Amino-Hexose-Reductones as Antioxidants. I. Vegetable Oils[1]

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REDUCTONES are resonance-stabilized enediols. They are strong reducing agents in acidic as well as in neutral and alkaline aqueous media. Members of this class include the ascorbic acids, triose-reductone, dihydroxymaleic acid, reductic acid, and dihydropyrogallol. The antioxygenic properties of ascorbic acid have been reviewed by Bauernfeind (1), and those of triose-reductone, dihydroxymaleic acid, and reductic acid have been investigated in fish (13) and fruits (14) by Tarr and Cooke. Butter oil prepared by heating to remove moisture and in presence of nonlipide materials exhibited improved oxidative stability (2, 9). Josephson and Dahle (9) believed that their results pointed to the formation of a reducing substance in heated butter through a lactose-protein reaction. The increased stability of sugar cookies has been attributed to the formation of reducing substance during baking (4). Lips (10) however found that lard heated in the presence of proteins and carbohydrates required temperatures of 280–296°C. before any improvement in stability was obtained.

New crystalline amino-reductones were prepared from hexoses and secondary amines in this laboratory (5, 6, 7). The physical and chemical properties, reactions, and structure of the amino-hexose-reductones will be presented by Hodge and Fisher in future publications. Investigation of these compounds as antioxidants has shown exceptionally strong inhibition of peroxide formation in a variety of animal fats, vegetable oils, and shortenings. This paper reports the results obtained in vegetable oils.

The amino-hexose-reductones are stable, colorless, neutral inner salts. Because of their salt-like nature they show very low solubilities in fats. They decompose below the melting points and do not withstand temperatures of oil deodorization. The anhydroamino-hexose-reductones, which are derived from the parent compounds by elimination of a molecule of water, possess the deep yellow color inherent in the molecules. They are less stable to heat, less soluble in water, and somewhat more soluble in fats than their precursors.

Methods of Evaluation

Extracted and refined vegetable oils were obtained from various commercial sources and were deodorized in a laboratory all-glass apparatus. For taste tests and oxygen absorption tests the reductones were added on the cooling side of deodorization. The temperature of the oil was lowered to 60°C., the reductones were added as a 1% solution in 90% aqueous ethanol, and deodorization continued for a half hour at 100°C. For the A.O.M. evaluations, deodorized oils were used and the appropriate amount of alcoholic reductone solution was added directly to the oil. The concentration of alcohol must be high enough so that a homogeneous solution is obtained in the oil. The alcohol was allowed to evaporate during the course of the aeration.

A.O.M. curves were run in the usual manner. The time to reach an arbitrary value of 20 milliequivalents of peroxides per kilogram of oil has been reported as the end-point. A.O.M. curves for the vegetable oils are logarithmic in shape and do not show the sharp break-points found for lard. Oxygen absorption curves for the fats and piecrust wafers were obtained with a constant-volume apparatus which has been previously described by the authors (12). Reductones are easily determined in aqueous or alcoholic solution by titration with standard iodine or indo-phenol solution. Because the above reagents are unsatisfactory in anhydrous systems, the reductones must be extracted from the fat into an aqueous solvent. The metaphosphoric-acetic acid-extracting solvent used for the determination of ascorbic acid (11) has proven satisfactory. Reductones present in the fat interfere with the Wheeler iodometric (16) peroxide determination. In this procedure, reductones present in the fat are extracted when water is added to the system, and they react with the iodine, which has been released by the fat hydroperoxides. Very little, if any, reaction is believed to take place directly between the peroxide and the reductone in the anhydrous fat system. Methods are being investigated for determination of reductones in anhydrous systems.

Results

The high antioxidant activity of the various reductones is easily demonstrated by the A.O.M. test. Figure 1 shows a typical set of curves for soybean oil. For those antioxidants which differ only slightly in their chemical structure the differences observed in

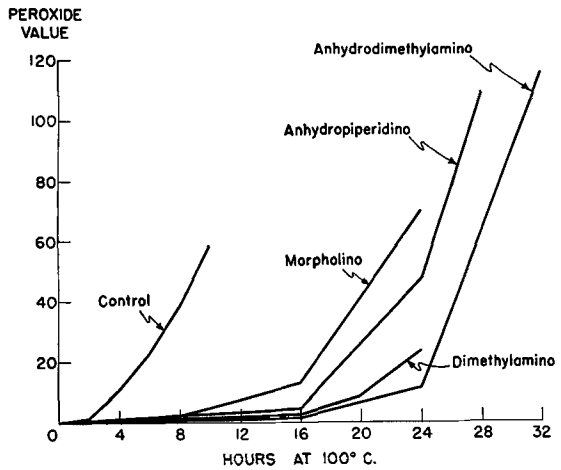

FIG. 1. Rate of peroxide development under A.O.M. conditions in soybean oil treated with different reductones at 0.01% concentration.

[1] Presented at the meeting of the American Oil Chemists' Society, Chicago, Ill., September 23–26, 1956.

activity are probably a result of the differences in molecular weight of the amine moiety. With groups having greater fat solubility, higher activity might be expected. However, for the reductones so far examined, the activity on a weight-basis decreases as the molecular weight increases but appears to hold rather uniformly on a molar basis.

The addition of certain groups to a phenolic antioxidant, such as a phenyl or tertiary butyl group, which would also be fat-solubilizing, exerts a large effect upon the electronic configuration of active centers and greatly influences the antioxidant activity in this way (3, 15). For example, we have found that phenyl hydroquinone is more active than hydroquinone at the 0.01% level. The molecular weight of phenyl hydroquinone is 69% greater than hydroquinone, thus indicating a much greater molar activity for the phenyl derivative. The greater activity in terms of current antioxidant theories would be attributed to the increased resonance-stabilization of the semiquinone radical imparted by the phenyl group rather than to improved fat solubility. In the reductones however, additives to the amine group appear to exert only a solubilizing effect and have little influence on the activity of the reducing groups. Because of the inner salt structure of the amino reductone, solubility in fats is only slightly improved by adding fat-soluble radicals.

If the free radical mechanism is operable in the autoxidation of fats, then the activity of antioxidants depends on the easy release or transfer of a hydrogen atom to chain-propagating, fatty acid hydroperoxide-free radicals (8, 15). Such a transfer results in a chain termination, and in the reductones there are two hydrogen atoms available for this purpose. Such a simple explanation would indicate a direct stoichiometric oxidation-reduction relationship. However each free radical chain that is allowed to start may supposedly develop many thousand moles of hydroperoxide. Thus it would be impossible to expect a stoichiometric relationship between the moles of peroxides formed and the moles of reductones oxidized. It is assumed that the oxidized (dehydro) form, having a lower potential, does not enter into further oxidizing reactions. Like other antioxidants the reductones probably disappear or are used up by the time the induction or break-point of the oxidizing oil has been reached.

TABLE I

Reductone Stabilization of Vegetable Oils

Antioxidants, 0.01% concentration	Hours to reach peroxide value of 20, A.O.M. conditions			
	Corn samples		Cotton-seed	Soy-bean
	A	B		
Control	3.5	6.3	4.5	5.5
Dimethylamino	8.3	30.0	27.5	23.0
Diallylamino	7.7	....	18.0	17.0
Morpholino	9.3	20.5	14.0	17.0
Piperidino	6.3	....	18.0	19.0
4-(5-nonyl)-piperidino	6.0	....	12.5	15.5
N-benzylpiperazino	5.7	....	13.5	16.0
Anhydrodimethylamino	10.0	30.0	34.0	25.0
Anhydropiperidino	7.0	....	25.0	19.0
BHA	2.5	4.8	3.5	5.6
Hydroquinone	9.0	....	13.5	18.0
Propyl gallate	4.0	....	17.0	4.8
Citric acid	8.3	13.0	4.5	10.0
Ascorbic acid	9.0	17.0	5.5	13.0

In Table I the activities of eight reductones are compared to those of several known antioxidants. The activity of the reductones as measured by this method is considerably greater than that of any of the approved antioxidants and frequently exceeds the activity of hydroquinone. Hydroquinone with its low molecular weight, about half that of the reductones, would occupy a much less favored position if the activities were expressed in molar terms. Reductone activity in cottonseed oil is equal to or slightly higher than that shown in soybean oil. One sample of corn oil however was not stabilized to nearly the same extent as soybean or cottonseed oil. Activity values for this corn oil are less than half that of the other oils. This particular lot of corn oil (Sample A) had been stored for a considerable length of time after its deodorization, and this may be a contributing factor in its low response to added antioxidants. The presence of free fatty acids in an oil is believed to reduce markedly the activity of the reductone through the formation and precipitation of an insoluble, reductone fatty acid salt. Tests on other lots of freshly deodorized oil indicate that the reductones have a high order of activity in corn oil equivalent to that shown for the other vegetable oils. The other data in Table I were verified with different lots of soybean and cottonseed oil.

Reductone activity is approximately a linear function of the concentration within the range of 0.0 to 0.02%. Table II indicates the effect of reductone concentration on the development of peroxides in soybean oil held under A.O.M. conditions for 8 hrs. Concentrations of only 0.001% reduce the peroxides by 2- to 5-fold over that found in the control oil. Although small variations occur in the data, the similarity in activity of all the reductones is evident. Trouble was encountered at 0.02% levels by the material crystallizing from the oil during storage. Titration of oil samples filtered after storage show 50 to 90% recovery of the added reductones. Solubility of the reductones in fats and a study of the factors involved will be reported separately.

TABLE II

Peroxide Development in Soybean Oils Treated with Different Reductones

Reductone	Peroxide values after 8 hours, A.O.M. conditions				
	Reductone concentration				
	Control	0.001%	0.005%	0.01%	0.02%
Diallylamino	40	16	2.0	1.2	0.5
Piperidino	40	....	2.0	1.5	0.5
Anhydropiperidino	40	8	0.9	0.4	0.0
4-(5-nonyl) piperidino	40	....	....	2.1	1.5
Morpholino	26	16	2.4	1.4	1.0
Hydroquinone	26	21	9.0	5.1	....

Practical use usually requires application of a mixture of one or more antioxidants plus one or more synergists and so-called acid activators. Table III shows the results of combinations of four different reductones with three other stabilizers in corn, cottonseed, and soybean oil. The synergistic effects are calculated as the percentage of the additional time necessary to reach the required peroxide level over that of the total time calculated from the known time of each component. Thus for corn oil (Sample A) containing a mixture of 0.01% anhydrodimethylamino-reductone and 0.01% ascorbic acid, the time required to reach a peroxide level of 20 was 25 hrs. The stability value for this combination calculated from the individual times is 3.5 for the control, plus 6.5 (10–3.5) for the reductone, plus 5.5 (9–3.5) for

TABLE III

Stabilizing Effects of Reductone, Antioxidant Combinations in Vegetable Oils

Reductone (0.01% concentration)	Antioxidants 0.01%						
	Control, hours[a]	Ascorbic acid		Citric acid		Propyl gallate	
		Hours	Synergism[b] %	Hours	Synergism, %	Hours	Synergism, %
Soybean Oil							
Control	5.5	13.0	....	10.0	....	5.0	....
Dimethylamino	23.0	33.0	8.0	32.0	16.0	22.0	0.0
Morpholino	17.0	25.0	0.0	26.0	21.0	18.0	0.0
Anhydrodimethylamino	25.0	32.5	0.0	37.0	25.0	25.0	0.0
Anhydropiperidino	19.0	32.0	21.0	29.0	23.0	....	....
Cottonseed Oil							
Control	4.5	5.5	....	4.5	....	17.0	....
Dimethylamino	27.5	30.5	7.0	28.0	0.0	37.0	0.0
Morpholino	14.0	28.0	87.0	26.5	89.0	32.0	21.0
Anhydrodimethylamino	34.0	35.5	0.0	37.0	9.0	....	....
Anhydropiperidino	25.0	32.0	23.0	26.0	0.0	....	....
Corn Oil							
Control Sample A	3.5	9.0	....	8.3	....	....	....
Control Sample B	6.3	17.0	....	13.0	....	....	....
Dimethylamino A	8.3	20.5	49.0	17.5	34.0	....	....
Dimethylamino B	30.0	44.5	9.3	36.5	0.0	....	....
Morpholino A	9.3	21.0	42.0	17.5	24.0	....	....
Morpholino B	20.5	35.5	14.0	31.0	14.0	....	....
Anhydrodimethylamino A	10.0	25.0	61.0	23.0	55.0	....	....
Anhydrodimethylamino B	30.0	41.0	0.0	39.0	6.3	....	....
Anhydropiperidino A	7.0	20.5	64.0	18.0	53.0	....	....

[a] Hours to reach a peroxide value of 20. [b] Synergism expressed as a percentage improvement.

the ascorbic acid, which equals 15.5 hrs. The synergistic effect was therefore 61%. In this particular lot of corn oil all the antioxidant mixtures of reductones with citric acid or ascorbic acid gave marked improvements amounting to a synergistic effect of approximately 50%. Similar tests conducted on other lots of corn oil, of which sample B is typical, showed that synergistic effects are not normally observed in corn oil. In both soybean and cottonseed oil only small, if any, synergistic effects were observed. In some cases the total additive effect was not observed. These low values could be a result of experimental errors or other undetermined factors, but it is believed that antagonistic effects are not present.

The synergistic effects obtained in tests with morpholino-reductone in cottonseed oil are not in agreement with the rest of the data. Such results would be obtained if a low value had been determined for the reductone control sample. Oxygen absorption tests with cottonseed oil indicate that morpholino-reductone does equal the activity of the other reductones. Citric acid-reductone mixtures have not shown increased stability in cottonseed oil; however, in soybean oil, a 20% improvement in the activity is observed for the citric acid-reductone mixtures. This agrees with previous observations that citric acid shows greater effects in soybean oil than in other oils.

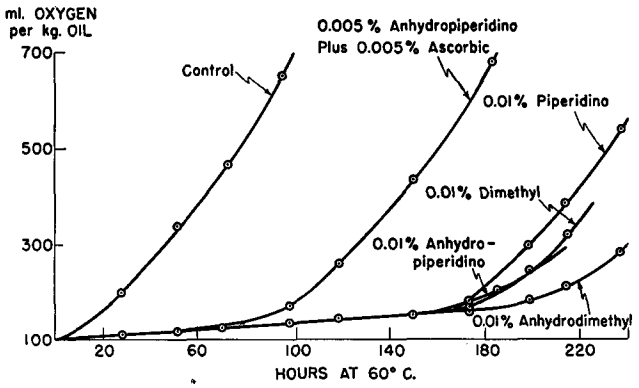

FIG. 2. Rate of oxygen absorption at 60°C. for cottonseed oil treated with various reductones.

Oxygen absorption tests with the different oils also show that high antioxidant activity is imparted by the various hexose-reductones. Figure 2 depicts the rate of oxygen uptake at 60°C. in cottonseed oil treated with four different reductones at the 0.01% level. The order of their activity is the same as determined under A.O.M. conditions. The lighter molecular weight reductones generally gave longer induction periods. If the time to reach an oxygen absorption equivalent to a peroxide value of 20 is taken as the basis of an induction period, then a relative index for these four reductones would be 4.1, 4.3, 4.6, and 4.9 times that of control. Calculation of a similar index from the A.O.M. data given in Table II gives 4.0, 6.1, 5.6, and 7.5, respectively. Considering the assumptions made in selecting the control value and the limitations of the peroxide method, these indexes are in satisfactory agreement. Figure 3 shows the oxygen uptake of anhydropiperidino-reductone at a series of concentrations in soybean oil. These curves show regular progression with increasing amounts of reductone added. Although such a series has not been run for each reductone in every oil examined, sufficient tests have been made to show that this is a typical set of curves applicable to the rest of the reductones.

Thiobarbituric acid (TBA) tests run on oils containing reductones have given the same indication of high antioxidant activity. Figure 4 shows long induction periods of 10 and 20 days for oils stored without shaking at 60°C. and stabilized with 0.0025% and 0.005% anhydropiperidino-reductone. The control sample stored in air did not show a significant TBA value until after 4 days while the control sample stored under oxygen showed a rapid development of oxidized products after 1 day. Peroxide values determined simultaneously with the above TBA values showed similar curves and virtually the same induction points. TBA values, run on lard extracted from piecrust wafers containing reductones, agreed with the results obtained from the organoleptic evaluation

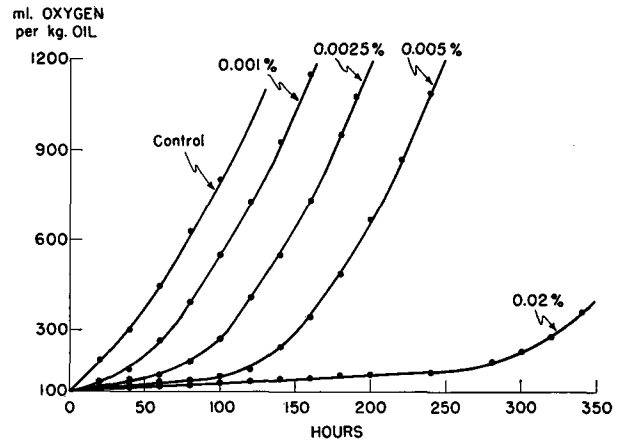

FIG. 3. Effect of concentration of anhydropiperidino-reductone on the rate of oxygen uptake at 60°C. in soybean oil.

of the piecrusts and also with the peroxide values of the extracted fats. Certain reductones, notably the anhydro derivatives, interfere with the color development in this test hence techniques using the TBA test in the presence of reductones in general must await further development.

Flavor Evaluation

Although excellent results were obtained from the chemical tests on the activity of reductones, the organoleptic evaluations of the treated oils failed to show a proportional degree of improvement in flavor stability. The initial flavor of freshly deodorized oils containing the reductones was high; therefore a taste inherent in the reductones did not appear to be the problem. Foreign odors and flavors, described as spicy and peppery, were noted in oils containing the diallylamino-reductone. Dibutylamino-reductone also contributed some flavor, which appeared to be intensified upon the storage and aging of the oils. In soybean salad oils only small improvement were observed in the flavor scores obtained by direct comparison of treated and untreated oils. The differences observed were mostly nonsignificant. Peroxide values determined on the oils at the time of tasting were uniformly lower in all treated oils. Flavor scores retained their same relative position even when storage of the oil was extended in order to develop very high peroxide values in the control oil and thus obtain an accentuated difference in peroxide levels. Table IV shows the results obtained with a series of evaluations for soybean oil. These results are a direct comparison of treated *versus* untreated oils; control scores for the comparisons are not shown. In each case the reductone-treated oil was slightly higher,

TABLE IV

Flavor Evaluation of Reductone-Treated Soybean Oils

Reductone 0.01%	Peroxide values 8 hrs. A.O.M.	Flavor evaluation			
		Initial		4 days, 60°C.	
		Score	Peroxide	Score	Peroxide
Control	32.0	7.2	0.7	4.5	5.9
Piperidino	1.8	8.5	0.0	4.9	0.8
Dimethylamino	1.7	8.0	0.0	4.7	0.6
Morpholino	1.7	7.4	0.0	4.9	0.6
Di-*n*-butylamino	2.2	7.8	0.2	3.8	1.0
Anhydropiperidino	1.4	7.4	0.0	4.1	0.6

but in no case was it significantly higher. Upon storage the flavor score of 3.8 for the dibutylamino reductone-treated oil was significantly lower because of the flavor developed by this additive. The flavor evaluations for cottonseed oil tabulated in Table V show results similar to those obtained with soybean oil where large differences in peroxide levels also failed to show differences in flavor scores. However cottonseed oil treated at the 0.01% level with an antioxidant mixture of equal parts of dimethylamino or anhydropiperidino-reductone and ascorbic acid did show a significant improvement in flavor stability after 4 and 7 days of storage. A similar test with ascorbic acid and piperidino-reductone failed to show this improvement after 4 days of storage. Combinations of reductone and citric acid were no more effective in preserving flavor quality than citric acid alone in either soybean or cottonseed oil.

Anhydropiperidino-reductone was used to replace propyl gallate in two multiple-component antioxidant mixtures. The antioxidant mixtures known in the trade as Tenox II and VI[2] and their counterparts containing the reductone were evaluated both oxi-

[2] Since the Department of Agriculture does not recommend the products of one company over those of another, these names are furnished for information only.

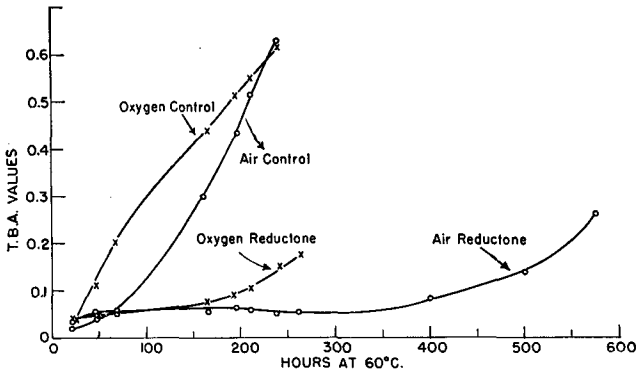

FIG. 4. Thiobarbituric acid tests on anhydropiperidino-reductone stabilized soybean oil stored at 60°C. The sample stored under oxygen contained 0.0025% reductone, and the sample stored in air contained 0.005% reductone.

TABLE V

Flavor Evaluation of Reductone-Treated Cottonseed Oil

Stabilizers (0.01% total concentration)	Peroxide values, 8 hrs. A.O.M.	Flavor evaluations					
		Initial		7 days, 60°C.		15 days, 60°C.	
		Score	Peroxide	Score	Peroxide	Score	Peroxide
Dimethylamino	0.0	8.7	0.0	6.6	0.4	5.5	1.4
Control	13.0	8.9	0.4	5.7	7.9	4.9	27.0
Anhydropiperidino	0.1	8.4	0.0	6.7[a]	0.8	5.5	1.6
Control	14.0	8.6	0.5	4.7	10.0	4.4	28.0
Dimethylamino plus ascorbic acid	1.0	8.3	0.0	7.8[a]	1.0	....	....
Control	11.0	8.3	0.5	5.9	9.6	....	....
Anhydropiperidino plus ascorbic acid	0.7	8.2	0.0	7.2[a]	1.0	....	....
Control	11.0	8.4	0.4	5.1	9.1	....	....

[a] Significant differences.

datively and organoleptically in soybean and cottonseed oils and in hydrogenated soybean oil. Table VI shows the results obtained in two evaluations at two antioxidant concentrations. Peroxide values were low in all tests where a reductone was included in the

TABLE VI

Flavor Evaluation of Oils Containing Antioxidant Mixtures

Antioxidant mixture	Peroxide values 8 hrs. A.O.M.	Flavor score		
		Initial	7 days, 60°C.	15 days, 60°C.
Soybean Oil				
Tenox VI 0.005%	3.8	8.4	6.7	6.5
Tenox VI 0.01%	3.4	8.7	7.8	6.6
NU VI 0.005%	1.2	8.7	7.7	6.1
NU VI 0.01%	1.0	8.7	7.4	4.6
Control	40.0	....	....	....
Cottonseed Oil				
Tenox II-0.005%	4.5	7.8	6.0	5.2
Tenox II 0.01%	3.2	7.7	6.5	4.9
NU II 0.005%	1.4	7.7	6.6	4.3
NU II 0.01%	0.9	7.7	6.5	5.4
Control	12.0	....	....	....

antioxidant mixture, likewise oxidative results were superior for the systems containing reductones. Flavor scores dropped consistently and at the same rate for both types of antioxidants, and no difference in their effectiveness for maintaining flavor could be established. Data for the same antioxidant combinations in other fats and oils gave similar results. It would appear that reductones could replace propyl gallate in these antioxidant mixtures with a corresponding improvement in oxidative stabliity. Color imparted by the reductone at these concentrations would not be visibly detectable.

Color

Reductones decompose on application of heat to yield brown melanoid pigments, and they might be expected to produce similar end-products in heated and stored oils. Aqueous or alcoholic solutions slowly turn brown on standing even at refrigerator temperatures. The anhydropiperidino-reductone has developed a more intense color, some 4-fold, over that of piperidino-reductone in oils stored at 60°C. At high concentrations and high temperatures, such as A.O.M. conditions, reddish brown colors quickly developed. The same oils however, show no increase over the initial color after standing at room temperature for several months. Table VII shows the changes in color of soybean oil containing three different concentra-

TABLE VII

Spectrophotometric Color Changes in Soybean Oil Containing Piperidino Reductone

Sample	Spectral color after storage, 60°C.				
	Initial	4	7	14	21 days
Control	1.2	1.3	1.2	1.8	1.5
Piperidino 0.005%	1.1	1.6	1.4	1.7	1.5
Piperidino 0.01%	1.4	1.7	2.3	2.8	2.9
Piperidino 0.02%	2.1	1.7	2.0	2.5	3.7

tions of piperidino-reductone when the samples are stored at 60°C. At concentrations of 0.01% and above, the depth of color continues to increase over a period of two to three weeks, and in cottonseed oil the brown color faded at a rather slow rate upon extended storage. Spectral absorptions run on oils containing reductones show no structural detail in the curves, and all indications are for an increased overall absorption beginning at about 4,000 Å.

A definite color problem exists, but when reductones are used at levels below 0.01%, color development does not impose a serious limitation on their use as antioxidants.

Summary

Amino-hexose-reductones were evaluated as antioxidants in soybean, cottonseed, and corn oils and were shown to be highly effective by all oxidative and chemical tests. The activity of the eight different reductones was approximately the same in any one substrate. Slightly higher activities were given by reductones of lower molecular weight. Activity was demonstrated at concentrations as low as 0.001% and was shown to be a linear function of the concentration up to 0.02%, the approximate limit of solubility. Outstanding features of the reductone-treated oils were long induction periods, slow absorption of oxygen, and low rates of peroxide development. Reductones are believed not to react directly with peroxides but to prevent peroxide formation by reacting with some precursor.

The combination of reductones with other antioxidants showed synergistic effects in only one sample of corn oil. The activity of combinations in soybean and cottonseed oils was for the most part strictly additive. In soybean oil, citric acid-reductone combinations with each at the 0.01% level gave a slight improvement over the expected activity. Oils stabilized with multiple-component, antioxidant mixtures in which an amino reductone replaced propyl gallate showed less peroxide development and were equally acceptable according to organoleptic scores. Aged oils did not show the organoleptic improvement that would be expected from the marked improvement observed in the oxidative stability. Significant improvements in flavor stability could be observed with reductones only when they were used in combination with another antioxidant. Reductone-treated soybean and cottonseed oils did not show an appreciable improvement in flavor stability. Only the di-n-butylamino- and diallylamino-reductones contributed foreign flavors to the oil. Atypical flavors are believed associated with the amine moiety of the reductone.

At high temperatures and at higher concentrations of reductones a brown melanoid color develops in the oil. The anhydro derivatives developed more color than the normal reductone. The reductones do not withstand oil deodorization conditions.

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