[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Chemistry of Vitamin E. XXXVI. Behavior at the Dropping Mercury Electrode of Quinones Related to Vitamin E[1]

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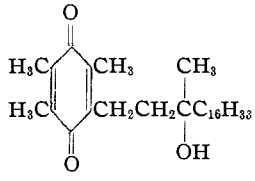
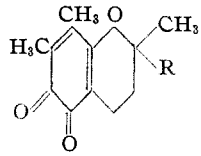
In previous communications the polarographic behavior of α-tocopherol[2] as well as that of related 6-hydroxychromans and 5-hydroxycoumarans[3] has been reported. Likewise, the polarographic waves of the para-quinones obtained by oxidation of various 6-hydroxychromans and 5-hydroxycoumarans have been studied.[3] The present study was undertaken in order to examine the behavior at the dropping mercury electrode of α-tocopherylquinone (I) and of orthoquinones of type II, which are obtained from α-tocopherol and various 6-hydroxychromans under certain conditions.[4]



I



II, R = CH_3
III, R = $C_{16}H_{33}$

No ortho-quinones, apparently, have hitherto been studied polarographically.

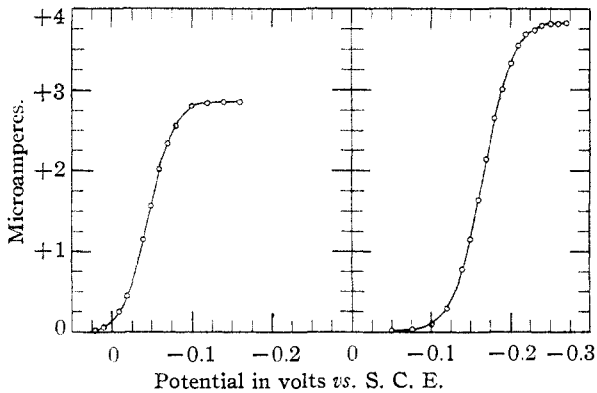


Fig. 1A.—0.1 *M* Aniline–0.1 *M* anilinium perchlorate.

Fig. 1B.—0.05 *M* sodium acetate–0.05 *M* acetic acid.

Fig. 1.—Current–voltage curves of α-tocoquinone in 0.05 *M* NaOAc–0.05 *M* HOAc in 75% ethanol and in 0.1 *M* $C_6H_5NH_2$–0.1 *M* $C_6H_5NH_3ClO_4$ in 75% ethanol.

Experimental

The apparatus and general experimental procedure have been described in previous papers.[2,3] In the present work, three drops of a 1% solution of methyl red acid in 50% ethanol were added to 90 ml. of the quinone solution, in order to suppress maxima. Buffered solutions were used in all cases, and the current–voltage curves were determined at 25°. The characteristics of the capillary were as follows: under a pressure of 62.7 cm. of mercury, the drop time in 0.1 *M* potassium nitrate, 0.001 *M* with respect to nitric acid, was 3.72 sec. (open circuit), *m* was 1.52 mg. per sec. and $m^{2/3}t^{1/6} = 1.646$.

α-Tocopherylquinone (I) was prepared from synthetic α-tocopherol by oxidation with ferric chloride and was purified via the hydroquinone.[5] Oxidation of tocopherylhydroquinone (from 1.91 g. of α-tocopherol) to the quinone was carried out with silver oxide (freshly prepared from 3.17 g. of silver nitrate)[6] as follows: to a solution of the hydroquinone in absolute ether (25 cc.) was added anhydrous magnesium sulfate (1.5 g.) and the mixture was shaken for five minutes with the silver oxide. The mixture was filtered and the ether was removed by distillation, finally under reduced pressure. The quinone, a viscous orange yellow oil, weighed 0.59 g.

2,2,7,8-Tetramethylchroman-5,6-quinone (II) was prepared by nitric acid oxidation of 2,2,5,7,8-pentamethyl-6-hydroxychroman.[4] This compound was quite unstable; after it had stood even for a few hours at room temperature the melting point became several degrees lower. Consequently, for accurate results, the current–voltage curve must be determined as soon as the quinone has been prepared.

2,7,8-Trimethyl-2-(4′,8′,12′-trimethyltridecyl-1)-chroman-5,6-quinone (III) was prepared by nitric acid oxidation of α-tocopherol,[4] but the product could not be obtained sufficiently pure to give well-defined waves.

Discussion of Results

The current–voltage curves for α-tocopherylquinone (I) in 75% ethanol solution were determined in two different buffers. In 0.05 *M* sodium acetate–0.05 *M* acetic acid (*p*H, 6.24) the half-wave potential was −0.158 v. (*vs.* S. C. E.) and i_d/c was 2.90 microamperes per millimole per liter (Fig. 1B). In 0.1 *M* aniline–0.1 *M* anilinium perchlorate (*p*H 4.02), the half-wave potential was −0.042 v. and i_d/c was 3.02 microamperes per millimole per liter (Fig. 1A). The change in half-wave potential, per unit change of *p*H, was 0.0523 v. in the *p*H range between 4.02–6.24, which agreed fairly well with the theoretical value of 0.0591 for reversible quinone–hydroquinone systems. Analysis of the current–voltage curves

(1) Paper XXXV, THIS JOURNAL, **64**, 447 (1942).
(2) Smith, Spillane and Kolthoff, Paper XXXV, *ibid.*, **64**, 447 (1942).
(3) Smith, Kolthoff, Wawzonek and Ruoff, *ibid.*, **63**, 1018 (1941).
(4) Smith, Irwin and Ungnade, *ibid.*, **61**, 2424 (1939).
(5) Tishler and Wendler, *ibid.*, **63**, 1532 (1941).
(6) Willstätter and Pfannenstiel, *Ber.*, **37**, 4744 (1904).

also agreed well for the reversible transfer of two electrons.

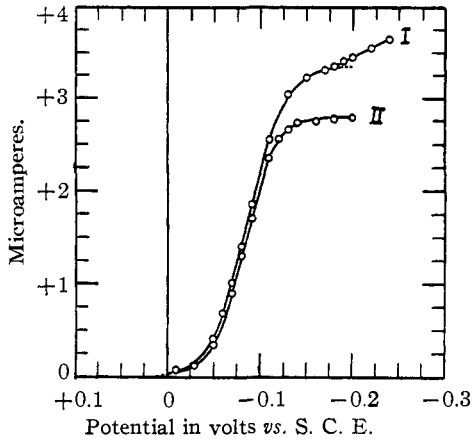
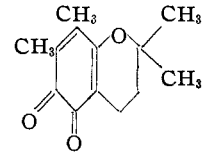


Fig. 2.—Current–voltage curve of 2,2,7,8-tetramethylchroman-5,6-quinone in 0.05 *M* NaOAc–0.05 *M* HOAc in 75% ethanol (corrected for *iR*).



Curve	M. p., °C.	Concn., $M \times 10^3$	i_d, microamp.	$\pi_{1/2}$, cor. for *iR*
I	107–108	0.718	3.30	−0.078
II	103–106	0.672	2.79	−0.078

The current–voltage curve of the ortho-quinone II in the acetate buffer is shown in Fig. 2. The half-wave potential (cor. for *iR*) was −0.078 v. (*vs.* S. C. E.) and i_d/c for the product melting at 107–108° was 4.60 microamperes per millimole per liter. The value for i_d/c of this ortho-quinone is markedly higher than the value (3.49) for the para-quinone obtained from the same chroman.[7] In the more acid aniline–anilinium perchlorate buffer, decomposition was so rapid that a current–voltage curve could not be obtained.[8]

(7) Ref. 3, p. 1021.

(8) A rapid decomposition, in the aniline–anilinium perchlorate buffer, is also shown by benzohydroquinone and current-voltage curves for this hydroquinone cannot be obtained in this buffer (see ref. 2).

It would be expected that the half-wave potential of the ortho-quinone III, derived from α-tocopherol, would correspond very closely to that of II. Unfortunately the red quinone III could not be obtained sufficiently pure to yield conclusive results. Although the current–voltage curves showed no well-defined waves in the acetate buffer, an approximate value of −0.073 v. (*vs.* S. C. E.) was obtained for the half-wave potential. This is in close agreement with the value of −0.078 obtained for II in this buffer (Fig. 3).

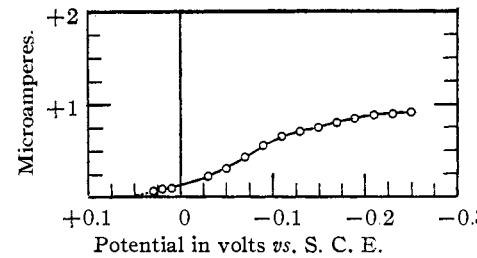


Fig. 3.—Current–voltage curve of (III), red oxidation product of α-tocopherol in 0.05 *M* NaOAc–0.05 *M* HOAc in 75% ethanol.

Concn., $M \times 10^3$	i_d, microamp.	$\pi_{1/2}$, cor. for *iR*., v.
0.946	0.90	−0.073

Summary

α-Tocopherylquinone gives well-defined current–voltage curves at the dropping mercury cathode in buffered 75% ethanol solutions.

2,2,7,8-Tetramethylchroman-5,6-quinone, the first ortho-quinone to be studied polarographically, gives well-defined waves in 75% ethanol solution buffered with acetic acid and sodium acetate. The half-wave potential was found to be independent of the concentration.

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