gave the acetoxychroman (100 mg., 44%) which melted at 69–71.5°. The analytical sample, prepared by crystallizing the material three times from petroleum ether (b. p. 28–38°), melted at 70.5–71.5°.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.64; H, 8.14.

2,2,7,8-Tetramethyl-6-hydroxychroman (I).—Hydrochloric acid (2 cc.) was added to a solution of the above acetate (190 mg.) in methanol (20 cc.). The mixture was allowed to stand for two days and then poured into water. The oil was removed by ether extraction, the ether solution was washed with aqueous sodium bicarbonate (5%) and then with water. Removal of the solvent left an oil which was crystallized from petroleum ether (b. p., 28–38°). The chroman I (110 mg. 70%) melted at 83–84.5°. A sample, recrystallized from petroleum ether (b. p. 28–38°) (Norite) several times, melted at 84.5–85.5°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.42; H, 8.81.

A mixture of the carbinol VII (from 0.21 mole of ketone VI), hydrobromic acid (20 cc., 48%), and acetic acid (60 cc.), was boiled for four hours. The solution was poured into water and extracted with ether. The ether solution was washed with aqueous sodium bicarbonate (5%) and then with water. Removal of the ether left an oil which, when crystallized from dilute methanol (Norite) gave the chroman I (2.5 g., 50% based upon the ketone VI) melting at 84–85°.

2,2,7,8-Tetramethyl-5,6-chromanquinone (II).—A mixture of the chroman I (500 mg.), dry ethanol (35 cc.), and silver nitrate (5 g.) was boiled for one hour and twenty minutes. The red solution was poured into water (300 cc.) and the mixture was extracted five times with ether. The combined ether solutions were washed with water and dried (sodium sulfate). Removal of the ether under reduced pressure at room temperature left a red oil which, when crystallized from ether at the temperature of Dry Ice gave the red *o*-quinone II (140 mg., 26%) melting at 100–107°. Three more crystallizations from ether gave 80 mg. of red crystals which melted at 109.5–110.5°.[3]

The successful synthesis of the hydroxychroman I suggested a possible independent synthesis of the red *o*-quinone II *via* the 5-nitroso compound of I, a tautomer of the 5-oxime of II, but this nitroso compound could not be prepared. A mixture of butyl alcohol (1 cc.), water (2 cc.), sodium nitrite (104 mg.) and sulfuric acid (1 drop) was shaken for three minutes. The alcohol layer was separated, washed once with water (1 cc.) and poured into a solution of the chroman I (150 mg.) in acetic acid (5 cc.) containing a drop of sulfuric acid. The solution soon became red. It was allowed to stand overnight and then was poured into water and extracted with ether. The ether solution was dried (sodium sulfate) and the ether was removed, finally under reduced pressure. The resulting red oil could not be crystallized.

Summary

1. 2,2,7,8-Tetramethyl-6-hydroxychroman, I, has been prepared in a pure state by an unequivocal synthesis. This chroman is a white solid which melts at 84.5–85.5°, and which is converted to the red *o*-quinone II in 26% yield when it is oxidized by action of silver nitrate in ethanol.

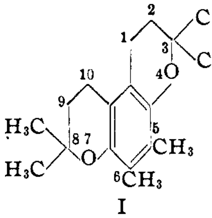
MINNEAPOLIS 14, MINNESOTA RECEIVED JUNE 2, 1944

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

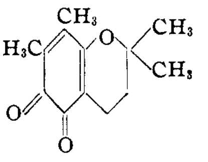
Vitamin E. XLIV.[1] Synthesis of 3,3,5,6,8,8-Hexamethylbenzo[1,2-b,4,3-b']dipyran,[2] and its Behavior upon Oxidation

BY LEE IRVIN SMITH AND ROY W. H. TESS[3]

It was stated in a previous paper[4] that the double chroman I, when oxidized by action of silver nitrate in ethanol, gave the red *o*-quinone II.



I



II

But the substance actually oxidized was the alkali-insoluble fraction of an oil obtained by condensation of *o*-xylohydroquinone with isoprene. As stated in the preceding paper,[1] some questions have arisen concerning the validity of certain statements made with reference to the formation of the red *o*-quinones from *p*-hydroxychromans, and it was therefore decided to prepare a pure specimen of I and to re-investigate its behavior toward alcoholic silver nitrate.

The double chroman I was prepared in yields of 63–84% by condensation of *o*-xylohydroquinone with isoprene according to methods previously published.[5] Practically no material insoluble in Claisen alkali resulted from this condensation, and the chroman I was isolated as a white solid melting at 102.5–103.5°. Contrary to the previous report,[4] the chroman I was recovered unchanged even when its solution in ethanol was boiled with silver nitrate for seven hours; no red color was produced, and no II whatever was formed. Oxidation of I by action of nitric acid in ethanol gave a red solution in a few minutes; however, no II could be isolated from the resulting red oil. When the red oil was adsorbed from carbon tetrachloride on Brockmann alumina, and the column then eluted with ethanol, the product was a red oil which formed a yellow solution in petroleum ether, and from which only a few crystals of a dull red solid could be isolated. This material was not the red *o*-quinone II.

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(1) Paper XLIII, THIS JOURNAL, **66**, 1523 (1944).

(2) This ring system is not represented in the Ring Index; the system most nearly resembling it is No. 1984.

(3) Abstracted from a thesis by R. W. H. Tess, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, March, 1944.

(4) Smith, Irwin and Ungnade, THIS JOURNAL, **61**, 2424 (1939).

(5) (a) Smith, Ungnade, Hoehn and Wawzonek, *J. Org. Chem.*, **4**, 311 (1939); (b) Smith and King, THIS JOURNAL, **65**, 441 (1943).

Experimental Part[6]

3,3,5,6,8,8-Hexamethylbenzo[1,2-b,4,3-b']dipyran (I).[2]—A mixture of *o*-xylohydroquinone (1 g.), zinc chloride (0.67 g., freshly fused), and acetic acid (25 cc.) was heated until the solids dissolved. The solution was cooled, and isoprene (2 g.) in acetic acid (10 cc.) was added. The mixture was allowed to stand for one hour at room temperature, and then was boiled for one hour. Sulfuric acid (2 drops) was added and the mixture was boiled for another hour. The mixture was poured into water and the oil was taken up in petroleum ether (b. p. 60–68°). Extraction of this solution successively with aqueous sodium bicarbonate (5%), aqueous sodium hydroxide (5%), and Claisen alkali, removed no material. Evaporation of the petroleum ether left an oily solid which was crystallized from methanol. The product then weighed 1.25 g. (63%). After several crystallizations from methanol, the substance melted at 102.5–103.5°.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.90; H, 9.82.

The same product was obtained in 84% yield in a duplicate of the above experiment, except that the reaction mixture was allowed to stand at room temperature for one week instead of being heated.

Silver nitrate (2.5 g.) was added to a solution of the chroman I (0.35 g., m. p. 93–101°) in dry ethanol (20 cc.), and the solution was boiled. The solution slowly acquired a yellow color; after seven hours, the solution (pale yellow) was poured into water and extracted with ether. The ether extracts were washed successively with water, aqueous sodium bicarbonate (5%), and water. Evaporation of the ether left a solid residue which, on crystallization from aqueous methanol, gave the chroman I (0.26 g.), m. p. and mixed m. p., 93–98°. Nitric acid (20 cc., 16 *N*) was added to a solution of the chroman I (150 mg.) in dry ethanol (100 cc.) and the solution was warmed on the steam-bath. After a few seconds, a red color developed; after ten minutes, the solution was poured into water and extracted with ether. The ether extracts were washed with water and dried (sodium sulfate). Removal of the ether left an orange-red oil. This was taken up in carbon tetrachloride and the solution was poured through a column of Brockmann alumina. The upper brown zone was eluted with ethanol; evaporation of the solvent left a red oil (80 mg.) which slowly dissolved in boiling petroleum ether (b. p. 60–68°) forming a yellow solution. This solution was concentrated to about 5 cc. and cooled; about 10 mg. of a dull red solid was deposited. This solid had an indefinite melting point, but it was completely liquid at 94°. No other solid could be obtained from the reaction product.

Summary

1. The double chroman I, a dipyrano-*o*-xylene, has been prepared in a pure state as a white crystalline solid melting at 102.5–103.5°. Contrary to the previous report, this substance is unattacked by action of silver nitrate in ethanol. However, the substance is attacked by action of nitric acid in ethanol, but no red *o*-quinone II could be isolated from the resulting red oil.

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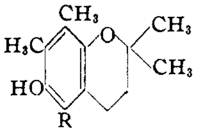
[6] Micro analyses by Stanley T. Rolfson.

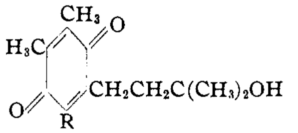
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Vitamin E. XLV.[1] Synthesis of 2,2,7,8-Tetramethyl-5-benzyl-6-hydroxychroman, and its Behavior upon Oxidation

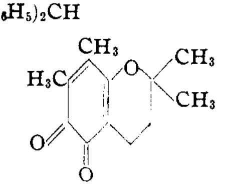
BY LEE IRVIN SMITH AND ROY W. H. TESS[2]



I, R = CH_3
II, R = $C_6H_5CH_2$
III, R = $(C_6H_5)_2CH$



IV, R = CH_3
V, R = $C_6H_5CH_2$



VI

It has been shown[3] that oxidation of the tocopherols and other *p*-hydroxychromans and -coumarans by a wide variety of reagents produces yellow *p*-quinones; thus, the quinone IV is produced from the *p*-hydroxychroman I. These yellow *p*-quinones can be reduced to hydroquinones, and the latter can be cyclized, regenerating, in most cases, the original heterocyclic compound. When silver salts, or nitric acid under carefully controlled conditions, are used as the oxidizing agents, certain of the initial yellow quinones IV are transformed into brilliant red substances, a fact first noted by John.[4] The study of these red compounds was continued by John and his associates[3,5b] and by Karrer and his collaborators,[6] but Smith, Irwin and Ungnade[7] first showed that the red compounds were *o*-quinones, I giving VI, and that the group originally present in the 5-position (R in I) was eliminated in the transformation of I into VI. No evidence as to the mechanism of the transformation of I into VI was obtained, however, although certain general conclusions were drawn as to the effect of the nature of the group in the 2-position of the quinone IV upon the elimination of the group R.

An interesting and suggestive mechanism for

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[1] (a) XLIV, THIS JOURNAL, **66**, 1525 (1944); (b) XLIII, **66**, 1523 (1944).

[2] Abstracted from a thesis by Roy W. H. Tess, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, March, 1944.

[3] (a) John, *Z. physiol. Chem.*, **252**, 201 (1938); (b) John, Dietzel and Emte, *ibid.*, **257**, 173 (1939); (c) Karrer, *et al.*, *Helv. Chim. Acta.*, **21**, 939 (1938); (d) Smith, Hoehn and Whitney, THIS JOURNAL, **62**, 1863 (1940); (e) Smith, Ruoff and Wawzonek, *J. Org. Chem.*, **6**, 236 (1941); (f) Tishler and Wendler, THIS JOURNAL, **63**, 1532 (1941); (g) Smith and King, *ibid.*, **65**, 441 (1943).

[4] John, *Z. physiol. Chem.*, **250**, 11 (1937).

[5] (a) John and Schmeil, *Ber.*, **72**, 1653 (1939); (b) John and Emte, *Z. physiol. Chem.*, **261**, 24 (1939).

[6] Karrer, Fritzsche and Escher, *Helv. Chim. Acta*, **22**, 661 (1939).

[7] Smith, Irwin and Ungnade, THIS JOURNAL, **61**, 2424 (1939).