The Oxidation of Purpurogallin by Oxygen and Hydrogen Peroxide

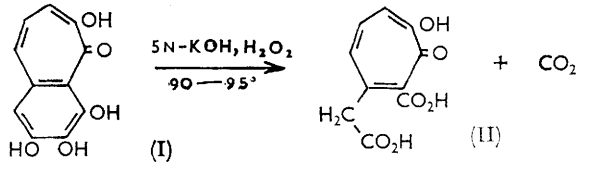
By P. D. Collier

The oxidation of purpurogallin in alkaline solution by oxygen and hydrogen peroxide is described. It is shown that initial attack on the purpurogallin anion is by oxygen (not hydrogen peroxide), producing a radical ion. This species is oxidised to, and exists in equilibrium with, purpurogalloquinone, which may undergo three separate reactions, two with hydrogen peroxide and one with solvent.

Hydrogen peroxide attacks the quinone in two ways; (i) to produce an intermediate thought to be a peroxy-purpurogallin, which decomposes to tropolone-αβ-anhydride and oxalic acid, this reaction predominates at room temperature and low alkali concentration and (ii) to produce α-carboxy-β-carboxymethyl tropolone in a reaction favoured by high temperature and alkali concentration. The solvent attacks the quinone to give an intermediate thought to be a hydroxy-purpurogallin, which is oxidised to tropolone-αβ-anhydride and oxalic acid.

Detailed paths for these reactions are proposed and discussed.

THE oxidation of purpurogallin (I) by hydrogen peroxide in strongly alkaline solution at 90—95° has been shown [1] to result in the formation of α-carboxy-β-carboxymethyl tropolone (II) in 30% yield. This compound (together with polymeric material) has also been obtained in 5% yield by ærobic oxidation of purpurogallin in 1N-potassium hydroxide at room temperature.[2] Further



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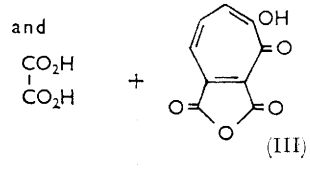


investigation of the peroxide reaction products has shown that oxalic acid and tropolone-αβ-anhydride (III) are formed in small amounts under the extreme reaction conditions employed.[3]

The present investigation is concerned with the intermediates giving rise to these products, and with the effects of pH and temperature on their distribution.

The First Two Reaction Steps.—Although hydrogen peroxide decomposes rapidly to oxygen in 5N-potassium hydroxide at 90°, no oxygen was evolved for some minutes from similar solutions containing purpurogallin. Similarly, evolution of oxygen from decomposing alkaline solutions of hydrogen peroxide was temporarily stopped by addition of purpurogallin. This indicates that the first reaction step consumes oxygen as fast as it is formed, or utilises a reactive intermediate in peroxide decomposition.

That hydrogen peroxide itself is not involved was shown by experiments in which degassed, EDTA-stabilised solutions of hydrogen peroxide were added to anærobic alkaline solutions of pyrogallol, gallic acid, and purpurogallin. Only when peroxide decomposition was provoked by heating or the addition of catalysts were these phenols attacked to produce (in the cases of pyrogallol and gallic acid) semiquinone radical-ions

[1] R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 1951, 561.
[2] R. D. Haworth, B. P. Moore, and P. L. Pauson, *J. Chem. Soc.*, 1948, 1045.
[3] W. D. Crow, R. D. Haworth, and P. R. Jefferies, *J. Chem. Soc.*, 1952, 3702.

identified by their electron spin resonance (e.s.r.) spectra.[4-6]

The orange solution of purpurogallin turned blue ($\lambda_{max.}$ 617mμ, Figure 1) and a transient e.s.r. signal of a

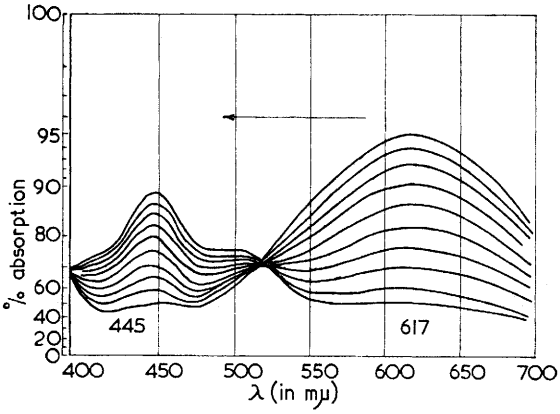


FIGURE 1 Visible absorption spectra of an oxygenated solution of purpurogallin (isosbestic point at 517 mμ)

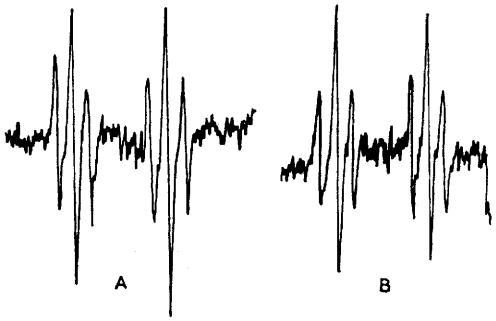


FIGURE 2 E.s.r. spectra of radical-ion of purpurogallin in basic solution. A, purpurogallin and O_2 at pH 12·0; B, purpurogallin and $K_3[Fe(CN)_6]$ at pH 12·0

doublet of triplets was observed (doublet splitting, 5·64 gauss; triplet splitting, 0·244 gauss, Figure 2). Similar changes in colour and magnetic properties were observed on admission of oxygen, which (by analogy with the behaviour of the other phenols) abstracts an electron from the purpurogallin anion. The e.s.r. signal amplitude decreased more rapidly in the presence of added peroxide. The blue colour of the ærated solution faded through green to yellow at a rate which increased with pH and added peroxide concentration. Alkaline solutions of purpurogalloquinone [11] (IV) above pH 10·0 were also blue ($\lambda_{max.}$ 617mμ), and displayed the same changes in visible absorption spectrum as ærated solutions of purpurogallin at the same pH. (At pH 12·0, an isosbestic point appeared at 517mμ and the final products absorbed at 445mμ.) No e.s.r. signal was obtained from these quinone solutions. When oxidised under Haworth's conditions,[1,3] the quinone was converted in 40% yield to α-carboxy-β-carboxymethyl tropolone (II), tropolone-αβ-anhydride (III) and oxalic acid being formed as side products.

In view of the lability of *ortho*-quinones to nucleophilic attack,[7-11] these observations indicate that (i) ærobic alkaline solutions of purpurogallin contain the quinone and semiquinone radical-ion in equilibrium, (ii) the transient blue colour of such solutions is due to the quinone, which undergoes irreversible nucleophilic attack by solvent and hydrogen peroxide, (iii) all the characterised products of reaction arise from purpurogalloquinone.

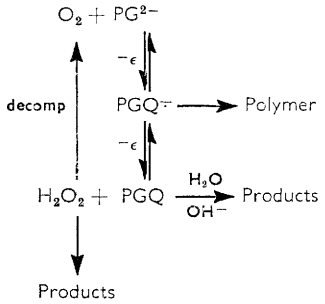
None of the products formed by ærobic [2] or peroxide [1,3] oxidation of purpurogallin were formed in the ærobic decomposition of purpurogalloquinone in alkaline solution. Evidently the generation of hydrogen peroxide in the ærobic oxidation of catechol and pyrogallol-type phenols [12] is essential for the formation of the characterised products of the reaction. Oxidation by hydrogen peroxide in 5N-alkali of the polymer obtained by ærobic oxidation of purpurogallin gave a 40% yield of α-carboxy-β-carboxymethyl tropolone; moreover, the infrared absorption spectrum of the polymer in Nujol was diagnostic of the tropolone ring system (3100, 1620, 1550, and 1245 $cm.^{-1}$).[13-16] Hence, no carbon-skeletal rearrangement can be involved in the formation of the polymer, which must arise by coupling of semiquinone radical-ions formed in the first reaction step. Similar coupling of semiquinone radical-ions has been directly observed by e.s.r.[17] in the ærobic oxidation of catechol to diphenylene dioxide-2,3-quinone.

Why the polymer is obtained only by ærobic oxidation of purpurogallin may be explained by considering the two types of process by which semiquinone radical-ions may be destroyed: (i) those which involve irreversible nucleophilic attack on the quinone existing in equilibrium with the semiquinone, and indirectly reduce the ambient semiquinone concentration without producing polymer, and (ii) those producing polymer, which involve the semiquinone directly.

Hydrogen peroxide and its anion would be expected to behave as nucleophiles towards the quinone; hence

[4] M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, 1958, **28**, 774.
[5] R. H. Hoskins and B. R. Loy, *J. Chem. Phys.*, 1955, **23**, 2461.
[6] Y. Matsunaga and C. A. McDowell, *Canad. J. Chem.*, 1960, **38**, 1158, 1167.
[7] L. Fieser and J. B. Conant, *J. Amer. Chem. Soc.*, 1924, **46**, 1858.
[8] R. Marshall, Part II, Thesis, Hon. School of Nat. Sci., Oxford Univ., 1962.
[9] P. D. Collier, Part II, Thesis, Hon. School of Nat. Sci., Oxford Univ., 1963.
[10] C. R. Dawson and J. M. Nelson, *J. Amer. Chem. Soc.*, 1938, **60**, 245.
[11] L. Horner and W. Dürckheimer, *Z. Naturforsch.*, 1959, **14***b*, 741; *Chem. Ber.*, 1961, **94**, 1267.
[12] W. Brackman, *Rec. Trav. chim.*, 1955, **74**, 937, 1021, and 1070.
[13] J. R. Bartels-Keith and A. W. Johnson, *Chem. and Ind.*, 1950, 677.
[14] G. P. Scott and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240.
[15] A. W. Johnson, N. Sheppard, and A. R. Todd, *J. Chem. Soc.*, 1951, 1139.
[16] R. E. Corbett, A. W. Johnson, and A. R. Todd, *J. Chem. Soc.*, 1950, **6**, 147.
[17] W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen, London, 1964, p. 145.

in the presence of added hydrogen peroxide (especially at high pH) it is likely that the combined rates of solvolysis and peroxide decomposition of the quinone are much faster than the coupling rate of the semiquinone. However, when hydrogen peroxide is formed only by autoxidation of purpurogallin, its ambient concentration can never be higher than that of purpurogalloquinone, so that the rates of direct semiquinone coupling and of its indirect destruction *via* the quinone should be less disparate, and radical coupling products appear. The position is summarised in Scheme 1.



Scheme 1

Effects of Temperature and pH *on Product Distribution.*—In contrast to the product distribution observed under Haworth's conditions,[1,3] oxidation of purpurogallin and purpurogalloquinone in solutions of hydrogen peroxide at pH 12 initially at room temperature gave tropolone-αβ-anhydride and oxalic acid as the major crystalline products. The reaction was exothermic, and if the reaction temperature was allowed to rise, so also did the yield of α-carboxy-β-carboxymethyltropolone. The same products and influence of temperature on their distribution were observed in exothermic oxygen oxidations of purpurogallin, with the addition of the polymer corresponding to the "humic acid" obtained by Haworth, Moore, and Pauson.[2]

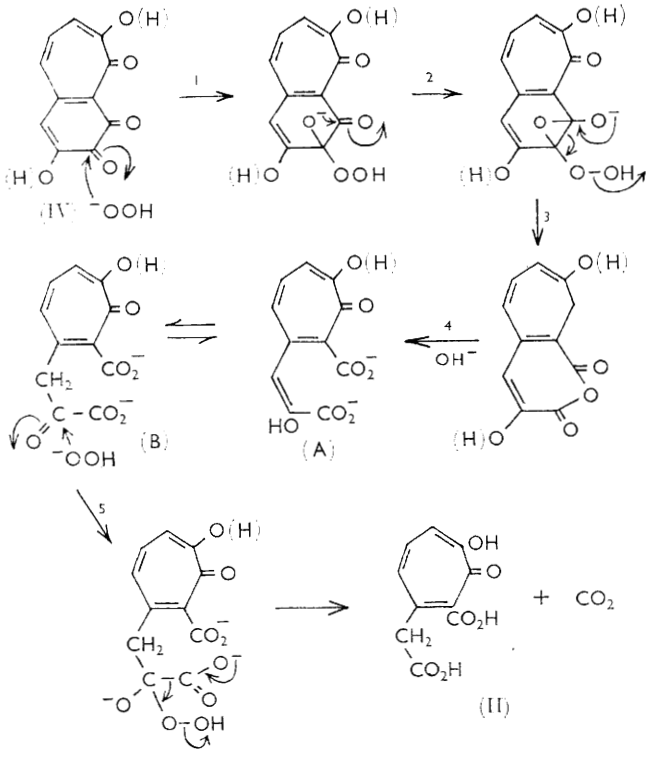
Ærobic decomposition of purpurogalloquinone in alkaline solution gave none of these products, indicating that the polymer is formed from the semiquinone radical-ion not present in this system. Purpurogallin was formed, together with two other substances separated by paper chromatography. Earlier work on the solvolysis of orthoquinones [7-11] suggests that these substances might be the hydroxylated purpurogallin (V) and the derived *para*-quinone (VI). The infrared absorption spectrum of material eluted from the leading spots on several chromatograms was consistent with structure (VI). (Absorption peaks at 3100, 2500—2550, 1620, 1550, and 1250 cm.$^{-1}$ were taken as diagnostic of tropolone OH groups, intramolecularly hydrogen-bonded OH groups, tropolone C=O groups, and tropolone ring deformations.) The visible absorption spectrum of this material in dilute solutions of hydrogen peroxide at pH 12 showed a peak diminishing with time at 445mμ: the final spectrum was identical with that obtained from reactions at room temperature of purpurogalloquinone with hydrogen peroxide, indicating that quinone (VI) might be an intermediate in the formation of tropolone-αβ-anhydride and oxalic acid.

Additional evidence supporting this view was obtained by examination of a further group of products isolated from peroxide oxidations of purpurogallin and purpurogalloquinone and ærobic oxidation of purpurogallin. This fraction was obtained in highest yield from low temperature reactions as a red viscous oil which decomposed on standing or in alkaline solution to tropolone-αβ-anhydride and oxalic acid. Paper chromatography and infrared spectroscopy on eluted material showed it to consist of tropolone-αβ-anhydride, quinone (VI), and a compound liberating iodine from acid solutions of potassium iodide. Reduction of the oil by this means produced a compound chromatographically identical with the hydroxylated purpurogallin (V) together with tropolone-αβ-anhydride.

Taken together, these product analysis studies suggest that purpurogalloquinone reacts with hydrogen peroxide at low temperature to produce an oxidising agent which decomposes to tropolone-αβ-anhydride *via* quinone (VI) and is reduced in acid solution to hydroxypurpurogallin (V). Such a species would be expected to be a peroxide of structure (VII). A yellow solid consisting of the same constituents and giving the same reactions as the oil was obtained by peroxide oxidation of purpurogalloquinone and purpurogallin in solutions of methanolic sodium methoxide. It decomposed more rapidly than the oil, and paper chromatography showed it to be richer in the iodide-oxidising constituent. Its infrared spectrum in Nujol included a sharp band at 860 cm.$^{-1}$, normally considered indicative of an –O–O– linkage.[18-20] Sodium peroxide, which is slowly precipitated from dilute solutions of hydrogen peroxide in methanolic methoxide, did not exhibit such an absorption.

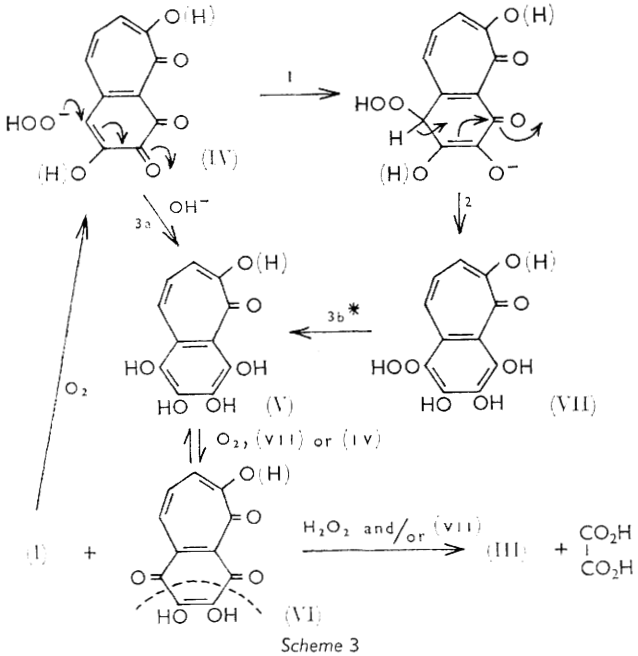
Proposed Reaction Mechanisms.—These investigations suggest that purpurogalloquinone undergoes two reactions with hydrogen peroxide in alkaline solution. The first predominates only at high temperature and alkali concentration, and results in the formation of α-carboxy-β-carboxymethyl tropolone. The reactions outlined in Scheme 2 are submitted as a tentative mechanism explaining many of the observations reported in this Paper. Steps 1 to 4 have been shown by Karrer,[21] and Kwart and Wegemer,[22] to occur both in oxidative ring-opening of *ortho*-quinones and the oxidative fission of α-diketones. The intermediate hydroxy-acid A is considered to be in base-catalysed equilibrium with the tautomeric keto-acid B. Nucleophilic attack by either the hydrogen peroxide molecule or its anion at the electrophilic α-keto group results in the formation of the observed product.

[18] L. J. Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1958, 2nd edn., pp. 120—122.
[19] C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1953, **75**, 6242.
[20] T. W. Campbell and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1496.
[21] P. Karrer, *Helv. Chim. Acta*, 1947, **30**, 859; 1948, **31**, 1210.
[22] H. Kwart and N. J. Wegemer, *J. Amer. Chem. Soc.*, 1961, **83**, 2746.



Scheme 2

The high-temperature oxidation of purpurogalloquinone by hydrogen peroxide in strongly alkaline solution

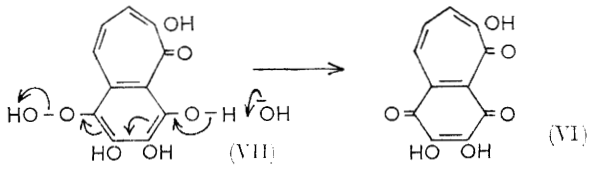


Scheme 3

The low-temperature oxidation of purpurogalloquinone by hydrogen peroxide in basic solution. [(H) denotes a hydrogen atom probably ionised under the conditions necessary for reaction.]

* Decomposition or reduction.

The second (Scheme 3) predominates at low temperature and with pH values up to 12. This reaction probably proceeds by nucleophilic attack of hydrogen peroxide or its anion at the *para*-position of the quinone to yield the peroxypurpurogallin (VII). This may decompose to the *para*-quinone (VI) either by direct attack of the hydroxyl ion or *via* the hydroxypurpuro-



gallin (V).[23,24] Although (V) has not been isolated from interrupted peroxide oxidations of purpurogallin, phentetrol (1,2,3,5-tetrahydroxybenzene) has been isolated from the analogous pyrogallol system.* Oxidative ring-opening of (VI) is expected to give tropolone-αβ-anhydride and oxalic acid. The fact that these two products always appeared together provides support for a mechanism in which they are formed in the same step of the reaction from the same intermediate.

Both these mechanisms fail to predict whether the most effective attacking species is the hydrogen peroxide molecule or its anion. Although in reactions involving uncharged electrophilic substrates the perhydroxyl ion normally behaves as the stronger nucleophile, the effect of charge repulsions on its reactivity is difficult to estimate. The proposed Schemes also give no idea of the relative rates of attack at the *para*-position of purpurogalloquinone by the solvent and hydrogen peroxide, since both reactions proceed through the same intermediate hydroxypurpurogallin (V) to the same products. Finally, neither Scheme enables any estimate to be made of the relative rates of the radical-ion coupling reaction and the other reactions in which the radical-ion is involved. All these points are at present being investigated.

EXPERIMENTAL

Hydrogen peroxide (30%, Pharmaceutical grade) was supplied by B.D.H.; all other chemicals unless otherwise stated were of AnalaR quality ex. B.D.H.

Paper chromatography was conducted by descending flow on Whatman's No. 1 paper with the solvent system n-butyl alcohol–acetic acid–water (4 : 1 : 2·2).

Visible and ultraviolet absorption spectra were measured using Perkin-Elmer Ultracord and Beckman DB spectrophotometers. Infrared spectra were measured using a Perkin-Elmer Infracord. E.s.r. spectra were measured by a Varian V-4500 spectrometer using a 6-in. magnet and 100 Kc. modulation.

Purpurogallin (I).—This compound was synthesised by the method of Evans and Dehn.[25] It was recrystallised from glacial acetic acid and purified by vacuum sublim-

* To be published.

[23] A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p. 110.

[24] A. F. Bickel and H. R. Gersmann, *Proc. Chem. Soc.*, 1957, 231.

[25] T. W. Evans and W. M. Dehn, *J. Amer. Chem. Soc.*, 1930, **52**, 3647.

ation to red needles, m. p. 275° (decomp.) (Found: C, 60·0; H, 3·7. Calc. for $C_{11}H_8O_5$: C, 60·0; H, 3·8%).

α-Carboxy-β-carboxymethyltropolone (II).—The title compound was prepared by the method of Haworth and Hobson [1] and recrystallised twice from glacial acetic acid to yield a white solid, m. p. 184° (decomp.). Yield: 30—35% (Found: C, 53·7; H, 3·6. Calc. for $C_{10}H_8O_6$: C, 53·6; H, 3·6%).

Tropolone-αβ-anhydride (III).—The title compound was prepared in the first instance by the method of Crow, Haworth, and Jefferies.[3] It was isolated from glacial acetic acid as golden plates, m. p. 250—253° (decomp.), and sublimed under slightly reduced pressure to give needles of unchanged m. p. [Found: C, 56·1; H, 2·3. Calc. for $C_9H_4O_5$: C, 56·3; H, 2·1%. *M* (Micro-Rast), 196; Calc. for $C_9H_4O_5$, 192]. Infrared maxima (Nujol mull and bromoform solution) were observed at 3100, 1820, 1765, 1630, 1550—1560, and 1255 $cm.^{-1}$.

Decarboxylation by heating under reflux in 10% aqueous solution yielded β-carboxytropolone, m. p. 217° (recrystallised from dioxan); the methyl ester was prepared and recrystallised from benzene (m. p. 116—118°).

The anilino-derivative was obtained by heating with aniline in glacial acetic acid under reflux. Recrystallisation from glacial acetic acid yielded yellow plates, m. p. 244—245°.

Experiments Under Anærobic Conditions.—All solutions were made up in water heated under reflux for at least 4 hr. with a stream of oxygen-free nitrogen passing through it. (The nitrogen was previously passed through Drechsel bottles containing alkaline solutions of pyrogallol.) Solutions of hydrogen peroxide were freed from oxygen immediately prior to use by several cycles of flushing with oxygen-free nitrogen followed by removal of gases by a vacuum (oil) pump. All solutions were made up under oxygen-free nitrogen, and all experiments were conducted with a stream of nitrogen passing through the reactant solutions.

Preparation of Tetrachloro-o-benzoquinone.—Pentachlorophenol (300 g., "Technical" grade ex. B.D.H.) was stirred in suspension with methylene dichloride (600 ml.) under reflux. Concentrated HNO_3 (40 ml.) was added over a period of 1 min., and a further addition (80 ml.) was made after the initial reaction had subsided. The mixture was heated under reflux for a further 15 min., allowed to cool, and water (225 ml.) added gradually. The mixture was cooled to 10°, and the yellow tetrachloro-*p*-benzoquinone filtered off. The methylene dichloride solution was washed with water until the washings were colourless, dried ($MgSO_4$), and distilled to dryness. The red solid so obtained was recrystallised from carbon tetrachloride to give scarlet crystals, m. p. 128—130°.

Preparation of Purpurogalloquinone (IV).—Purpurogallin (10 g., resublimed needles) was dissolved in dioxan (220 ml.) with warming. A solution of tetrachloro-*o*-benzoquinone (12·5 g.) in ether (150 ml.) was added, and the solution cooled in ice–water. After 2 hr., a violet microcrystalline powder was filtered off and washed with ether. This could not be recrystallised without decomposition and melted at 215—220° (decomp.). Yield: 75—80% (Found: C, 60·62; H, 2·81. Calc. for $C_{11}H_6O_5$: C, 60·55; H, 2·75%).

Purpurogallin Oxidations.—(a) *By oxygen.* (i) Solutions of sodium hydroxide (500 ml.) containing purpurogallin (10 g.) at pH 12 were prepared. Oxygen was passed in through a glass sinter for 12 hr., the pH being kept constant by additions of N-NaOH as required. The temperature of the solution rose steadily in all cases to 35—37° over the first 40 min., remained steady for 2—3 hr., then fell to room temperature for the remainder of the reaction time. The solution was acidified, with cooling, and a dark brown powder was precipitated. This was filtered off and dried in a vacuum desiccator. It did not melt below 250°, but softened and darkened over the range 280—300°. It could not be recrystallised from any common organic solvent, and paper chromatography against a purpurogallin standard showed it to be much more strongly adsorbed on paper. Yield: 5·5—6·5 g.

The filtrate was extracted with ether (1 l.) in a liquid–liquid extractor for 8 hr. The extract solution was dried ($MgSO_4$), concentrated, and cooled. The first material precipitated was a yellow powder (0·7—1·0 g.) recrystallised from glacial acetic acid to yield golden plates, m. p. 251—253°, undepressed by admixture with an authentic specimen of tropolone-αβ-anhydride (III). Its infrared absorption spectra in Nujol mull and bromoform solution confirmed this identification.

Pale yellow crystals were deposited from the mother-liquors after further concentration (0·40—0·60 g.). Paper chromatography indicated the presence of a small quantity of (III). Recrystallisation from water yielded colourless prisms, m. p. 100—102°, acid Equiv. 62·6. These were oxidised by both hot sulphuric acid and acid permanganate to carbon dioxide, which suggested that the material was oxalic acid monohydrate (Equiv. 63). The infrared spectrum of the dehydrated crystals in Nujol mull confirmed this identification.

Cooling of the remaining mother-liquors (*ca.* 50 ml.) in a salt–ice bath caused further white crystals to be precipitated (0·26—0·37 g.). Recrystallisation from glacial acetic acid yielded white plates, m. p. 183—184° (decomp.), undepressed by admixture with an authentic specimen of (II), α-carboxy-β-carboxymethyl tropolone. The infrared spectrum in Nujol confirmed this identification. Removal of the last of the ether from the cold solution at the pump gave a small quantity of a viscous red oil smelling like peracetic acid. This oil liberated iodine from acidified potassium iodide solution on warming and deposited yellow crystals of tropolone-αβ-anhydride (III) on standing.

(ii) Series of experiments conducted at 95 and 20° gave the product distributions shown in Table 1:

TABLE 1

	Polymer	(II)	(III)	Oxalic acid	Oil
95° (time, 3 hr.)	3·2—4·5 g.	2·0—2·2 g.	0·40—0·82 g.	0·25—0·42 g.	None
20° (time, 12 hr.)	6·0—6·8 g.	None	0·75—1·3 g.	0·45—0·80 g.	Up to 1 ml.

When the experiments were repeated in 5N-sodium hydroxide initially at room temperature, a rapid rise in temperature to 40—45° was observed. After 1—1·5 hr., the solutions had cooled to room temperature; after 8 hr., the oxygen flow was stopped and the reactions worked up. The following product distributions were obtained: polymer (4·6—5·4 g.), (II) (1·1—1·9 g.), (III) (0·61—0·92 g.), oxalic acid (0·24—0·55 g.), oil (very little).

(iii) Oxidation of polymeric material. Polymeric material isolated from the above experiments (2·0 g.) was dissolved in 5N-sodium hydroxide (100 ml.) and the dark solution heated to 95°. Hydrogen peroxide (5 ml. of 30%) was

added dropwise with stirring: heating was stopped until the vigorous reaction subsided, when the solution (now yellow-brown) was boiled for 5 *min*. The solution was allowed to cool to room temperature, acidified with cooling, and was extracted exhaustively with ether.

Concentration and cooling of the extract solution gave yields ranging from 0·70—0·81 g. of α-carboxy-β-carboxymethyltropolone, m. p. 183—184° (decomp.) from glacial acetic acid, undepressed by admixture with an authentic specimen. The identification was confirmed by infrared spectroscopy (Nujol mull).

(b) *By hydrogen peroxide.* (i) Solutions of sodium hydroxide (500 ml.) containing hydrogen peroxide (25 ml. of 30% solution) at pH 12 were prepared. Purpurogallin (10 g.) was added in small portions with vigorous stirring, the pH being kept at 12 by the addition of N-sodium hydroxide as needed. Transient blue colours were observed after each addition, and in experiments in which the rate of addition of purpurogallin was too fast, the temperature of the solution rose to 32—35° for short periods. When all the purpurogallin was added at once, a rapid rise in temperature to 50—55° was observed: after 1—1·5 hr. the solutions cooled to room temperature. The pale orange solutions resulting from all these experiments were allowed to stand overnight; the excess of hydrogen peroxide was destroyed with sodium hydrogen sulphite, the solutions acidified with cooling, and extracted exhaustively with 1 l. aliquots of ether. Products were isolated from these extracts as described in the previous section, and typical product distributions are given in Table 2.

TABLE 2

Max. temp.	(II)	(III)	Oxalic acid	Oil
20°	None	3·5—4·1 g.	2·0—2·3 g.	1·5—2·0 ml.
35	1·0—1·3 g.	2·8—2·1 g.	1·7—2·1 g.	0·5—1·0 ml.
55	2·0—2·2 g.	2·5—2·9 g.	1·4—1·6 g.	Very little

No polymeric material was precipitated on acidification.

Reactions of Purpurogalloquinone.—(a) *With hydrogen peroxide.* (i) Purpurogalloquinone (V) (10 g.) was added to 5N-sodium hydroxide (500 ml.) containing hydrogen peroxide (25 ml. of 30% solution) at 90%. When the vigorous reaction had subsided, the solution was allowed to cool to room temperature overnight. The excess of hydrogen peroxide was destroyed by the addition of sodium hydrogen sulphite, the solution was acidified with cooling and extracted exhaustively with ether. Concentration and cooling of the extract solution precipitated white plates from solution (3·2—3·5 g.), m. p. 183—184° (decomp.) from glacial acetic acid, undepressed by admixture with an authentic sample of α-carboxy-β-carboxymethyltropolone.

The red oil remaining after removal of ether from the mother-liquors was taken up in a minimum quantity of acetone–ether (1 : 3 v/v). The solution was put aside overnight, when yellow crystals were deposited (0·2—0·32 g.). These were recrystallised from glacial acetic acid to yield golden plates, m. p. 251—253°, undepressed by admixture with an authentic sample of tropolone-αβ-anhydride. Infrared spectra in Nujol mull and bromoform solution confirmed this identification. Further crops of a paler material were later precipitated (0·1—0·15 g.): these were shown by paper chromatography to contain traces of the anhydride (III) and were recrystallised from water to give oxalic acid monohydrate (m. p. 101—102°), identified by its acid Equiv., infrared spectrum, and permanganate reaction.

(ii) Purpurogalloquinone (V) (5·0 g.) was added in small portions with stirring to solutions of sodium hydroxide (250 ml.) containing hydrogen peroxide (12·5 ml. of 30% solution) maintained at pH 12 and initially at room temperature. In those experiments in which the rate of addition of quinone was faster, the temperature of the solution rose to 35—40°; when all the quinone was added at once the temperature rose rapidly to 55—58°. The resulting pale orange solutions were allowed to stand overnight, the excess of hydrogen peroxide was destroyed by sodium hydrogen sulphite, and the solutions extracted exhaustively with ether. Products were isolated from these extract solutions as described in (a) (i) and typical distribution ranges are given in Table 3.

TABLE 3

Temp.	(II)	(III)	Oxalic acid	Oil
20° (cooling)	None	1·7—2·0 g.	0·9—1·2 g.	0·7—1·3 ml.
35	0·4—0·6 g.	1·2—1·6 g.	0·7—1·6 g.	Up to 0·8 ml.
55	1·0—1·2 g.	1·2—1·4 g.	0·6—0·8 g.	Very little

(b) *By solvent.* Purpurogalloquinone (5·0 g.) was added in small portions with stirring to solutions of sodium hydroxide (250 ml.) at pH values 10, 11, 12, and 13. The blue colour of the quinone faded through green to yellow after each addition, and the pH values of the solutions dropped. The solutions were allowed to stand overnight, when an orange solid was deposited from solutions originally at pH values of 10 and 11. This was filtered off (pH 10, 300—450 mg.; pH 11, 100—250 mg.) and its infrared spectrum taken in Nujol. This, together with a m. p. and mixed m. p. of 275° (decomp.) confirmed that the solid was purpurogallin. (Tetramethyl derivative, m. p. 94° from cyclohexane.)

The filtrates were acidified, thus precipitating red-brown solids which were filtered off and dried *in vacuo* (3·2—3·6 g.). Paper chromatography of these solids showed them to contain two compounds in addition to purpurogallin. The filtrates were exhaustively extracted with ether, and the dried extract solutions evaporated to yield red-brown solids (0·9—1·1 g.) shown by paper chromatography to consist of purpurogallin together with the two compounds present in the acid-precipitated solids. Neither spot corresponded with tropolone-αβ-anhydride or α-carboxy-β-carboxymethyl tropolone.

Reactions of the Peroxy-fraction.—(a) *Decomposition in alkaline solution.* Samples of the red oily peroxy-fractions obtained from oxidations of purpurogallin and purpurogalloquinone (2·0 g.) were dissolved in N-sodium hydroxide (100 ml.) and gently warmed for 15 min. After being allowed to stand for 2 hr., these solutions were acidified and exhaustively extracted with ether. The dried solutions were concentrated and cooled: the first yellow deposits melted at 251—253° (recrystallised from glacial acetic acid), and gave an emerald-green ferric chloride test and an infrared spectrum identical with that of tropolone-αβ-anhydride. Later crops consisted of oxalic acid, whilst intermediate crops were shown by paper chromatography to contain traces of the anhydride mixed with oxalic acid. Yields of the anhydride ranged from 0·7—0·9 g., and 0·3—0·5 g. of oxalic acid were obtained.

(b) *Reduction in acid solution.* Samples (2 g.) of the peroxy-fractions were dissolved in 2N-sulphuric acid (50 ml.) and saturated potassium iodide solution (5 ml.) was added. After gentle warming for 5 min., the solutions were allowed to cool, iodine was extracted with carbon

tetrachloride, and the remaining solutions exhaustively extracted with ether. The concentrated ethereal extracts were examined by paper chromatography, which showed them to contain principally the compound formulated as hydroxypurpurogallin (VI), together with a small amount of tropolone-αβ-anhydride.

Preparation of Peroxy-intermediate (VIII).—Resublimed purpurogallin was added in small quantities with stirring to solutions of methanolic sodium methoxide (100 ml., containing 2 g. of sodium) containing hydrogen peroxide (10 ml. of 30% solution). A bright yellow precipitate was formed and was quickly filtered off. It rapidly liberated iodine from acidified potassium iodide solution, and its infrared spectrum in Nujol included a sharp band at 860 $cm.^{-1}$.

Freshly precipitated material (2·0 g.) was dissolved with warming in N-sodium hydroxide (100 ml.) with the evolution of oxygen: the solution was acidified after 15 min. and extracted with ether. Paper chromatography of this extract showed it to contain tropolone-αβ-anhydride and substance (VII). Concentration of the ethereal solution precipitated the anhydride (III) and oxalic acid (0·3 and 0·15 g., respectively).

Freshly precipitated material (5·0 g.) was dissolved quickly in 0·1N-sulphuric acid (100 ml.) and the solution quickly extracted with ether. Paper chromatography of the extract solution showed it to contain compound (VII), tropolone-αβ-anhydride, and a species liberating iodine from acidified iodide solutions. Concentration of the ethereal solution resulted in an exothermic decomposition and precipitation of tropolone-αβ-anhydride and oxalic acid (1·2 and 0·8 g., respectively, were isolated pure).

The yellow solid precipitated by addition of purpurogalloquinone in small quantities to solutions of methanolic methoxide containing 10% (v/v) of 30% aqueous hydrogen peroxide showed entirely similar properties.

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