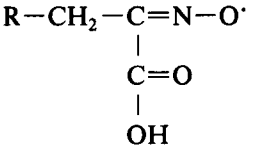
LETTER TO THE EDITOR

(Received Jue 22nd, 1994)

Dear Editor

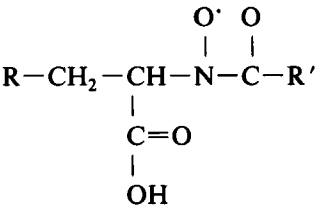
In response to Dr Janzen's letter, I would like to emphasise the fact that the radical corresponding to the ESR spectrum depicted on Figure 4 in our paper[1] is a nitroxide. Actually this fact is not disputed by Dr Janzen. That is the important point as it positively proves the involvement of phospholipids possessing primary amine groups in the radical reactions which sustain the antioxidant activity of vitamin E, vitamin C and phospholipid mixtures.

As reported in our paper the structure (**I**) of the radical we proposed for this spectrum was only tentative.



I

The small hyperline coupling a_N we observed (8.2 G) is effectively not likely associated with the nitrogen atom in (**I**). Based on this hyperfine coupling, the α-acyl aminoxyl (**II**) described by Dr Janzen is a better candidate.

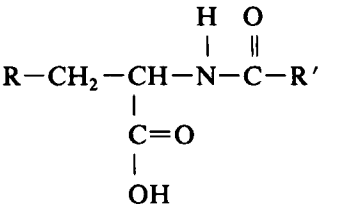


II

The very low hypertine coupling constant (<1.5 Gauss) associated with the β-hydrogen in **II** is consistent with the 1.3 Gauss splitting observed for the β-hydrogen in 1-(3′-hydroxypropyl) pentyl octanoyl nitroxide.[2] Besides, the great stability of radical **II** as compared to that of the radical formed in the presence of phosphatidylethanolamine is certainly due to hydrogen bonding between the carboxyl group and the aminoxyl function.

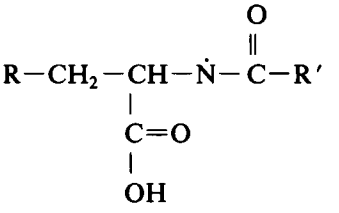
However, the pathway proposed by Janzen for the formation of the radical **II** seems unlikely. Indeed, although nitroso compounds can be formed by oxidation of primary amines followed by dehydration, although nitroso compounds react with acyl radicals to form α-acyl aminoxyls,[2] the presence of acyl radicals in the lipid system used in our study is, however, unlikely.

A more probable pathway will involve the reaction of the primary amine of the phospholipid with the ester of the triglyceride to form an amide (**III**).



III

The hydrogen atom located on the nitrogen in the amide **III** is activated. The amide **III** will therefore be able to regenerate vitamin C from the ascorbyl radical throughout an hydrogen atom transfer reaction. During this reaction the amide **III** will be converted into an aminyl radical (**IV**) which in turn will react with oxygen to produce the aminoxyl radical (**II**)[3,4,5] via the formation of a nitrogen peroxy radical.[6]



IV

Acknowledgements

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References

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