

# Monohydroxylation of Unsaturated Oils:

## II. Autoxidation-Reduction

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### Abstract

After an initial induction period the rate of autoxidation of safflower oil was linear at 0–5 C under ultraviolet illumination in glass and proceeded to a maximum peroxide value of 2200. Reduction of hydroperoxy to hydroxy groups was easily accomplished by shaking with stannous chloride solution. The product showed hydroxyl value (HV) 76, iodine value (IV) (total) 122 and conjugated diene 20%. Attempts to increase the degree of this hydroxylation either by controlled oxidation, or by additional autoxidation after blocking the hydroxyl in the once-hydroxylated oil, or by autoxidizing in the presence of silver nitrate or stannous chloride, were unsuccessful. After preliminary treatment with an acidic earth, the rate of autoxidation of a commercial linseed oil was linear up to a PV of 1840. Reduction with stannous chloride gave a product with a HV of 50 containing 15% diene and 3% triene conjugation.

### Introduction

Previous papers describe two routes for the introduction of monohydroxy groups by reaction of the double bonds of unsaturated oils to increase their reactivity (1–3). One route involved epoxidation and selective hydrogenation of epoxy to hydroxyl groups, and the other involved sulfation followed by hydrolysis of sulfate to hydroxyl groups. This paper describes a third approach, the autoxidation of safflower and linseed oils to introduce hydroperoxy groups and reduction of the latter to hydroxy groups. Perlstein et al. (4) applied similar autoxidation-reduction reactions to methyl oleate and linoleate and the hydroxy esters were dehydrated to yield conjugated dienes and trienes.

Autoxidation of mono- and polyunsaturated material occurs at carbon atoms adjacent to double bonds with no loss of unsaturation. A shift of the double bond location as well as from *cis* to *trans* forms takes place, and conjugated diene systems are created in linoleate and linolenate (5). Side reactions can be minimized, but never completely suppressed, and become especially important as higher peroxide levels are attained. Hence the first objective is a reasonable level of hydroperoxidation without excessive development of secondary products such as ketones, aldehydes or polymers. Low but practicable temperatures of autoxidation, efficient dispersal of oxygen and accelerators such as ultraviolet light are indicated. Suitable indices of proper autoxidation are linear peroxide increase with time, and a steady increase in the degree of conjugated unsaturation. For the reduction of hydroperoxides to hydroxy groups, a simple and efficient method is desirable.

Some factors in the autoxidation-reduction of safflower and linseed oils have been studied. Hydroxy glycerides of the highest hydroxyl value (HV) attainable without an excess of secondary products were sought. The products obtained were characterized as an aid to further use.

### Materials and Methods

#### Oils

Safflower oil was extracted in the laboratory from crushed whole seeds and refined with strong alkali, washed and dried (iodine value 126). Linseed oil was a commercial, probably acid-refined material (iodine value 180).

#### Autoxidation

The oil (20 g) was air-blown in a large glass test tube using a sintered filter stick while the whole was exposed to UV irradiation from a Hanovia lamp. Autoxidations were conducted either at ambient temperature (generally 25–30 C) or at 0.5 C by immersing the test tube in an ice-bath.

#### Reduction

The hydroperoxides in autoxidized materials were reduced to hydroxy groups by a variety of means. An aqueous solution of potassium iodide (20 g in 15 ml water) was shaken with the fatty material (5 g) dissolved in a mixture of chloroform (100 ml) and acetic acid (200 ml) and the liberated iodine destroyed with aqueous sodium sulfite (6).

Stannous chloride (200% excess based on peroxide value) was dissolved in alcohol (0.5% solution) and stirred with the autoxidized fatty material (5 g) for 2–4 hr under nitrogen. The mixture was washed with 50% alcoholic HCl to remove excess of the metal salt (7) and the fat extracted with ether.

For sodium borohydride reduction (8), the autoxidized fat was added as a methanol solution to methanolic sodium borohydride in excess over 2.5 hr and refluxed for 1 hr more.

Two procedures were used for reduction by low-pressure catalytic hydrogenation. One employed 1% Lindlar's catalyst (9) with the fat dissolved in ether solution. In the other, the catalyst was 10% palladium-on-carbon and the autoxidized fat (5 g) was treated with a methanolic solution of silver nitrate (2.5 g in 50 ml) prior to hydrogenation in an attempt to protect the unsaturation present (1).

#### Analysis

Peroxide values were determined according to Wheeler (10). For total iodine values the Rosenmund-Kuhnenn procedure catalyzed by mercuric acetate was used (11). Other determinations were carried out by standard procedures.

### Results and Discussion

#### Autoxidation and Reduction

*Autoxidation.* In a preliminary experiment to determine the oxidation pattern with time, a methyl linoleate concentrate (IV 159, PV 9) when autoxidized at ambient temperature (25–30 C) showed peroxide value (PV) as follows: 6 hr, 1039 and 12 hr, 2010. The PV of pure methyl linoleate monohydroperoxide is 6145. The product of PV 2010 therefore corresponds to about one third total hydroperoxidation.

Autoxidation of safflower oil at ambient tempera-

TABLE I  
Reduction of Autoxidized Lipids to Hydroxy Products

Reagent	Hydroxy product				
	Total IV	Wijs IV	HV	PV	AV
Autoxidized methyl linoleate (PV 2010)					
Potassium iodide	.....	.....	74.2	Nil	2.4
Stannous chloride	.....	.....	76.9	Nil	2.3
Sodium borohydride	.....	.....	88.9	Nil	2.3
Autoxidized safflower oil (PV 2219, Total IV 132.9)					
Potassium iodide	116.8	92.4	63.1	Nil	3.8
Stannous chloride	121.5	92.5	76.2	Nil	3.7
Sodium borohydride	120.8	92.3	76.9	Nil	3.6
Catalytic hydrogenation (10% Pd/C, AgNO <sub>3</sub> )	112.4	83.3	76.8	Nil	3.5
Lindlar hydrogenation	122.7	92.7	76.4	Nil	3.6
Autoxidized linseed oil (PV 1840)					
Potassium iodide	176.2	.....	45.8	3.8	2.8
Stannous chloride	.....	.....	50.5	Nil	3.6
Sodium borohydride	184.0	.....	51.2	Nil	2.5
Lindlar hydrogenation	181.2	.....	49.2	Nil	2.8

ture yielded the following results: Hours of oxidation, nil; PV 7; 8 hr, 56 PV; 16 hr, 486 PV; 24 hr, 1428 PV; 32 hr, 1971 PV; 40 hr, 2219 PV; 42 hr, 2225 PV. Hydroperoxide development is much slower in safflower oil than in methyl linoleate. There is a marked induction period. Thereafter the plot of PV against time was linear but the same rate of increase was not maintained after 40 hr. Further hydroperoxide reactions apparently occur.

Commercial linseed oil was autoxidized at ambient temperature under UV illumination. After 24 hr a low PV of 103 had developed. To remove the inhibitor, the oil was bleached with 4% of acid-activated earth at 70 C and filtered hot. Autoxidation of the bleached oil at room temperature (25–30 C) for 56 hr gave a viscous product (PV 920). After 40 hr of reaction the product was very viscous (PV 741).

Another sample of bleached linseed oil was autoxidized at a temperature below 10 C under UV illumination. The PV increase after 56 hr was 1840 or twice as much as before. The PV development was still linear, and further autoxidation may be possible.

*Reduction of Hydroperoxide to Hydroxy Groups.* Various methods were applied for the reduction of autoxidized methyl linoleate, safflower and linseed oils. The results are shown in Table I. Satisfactory reduction of autoxidized products occurs by Lindlar hydrogenation, or by treatment with stannous chloride or by sodium borohydride reduction. Of these stannous chloride treatment is the simplest. With potassium iodide, a slight drop in total IV is noticed, and the liberation of a large amount of iodine causes handling difficulties. Catalytic hydrogenation in the presence of silver nitrate shows a drop of 8–10 units in IV; this could be caused by comparatively weak  $\pi$ -complex formation between conjugated double bonds and silver nitrate, which therefore does not exert its usual protective effect during hydrogenation (1).

Autoxidation-reduction of safflower oil thus yields a product of HV 76, AV 3.6 and total IV 122. Similar procedures from linseed oil yield a product of HV 50, AV 3.0, total IV 180, conjugated diene 15% and conjugated triene 3%. For comparison, the calculated values for methyl ricinoleate are HV 180 and IV 81.

A product derived from ambient temperature autoxidation of safflower oil and stannous chloride reduction, of HV 73, showed diene conjugation of 10.2%. This is low in relation to the degree of autoxidation. Autoxidation of safflower oil under UV

illumination of 0–5 C resulted in a slower PV build up of ca. 30 units per hour against 50 at ambient temperature. A product of PV 1930, obtained after 56 hr of autoxidation, yielded on stannous chloride reduction hydroxy glycerides of HV 58, AV 3.6, PV Nil, and diene conjugation 18.6%, which corresponds more closely to the peroxide development. Thus autoxidation at low temperatures leads to a high conjugated diene content.

Short-chain aldehydes and ketones are early breakdown products of autoxidation and may usefully serve as an indication of side reactions. Estimation of carbonyls was carried out by the method devised by Bhalerao et al. (15) for thermally-oxidized fats. Hydroxylamine hydrochloride was the reagent and *n*-octyl alcohol, the fat solvent. A sample of reduced safflower oil of HV 76 showed a carbonyl content of only 571 mg/kg, equivalent to about 0.057% of the fat or 1.7% of the hydroperoxides formed.

#### Attempts to Increase the Hydroxyl Value

Linear autoxidation of safflower oil proceeds only to a PV of ca. 2200. After catalytic reduction with stannous chloride, hydroxy glycerides of HV 77 result. Various attempts were made to increase this HV by increasing the degree of peroxide build-up of safflower oil.

Air was bubbled through safflower oil under ultra-violet illumination in the presence of added stannous chloride. The product after 24 hr showed no hydroxyl value and was mostly unchanged safflower oil.

Safflower oil (10 g) containing silver nitrate (4.8 g) dissolved in 20 ml of ethanol was autoxidized as usual. A sample of the product withdrawn after 24 hr (PV 510) was very viscous. Autoxidation was continued for 40 hr (PV 840). Reduction with stannous chloride yielded glycerides with HV 10, AV 3.2 pointing to cross-linking reactions.

Safflower oil was autoxidized to a PV of 1161, and the product reduced with stannous chloride to a glyceride of HV 43, AV 3.4. This hydroxy oil was now autoxidized with some difficulty to a PV of 1120. This oxidized product was reduced with stannous chloride to yield a dark, viscous material of HV 38, AV 4.8,  $n_D^{25}$  1.4851 and absolute viscosity of 17.6 poises at 25 C. The HV of the hydroxylated oil which was 43 has actually gone down on further autoxidation. It is relevant that autoxidation of castor oil produces a product with a PV of only 15–30 (12,13). The autoxidized products are thick and dark, and it has been suggested on the basis of IR evidence that initial hydroperoxy free radicals stabilize themselves by linking with another hydroxy group. Such links by way of oxygen occur for example in the bodying of unsaturated oils by air blowing, and result in an increase in viscosity.

Methyl linoleate was autoxidized (PV 2000) and reduced with stannous chloride (HV 70, AV 3.8). The hydroxylated ester was converted to the pyranil ether by refluxing with excess dihydropyran in the presence of HCl (14). Any unconverted hydroxy ester was removed by extraction with light petroleum ether. Autoxidation of the pyranil ether for four days yielded a product of PV 1000. This was reduced with stannous chloride and the blocking agent was removed by treatment with 2 N sulfuric acid at 0 C for 5 min to yield a product of HV 39. This HV corresponds only with the second autoxidation, though this could be a coincidence. The blocked hydroxyls are not restored, though no reason is apparent.

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