Antioxidant Activity of Squalene

TOCOPHEROLS OCCUR in isolated natural fats to the extent of 40–90 mg/100 g of oil (1,2) and function as antioxidants. The hexaene hydrocarbon squalene is present in quantity in fish fats but also occurs ubiquitously (3) in vegetable fats in widely varying amounts. Quantities present in 100 g of various oils are: safflower 4–7 mg, soybean 7–17 mg, rice bran 332 mg, and olive 136–708 mg (4).

The effect of squalene on autoxidation does not appear to have been studied. It has been used as a stabilizer for vitamin A (5) and in the preparation of polyurethane base (6), and the kinetics of its autoxidation to hydroperoxide have been examined (7). The polar compounds of the unsaponifiable matter of soybean oil, which would include squalene, have been identified as likely to cause flavor problems though to a milder extent than air, metals, or linolenate; addition of 0.1-0.2% of squalene to soybean oil lowered its flavor score on subsequent storage (8).

In this study, concentrates of methyl oleate (I.V., 86.5) and linoleate (I.V., 162.5) of initial peroxide value (POV), 2 and 11 respectively, were kept in glass beakers in an oven at 63C with and without incorporation of 0.02% each of squalene and tocopherols. POVs were determined at 24-hr intervals by Wheeler's method. Squalene was isolated by repeated chromatography (5) of the unsaponifiables of a specimen of olive oil which contained 183 mg of squalene in 100 g of oil, as determined by the AOAC method (9). The tocopherols employed for comparative study were the unsaponifiables of safflower oil (tocopherol content, 90 mg/100 g of oil), freed of sterols by digitonin precipitation.

This tocopherol concentrate has strong antioxidant action, and the squalene and other unknown unsaponifiable constituents present have probably only a small effect on the protective action. Safflower oil mixed tocopherols consist of about 50% of the α-form with about 25% each of γ- and δ-tocopherols (10).

Fig. 1 shows the results of the stability trials. The increase in POV is approximately linear for the first four days. During this period squalene shows good protective action: in methyl oleate the POV increase per day was approximately 7 units and 22 units in the presence and absence respectively of 0.02% squalene, and for methyl linoleate the corresponding figures were 11 units and 50 units.

In fact, within this period, squalene has a better protective action than the same quantity of mixed

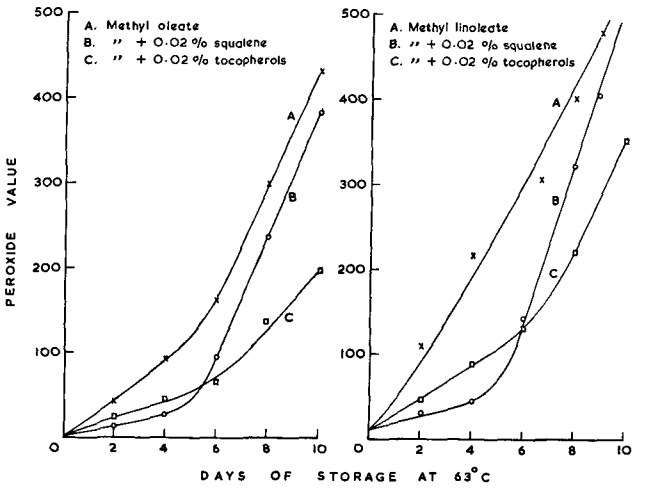

FIG. 1. Peroxide values of methyl oleate and linoleate at 63C in the presence and absence of 0.02% of squalene and safflower oil mixed tocopherols.

tocopherols. In the subsequent storage period, while the tocopherols continue to exert their protective effect, that of squalene is lost, and the rate of POV increase becomes greater than that of the control. The oxidation products of squalene may perhaps be pro-oxidant, as has also been suggested for other polyene materials, such as carotene (11). Thus squalene per se is initially an antioxidant but subsequently behaves as a pro-oxidant.

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