

## Ascorbic Acid and Ascorbyl Palmitate as Synergistic Antioxidants for Methyl Linoleate in Presence of Water

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The efficiency of ascorbic acid and ascorbyl palmitate as synergistic antioxidants in methyl linoleate containing 0.0025 % phenyl- $\alpha$ -naphthylamine in the presence of water decreases with increasing pH-value. At pH 5.1 ascorbyl palmitate is very efficient and, due to its higher fat-solubility, more active than ascorbic acid. Ascorbic acid is more effective in dry methyl linoleate. At pH 9.2 neither substance has any effect.

Ascorbic acid and its fatty acid ester have been proposed as antioxidants for fats<sup>1,2</sup> and shown to be highly effective in dry fat (*e.g.* by Golumbic and Mattill<sup>3</sup>, Riemenschneider *et al.*<sup>4</sup>). In presence of water ascorbic acid has been reported to be efficient in some cases<sup>5</sup>.

Ascorbic acid is known to autoxidize readily in water solution, especially if the water is alkaline<sup>6</sup>. Its efficiency as a synergistic antioxidant may therefore be supposed to be influenced by the presence of water and vary with the pH-value. This has earlier been shown to be the case for some autoxidizable, polyphenolic antioxidants<sup>7</sup>.

### EXPERIMENTAL

A system of methyl linoleate and borate buffers under oxygen in darkness at 40° C (*cf.* Ref.<sup>8</sup>) has been studied. Phenyl- $\alpha$ -naphthylamine was used as primary antioxidant, since it has been proved active within the investigated range of pH 5.1—9.2.

*Chemicals: Methyl linoleate and borate buffer solutions.* (Preparation *cf.* Ref.<sup>8</sup>).

*Phenyl- $\alpha$ -naphthylamine* (Eastman).

*Ascorbic acid* (Hoffmann-la Roche),

*Ascorbyl palmitate.* Ascorbic acid was esterified with palmitic acid according to Riemenschneider and Turer<sup>10</sup> and gave ascorbyl palmitate, m. p. 116° C.

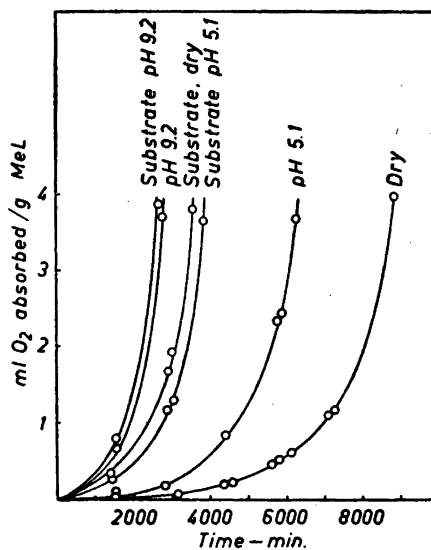


Fig. 1. The influence of pH on the stability of methyl linoleate + 0.0025 % phenyl- $\alpha$ -naphthylamine (substrate) + 0.0025 % ascorbic acid.

## RESULTS

Figs. 1 and 2 give the oxygen absorption curves for the two systems methyl linoleate + 0.0025 % phenyl- $\alpha$ -naphthylamine + 0.0025 % ascorbic acid, and methyl linoleate + 0.0025 % phenyl- $\alpha$ -naphthylamine + 0.0025 % ascorbyl palmitate, in a dry state and after addition of equal amounts of buffers of pH 5.1 and 9.2, respectively. For comparison the corresponding curves for the system methyl linoleate + 0.0025 % phenyl- $\alpha$ -naphthylamine<sup>9</sup> have been added.

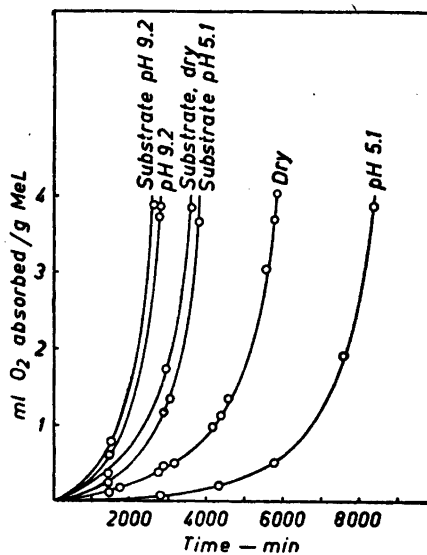


Fig. 2. The influence of pH on the stability of methyl linoleate + 0.0025 % phenyl- $\alpha$ -naphthylamine (substrate) + 0.0025 % ascorbyl palmitate.

Both ascorbic acid and ascorbyl palmitate are powerful antioxidants. In dry methyl linoleate ascorbic acid is most efficient due to its lower molecular weight. In presence of a water phase of pH 5.1, ascorbyl palmitate is, however, the more active. At pH 9.2 both substances are inefficient.

#### DISCUSSION

The experimental results show that ascorbic acid and ascorbyl palmitate are affected by water, and its pH-value, in the same way as are the autoxidizable polyphenolic antioxidants. The two substances have their maximal effect at pH 5.1. Ascorbyl palmitate is most effective because of its higher fat solubility resulting in a higher concentration in the ester phase. Like the fat-soluble, primary antioxidants it is actually more active in the presence than in the absence of water. Both ascorbic acid and ascorbyl palmitate are inactive at pH 9.2, their autoxidation products then being without stabilizing effect.

#### REFERENCES

1. Gray, P. P. and Stone, I. *Food Inds.* **11** (1939) 629.
2. Wells, P. A. and Riemenschneider, R. W. (to Secretary for Agriculture of the U.S.A.) *U. S. Patent* 2.368.435 (1945).
3. Golumbic, C. and Mattill, H. A. *J. Am. Chem. Soc.* **63** (1941) 1279.
4. Riemenschneider, R. W., Turer, J., Wells, P. A. and Ault, W. C. *Oil and Soap* **21** (1944) 47.
5. Watts, B. M. and Wong, R. *Arch. Biochem.* **30** (1951) 110.
6. Weissberger, A., Lu Valle, J. C. and Thomas, D. S. *J. Am. Chem. Soc.* **65** (1943) 1934.
7. Spetsig, L. O. *Svensk Kem. Tidskr.* **64** (1952) 191.
8. Spetsig, L. O. *Acta Chem. Scand.* **8** (1954) 1643.
9. Spetsig, L. O. *To be published.*
10. Riemenschneider, R. W. and Turer, J. (to Secretary of Agriculture of the U.S.A.) *U. S. Patent* 2.383.815 (1945).

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