol. I, Third edition, AOCS, Champaign, Ill., 1964 (revised to 1972), Method CD 8-53.
10. Farmer, E.H., Trans. Faraday Soc. 38:348 (1942).
11. Rawls, H.R., and P.J. van Santen, JAOCS 47:121 (1970).

[Received April 17, 1972]