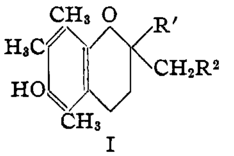
[Contribution from the School of Chemistry of the University of Minnesota]

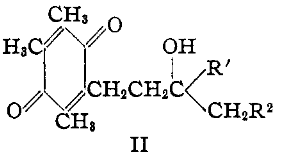
The Chemistry of Vitamin E. XVII. The Oxidation Products of α-Tocopherol and of Related 6-Hydroxychromans[1]

By Lee Irvin Smith, Willa B. Irwin and Herbert E. Ungnade

When α-tocopherol (I, R^1 = CH_3; R^2 = $C_{16}H_{31}$), 2,2,5,7,8-pentamethyl-6-hydroxychroman (I, R^1 = CH_3; R^2 = H) and similar substances are oxidized by ferric chloride, gold chloride or, under certain circumstances by silver nitrate, the products are yellow para-quinones, II.[2]



I



II

When, however, the action of silver nitrate is prolonged, the oxidation proceeds beyond the yellow para-quinone stage and brilliant red solutions are obtained.[2,3] Red solutions also result when nitric acid is used as the oxidizing agent, and Furter and Meyer[4] have developed an elegant photometric method of analysis for tocopherols based upon the production of these red solutions with nitric acid. This reaction has been extended in this Laboratory to para hydroxy coumarans and chromans in general.[5]

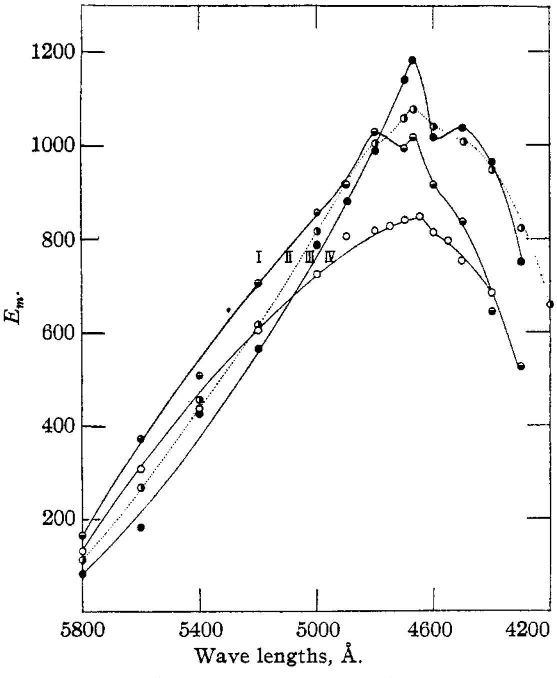


Fig. 1.—◒, Curve I, pure $C_{13}H_{16}O_3$ (IV) m. p. 109–110° in 5 cc. abs. ethanol + 1 cc. concd. HNO_3; ◑, Curve II, $C_{13}H_{16}O_3$ (IV) m. p. 107.5–108.5° from $AgNO_3$ method in abs. ethanol; ●, Curve III, pure $C_{13}H_{16}O_3$ (IV) in absolute ethanol; ○, Curve IV, further reaction on pure 2,2,5,7,8-pentamethyl-6-hydroxychroman.

We have obtained, from the chroman I (R^1 = CH_3, R^2 = H), the same red crystalline compound using either silver nitrate or nitric acid as the oxidizing agent. The substance forms brilliant red needles which have a melting point (and mixed melting point) of 109–110°.[6] These results show that this compound, m. p. 109–110°, is the substance responsible for the color in the Furter and Meyer reaction with the pentamethylchroman. This is also shown by the curves in Fig. 1. In these curves, the molecular extinction coefficient, E_m, is plotted against the wave length in Ångström units. Curve IV represents the data obtained when the pentamethylchroman was analyzed photometrically by the method of Furter and Meyer; curve III represents the data for the pure (m. p. 109–110°) red substance in absolute ethanol; curve II represents the data for a slightly less pure specimen (m. p. 107.5–108.5°, obtained by silver nitrate oxidation of the chroman) in absolute ethanol, while curve I was obtained using a solution of the pure substance (m. p. 109–110°) in absolute ethanol (5 cc.) containing nitric acid (1 cc.) in the proportions in which they are used in the photometric method of analysis. Comparison of the curves shows that the effect of the nitric acid is to decrease the maxima at 4670 and 4500 Å. (curve III) and to produce a new maximum at 4800 Å. (curve I). These effects, however, are not sufficient to account for the curve obtained in the Furter reaction (curve IV), and it appears that in the Furter reaction the yield of the red compound is not quantitative, due either to incomplete reaction or to the slow destruction of the red compound by the nitric acid, a reaction which is known to occur. How-

---

[1] (a) XVI, *Science*, in press (1939); (b) XV, *J. Org. Chem.*, **4**, 298 (1939).

[2] (a) John, Dietzel and Emte, *Z. physiol. Chem.*, **257**, 173 (1939); (b) Karrer, Fritzsche and Escher, *Helv. Chim. Acta*, **22**, 661 (1939).

[3] Evans, Emerson and Emerson, *Science*, **88**, 38 (1938).

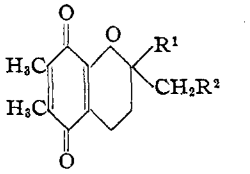
[4] Furter and Meyer, *Helv. Chim. Acta*, **22**, 240 (1939); see also ref. 2b.

[5] Paper XV in this series, ref. 1b.

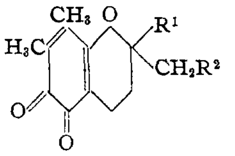
[6] John, Dietzel and Emte, ref. 2a, give the m. p. as 109°.

ever, the reproducibility of the Furter and Meyer reaction under standard conditions is very good.

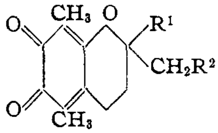
John and his associates[2a] established that the red compounds differed in composition from the para-quinones II by one carbon atom and four hydrogen atoms; thus the red compound from the pentamethylchroman had the composition $C_{13}H_{16}O_3$, and Karrer and his associates[2b] established that there was a similar change in composition when the quinone (II, $R^1 = R^2 = H$) from 2,5,7,8-tetramethyl-6-hydroxychroman (I, $R^1 = R^2 = H$) was converted into the analogous red compound $C_{12}H_{14}O_3$, m. p. 140°. In their recent paper, Karrer, Fritzsche and Escher[2b] have shown that the red compound obtained from 2,5,7,8-tetramethyl-6-hydroxychroman (I, $R^1 = R^2 = H$) contains no active hydrogen atoms and that it is a quinone, for on reduction it absorbs two atoms of hydrogen to give a colorless hydroquinone. They have proposed a tentative structure for this red compound, which by analogy would become III ($R^1 = CH_3$; $R^2 = H$) when applied to the pentamethylchroman I ($R^1 = CH_3$; $R^2 = H$).



III



IV



V

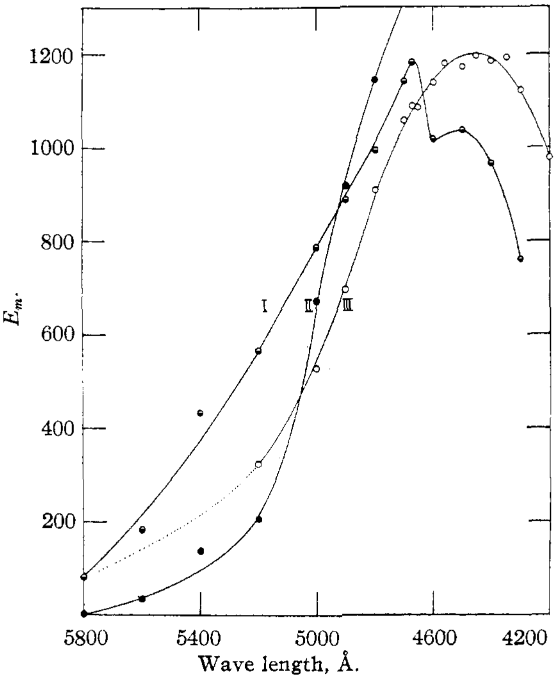


Fig. 2.—◐, Curve I, $C_{13}H_{16}O_3$ (IV), m. p. 109–110°, in absolute ethanol; ●, Curve II, β-lapachone in absolute ethanol; ○, Curve III, tetramethyl-*o*-benzoquinone.

The red substance, however, is not a para-quinone, but is an ortho-quinone. First of all, the red color is in itself a strong argument against such a formulation as III. It has been shown by Hooker and his associates, in a series of remarkable papers, that in the naphthoquinone series all of the hydroxy-α-quinones and the chromans and coumarans derived from them are yellow, the only exceptions being those 2-hydroxy-α-naphthoquinones with a side chain in the 3-position containing a double bond α,β- to the ring—these, and only these, are red, whereas *all* of the derivatives of 4-hydroxy-β-naphthoquinone, as well as the chromans and coumarans derived from them, are red.[7] In Fig. 2 are given the absorption curves for the red compound (pure; m. p. 109–110°) in ethanol, together with curves for two known ortho-quinones—tetramethyl-*o*-benzoquinone[8] and β-lapachone.[9] The curves for the red compound (curve I) and tetramethyl-*o*-benzoquinone (curve III) show good agreement, particularly with respect to the molecular extinction coefficient at the maximum. The shift of the maximum from about 4460 Å. in curve III to 4670 Å. in curve I may be ascribed to the 6-membered hetero ring, because this maximum is characteristic of the red oxidation products of all 6-hydroxychromans which have so far been investigated. The curves reported previously for the red solutions obtained in the Furter reaction from 5-hydroxycoumarans[1b] show a maximum at 4400 Å., which agrees well with an *o*-quinone structure as for instance with tetramethyl-*o*-benzoquinone. Our absorption curve for β-lapachone (curve II, Fig. 2) does not allow for inferences as to structural units, because the range of our instrument was not sufficiently great to include all of the significant parts of the curve. However, while this work was under way, Cook, Macbeth and Winzor[10] have pub-

---

[7] Hooker, *et al.*, THIS JOURNAL, **58**, 1163, 1168, 1179, 1181, 1198, 1202 (1936). References to previous work by Hooker are given in these papers. See also Fieser, *ibid.*, **49**, 857 (1927).

[8] Smith and Hac, *ibid.*, **56**, 477 (1934).

[9] The authors are greatly indebted to Dr. L. F. Fieser for generous samples of β-lapachone and lapachol.

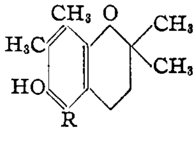
[10] Cook, Macbeth and Winzor, *J. Chem. Soc.*, 878 (1939).

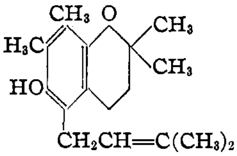
lished the results of a thorough investigation of the absorption spectra of some naphthoquinones and their derivatives. They conclude that a maximum of about 4000–4400 Å. is characteristic of ortho-naphthoquinones, while it is absent in the para-quinones. Our curve for β-lapachone is identical with theirs in the range accessible to us. The location of the characteristic maximum in ortho-benzo- and β-naphtho-quinones is not identical, but involves a slight shift to the longer wave lengths in the case of the benzoquinones, which accounts for the deeper color of these substances. The fact that the red oxidation products absorb most strongly in the region of 4500 Å. may be taken as good evidence that the o-quinoid structure is present.

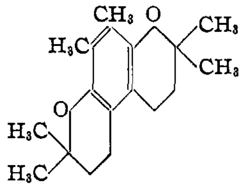
On the chemical side, the results are decisively in favor of the o-quinoid structure IV for these red oxidation products. The red substance, m. p. 109–110° (IV, $R^1 = CH_3$; $R^2 = H$), forms a phenazine with m. p. 151–152° with o-phenylenediamine, and a tetramethylphenazine of m. p. 204–205° with tetramethyl-o-phenylenediamine. These phenazines are yellow and their alcoholic solutions show a pale green fluorescence; in ultraviolet light the fluorescence is quite brilliant.[11] Hooker found that most of the azines of the lapachol group exhibited this greenish fluorescence. The phenazine from tetramethyl-o-benzoquinone[8] also exhibits a strong green fluorescence in ultraviolet light although this is lacking in ordinary light. When reduced the bright red solution of IV ($R^1 = CH_3$; $R^2 = H$) becomes completely decolorized in a few minutes. The reduction product, however, is oxidized in the air with extreme rapidity—so rapidly that the compound becomes reoxidized and the solution turns bright red before the insoluble material (catalyst, zinc, etc.) can be filtered off.

In order to prove structure IV, it was necessary to locate definitely the position occupied by the methyl group eliminated in the conversion of the quinone II to the red compound IV. This methyl group must be one of those in the benzene ring, for Karrer, Fritzsche and Escher showed that 2,5,7,8-tetramethyl-6-hydroxychroman (I, $R^1 = R^2 = H$) gave a red compound $C_{12}H_{14}O_3$ which was a lower homolog of IV, $C_{13}H_{16}O_3$. Since all of the substituents in the benzene ring of the pentamethylchroman are alike, structure V for the red compound, although improbable, is not rigidly excluded.

It is obvious that, if structure IV is correct, the same red compound must result from any 6-hydroxychroman of the type of VI. Accordingly, o-xylohydroquinone was condensed with isoprene. The product was a mixture, as is usual in these condensations when the hydroquinone possesses more than one vacant position ortho to the hydroxyl groups. Unchanged hydroquinone was removed from this product by extraction with aqueous sodium hydroxide, and the insoluble portion was then separated by extraction with Claisen's alkali into (a) a phenolic constituent, the chroman VI, $R = H$, possibly containing also the chroman VII and (b) a non-phenolic constituent, the double chroman VIII. These materials were not further purified, but were subjected directly to oxidation, the non-phenolic constituent by silver nitrate, and the phenolic constituent by nitric acid under the conditions of the Furter reaction. *Both of these substances gave in excellent yield, the same red compound IV*, m. p. and mixed m. p. 109–110°. In fact, the red compound from the phenolic constituent melted at 109.5–110.5°, the highest melting point so far recorded for this compound. It is thus apparent that the group eliminated in these oxidations of 6-hydroxychromans is the one in the 5-position, and that this reaction will occur even though both oxygen atoms of the hydroquinone are involved in heterocyclic systems; furthermore, when hydrogen occupies the 5-position, the composition of red compound IV will be that of the quinone II minus two hydrogen atoms only.


VI


VII


VIII

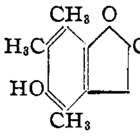
α-, β- and γ-tocopherols give deep red compounds when they are oxidized by nitric acid in alcohol solution. These substances are obtained in good yield, but they are oils which we have so far been unable to crystallize. The red oil (IV,

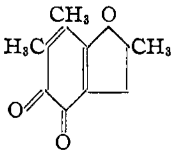
---

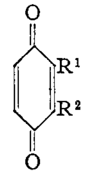
(11) Hooker, *J. Chem. Soc.*, **63**, 1376 (1893).

$R^1 = CH_3$; $R^2 = C_{15}H_{31}$)[12] from α-tocopherol (I, $R^1 = CH_3$; $R^2 = C_{15}H_{31}$) gives a phenazine, which is also an oil, but which shows the same strong green fluorescence in ultraviolet light as is shown by the simpler phenazine of IV ($R^1 = CH_3$; $R^2 = H$).[13]

Formation of the red ortho quinones by oxidation is not limited to 6-hydroxychromans. It has been shown by Furter[14] and in a previous paper from this Laboratory[1b] that the reaction occurs also in the case of 5-hydroxycoumarans such as IX. By analogy the red compounds derived from these substances would have structures such as X, although this point has not yet been investigated thoroughly.


IX


X


XI

With regard to the mechanism whereby these red compounds are produced from the chromans (I) and the related quinones (II), it is not possible at present to do more than speculate. Certain facts, however, have been discovered which must be taken into account in formulating a mechanism; since these facts have a bearing upon the applicability of the Furter and Meyer method of photometric analysis, they are given here.

An alcohol or possibly a phenol is necessary as a solvent in order to produce the red solutions from the tocopherols and related substances. Using 2,4,6,7-tetramethyl-5-hydroxycoumaran (IX) as the test substance, red solutions were obtained in methanol, ethanol, 2-propanol, *t*-butyl alcohol, and mesitol. The *intensity* of the color developed in the alcohols in a given time, however, decreased in the order they are named—that is, primary alcohols were more effective than secondary, and these more so than tertiary. Red solutions are not formed in petroleum ether, acetic acid, or acetone, although Furter and Meyer observed that a mixture of ethanol and acetone could be used in the case of the tocopherols. It appears from these results that alcohols are essential for the production of the red color, and this leads to the suspicion that the alcohol plays the role of a reagent as well as that of a solvent in the reaction, especially when taken along with the fact that acetone (negative) is the oxidation product of isopropyl alcohol (positive). There is definite evidence that the alcohol is oxidized during the reaction: in methanol, formaldehyde was detected, and in ethanol, acetaldehyde. Naturally these oxidation products might have been produced by the nitric acid in the absence of any substance capable of giving a red solution, but it is perhaps significant in this connection that the color in *t*-butyl alcohol was developed *very* much more slowly than in the other three alcohols tested, and all of the solvents giving negative results are substances quite resistant to the action of nitric acid over fairly short periods of time.

As to the nature of the substances capable of giving the red colors, the following can now be added to those previously reported:[1b,4] *m*-xylotocopherol (synthetic), 2,4,6-trimethyl-7-allyl-5-hydroxycoumaran, *o*-allyl-*p*-aminophenol, tetramethyl-*o*-benzohydroquinone, catechol, and the substances described in this paper. The positive reaction with catechol is important in connection with the Furter and Meyer method of analysis for tocopherols when applied to preparations or concentrates obtained from natural sources, for catechol derivatives are very common among certain classes of natural products. In the case of the *o*-quinones and catechol the red color is developed in the cold, as soon as the nitric acid is added, but it fades to yellow on standing, a behavior which also is shown by the red *o*-quinones such as IV, although here the color persists for a day or so. These substances did not give a red color under the conditions of the Furter and Meyer reaction: duroquinone, trimethylethylquinone, 2,5,7,8-tetramethyl-6-hydroxychromone, 2,4,5-trimethyl-3,6-diacetoxybenzyl chloride, trimethyl-(β-carboxy ethyl)-*p*-benzoquinone, mesitol.

When the results obtained from all of the compounds so far tested are assembled, they lead to the conclusion that if the heterocyclic compound can be oxidized readily to a quinone of type XI (vacant positions may be occupied by alkyl or substituted alkyl groups), *a positive reaction* (formation of a red ortho quinone of type IV, with elimination of the group R^2) will occur when the group R^1 is any of the following:

(a) $-CH_2CH_2CH(OH)CH_3$
(b) $-CH_2CH_2C(OH)(CH_3)_2$
(c) $-CH_2CHOHCH_3$
(d) $-CH(CH_3)CHOHCH_3$
(e) $-CH(C_2H_5)CHOHCH_3$
(f) $-CH_2CH_2C(OH)(CH_3)R$
(g) allyl

---

[12] Dr. H. M. Evans has assayed this red oil for vitamin E activity; it is inactive at 3 and 6 mg. doses.

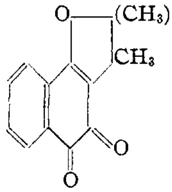
[13] Furter and Meyer[4] carried out this reaction with α- and β-tocopherols; our experiments were limited to α- and γ-tocopherols.

[14] Private communication.

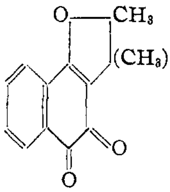
No red color will result when R^1 is in any of the following:

(a) $-CH_2CH_2COOH$ (b) $-CH{=}C(COOH)COOC_2H_5$
(c) $-CH_2COCH_3$ or the tautomeric form $-CH{=}C(OH)CH_3$
(d) $-COCH_2COCH_3$ or the tautomeric forms
(e) $-CH_2Cl$ (f) CH_3 (g) C_2H_5

It is interesting in connection with structure IV for the red compounds that Price and Robinson[15] have investigated a naturally occurring *red* pigment, dunnione, for which they propose structure XII or XIII, and that as a result of their study of the absorption spectra of naphthoquinone derivatives, Cook, Macbeth and Winzor[10] agree with Price and Robinson that dunnione is either XII or XIII.



XII



XIII

Experimental Part[16]

The apparatus and procedure used for obtaining the absorption curves have been described in a previous paper.[1b]

2,2,7,8-Tetramethylchroman-5,6-quinone (IV, R^1 = CH_3; R^2 = H).—A solution of 2,2,5,7,8-pentamethyl-6-hydroxychroman (I, R^1 = CH_3; R^2 = H) (500 mg.) in absolute ethanol (500 cc.) and concd. nitric acid (100 cc.) was warmed for ten minutes on the steam-bath. The solution was cooled rapidly, diluted with water (1800 cc.) and extracted thoroughly with ether (six times). The combined extracts were washed with water until the washings were neutral to litmus, then once with dilute sodium carbonate and finally twice with water. The ether was removed on the steam-bath, the last traces being taken off under reduced pressure. The residue solidified to a red solid which was crystallized, first from petroleum ether (b. p. 28–38°) and then from ether–petroleum ether. The substance formed red needles which melted at 109–110° and which did not depress the melting point of a specimen made by the action of silver nitrate upon the chroman according to the directions of John.[2a]

The red compound forms deeply colored, red-violet solutions with cold, concd. hydrochloric acid, cold concd. sulfuric acid, or with hot dilute aqueous alkali. When hydrochloric acid is used, the solution finally deposits a brown amorphous solid melting above 200°. This brown solid gives a yellow solution in ether and a deep red solution in alcohol. All of these yellow and colorless transformation products are very soluble and so far we have not been able to isolate any pure compounds from them. These color changes with acids and alkali parallel strongly those observed by Hooker[17] in the lapachol series when an *o*-quinone of the type of IV (red) was transformed, by opening the hetero ring and recyclizing, into a *p*-quinone of type III (yellow), and the new pigment, dunnione, shows a similar series of color changes under the same circumstances.[10]

Phenazine.—The crude, moist quinone (0.43 g.) was dissolved in acetic acid (25 cc.) and warmed on the steam-bath. To this solution was added *o*-phenylenediamine (0.25 g.) and the solution was heated for ten minutes. It was then diluted with water to incipient cloudiness, and cooled. The fine yellow needles (0.11 g.) were removed and crystallized twice from dilute acetic acid. The substance formed glistening yellow needles which melted at 151–151.5°; the compound could be sublimed *in vacuo*, but this did not result in a higher melting point.

Anal. Calcd. for $C_{19}H_{20}ON_2$: C, 78.08; H, 6.85; N, 9.59. Found: C, 77.43; H, 7.10; N, 9.51.

Tetramethylphenazine.—To a boiling solution of the red quinone (50 mg.) in acetic acid (2 cc.) was added a solution of prehnitenediamine hydrochloride (60 mg.) in acetic acid (5 cc.) containing a crystal of sodium acetate. On cooling, a yellow granular solid precipitated, which was removed and crystallized twice from acetic acid. It melted at 204–205°, but the amount of it was too small to crystallize to analytical purity.

Anal. Calcd. for $C_{23}H_{28}ON_2$: C, 79.31; H, 8.05. Found: (2 mg. sample) C, 77.1; H, 8.04.

In ultraviolet light, these phenazines show a powerful green fluorescence, which is visible, though much fainter, even in daylight. Neither of these phenazines gives a positive phenol test (Folin). When, however, the phenazine of m. p. 151–151.5° is reduced catalytically (platinum oxide), the colorless solution gives a positive phenol test. The colorless solution of the reduction product is reoxidized rapidly in the air.

Bisulfite Reduction of IV.—When shaken with 20% aqueous sodium bisulfite, the red quinone dissolved, giving a pale straw colored solution. Acidification and boiling to remove sulfur dioxide regenerated the deep red color; similarly, the red color reappears on boiling with a little nitric acid or alkali. In the latter case, the solution becomes red, then purple.

Reaction of IV with Alkali.—The quinone IV (1.7 mg.) was added to potassium hydroxide solution (1 cc., 5%). On warming, the solution became deep violet. It was boiled for ten seconds, then cooled and acidified with acetic acid (0.2 cc.). The color at once became yellow. Water was added and the solution was extracted with ether. Evaporation of the ether left an oil, soluble in benzene and insoluble in petroleum ether. This oil gave a positive phenol test but it could not be crystallized.

Cleavage of IV.—When the red quinone was boiled with acetic acid, potassium acetate and hydrogen peroxide (3%), the solution decolorized completely. An attempt was made to isolate the cleavage product as the barium salt, but no product could be obtained.

Addition of Isoprene to *o*-Xylohydroquinone.—Isoprene (2.2 cc.) was added to a hot solution of the hydroquinone

---

[15] Price and Robinson, *Nature*, **142**, 147 (1938).

[16] Microanalyses by J. W. Opie, C. O. Guss and H. H. Hoehn.

[17] Hooker, THIS JOURNAL, **58**, 1202, 1207 (1936); *J. Chem. Soc.*, **65**, 76, 321, 717 (1894).

(2.5 g.) and zinc chloride (0.5 g.) in acetic acid (25 cc.). The mixture was allowed to stand for thirty minutes, a drop of sulfuric acid was added, and it was then refluxed for thirty minutes. The cooled solution was poured into water and extracted with petroleum ether. The extract was washed with water, and then extracted exhaustively first with aqueous sodium hydroxide (5%) and then with Claisen's alkali. The petroleum ether layer was then washed with water and dried.

From the aqueous alkali extractions, carbon dioxide precipitated a gummy solid (300 mg.), principally unchanged hydroquinone. Acidification and extraction of the Claisen's alkali extract gave 700 mg. of a brown, viscous oil. This was the chroman VI (R = H), possibly containing the chroman VII. The original petroleum ether solution, after extraction, yielded 700 mg. of a viscous oil, the double chroman VIII.

Oxidation of the Non-phenolic Constituent (VIII).—This material (700 mg.) was dissolved in absolute ethanol (35 cc.) and the solution was refluxed with silver nitrate (5 g.) for an hour and forty-five minutes. It was then diluted with water and extracted with ether. Removal of the ether left a red oil which was taken up in petroleum ether. This solution, on cooling, deposited the red quinone IV, m. p. and mixed m. p. 109–110°.

Oxidation of the Phenolic Constituents (VI and VII).—This material (700 mg.) was dissolved in absolute ethanol (500 cc.) and nitric acid (100 cc.) was added. The solution was heated on the steam-bath for fifteen minutes, then diluted with ice water (3000 cc.) and cooled to 0°. The cold solution was extracted exhaustively with ether and the extracts were washed free from acid. Removal of the ether left a red oil (400 mg.) which was taken up in ether–petroleum ether and crystallized. The product was the red quinone IV, m. p. 109.5–110.5°; mixed m. p. 109–110°.

Oxidation of α-Tocopherol; 2,7,8-Trimethyl-2-(4′,8′,12′-trimethyltridecyl-1)-chroman-5,6-quinone (IV, R = $C_{15}H_{31}$).—To a solution of synthetic *dl*-α-tocopherol (1.190 g.) in absolute ethanol (1190 cc.) was added concd. nitric acid (238 cc.). The solution was heated on the steam-bath for twenty-five minutes, then cooled and diluted with a large excess of ice water (3000 cc.). The mixture was extracted with ether, and the extracts were washed with water until free from acid. After drying the ethereal solution, the solvent was distilled off. The residue was a red oil which could not be crystallized.[18]

Phenazine.—The red oil from oxidation of α-tocopherol (0.225 g.) was dissolved in acetic acid (4.5 cc.) and *o*-phenylenediamine (0.159 g.) was added. After standing for three and a half hours, excess water was added and the product was extracted with a mixture of ether and petroleum ether. The extracts were washed with water and dried over sodium sulfate. The dry solution was chromatographed, using a column of Brockman alumina. The bulk of the material appeared in a wide yellow zone which fluoresced strongly in ultraviolet light. This zone was cut out and eluted with ether. The yellow ethereal solution showed a strong greenish fluorescence both in daylight and in ultraviolet light. The solvent was removed, but the residue was an orange oil which could not be crystallized.

Summary

1. When 6-hydroxychromans are oxidized by silver nitrate or by nitric acid, the products are red chroman-5,6-quinones. Any group in the 5-position of the hydroxychroman is eliminated in this reaction. Certain facts having a bearing on the mechanism of this reaction are reported.

2. The structure of the *o*-quinone from 2,2,5,7,8-pentamethyl-6-hydroxychroman has been proved by synthesizing it from derivatives of *o*-xylohydroquinone.

3. Certain similarities between the absorption spectra of these red compounds and known ortho quinones are discussed.

4. The quantitative aspects of the photometric method of Furter and Meyer are discussed, and the limits of the reaction have been further defined and extended. It is pointed out that catechol derivatives, if present, may interfere.

5. The red chroman-5,6-quinone from α-tocopherol is an uncrystallizable oil. Evidence is presented to show that this substance forms a phenazine, although the latter is also an oil.

MINNEAPOLIS, MINN. RECEIVED JULY 10, 1939

---

[18] Professor Furter, in a private communication, states that he also was unable to purify this compound.