Tetrahedron Letters No.1, pp. 105-111, 1966. Pergamon Press Ltd.
Printed in Great Britain.

A SOLID PHENOXY RADICAL FROM DISYRINGYLMETHANE--

A MODEL FOR LIGNIN RADICALS

Cornelius Steelink*
Forest Products Laboratory,** Forest Service
U.S. Department of Agriculture

and

Raymond E. Hansen
Institute for Enzyme Research
Madison, Wisconsin

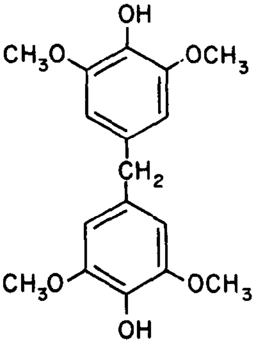
(Received 25 October 1965)

The oxidation of disyringylmethane (I) gives a purple solid free radical, which we have tentatively identified as 2,6-dimethoxy-4-(3,5-dimethoxy-4-oxo-2,5-cyclohexadien-1-ylidenemethyl)-phenoxyl, II. We have assigned the trivial name of syrinoxyl to this radical. The radical and its precursor (I) are of significant interest to lignin chemists, since both have been recently proposed (1,2) to represent structural units in alkali hardwood lignins. Because of its stability and relative insensitivity to oxygen, syrinoxyl may represent the moiety responsible for part of the paramagnetism of hardwood lignin preparations (3).

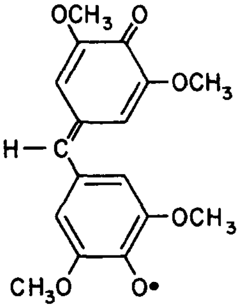
---

[*] On sabbatical leave from the University of Arizona, Department of Chemistry, Tucson, Ariz.

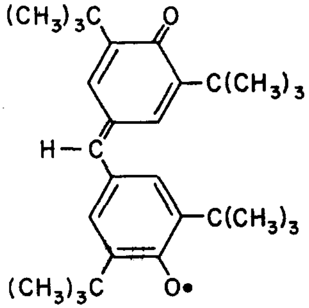
[**] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.



I



II



III

Syrinoxyl (II) was prepared by the PbO_2 oxidation of disyringylmethane (I) in dichloromethane under nitrogen, according to the method of Bartlett (4). Upon removal of the solvent and PbO_2, a purple-black solid was obtained. This contained more than 50-mole % unpaired electrons, as estimated by comparison with diphenylpicrylhydrazyl. The infrared spectrum of syrinoxyl revealed no OH bands; well-defined bands appeared at 6.12μ, 6.35μ, and 6.45μ, the latter being characteristic of phenoxy radicals. The visible spectrum revealed bands at 413mμ, 458mμ, 650mμ, and 850mμ (weak). The solid sintered at 190° C. and melted around 250° C. Thin layer chromatography revealed a minor contaminant present in syrinoxyl, which could be the red *orthoquinone* derivative. Similar side products were observed by us in the oxidation of simple syringol derivatives in dichloromethane (5).

When exposed to air in an open container for a week, the spin content of syrinoxyl decreased to one-fifth of its original value; under nitrogen, this decrease was limited to one-half of its original value.

The e.s.r. spectrum of syrinoxyl is shown in Figure I; that of galvinoxyl (6) (III) is also shown for comparison. Both radicals yield single line spectra in the solid state, and both show a broad doublet pattern in solution, indicative of the interaction of the unpaired electron with the methide hydrogen atom. At least 25 prominent lines are observed in the syrinoxyl spectrum; each of these is further split into five components of relative intensities 1:4:6:4:1.

We interpret these results to indicate that the methide proton is responsible for the main doublet pattern of five gauss separation; the hyperfine pattern of 25 lines (or more) is caused by the 12 methoxyl protons, and finally, the subsidiary 5-line splitting is caused by the 4 equivalent ring protons. The number and intensity pattern of the 25 lines do not agree with those expected for 12 equivalent methoxyl protons, but rather suggest that 6 of these protons are different from the other 6. A synthetic spectrum, which is a very close approximation of the experimental e.s.r. spectrum, was computed by assigning the coupling constants to syrinoxyl, as shown in Table I.

TABLE I Coupling Constants for Syrinoxyl

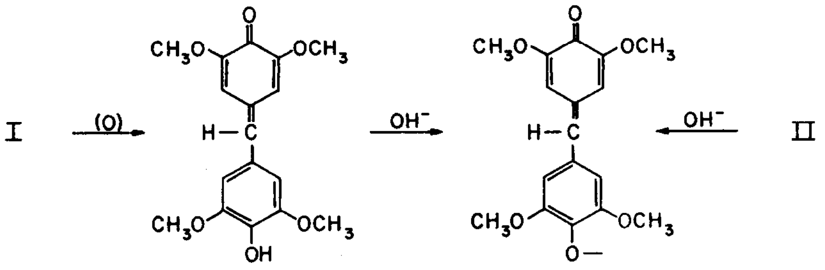
Proton	A^H (gauss)	Number of protons
Methide	5.60	1
Ring	.14	4
OCH_3(a)	.70	6
OCH_3(b)	1.40	6

Assumed line width = 0.125 gauss.

The striking difference in coupling constants between the methoxyl sextets (a) and (b) may be caused by the asymmetry of the syrinoxyl molecule, which makes the 2- and 6-positions nonequivalent.

Disyringylmethane (I) was synthesized from 2,6-dimethoxyphenol, formaldehyde and aqueous sodium hydroxide by the method that Bailey (7) used for the preparation of diguaiacylmethane. White plates crystallized from water, melting at 111° to 112° C. (*Anal*. Found: C, 63.92; H, 6.21. Calc.: C, 63.74; H, 6.29). The molecular weight was 315 (calc. 320), as determined by osmometry. The ultraviolet absorption spectrum was practically identical to that for 2,6-dimethoxyphenol; principal bands in the infrared spectrum were 2.95μ(s), 3.40 and 3.55μ(m), 6.2μ(s), 6.6μ(s), 6.75μ(s), 7.0μ(s), 7.55μ(s), 8.3μ(s), and 9.0μ(s), consistent with the structure for I. Unambiguous confirmation of the structure of I was obtained from a n.m.r. analysis in deuterochloroform: τ 3.59(4H, singlet), τ 4.57(2H, singlet), and τ 6.17 (14H, singlet). The integrated intensities were consistent with the assignments of 4 aromatic protons, 2 hydroxyl protons, and 14 protons (2 methylene and 12 methoxyl), respectively.

An interesting color reaction lent additional support to our assignment of II to syrinoxyl. When this radical was dissolved in aqueous base, an immediate blue color developed (259mμ, 285mμ, and 613mμ (intense)). When disyringylmethane was subjected to mild oxidation with air or PbO_2, a yellow color was observed in neutral solution (275mμ, 281mμ, 319mμ, and 434mμ (intense)), which is most likely the quinone-methide, IV. Upon basification, this yellow solution turned deep blue with the same spectral bands as those of syrinoxyl in base. The blue compound is probably the anion, V. The results are summarized below:



IV V

These reactions parallel those reported by Kharasch and Joshi (8) for galvinoxyl and its diphenylmethane precursor.

The results confirm our previous conclusions (5) that 2,6-dimethoxyphenols are capable of forming unusually stable radical species, if they are substituted in the 4-position with conjugated systems. However, the radicals obtained from these compounds are not as stable as those with tertiary-butyl groups in the 2- and 6-positions.

Of particular interest to lignin chemistry is the stability and deep color of the syrinoxyl radical. Alkali lignins, especially hardwood lignins, have relatively high stable radical contents, as well as deep colors (3,9,10). This could arise from the facile oxidation of disyringylmethane moieties and their subsequent one-electron conversion to the deeply colored radical. Syrinoxyl appears to be a reasonable model to account for both color and paramagnetism. Its stability would probably be increased if trapped in a polymeric lignin or cellulose matrix. Therefore, a study of its reactions with a variety of reagents should be useful in interpreting the complex chemistry of lignin.

An X-band e.s.r. spectrometer equipped with a microwave circulator circuit and a TE 102 cavity was used (11). Proton resonance frequency measurements for determining magnetic field strength and microwave frequency measurements were made with a Hewlitt-Packard 5253B Electronic Counter and a Hewlitt-Packard 540B Transfer Oscillator phase locked with a Dymec DY5796 Transfer Oscillator Synchronizer.

Acknowledgments

We are indebted to Prof. John Harriman of the University of Wisconsin, Department of Chemistry, for his invaluable aid in computing the synthetic spectra, and to Mr. David Johnson and Mrs. Carole Southerland of the Forest

Products Laboratory for the n.m.r. and molecular weight analyses, respectively. Part of this work was supported by a grant from the National Institutes of Health (GM-12394).

REFERENCES

(1) S. Rothenberg and P. Luner, Abstracts, Symposium on Lignin, Structure and Reactions, 150th National Meeting, Amer. Chem. Soc., Atlantic City, N.J., Sept. 12, 1965.

(2) J. M. Harkin, *ibid*.

(3) C. Steelink, *ibid*.

(4) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc*., **84**, 2596 (1962).

(5) C. Steelink, *J. Amer. Chem. Soc*., **87**, 2056 (1965).

(6) Purchased from Aldrich Chem. Co., Milwaukee, Wis.

(7) H. C. Bailey, *Brit. Pat*., 845, 608 (CA **55**, P7365e).

(8) M. S. Kharasch and B. S. Joshi, *J. Org. Chem*., **22**, 1435 (1957).

(9) C. Steelink, T. Reid and G. Tollin, *J. Amer. Chem. Soc*., **85**, 4048 (1963).

(10) C. Steelink, *Geochim. Cosmochim. Acta*, **28**, 1615 (1964).

(11) H. Beinert and B. Kok, *Biochim. Biophys. Acta*, **88**, 278 (1964).

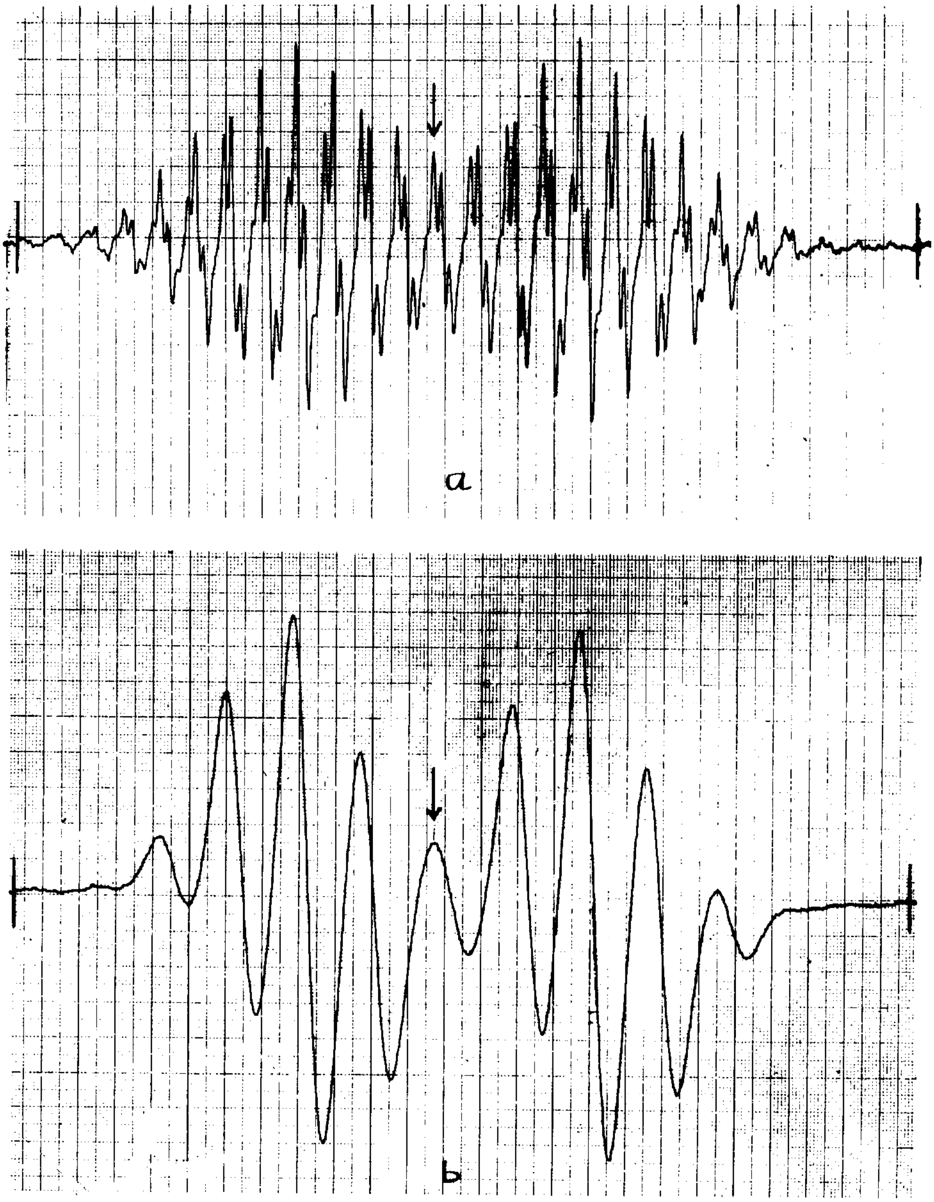


FIG. I

First derivative e.s.r. spectra: (a) Syrinoxyl in CH_2Cl_2: g = 2.0060 (arrow); (b) galvinoxyl in CH_2Cl_2: g = 2.0044 (arrow). Distance between dark lines is 18 gauss in both spectra.

M 128 908