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[Received August 12, 1985]

Oxidative Stability of Avocado Oil

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This study is concerned with the extent of oxidative deterioration and oil stability as determined by measuring peroxide and conjugable oxidation products (COP) values and AOM time of refined bleached avocado oil in comparison with refined soybean and olive oil. The formation of peroxides in avocado oil exposed to daylight at room temperature is similar to that of soybean oil but greater than that of olive oil. No differences were found in peroxide formation, oxodiene values and COP values between the tested oil stored in the dark, at 60 C and at room temperature. The COP ratio in oils stored at 60 C is similar for avocado and olive oil, but differs from that of soybean oil.

The AOM stability time both for refined avocado and soybean oil was approximately 14 hr, and for refined olive oil was 15 hr.

The extent of oxidative stability of crude avocado oil was determined by measuring peroxide value compared with crude olive oil. Crude avocado oil is very sensitive to oxidation when exposed to daylight and fluorescent light, in contrast to its stability in the dark at room temperature. The chlorophyll content in crude avocado oil is reduced rapidly on exposure to daylight and fluorescent light.

The large oil content, 15-30%, is one of the distinguishing features of the avocado fruit. In fact, of all fruits, only the olive and palm fruit can rival the avocado in oil content. The oil is unsaturated and the predominant fatty acid is oleic. Mazliak (1) reported that the edible avocado oil contained 13-16.7% palmitic acid, 3-5.1% palmitoleic acid, 67-72% oleic acid, 10.4-12% linoleic acid and traces to 1.5% linolenic acid.

Large surpluses of avocado are expected in the near future. One way of utilizing these surpluses is by extracting the oil from the fruit. Crude avocado oil is utilized mainly in the cosmetic industry. Refined avocado oil has only recently been introduced in the food industry and the world food market. Thus, there are few reports, if any, dealing with the oxidative stability of avocado oil.

The oxidative deterioration of edible oils and fats is a complex process leading to varied decomposition products (2). These oxidative processes, which occur slowly at normal ambient temperature, are known as autoxidation. Several mechanisms are possible, yet it is known that the oxidation process is initiated by the formation of radicals as a result of homolytic splitting-off of hydrogen atoms in the α-position with respect to the double bond (3). For this reason oils and fats containing unsaturated fatty acids are susceptible to oxidation. Because crude avocado oil contains small amounts of natural antioxidants (4-5) and large amounts of chlorophyll, the rate of its photo-oxidation is greater than that of other oils.

The susceptibility of an oil or fat to autoxidative degeneration can be assessed in terms of oxidative stability. The quality control of oils and fats, in the food industry, can be carried out by either static or dynamic methods. In the static methods, analytical determinations are made of various characteristics (such as peroxide value and the COP assay) relating to the degree of oxidation which already has taken place. In the dynamic methods, the oil is subjected to a stream of air at elevated temperatures. This method is the AOM stability test. Autoxidation can be inhibited by natural or synthetic antioxidants, whose effectiveness may be enhanced still further by synergistic agents such as ascorbic and citric acids (6).

In this work, oxidative stability of avocado oil was determined in comparison with olive and soybean oil, at several oxidative conditions.

EXPERIMENTAL PROCEDURES

Materials. Refined and crude avocado oil was obtained from Avochem (Santa Paula, California), refined olive

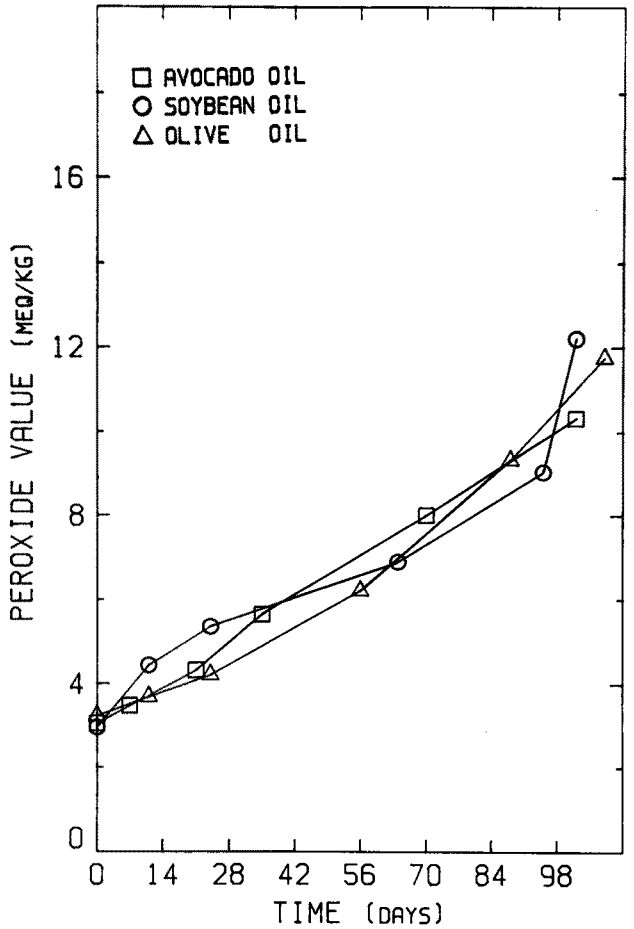

FIG. 1. Peroxide formation in refined avocado, soybean and olive oil during storage at room temperature (darkness).

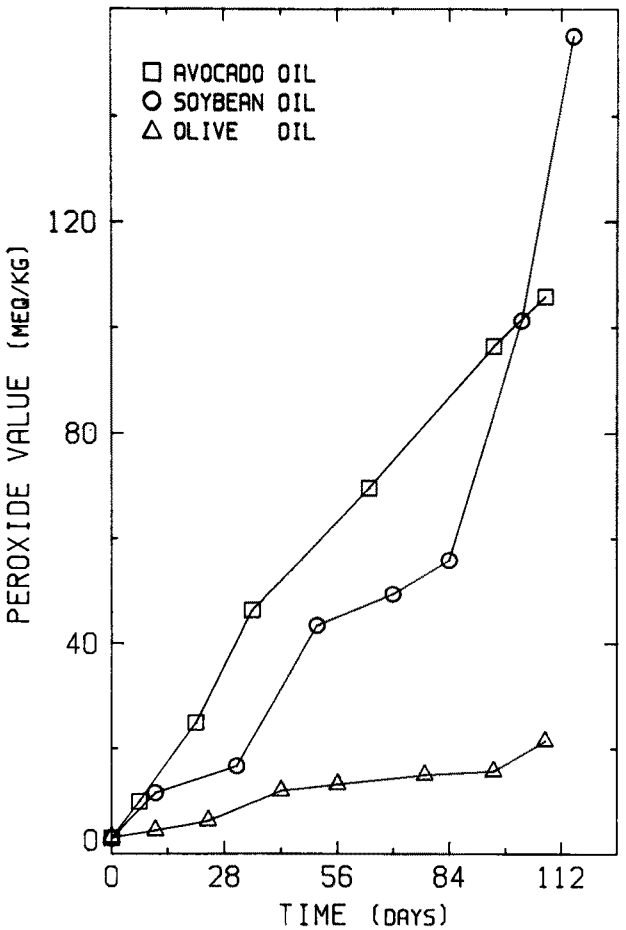

FIG. 2. Peroxide formation in refined avocado, soybean and olive oil during storage at room temperature (exposed to daylight).

and soybean oil from Shemen (Haifa, Israel) and crude olive oil from a local oil press (West Galilee, Israel). According to the manufacturers, the oils were free of added antioxidants and preservatives.

Sample preparation. Samples of oil, 10 ml each, were placed in a series of transparent glass bottles having a 5 cm^2 cross section and a volume of 20 ml each. The bottles remained loosely capped, enabling direct contact between oil surface and atmospheric air.

Crude avocado and olive oils were exposed to three oxidative conditions at room temperature (22 ± 1 C); these were absolute darkness, "on the shelf" exposure to daylight for 12 hr per day and exposure to 40 W fluorescent lamp for 24 hr per day. Oil samples were placed 50 cm beneath the fluorescent lamp.

Refined avocado, olive and soybean oils were exposed to three oxidative conditions: opaque laboratory oven at 60 C, absolute darkness, and "on the shelf" exposure to daylight for 12 hr per day at room temperature (22 ± 1 C).

Sample analysis. Periodic determination of chlorophyll content, peroxide values and AOM stability tests (carried out at 98 C and air flow rate of 1 ml/sec) were made in accordance with AOCS official methods (7-9). The assay of conjugable oxidation products (COP) was applied to the refined oil samples stored at 60 C (10).

RESULTS AND DISCUSSION

The results showing the oxidative stability of crude and refined avocado oil are presented in Figures 1–7 and Table 1. The values that appear in these figures and table are the average of three determinations.

The traditional method for determining peroxide value serves as an indicator of oil quality. This method does not distinguish between the various unsaturated fatty acids that undergo oxidation; it also does not supply information about the secondary oxidative products formed by hydroperoxide decomposition. It generally can be stated that the peroxide value is an indicator of the primary level of oil oxidation (11). The change in peroxide values vs time exhibits both an induction stage, where no secondary oxidative products are formed, and an oxidative stage, where a steep increase in peroxide value occurs. The induction stage usually serves as an indicator of oil quality. Low quality oil will have a shorter induction period (12).

Primary oxidation. Comparison of peroxide values for the oils stored in the dark at room temperature for three mo (Fig. 1) suggests no apparent differences between the oil samples. During storage the peroxide value of the oils remained less than 12 meq/kg. The rate of increase in peroxide values suggests that the oils are still in the induction stage.

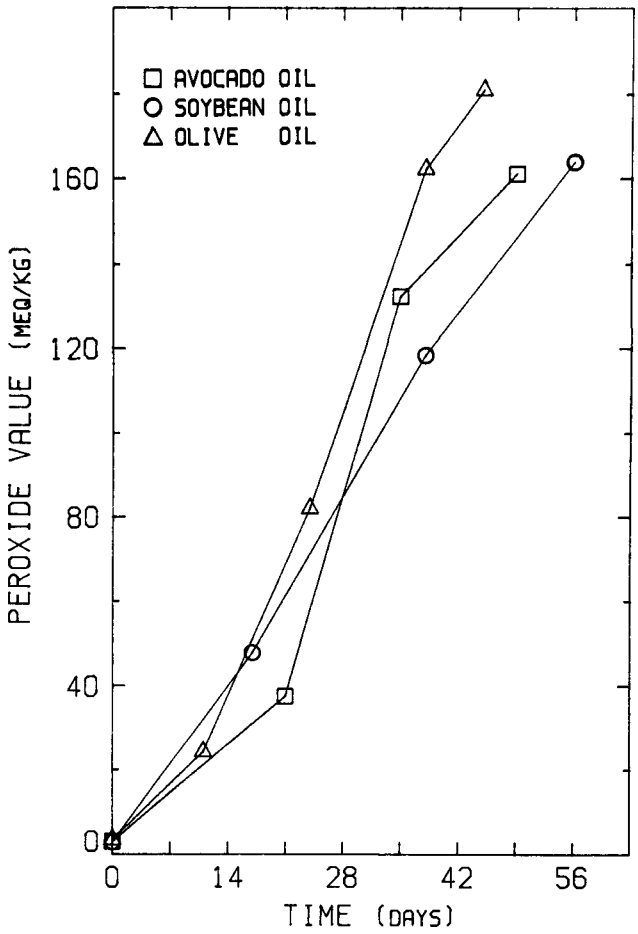

FIG. 3. Peroxide formation in refined avocado, soybean and olive oil during storage at 60 C.

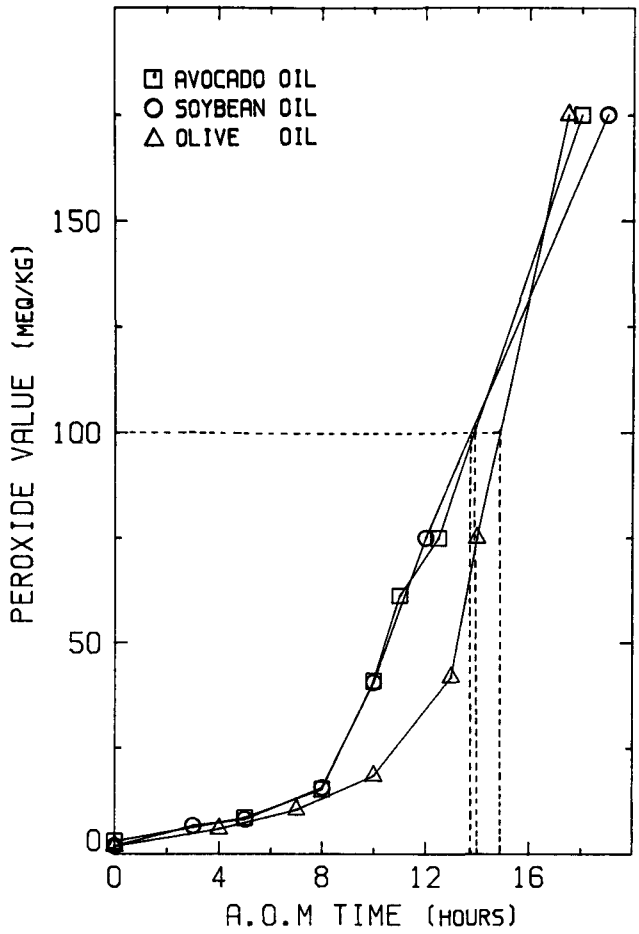

FIG. 4. Peroxide formation in refined avocado, soybean and olive oil during AOM evaluation.

TABLE 1

Peroxide Value and Chlorophyll Content of Crude Avocado and Olive Oil at Various Oxidative Conditions

Storage at room temperature (days)	Peroxide Value (PV) and Chlorophyll Content											
	Absolute darkness				Daylight "on the shelf"				Fluorescent light			
	PV		Chlorophyll (ppm)		PV		Chlorophyll (ppm)		PV		Chlorophyll (ppm)	
	Avocado oil	Olive oil	Avocado oil	Olive oil	Avocado oil	Olive oil	Avocado oil	Olive oil	Avocado oil	Olive oil	Avocado oil	Olive oil
0	5.85	5.10	41.36	6.26	5.85	5.10	41.36	6.26	5.85	5.10	41.36	6.26
7	5.95	5.31	40.97	6.15	9.95	8.82	40.60	6.10	18.61	16.97	38.02	5.59
10	—	—	39.85	6.10	—	—	40.28	5.76	64.62	—	35.41	4.49
14	6.20	5.95	38.45	6.03	31.65	24.38	38.12	5.68	85.02	54.45	32.92	4.62
22	6.60	6.07	35.33	5.85	43.67	38.0	31.08	5.41	154.93	81.07	16.29	3.62
27	—	—	35.06	5.80	—	—	30.86	5.32	187.50	96.66	7.57	3.01
31	7.60	6.71	34.27	5.79	62.75	45.06	29.97	5.27	208.34	119.70	1.95	2.70
38	8.83	7.85	34.00	5.77	67.86	58.19	28.32	5.12	206.71	189.02	—	1.46
45	9.32	8.44	33.59	5.78	80.11	69.89	27.36	4.96	193.88	171.82	—	—
52	9.55	9.18	33.32	5.75	93.79	78.80	25.03	4.84	175.34	169.80	—	—
59	9.78	10.42	32.65	5.74	117.58	81.65	24.97	4.71	152.49	147.94	—	—
65	10.45	12.75	32.14	5.74	123.43	87.31	24.04	4.41	—	127.93	—	—
71	11.03	15.45	32.03	5.72	140.92	98.82	22.91	4.27	—	—	—	—

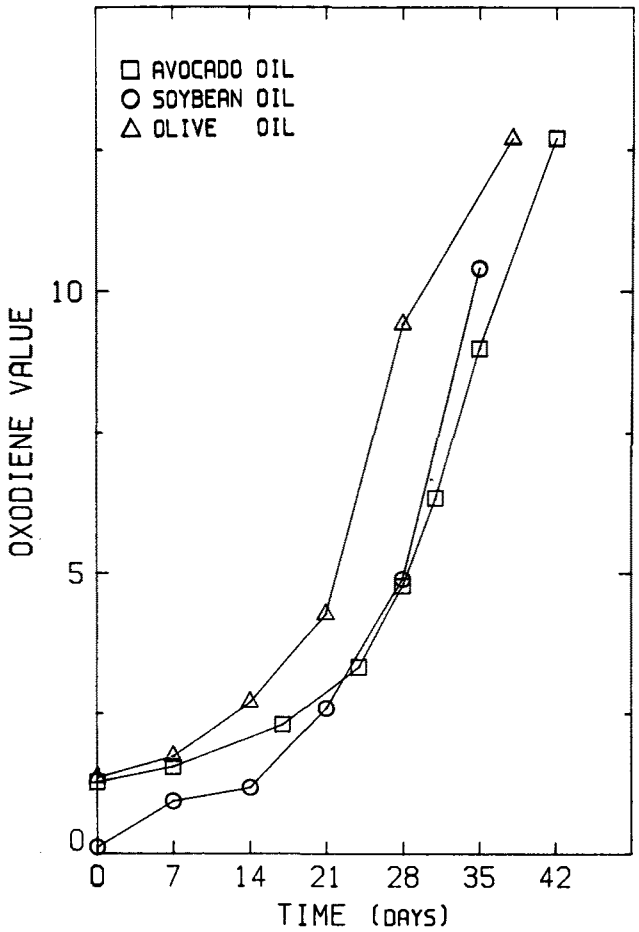

FIG. 5. Development of "oxodiene value" in refined avocado, soybean and olive oil during storage at 60 C.

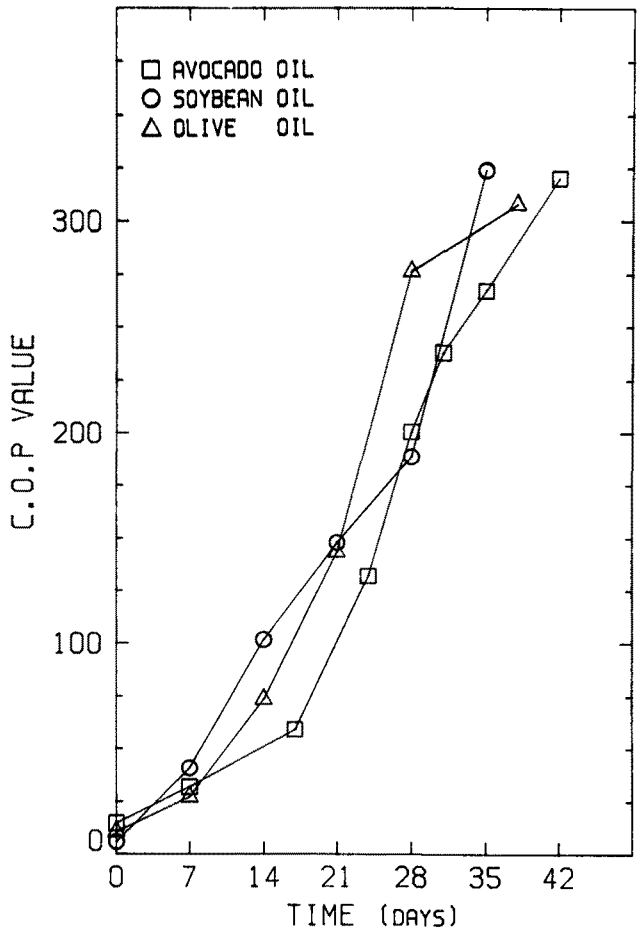

FIG. 6. Development of "COP value" in refined avocado, soybean and olive oil during storage at 60 C.

The increase in peroxide value in refined oils stored "on the shelf" exposed to daylight at room temperature (Fig. 2) shows that refined avocado oil is sensitive to oxidation in the presence of light containing ultraviolet (UV) radiation. Exposure to diffuse daylight or artificial light is well known to cause a marked acceleration in the deterioration of unsaturated oils (13). Photosensitizers and UV radiation can cause photo-oxidation of oil (3). Because chlorophyll is hardly present in refined oils, it does not act as a photosensitizer in this particular oxidative process "on the shelf." The deterioration probably is sensitized by chromophoric impurities in the oils, especially residual dyes and pigments (pheophytin, myoglobin, porphyrins, etc.) which absorb strongly in the visible or near UV light (13).

In contrast to thermal oxidation, it has been suggested (3) that light deterioration does not involve free radicals, but instead results from the generation of singlet oxygen by the transfer of excitation energy from excited chromophoric impurities to oxygen. Singlet oxygen reacts directly with double bonds of unsaturated fatty acids by concerted addition yielding allylic hydroperoxides in the *trans* configuration(3).

The greater rate of photo-oxidation of refined avocado oil relative to refined soybean and olive oil up to 84 days of storage is due to greater absorbtion of UV light (14). However, the greater rate of photo-oxidation of refined soybean oil relative to refined avocado oil after 84 days of storage may be due to the much greater concentration of linoleic and linolenic acid in soybean oil.

Oil stability usually is determined at accelerated conditions (60 C and more) because ambient conditions demand an excessively long period of time (15-16). The stability of refined avocado oil at 60 C is assessed in comparison to refined soybean and olive oil (Fig. 3). There is no apparent difference in the increase of peroxide value for the oils examined.

Results obtained from exposure of the oils to daylight show that it is desirable to avoid exposure to light of avocado oil or products containing the oil, for example by use of suitable packaging.

Examination of oil stability under dynamic conditions in the AOM stability test indicates no apparent difference between the oils (Fig. 4). Refined avocado and soybean oil have an AOM time of 14 hr, and refined olive oil of about 15 hr.

Secondary oxidation. The peroxide value does not serve as an absolute indicator of oxidative condition of the oil because of the peroxide's transitory nature (2). In contrast, the COP assay supplies information about the secondary deposition products formed during oil oxidation. In this assay, hydroperoxides formed from

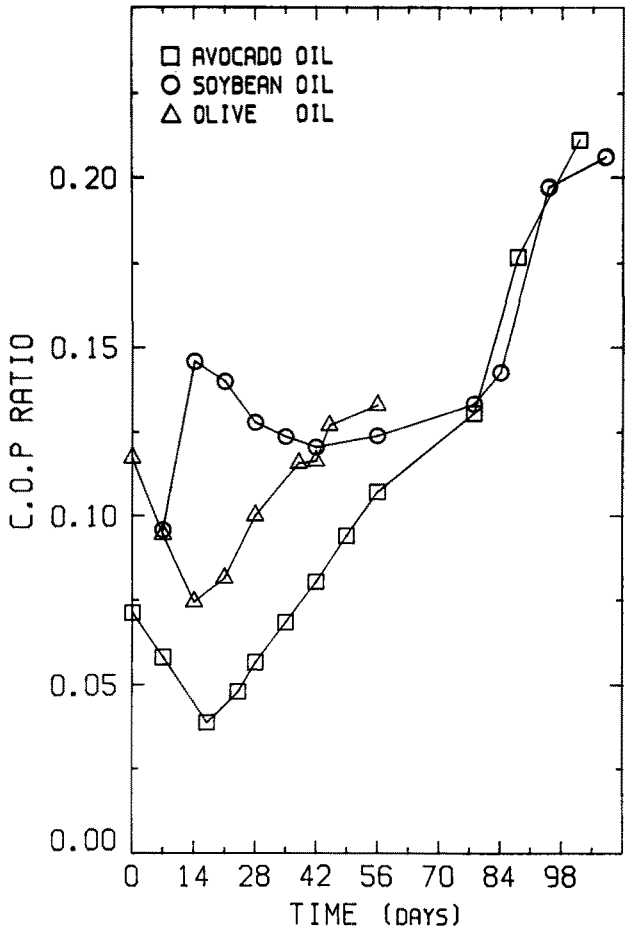

FIG. 7. Development of "COP ratio" in refined avocado, soybean and olive oil during storage at 60 C.

polyunsaturated fatty acids, and hydroxy and carboxy groups derived from them, are transformed by reduction and dehydration into conjugated chromophores. During reduction, the characteristic absorbance of the carbonyl groups in the UV range disappears. The decrease in absorbance at 275 nm as a result of reduction is defined as oxodiene value (10). Changes in absorbance at 268 and 301 nm during dehydration indicate formation of conjugated trienes and tetraenes. The sum of absorbance at both these wavelengths is defined as the COP value (10). The ratio between tetraene and triene content is measured by changes in absorbance at these two wavelengths, and is defined as the COP ratio (10).

From results obtained in determination of COP it can be seen that initial unsaturated carbonyl content is similar in olive and avocado oil, about one unit, while soybean oil has a lower initial content, about zero units (Fig. 5).

Initial unsaturated carbonyl content can serve as an indicator of the oil's oxidative history. Fresh oil stored under appropriate conditions is supposed to have low unsaturated carbonyl content.

During oxidation of the examined oils, oxodiene and COP values are markedly increased (Figs. 5-6). On the other hand, the change in COP ratio of soybean oil during oxidation is different from that of avocado and olive oil (Fig. 7). During oxidation of soybean oil there is an increase in COP ratio up to 14 days, then a gradual decrease until 42 days, followed by a gradual increase. On the other hand, avocado and olive oil show a steep decrease in COP ratio during 15 days; afterward there is a steep increase during the remainder of the oxidation period.

The differences in COP ratio may just reflect the differences in linoleic and linolenic concentration between the oils, because olive oil has linoleic and linolenic concentration similar to that of avocado oil, approximately 13% and 1%, respectively, for olive oil. On the other hand, soybean oil contains approximately 50% and 8%, respectively.

However, there is a possibility that the differences in COP ratio are due to the different oxidative histories of the examined oils. Since the history of the tested oils is unknown, it seems that the initial COP ratio of avocado and olive oil may indicate an oxidative stage which soybean oil has reached only after 14 of oxidation (Fig. 7). The carbonyl content of one unit suggests that refined avocado and olive oil have an oxidative history in comparison to refined soybean oil havng no carbonyl content (Fig. 5).

Peroxide value and chlorophyll content in crude avocado and olive oil. The green color of crude avocado oil is an attractive effect, imparting to the cosmetic products to which it is added the appearance of a natural product. This is a desirable characteristic because of the recent trend toward consumption of products derived from natural sources. Chlorophyll imparts the green color to the crude oil. Because there is a possibility of utilizing crude avocado oil in the food industry in a way similar to the use of that crude olive oil, the stability of these crude oils was determined at ambient temperature, with peroxide value serving as an indicator of oil quality. At the same time, chlorophyll content also was determined. Crude avocado oil has a very high chlorophyll content, 41.36 ppm, in contrast to crude olive oil, 6.26 ppm only. Chlorophyll concentration of crude avocado oil "on the shelf" decreased from 41.36 to 30.86 ppm after 27 days of storage. During the same period, chlorophyll content of crude olive oil decreased from 6.26 to 5.32 ppm (Table 1). Chlorophyll content of crude oils exposed to fluorescent light decreased very rapidly; after 27 days of storage only 7.57 ppm were left in crude avocado oil and 3.01 ppm in crude olive oil. On the other hand, chlorophyll content of crude oils stored in the dark decreased very slowly in comparison to the two other oxidative conditions examined.

Examination of chlorophyll content during storage indicates that chlorophyll is very sensitive to light, especially light containing radiation in the UV range. UV causes an excitation of the chlorophyll molecule which then reacts with oxygen, producing singlet oxygen. This active oxygen species reacts with components of the oil producing hydroperoxides. These compounds, in the presence of light, are transformed into peroxy-radicals that react with the chlorophyll, producing oxidized colorless chlorophyll (17). The chlorophyll serves as a sensitizer in photo-oxidative processes. On the other hand, it has been reported that chlorophyll has no effect, or is even an antioxidant, in the dark (18).

The initial peroxide content of crude avocado and olive oil was found to be 5.85 and 5.10, respectively. From the results obtained for storage "on the shelf" exposed to daylight and those exposed to fluorescent light, it seems that crude avocado oil is more sensitive to photo-oxidation than crude olive oil. This can be explained by the high chlorophyll concentration in crude avocado oil and by the fact that crude olive oil contains higher amounts of polyphenols, serving as antioxidants, than crude avocado oil (16). On the other hand, no effects have been apparent in the samples oxidized in the dark, even though the natural antioxidant polyphenols exist in greater concentration in the crude olive oil than in the crude avocado oil. This may be due to chlorophyll acting as an antioxidant in the dark (18). The rate of peroxide formation in the dark was much lower than that obtained with crude oils that underwent oxidation at the two additional conditions tested. The gradual decrease of chlorophyll content in oils stored in the dark can be attributed to the presence of hydroperoxides, formed as a result of an earlier oxidation, reacting with chlorophyll.

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[Recieved June 24, 1985]

Chemical and Nutritional Studies on *Terminalia bellirica* Roxb. Kernel and Its Oil

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Terminalia bellirica **Roxb. is a valuable tree of Indian forests. The seeds are valued medicinally and also industrially, for tanning purposes. The kernels, which are not currently used for edible purposes, have 40% oil and 35% protein. The oil extracted from the kernels is sweet-smelling and has palmitic (35%), oleic (24%) and linoleic (31%) acids as major fatty acids. The proximate principles, antinutritional factors and amino acid composition of the protein of the kernel are analyzed. Short term feeding of the oil at 10% level in a 10% casein protein diet to rats for 4 weeks resulted in growth comparable to that observed with animals fed a similar diet containing 10% groundnut oil. The protein utilization of casein used in the diet, as judged by the protein efficiency ratio (PER) and net protein utilization (NPU), was not adversely affected by the *T. bellirica* oil in the diet. The liver and heart lipid profiles of both the groups as reflected by the parameters, total lipids, total cholesterol and triglycerides content were comparable except for the heart triglycerides of the TBO-fed group, which were elevated. The absorption of nutrients like calcium, phosphorus and nitrogen was not adversely affected by the intake of *T. bellirica* oil. *T. bellirica* oil is absorbed to the same extent as groundnut oil. The results of this preliminary study indicate that *T. bellirica* kernel oil may be used for edible purposes because it is a good source of linoleic acid. However, long term toxicological studies are necessary to establish its safety before it can be recommended as an edible oil for human consumption.**

Feeding a diet containing 10% *T. bellirica* kernel protein as a raw diet as well as a cooked diet to rats, mice and chicks resulted in low food intake and death in all three species, probably due to heat stable antinutritional factors in the kernel.

An acute shortage of traditional edible oils in India has created considerable interest in developing new sources of oils and fats and in evaluating their nutritional and toxicological properties to establish their suitability for edible purposes. Studies on *Hibiscus sabdariffa* oil, *Cleome viscosa* oil and mango kernel oil have been reported (1,2) from these laboratories.

Terminalia bellirica Roxb. *(combritaceae)* is a valuable tree of Indian forests (3). The fruit is known as myrobalan and is one of the constituents of 'triphala,' an indigenous system of medicine (4), which is considered to cure a variety of disorders. The fruit provides a valuable export