Observations on the Destruction of Cyclopropene Fatty Acids of Cottonseed Oil on Exposure to Visible Light

Y. SITA RAMA SASTRY and GOLLAMUDI LAKSHMINARAYANA,
Regional Research Laboratory, Hyderabad-9, India

Abstract

The destruction of cyclopropene fatty acids of cottonseed oil on exposure to light from a 500 W tungsten bulb was studied under various conditions in the laboratory. The Halphen test was used to determine the destruction. Visible light exerted a strong catalytic effect and oxygen, at least in traces, was necessary. In 4–12 hr the Halphen response was negative for refined cottonseed oil (0.2–10 ml) sealed in a 50 ml flask at 1 mm Hg without apparent peroxide development. No significant difference was noticed in the peroxide development pattern of the exposed and unexposed samples in the air-oven stability test.

Introduction

Various biological effects have been attributed to the ingestion of cyclopropene fatty acids (CFA), which occur in some seed fats of Malvaceae (e.g., cottonseed), Sterculiaceae (e.g., *Sterculia foetida*) and other families (1,2). Raw and refined cottonseed oils (CSO) contain ca. 0.6–1.0% and 0.6% CFA, respectively while salad oils contain ca. 0.04–0.42% (3,4). Destruction of the CFA is thus incomplete in refining, bleaching and deodorizing operations (4,5). A large number of treatments have therefore been proposed for the destruction of the CFA of CSO: hydrogenation (2,6–8); treatment with either HCl (1,2), SO_2 (1) or alumina activated with sulfurous acid (1,2); heating with either aluminum silicate catalyst (2), fatty acids, citric acid, phosphoric acid (5,9) or metal halides (10); heating to high temperature in air (1,2); heating with hydrogenation catalysts (Pt or Pd) under nitrogen (11); and exposure to either infrared radiation or sunlight with or without sulfur in the presence of air (1). Exposure to visible light appears to be a simpler operation than the catalytic and chemical treatments mentioned and deserved further study. Conditions investigated in the laboratory for the destruction of CFA, without apparent development of peroxides, are reported here.

Experimental Procedures

CSO was freshly extracted in the laboratory, refined with aqueous alkali and bleached with Fuller's earth. This was neutral and used in exposure studies as such and after further purification by alumina column chromatography (12). Freshly extracted *S. foetida* oil was also purified by alumina column chromatography.

Light from a 500 W tungsten bulb was allowed to pass through a 3 cm layer of water kept in a flat glass trough resting on a tripod stand. The trough was placed midway (8 cm) between the light bulb and the flask containing the oil sample clamped above. The oil sample (0.2, 2 and 10 ml) was taken in a 50 ml round bottomed flask with a long neck drawn to a narrow width for sealing. While 0.2 ml of oil gave a thin film, 2 ml and 10 ml gave 0.4 cm and 1.6 cm deep layers, respectively. The whole assembly was enclosed in a chamber covered with a black cloth. By alternate periods of exposure for 15 min to light and darkness the temperature of the oil was kept below 40 C. The flask was rotated at 15 min intervals in order to expose a fresh film. Studies were made under different conditions, as described in Table I.

The AOCS methods were used on a semi-micro scale for peroxide value and the Halphen test (13). About 0.7 g of oil was taken for peroxide value and 0.01 N thiosulfate solution used. For the Halphen test ca. 0.5 ml of the oil was taken and an equal volume of reagent added. CFA were estimated by the HBr titration method (14). The Emmerie-Engel method (15) was used for estimation of tocopherols. Peroxide development was studied by placing 50 ml beakers containing oil samples in an air oven at 63 C and determining the peroxide values at intervals.

Results and Discussion

It is evident from the observations recorded in Table I that visible light exerted a strong catalytic effect on the destruction of CFA of CSO. In addition, oxygen was necessary at least in traces. There was no reduction in the intensity of the Halphen response even after 28 hr of exposure of CSO to light when the oxygen atmosphere was replaced by nitrogen. Freer accessibility to oxygen caused faster destruction of the CFA than limited accessibility, although peroxides developed to a greater extent in the former case. The residual oxygen present at 1 mm Hg was adequate to cause destruction of the CFA of CSO present in low concentration (0.6%) without giving

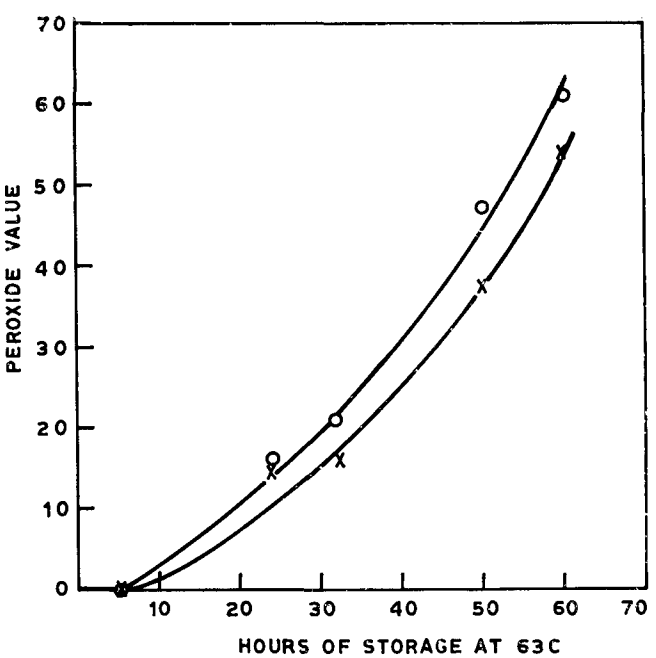

FIG. 1. Peroxide development at 63 C of refined and bleached cottonseed oil before (X) and after (O) exposure to visible light under 1 mm Hg.

TABLE I

Destruction of Cyclopropene Fatty Acids (CFA) on Exposure to Light from a 500 W Tungsten Bulb

Sample (2 ml, unless otherwise mentioned)	Experimental condition	Exposure period for Halphen negative response, hr	Peroxide value after exposure
CSO[a] refined and bleached (0.081 % tocopherols)	Sealed, 1 mm Hg	12	0
CSO, chromatographed (0.060 % tocopherols)	Open	2	18
CSO, chromatographed	Open in the dark	120	10
CSO, chromatographed	Sealed, atm. pressure	4	21
CSO, chromatographed	Sealed, 150 mm Hg	7	16
CSO, chromatographed	Sealed, 1 mm Hg	10	0
CSO, chromatographed	Sealed, N_2 atm.	No reduction in Halphen response after 28 hr	0
CSO, chromatographed (0.02 % butylated hydroxyanisole incorporated)	Sealed, 1 mm Hg	No reduction in Halphen response after 28 hr	0
CSO, chromatographed (6% cottonseed fatty acids incorporated)	Sealed, 1 mm Hg	10	0
CSO, chromatographed (0.2 ml)	Sealed, 1 mm Hg	4	0
CSO, chromatographed (10 ml)	Sealed, 1 mm Hg	10	0
S. foetida oil	Sealed, 1 mm Hg	No reduction in Halphen response after 40 hr	0
Saturated paraffin oil mixed with *S. foetida* oil to give 0.6% CFA concentration		10	0

[a] CSO, cottonseed oil.

rise to an apparent peroxide value. However, the concentration of CFA in *S. foetida* oil (50.5% calculated as sterculic) could be reduced to 47.7%, 44.9%, 44.1% and 44.0% only after 10, 20, 30 and 40 hr respectively of exposure to light at 1 mm Hg, due to the inadequate availability of oxygen. The role of oxygen can further be seen from the effect of antioxidants on the period of exposure for the destruction of CFA. The destruction period was shorter (10 hr) for chromatographed CSO containing 0.060% tocopherols than for the refined and bleached oil (12 hr) containing 0.081% tocopherols. When the natural tocopherols of chromatographed CSO were supplemented with 0.02% of butylated hydroxyanisole, there was no reduction in intensity of the Halphen response even after 28 hr of exposure. Oxygen seems to play a definite part either by direct reaction with CFA or by way of free peroxy radicals of other unsaturated fatty acid moieties of CSO. The latter mechanism does not seem to operate since the period of exposure for elimination of the Halphen response was the same both for chromatographed CSO and for saturated paraffin oil to which *S. foetida* oil was added to give the same CFA concentration as in chromatographed CSO, i.e., 0.6%. The reaction products of CFA with oxygen could not be identified from the UV, IR and NMR spectra of the exposed samples. Further attempts were not made to concentrate and identitfy these products.

A few experiments were directed to reduce the exposure period for elimination of the Halphen response of CSO. The destruction of CFA was not hastened when fatty acids of CSO were incorporated, unlike in deodorization (5). By reducing the sample size from 2 ml (0.4 cm deep layer) to 0.2 ml (film) the CFA of CSO could be destroyed in 4 hr instead of 10 hr. By increasing the sample size to 10 ml (1.6 cm deep layer), the CFA could still be eliminated in 10 hr. Studies with larger quantities were not carried out. It may be possible to further reduce the destruction period to practical limits by exposing a moving film in a continuous system to a more intense light. Further investigations are necessary to determine the commercial feasibility of the observations reported in this paper.

There was a reduction in tocopherol concentration on exposure to light from 0.081% to 0.054% in refined and bleached CSO and from 0.060% to 0.046% in the chromatographed CSO. Nevertheless, the induction periods were almost the same for the exposed and unexposed refined and bleached CSO (Fig. 1). Subsequent peroxide development was a little faster for the exposed sample than for the unexposed. No difference was noticed in odor and taste of the exposed and unexposed samples. The stability of the Halphen negative CSO obtained by exposure to visible light under 1 mm Hg is therefore not expected to be much different from that of the original refined and bleached CSO.

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