

September 1958

## An ESR Study of Stable Free Radicals in Natural and Synthetic Melanins

Juana Acrivos  
*San José State University*

Follow this and additional works at: [https://scholarworks.sjsu.edu/chem\\_pub](https://scholarworks.sjsu.edu/chem_pub)

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

Juana Acrivos. "An ESR Study of Stable Free Radicals in Natural and Synthetic Melanins" *Informal Discussion on Free Radical Stabilization, Faraday Society* (1958).

This Presentation is brought to you for free and open access by the Chemistry at SJSU ScholarWorks. It has been accepted for inclusion in Faculty Publications, Chemistry by an authorized administrator of SJSU ScholarWorks. For more information, please contact [scholarworks@sjsu.edu](mailto:scholarworks@sjsu.edu).

**THE FARADAY SOCIETY**

**INFORMAL DISCUSSION**

**ON**

**FREE RADICAL STABILISATION**

**PROGRAMME**

**AND**

**SUMMARIES OF PAPERS**

**SHEFFIELD UNIVERSITY, SEPTEMBER 4TH & 5TH, 1958**

AN ELECTRON SPIN RESONANCE STUDY OF STABLE FREE RADICALS  
IN NATURAL AND SYNTHETIC MELANINS.

J. L. Vivo-Acrivos and M. S. Blois, Jr.

The observation of an electron spin resonance (e.s.r.) absorption in natural melanin was reported by Commoner and coworkers in 1954<sup>(1)</sup>, who speculated that these permanently unpaired electrons were associated with free radicals that had become trapped in the lattice of the melanin polymer.

Relative to the more general question of the roles of free radicals in biological systems, it is of particular interest to determine whether intracellular melanin production is a biological free radical mechanism. As employed herein, we shall use the term natural melanin to refer to the polymeric biological pigment ordinarily considered to result from tyrosine oxidation and polymerization, and by synthetic melanins, to refer to the polymerization products of polyphenols or aromatic amines by auto-oxidative or enzymatic reactions.

The observations reported here were obtained with a paramagnetic resonance spectrometer operating in the 3 cm band and utilizing a reflection cavity.

Free Radical Intermediates in the Auto-oxidation and Enzymatic  
Oxidation of catechol, 3,4 dihydroxyphenylalanine (DOPA)  
and pyrogallal.

The e.s.r. spectra of the semiquinones of these compounds have been previously reported<sup>(2,3,4)</sup>.

If these reaction mixtures are then examined over longer periods of time, further intermediates are found. For the para<sup>5</sup> and orthobenzoquinones the dimer intermediate semiquinone has been observed by means of e.s.r. The structure of these have been inferred directly from the hyperfine structure arising from the unpaired electron-nuclear moment interactions in the free radical. In both cases the dimerization occurs through a C-C bond between the two rings. In DOPA and pyrogallal multiple spectra are also observed with time. The observed hyperfine structure in the case of DOPA is consistent with the proposed reaction mechanism.

The most important feature of the monomer and dimer spectra is the lowering of the g-factor by one part in  $10^5$  and the reduction of the total hyperfine splitting.

The first effect is explained as an increase in the diamagnetic shielding of the now larger  $\pi$ -electron system and the second is due to the fact that the

Oxygen atoms in the diquinone are more electro-negative and thus the unpaired electron density is reduced at the in-plane aromatic protons.

#### g-values of Natural and Synthetic Melanins.

In comparing the g-values of a number of polyphenolic semiquinones with those of the resulting synthetic melanins, it appears that the stable free radicals trapped are those of the monomeric form or quite small polymers inasmuch as the expected diamagnetic shielding is very slight. In contrast with this we find a significantly lower g-value for the enzymatically produced DOPA melanin than for the auto-oxidized DOPA melanin. The natural melanin from squid ink and from the Harding-Passey mouse melanoma is found to give a g-value intermediate between the former two.

This research was supported by the United States Air Force through AF Office of Scientific Research, Air Research and Development Command.

#### References.

1. B. Commoner, J. Townsend, and G. E. Pake, Nature 174, 689, (1954).
2. R. H. Hoskins, J. Chem. Phys. 23, 1975 (1955).
3. M. Adams, M. S. Blois, R. H. Sands, J. Chem. Phys. 28, 774 (1958).  
J. L. Vivo-Acrivos and J. E. Wertz, *ibid.* in press.