tude of the dipole moment of the solvent and the solubility of 1-monostearin in it.

Available data on the solubility of tristearin (6), which is non-polar, show that it is relatively insoluble in the alcohols, which are polar. Because the reverse is true for 1-monostearin, this difference in solubility can be used to advantage in the fractional crystallization of the monoglycerides from the triglycerides concomitantly formed in the normal preparation of monoglycerides. Daubert and King (3) found this same relationship with mono- and tripalmitin in the alcohols.

Summary

The practical limits of the solubility of pure monostearin in various solvents at different temperatures has been determined for isopropyl alcohol, ethanol, acetone, methanol, and commercial hexane. The synthetic method was employed, in which the temperature of known quantities of solvent and solute was decreased until crystallization of the solute began. This temperature, corrected for supercooling and heat loss to the surrounding bath, was taken as the equilibrium temperature between the known weight of solute and the known weight of solvent.

The solubility-temperature data of monostearin in each of the various solvents are presented both graphically and in tabular form.

A comparison of the solubility of monostearin in the various solvents at comparative temperatures indicates that its solubility is greatest in isopropyl alcohol and decreases in the order ethanol, acetone, methanol, and hexane.

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Tocopherol Retention in Oils Aerated in Glass and Iron Tubes

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VEGETABLE SEED FATS normally contain a natural "built-in" phenolic type of antioxidant. This is not true of animal fats. Hence the two types of fat require different protective supplementation. Vegetable seed fats with their normal content of tocopherols seldom require added phenolic type of antioxidants but do require a) getting the most use possible out of the tocopherols present and b) protection against metals which act as pro-oxidant catalysts.

In a preceding paper (1) a modification of the conventional A.O.M. test for evaluating the keeping qualities of fats and oils was presented. This method involves the substitution of an iron tube for the glass tube normally used in the A.O.M. test. The greater susceptibility of oils to oxidative deterioration in iron tubes was found to be due not to the pro-oxidant effects of dissolved iron but primarily to contact metal catalysis. Isopropyl citrate esters, predominantly monoisopropyl citrate, minimize the deleterious effects due to both dissolved iron and contact metal catalysis.

In reporting the results previously obtained, it was postulated that a) the tocopherols (very weak acids) in the oils are either adsorbed by the metal wall and rendered ineffective or are destroyed during the period of aeration, and b) the competition for metal between tocopherols and the monoisopropyl citrate (a very much stronger acid) is in favor of the latter. Regardless of which mechanism is involved, the tocopherols were expected to remain in the oil as effective antioxidants for longer periods of time when monoisopropyl citrate is also present. That acid synergists inhibit tocopherol destruction has been reported (2-4).

In the present study the fate of the tocopherols in the aerated oils was investigated. The experimental design called for tests conducted on the oils aerated in both glass and iron tubes and in the absence and in the presence of added monoisopropyl citrate. In addition, the influence on tocopherol retention of iron in solution, as the only source of the pro-oxidant catalyst, was evaluated.

Experimental

The aeration methods of test have been described in the previous publication (1). Tocopherol analyses were conducted according to the Rawlings' (5, 6) modification of the Emmerie-Engel (7) colorimetric method. In order to liberate tocopherols, possibly adsorbed to the walls of the iron tubes, the tubes were drained of the test oil and then filled to the same 20-ml. volume with coconut oil containing 0.08% of isopropyl citrate esters, predominantly monoisopropyl citrate. The oils were heated to 98°C. in the tubes and then tested for increased tocopherol content on the assumption that the presence of the more acid monocitrate would displace adsorbed tocopherols. The tocopherol analyses of the test oils were conducted serially on each oil as it was progressively oxidized during the period of aeration. The tocopherol analyses on the coconut oil with added monoisopropyl citrate were conducted on the wash-outs of different tubes, following specific periods of aeration.

The test systems were all-hydrogenated soybean oil shortenings of the same type, with the following average constants: melting point (Wiley) 111.0°F.; setting point (maximal titer heat rise), 28.0°C., iodine value (Wijs), 76.0. In those systems containing added iron, iron stearate was dissolved in the oils.

TABLE I

Illustrative Findings on Tocopherol Retention in Vegetable Oil Shortenings Aerated in Glass and Iron Tubes

Aerated at 98°C.	I.C.[a] added	Aerated in glass tubes		Aerated in iron tubes		
		Oil[b] itself	Fe added, 2.0 p.p.m.	Oil itself	Wash-out[c]	Oil + Wash-out[d]
hours	%	*% tocopherol content*				
0	0	0.087	0.087	0.087	....	0.087
5	0	0.050	0.027	0.029	0.0052	0.030
10	0	0.027	0.015	0.015	0.0041	0.015
20	0	0.019	0.011	0.010	0.0030	0.010
to 100 p.v.	0	0.017	0.008	0.008	0.0019	0.008
hrs. to 100 p.v.	....	114	56	38	....	....
0	0.08	0.087	0.087	0.087	....	....
5	0.08	0.084	0.070	0.080	....	....
10	0.08	0.064	0.048	0.049	....	....
20	0.08	0.029	0.029	0.033	....	....
to 100 p.v.	0.08	0.012	0.009	0.021	....	....
hrs. to 100 p.v.	....	176	168	113	....	....

[a] Isopropyl citrate esters, predominantly monoisopropyl citrate.
[b] Basic oils contained an average of 0.2 p.p.m. of iron. When iron was added, it was as the stearate.
[c] Coconut oil + 0.08% isopropyl citrate esters.
[d] After correcting for the 0.0035% of tocopherols in the coconut oil wash-out, and the 0.5 g. of residual test oil in the tube prior to addition of the coconut oil.

In Table I are summarized typical findings obtained in the course of the present investigation. As the oil was aerated in the glass tube, there was a progressive decrease in tocopherol concentration. In the presence of added iron in solution, the tocopherol loss was more precipitous. This was associated with a marked lowering in the A.O.M. value of from 114 to 56 hrs. When the oil was aerated in iron tubes, there appeared again a very rapid loss of tocopherols apparently of the same order of magnitude as noted when the same oil, with the added iron in solution but at much higher concentration (1), was aerated in glass tubes.

The quantity of tocopherol adsorbed on the walls during the aeration of the oils in the iron tubes was negligible. The coconut oil with the added 0.08% isopropyl citrate esters contained 0.0035% tocopherols. This wash-out solution also contained tocopherols from the 0.5 g. of original test oil that had adhered to the walls after drainage. The tocopherol content of each of the wash-out oils was corrected for these other sources of tocopherols, and the extra amount was added to that found in testing the oil as it was progressively aerated. The total tocopherol contents of the test oils were practically the same as those found by analyzing only the test oils themselves.

Of some interest was the observation that the tocopherol contents of wash-outs of the iron tubes, containing the oils aerated 20 hrs. and more in the iron tubes, were actually less than the tocopherol content of the coconut oil used for this purpose. Apparently a peroxide value of 40 and more (1) of the residual oil film and the pro-oxidant catalytic effect of the iron wall are sufficient to cause instantaneous destruction of tocopherols.

When the oil in glass was supplemented with isopropyl citrate esters, predominantly monoisopropyl citrate, the tocopherol loss was retarded. This was reflected by a greater A.O.M. value, 176 as compared to 114 hrs. The addition of 2 p.p.m. of iron to the oil increased somewhat the rate of tocopherol loss but to a much less degree than when the test system contained no monoisopropyl citrate. The A.O.M. values were again in agreement with the findings on tocopherol retention; 168 relative to 176 hrs. in the presence of monoisopropyl citrate and 56 relative to 114 hrs. in the absence of the metal-sequestering monocitrate.

When the oil supplemented with monoisopropyl citrate was aerated in iron tubes, tocopherol retention was markedly superior to that noted in the absence of the monocitrate ester. The same was true for the A.O.M. values, 113 as compared to 38 hrs. In this case also, despite a lower content of iron in solution (1) and a somewhat better retention of tocopherols, the oil aerated in the iron tube exhibited a lower A.O.M. value (113 hrs.) than the same oil with added iron aerated in the glass tube (168 hrs.).

It may be concluded that monoisopropyl citrate is very effective in protecting aerated oils against soluble iron (in such concentrations commonly found) by sequestering the iron so completely that both tocopherol retention and A.O.M. value are not substantially affected. Monoisopropyl citrate also protects oils against contact metal catalysis by preventing excessive tocopherol destruction.

Summary

Aeration of vegetable oils according to a modified A.O.M. test, involving the substitution of iron tubes for the conventional glass tubes, results in a more rapid destruction of the tocopherols present. Isopropyl citrate esters, predominantly monoisopropyl citrate, greatly retard the rate of tocopherol loss by sequestering soluble iron and by protecting the oil against further tocopherol loss by minimizing the effect of contact metal catalysis. Adsorption of tocopherols on the metal wall is insignificant.

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