710. *Purpurogallin. Part X.* Further Studies on the Oxidation Products of Purpurogallin and Purpurogallincarboxylic Acid.*

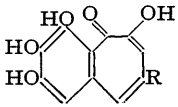
By W. D. Crow, R. D. Haworth, and P. R. Jefferies.

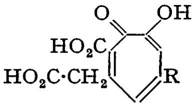
The methylation and decarboxylation of the acids (II; R = CO_2H) and (III; R = CO_2H), described in earlier papers, has been examined; the acid (III; R = CO_2H) has been converted by Curtius degradation into the β′-amine (III; R = NH_2) which with nitrous acid gave the corresponding β′-hydroxy-derivative. The acids (II; R = H and CO_2H) gave crimson anhydrides (X; R = H and CO_2H), and enol acetates and benzylidene derivatives are described. The anhydride constitution is supported by a study of the products obtained by reaction with (*a*) methyl alcohol and (*b*) ammonia, but the infra-red evidence suggests that the anhydride (X) exists entirely in an enolic form.

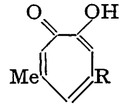
The yellow anhydride (XVII; R = O), now isolated in small yield from the oxidation of purpurogallin with hydrogen peroxide, resembles puberulonic acid in appearance and properties.

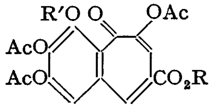
γ-Hydroxy-β-methyltropolone has been prepared by the action of potassium persulphate on β-methyltropolone, together with a smaller yield of the α- or α′-isomer.

In Part VII (*J.*, 1951, 1325) convenient methods for the preparation of purpurogallincarboxylic acid (I; R = CO_2H), β-carboxymethyltropolone-αβ′-dicarboxylic acid (II; R = CO_2H), and β-methyltropolone-β′-carboxylic acid (III; R = CO_2H) were described and these acids have now been investigated in more detail.


(I)


(II)


(III)


(IV)

Perkin and Perkin (*J.*, 1903, **83**, 200; 1908, **93**, 1189) failed to prepare acetyl derivatives from purpurogallincarboxylic acid (I; R = CO_2H), but tri-, tetra-, and penta-acetates have now been obtained. The yellow triacetate probably (IV; R = R′ = H), was best prepared by the action of acetic anhydride and pyridine, and when warmed with acetic anhydride and potassium carbonate in acetone it was converted into a colourless tetra-acetate, probably (IV; R = H; R′ = Ac), which decomposed slowly in air to the yellow triacetate. Both these acetates were acidic, but a penta-acetate (IV; R = R′ = Ac), insoluble in sodium hydrogen carbonate solution, was obtained by the action of warm acetic anhydride on the tetra-acetate; the penta-acetate was readily hydrolysed to the tetra-acetate during attempted recrystallisation from aqueous alcohol.

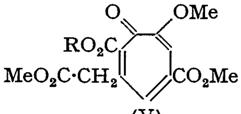
β-Carboxymethyltropolone-αβ′-dicarboxylic acid (II; R = CO_2H) with methyl sulphate and sodium hydroxide yielded a yellow trimethyl ester, which gave a crimson ferric test and dissolved readily in aqueous sodium carbonate. Further methylation with ethereal diazomethane gave a neutral trimethyl ester methyl ether-A (V), m. p. 132—133°. The isomeric ether-B was obtained as an oil, and the constitution (V) assigned to the ether-A is based on analogy with the observations reported in Part IX (*J.*, 1951, 3427).

Methylation of β-methyltropolone-β′-carboxylic acid (III; R = CO_2H) with methyl sulphate and sodium hydroxide afforded the methyl ester (III; R = CO_2Me), m. p. 118—119°, which on further treatment with ethereal diazomethane gave a mixture of the methyl ethers-A (VI) and -B (VII), m. p. 117° and 81° respectively, but the constitutions of these ethers are again based on the experiments described in Part IX (*loc. cit*). It is noteworthy that the ether-B (VII), like tropolone methyl ether (Cook, Gibb, Raphael, and Somerville, *J.*, 1951, 503), was hydrated in the crystalline form, m. p. 81°, which liquefied on dehydration

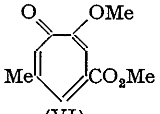
---

* Part IX, *J.*, 1951, 3427.

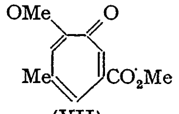
and resolidified on exposure to air. β-Methyltropolone methyl ether-B (Part IX, *loc. cit.*) is crystalline in the anhydrous state, but in this form it is hygroscopic and liquefies by hydration in air.



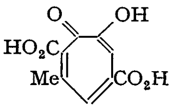
(V)



(VI)

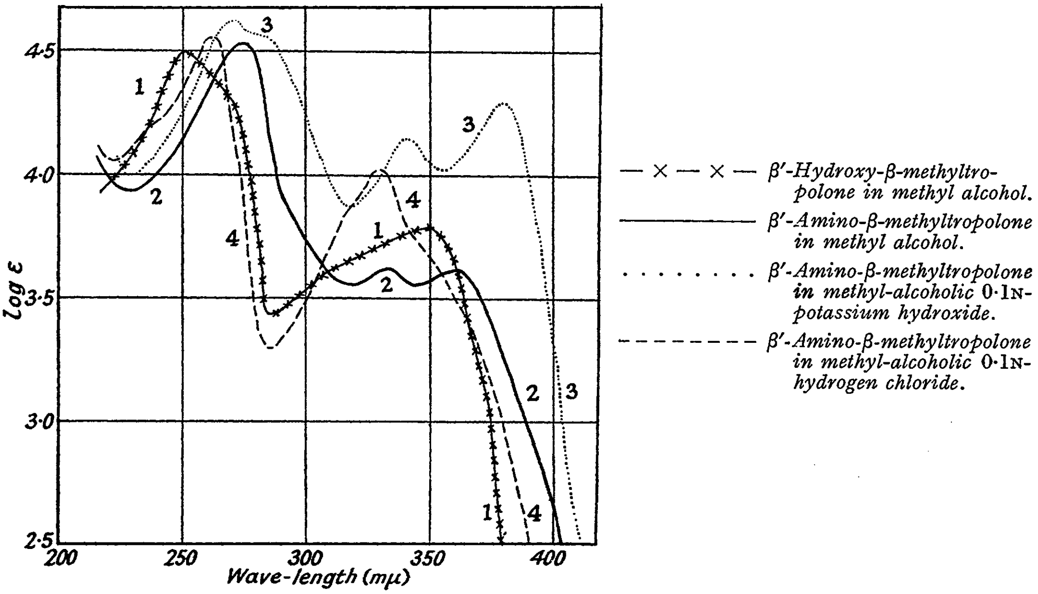


(VII)



(VIII)

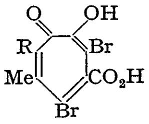
Heating β-carboxymethyltropolone-αβ′-dicarboxylic acid (II; R = CO_2H) in nitrobenzene afforded β-methyltropolone-αβ′-dicarboxylic acid (VIII) which melted at 245° (decomp.) with elimination of carbon dioxide and conversion into β-methyltropolone-β′-carboxylic acid (III; R = CO_2H). The dicarboxylic acid (VIII) with methyl sulphate and sodium hydroxide gave a dimethyl ester, and this or the acid (VIII) was converted into dimethyl β-methyltropolone-αβ′-dicarboxylate methyl ether-A, m. p. 137—138°, by ethereal diazomethane; the more soluble ether-B could not be crystallised.



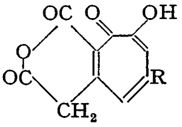
β-Methyltropolone-β′-carboxylic acid gave a dibromo-derivative, probably (IX; R = H), but even in the presence of excess of bromine tribromination could not be brought about. When, however, β-methyltropolone-αβ′-dicarboxylic acid (VIII) was treated with bromine in acetic acid solution, brominative decarboxylation took place and the tribomo-acid (IX; R = Br) was readily formed.

Methyl β-methyltropolone-β′-carboxylate (III; R = CO_2Me) reacted with hydrazine, and the product was converted by nitrous acid into a yellow amorphous azide (III; R = CON_3) from which the ethyl- and benzyl-urethanes (III; R = $NH\cdot CO_2Et$ and $NH\cdot CO_2\cdot CH_2Ph$ respectively) were prepared. The former was unaffected by acids or alkalis, and the benzylurethane gave a small amount of β′-amino-β-methyltropolone (III; R = NH_2) on hydrogenolysis. This amine was, however, more readily prepared by hydrolysis of the azide (III; R = CON_3) with a mixture of acetic and hydrochloric acid, and the ultra-violet absorption curves measured in neutral, acid, and alkaline solutions are shown in the Figure. The amine reacted with nitrous acid, nitrogen being eliminated and β′-hydroxy-β-methyltropolone (III; R = OH) produced. The ultra-violet absorption curve of the hydroxy-compound (see Figure) shows that the tropolone structure has been retained and that ring contraction to salicylic acid derivatives, encountered during the decomposition of the α- and α′-amines (Part VIII, *J.*, 1951, 2067), is not observed in the case of the β-compound. Consequently the β-compound resembles the γ-derivative in this feature, although the failure to detect a diazonium salt at −20° from (III; R = NH_2) indicates a marked difference between the β- and the γ-position in other respects. This failure is probably connected with the fact that β-aminotropolone is the divinyl analogue of an acid amide and in this connection it is interesting that 2-amino-6-methyl*cyclo*heptatrienone (Part IX, *loc. cit.*) also fails to give a diazonium salt. This reaction will be discussed more fully in a later communication.

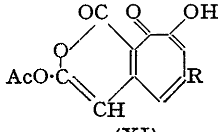
Although several reactions characteristic of phenols have failed with β-methyltropolone, the activity to certain electrophilic reagents led to an examination of the action of potassium persulphate. When the reaction was carried out under the conditions of Baker and Brown's experiments (*J.*, 1948, 2303), γ-hydroxy-β-methyltropolone, m. p. 232—233°, was obtained and identified by comparison with an authentic sample (Part IV, *J.*, 1951, 566); with acetic anhydride and pyridine it gave a diacetate, giving a negative ferric reaction and rapidly hydrolysed by alkali. An isomeric hydroxytropolone, m. p. 104—105°, was also obtained in smaller yields; it is probably α- or α′-hydroxy-β-methyltropolone and interaction of the α- or α′-hydroxyl group with the enolone system would account for the low melting point, the volatility, and the solubility properties of this compound.



(IX)

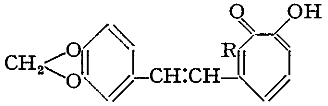


(X)

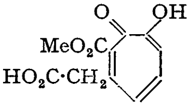


(XI)

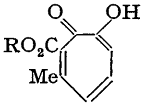
When β-carboxymethyltropolone-αβ′-dicarboxylic acid (II; R = CO_2H) was warmed with concentrated sulphuric acid it was converted into a crimson compound, $C_{11}H_6O_7$, m. p. 249—251°, which is regarded as the anhydride (X; R = CO_2H). This formulation, which is consistent with the formation of an enol acetate (IX; R = CO_2H) is supported by the more detailed examination of the anhydride (X; R = H), which was prepared similarly by the action of warm sulphuric acid on β-carboxymethyltropolone-α-carboxylic acid (II; R = H). The anhydride (X; R = H) was readily converted into the corresponding acid (II; R = H) by boiling its aqueous solution, and Zerevitinoff estimation indicated the presence of two active hydrogen atoms, derived from the tropolone and enol-anhydride groupings respectively. The enol acetate (XI; R = H), which contained one active hydrogen atom on the basis of Zerevitinoff test and gave molecular-weight values in good agreement with the structure (XI; R = H), could be recovered from its solution in sodium hydrogen carbonate, although it was hydrolysed to the anhydride (X; R = H) by cold aqueous sodium hydroxide. The anhydride (X; R = H) condensed readily with aromatic aldehydes at 80° and yellow benzylidene, *o*-nitrobenzylidene, and piperonylidene (XII; R = CO_2H) derivatives have been obtained. Carbon dioxide is eliminated during the condensation and further decarboxylation to (XII; R = H) was effected when the piperonylidene derivative was heated to 230° in dibutyl phthalate. The enol acetate (XI; R = H) did not react with benzaldehyde.



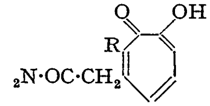
(XII)



(XIII)



(XIV)

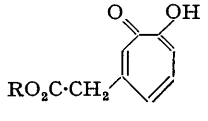


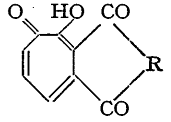
(XV)

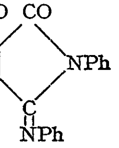
When the anhydride (X; R = H) was warmed with methyl alcohol it afforded largely methyl β-carboxymethyltropolone-α-carboxylate (XIII), which was readily decarboxylated to methyl β-methyltropolone-α-carboxylate (XIV; R = Me), both descirbed in Part IV (*loc. cit.*). The acid (XIV; R = H) has now been obtained by partial decarboxylation of (II; R = H) in dibutyl phthalate or nitrobenzene at 170°. Rigid proof of the structure was not then available but it has now been obtained by alkali fusion of β-methyltropolone-α-carboxylic acid (XIV; R = H): although a temperature of 320—340° was required, a 40% yield of 3-methylphthalic acid was obtained.

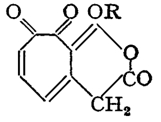
Treatment of the anhydride (X; R = H) with ammonia gave the amic acid, m. p. 167—169° (XV; R = CO_2H) which was decarboxylated in hot quinoline to the amide (XV; R = H). The amide was readily hydrolysed to β-carboxymethyltropolone (XVI; R = H), which was converted into β-methyltropolone on fusion and gave a methyl ester (XVI; R = Me) with methanolic hydrogen chloride. Thus ammonia and methyl alcohol attacked different seats of the anhydride (X; R = H) and, whilst this difference is not readily explained, it provides adequate proof of the anhydride structure.

Oxidation of purpurogallin (I; R = H) with hot alkaline hydrogen peroxide has been shown (Part IV, *loc. cit.*) to yield β-carboxymethyltropolone-α-carboxylic acid (II; R = H). Although it was not possible to oxidise this acid further without rupture of the tropolone nucleus, an examination of the residue from which the acid had been isolated yielded, in addition to oxalic acid, about 3% of the anhydride (XVII; R = O). This yellow anhydride gave a typical tropolone ferric test and formed an orange salt with sodium hydrogen carbonate; with hot sodium hydroxide it gave a pale yellow solution, back-titration of which showed the presence of three acid groups, but acidification yielded the anhydride (XVII; R = O), which was unaffected by hot alcohol either alone or in the presence of acids. The stability of the anhydride group is in agreement with the results obtained with puberulonic acid (Corbett, Hassall, Johnson, and Todd, *J.*, 1950, 1; Aulin-Erdtman, *Acta. Chem. Scand.*, 1951, **5**, 301). The anhydride was decarboxylated in water at 180°, affording tropolone-β-carboxylic acid. The position of the remaining carbon atom was established by fusion of the anhydride with sodium hydroxide at 180°, which yielded hemimellitic acid. Corbett *et al.* (*loc. cit.*) describe the preparation of an *o*-phenylenediamine condensation product of puberulonic acid, but although the anhydride (XVII; R = O) reacted rapidly with *o*-phenylenediamine the basic product was probably an *o*-amino-*N*-phenylimide. The anhydride (XVII; R = O) gave a yellow *N*-phenylimide (XVII; R = NPh) with aniline in acetic acid, but when this or the anhydride was heated with a large excess of aniline a scarlet compound, m. p. 281—283°, containing two aniline residues and possibly (XVIII) was obtained. Both the *N*-phenylimide and the aniline derivative gave tropolone colour tests, are virtually non-basic and very weak acids, on hydrolysis slowly regenerate the anhydride.


(XVI)


(XVII)


(XVIII)


(XIX)

We are very much indebted to Drs. R. N. Haszeldine and A. W. Johnson for the infrared absorption spectra which were measured in paraffin mull. The following strong bands were observed in the 6-μ region.

Anhydride of	Bands (μ)						
Tropolone-αβ-dicarboxylic acid (XVII)	5·47	5·61	6·1		6·15		6·34
β-Carboxymethyltropolone-α-carboxylic acid (X; R = H)		5·89		6·15			6·53
Homophthalic acid	5·63	5·7				6·23	
Glutaconic acid	5·59	5·73					

The spectrum of the anhydride (XVII) is in full accord with the structure; the doublet at 6·1 and 6·15 μ, and the 6·34-μ band, are assigned to the basic tropolone structure (Koch, *J.*, 1951, 512; Scott and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240), and the absorptions at 5·47 and 5·61 μ are assigned to the anhydride doublet, in close agreement with the values 5·46 and 5·65 μ found in puberulonic acid (Johnson, Sheppard, and Todd, *J.*, 1951, 1139; Aulin-Erdtman and Theorell, *Acta Chem. Scand.*, 1950, **4**, 1490). On the other hand, the spectrum of β-carboxymethyltropolone-α-carboxylic anhydride is inconsistent with structure (X; R = H), and the anhydride doublet, observed in homophthalic and glutaconic anhydrides at 5·63 and 5·7 μ and 5·59 and 5·73 μ respectively, is absent. This abnormal result is probably best explained by postulating an enolic structure for the tropolone anhydride. In this connection it is noted that Nozoe *et al.* (*Proc. Jap. Acad.*, 1952, **28**, 32), in a communication which became available when this paper was in manuscript form, suggested a structure such as (XIX; R = Ac) for the enol acetate (XI; R = H) in order to account for the pronounced colour of this compound.

EXPERIMENTAL

Acetylation of Purpurogallincarboxylic Acid.—The acid (I; R = CO_2H) (1 g.) was warmed for 30 minutes with acetic anhydride (2 c.c.) containing a few drops of pyridine; the *triacetate* (IV; R = R′ = H), isolated by dilution with water and extraction with ether, separated from toluene containing a little acetone in yellow needles (0·6 g.), m. p. 219—220° (Found: Ac, 33·1. $C_{18}H_{14}C_{10}$ requires Ac, 33·1%), soluble in sodium hydrogen carbonate. The triacetate (0· 5g.) was refluxed for 30 minutes in acetone (25 c.c.) with acetic anhydride (2 c.c.) and anhydrous potassium carbonate (5 g.). The solid was collected, washed with acetone, and decomposed with dilute hydrochloric acid; the *tetra-acetate* (IV; R = H, R′ = Ac), isolated with ether and crystallised from acetic acid, formed colourless needles (0·35 g.), m. p. 207—208° (Found: C, 55·5; H, 3·9; Ac, 41·2. $C_{20}H_{16}O_{11}$ requires C, 55·6; H, 3·7; Ac, 39·8%). Crystallisation from acetic anhydride gave the *penta-acetate* (IV; R = R′ = Ac) as colourless prisms, m. p. 156—157° (Found: Ac, 45·2. $C_{22}H_{18}O_{12}$ requires Ac, 45·3%), which was insoluble in sodium hydrogen carbonate solution and decomposed to the tetra-acetate, m. p. 207—208°, during attempted recrystallisation from aqueous alcohol. The tri-, tetra-, and penta-acetate were hydrolysed by methyl-alcohlic hydrochloric acid to purpurogallincarboxylic acid.

Methylation of β-*Carboxymethyltropolone*-αβ′-*dicarboxylic Acid* (II; R = CO_2H).—The acid (1 g.) in 10% sodium hydroxide (5 c.c.) was shaken with methyl sulphate (1·4 c.c.), for 15 hours. The solid was collected and crystallised from carbon tetrachloride; the *trimethyl* ester (0·6 g.) was obtained as yellow needles, m. p. 161—162° (Found: C, 54·3; H, 4·5. $C_{14}H_{14}O_8$ requires C, 54·2; H, 4·5%), which gave a crimson ferric test and dissolved in sodium carbonate solution.

Further treatment of the trimethyl ester (0·5 g.) with a small excess of ethereal diazomethane yielded a yellow gum, insoluble in sodium hydroxide and showing no ferric reaction. Trituration with ether gave the *trimethyl* ester *methyl ether-A* (V) as a pale yellow solid (0·3 g.), crystallising from benzene–light petroluem (b. p. 60—80°) in yellow prisms. m. p. 132—133° (Found: C, 56·0; H, 5·1. $C_{15}H_{16}O_8$ requires C, 55·6; H, 5·0%). The ether-soluble fraction could not be induced to crystallise.

Methylation of β-*Methyltropolone*-β′-*carboxylic Acid* (III; R = CO_2H).—Treatment of the acid (III; R = CO_2H) with methyl sulphate in the usual way gave the *methyl* ester (III; R = CO_2Me) which crystallised from aqueous acetone in yellow needles, m. p. 118—119° (Found: C, 61·7; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%), soluble in sodium carbonate solution and giving a red ferric test.

Further methylation with excess of ethereal diazomethane gave an oil which was repeatedly extracted with boiling light petroleum (b. p. 60—80°); the combined extracts were evaporated, and the residual oil crystallised from light petroleum (b. p. 45—60°). The less soluble *methyl* β-*methyltropolone*-β′-*carboxylate methyl ether-A* (VI) was obtained as pale yellow needles, m. p. 117—118° (Found: C, 63·4; H, 6·1. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%), and the more soluble *ether-B* (VII) as pale yellow hydrated needles, m. p. 80—81° (Found: C, 61·7; H, 5·9; H_2O, 3·1. $C_{11}H_{12}O_4,\frac{1}{3}H_2O$ requires C, 61·7; H, 6·0; H_2O, 2·9%), which liquefied when dried over phosphoric oxide and resolidified on exposure to the air. Both ethers gave a negative ferric test and were insoluble in dilute sodium hydroxide solution although with cold 10% sodium hydroxide they were gradually hydrolysed to the ester (III; R = CO_2Me), m. p. 118—119°; both ethers were converted into the acid (III; R = CO_2H), m. p. 222—223°, by warm 10% sodium hydroxide.

β-*Methyltropolone*-αβ′-*dicarboxylic Acid* (VIII).—The acid (II; R = CO_2H) (1 g.) was heated in nitrobenzene (10 c.c.) at 180° for 5 minutes and finally boiled for 1 minute. The product was diluted with light petroleum (b. p. 60—80°) (20 c.c.), filtered, recovered by evaporation under reduced pressure, and crystallised from water (charcoal). β-*Methyltropolone*-αβ′-*dicarboxylic acid* was obtained as yellow plates (0·72 g.), m. p. 247—248° (decomp.) (Found: C, 53·4; H, 3·8. $C_{10}H_8O_6$ requires C, 53·6; H, 3·6%), readily soluble in sodium hydrogen carbonate solution, giving a red ferric test, and decarboxylated to β-methyltropolone-β′-carboxylic acid (III; R = CO_2H), m. p. 222—223°, at 250°. The *dimethyl* ester, prepared from (VIII)

(0·5 g.), 20% aqueous sodium hydroxide (1·25 c.c.), and methyl sulphate (0·6 c.c.), separated from carbon tetrachloride in pale yellow needles (0·4 g.), m. p. 106—107° (Found: C, 56·8; H, 4·7. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8%), which dissolved slowly in aqueous sodium hydrogen carbonate and gave a red ferric test. *Dimethyl* β-*methyltropolone*-αβ′-*dicarboxylate methyl ether-A*, prepared by the action of ethereal diazomethane on the acid (VIII) or its dimethyl ester, crystallised from benzene–light petroleum (b. p. 60—80°) in yellow prisms, m. p. 137—138° (Found: C, 58·6; H, 5·4. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%), which were alkali-insoluble and no longer gave a ferric test. The mother-liquors yielded a clear gum which could not be crystallised.

Bromination of β-*Methyltropolone*-β-*carboxylic Acid* (III; R = CO_2H).—The acid (0·5 g.) in 90% acetic acid (5 c.c.) was treated with bromine (0·6 c.c.), and after 24 hours at room temperature the mixture was diluted with water and the *dibromo-acid* (IX; R = H) was collected and crystallised from acetic acid; yellow needles (0·5 g.), m. p. 214—215° (decomp.) (Found: C, 32·3; H, 1·9; Br. 46·7. $C_9H_6O_4Br_2$ requires C, 32·0; H, 1·8; Br. 47·3%), were obtained, which were unaffected by boiling with 20% sodium hydroxide solution and gave a red ferric test.

Bromination of β-*Methyltropolone*-αβ′-*dicarboxylic Acid* (VIII).—This, when carried out as described above, yielded the *tribromo-acid* (IX; R = Br), yellow plates (from acetic acid), m. p. 222—223° (decomp.) (Found: C, 26·5; H, 1·4; Br, 57·6. $C_9H_5O_4Br_3$ requires C, 25·9; H, 1·2; Br, 57·3%), which gave a red ferric test but was unaffected by boiling 20% sodium hydroxide solution.

β-*Methyltropolone*-β′-*carboxylic Azide* (III; R = CON_3).—Methyl β-methyltropolone-β′-carboxylate (III; R = CO_2Me) (2·0 g.) was heated at 100° for 3 minutes with 90% hydrazine solution (1 c.c.), then allowed to cool, and the yellow water-soluble product (1·9 g.), m. p. 171—172° (decomp.), precipitated by the addition of alcohol (35 c.c.), collected, and dissolved in 5% hydrochloric acid (20 c.c.). Addition of 7·5% sodium nitrite (10 c.c.) at −10° then precipitated the *azide* (III; R = CON_3), which was collected, washed, and dried in a vacuum. The amorphous product (1·35 g.), m. p. 119—120° (decomp.) (Found: N, 21·0. $C_9H_7O_3N_3$ requires N, 20·4%), gave a red ferric test.

β-*Methyltropolone*-β′-*carboxylic acid* N-*ethylurethane* (III; R = $NH{\cdot}CO_2Et$), prepared by evaporation of a solution of the azide (III; R = CON_3) (0·5 g.) in ethyl alcohol (20 c.c.), was purified first by sublimation and then by crystallisation from water; it separated in colourless needles (0·45 g.), m. p. 174—175° (Found: C, 59·5; H, 5·6; N, 6·5. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9; N, 6·3%), insoluble in dilute acids, soluble in sodium hydroxide solution, and giving a red ferric test.

β-*Methyltropolone*-β′-*carboxylic acid* N-*benzylurethane* (III; R = $NH{\cdot}CO_2{\cdot}CH_2Ph$), prepared by heating the azide (0·5 g.) with benzyl alcohol (0·5 c.c.) for a few minutes at 150°, crystallised from ethyl alcohol in colourless needles (0·6 g.), m. p. 185—186° (Found: C, 67·6; H, 5·6. $C_{16}H_{15}O_4N$ requires C, 67·4; H, 5·3%).

β′-*Amino*-β-*methyltropolone* (III; R = NH_2).—(*a*) This was prepared in small yield by shaking the above *N*-benzylurethane in alcohol with 10% palladium–charcoal and hydrogen for 1 hour.

(*b*) It was obtained in better yield by refluxing for 2 hours a solution of the azide (III; R = CON_3) (1 g.) in acetic acid (10 c.c.) containing 10N-hydrochloric acid (2 c.c.); the acetic acid was removed in steam, and the residual solution neutralised by careful addition of sodium hydrogen carbonate and continuously extracted with ether. The ether was removed and the *amine* (III; R = NH_2) crystallised from water, forming cream-coloured needles (0·48 g.), m. p. 199—200° (Found: C. 63·5; H, 6·3; N, 9·3. $C_8H_9O_2N$ requires C, 63·6; H, 6·0; N, 9·3%), readily soluble in dilute hydrochloric acid or aqueous sodium hydroxide and giving a red ferric test.

β′-*Hydroxy*-β-*methyltropolone* (III; R = OH).—The amine (III; R = NH_2) (0·3 g.) in 5% sulphuric acid (20 c.c.) was treated with a solution of sodium nitrite (0·15 g.) in water (5 c.c.) at −20°. Nitrogen was evolved and the solution, which did not couple with an alkaline solution of β-naphthol, was treated with urea and boiled for a few minutes; the cooled solution extracted continuously with ether. The concentrated extract was sublimed at 0·1 mm., and the *product* (III; R = OH) crystallised from alcohol, forming straw-coloured prisms (0·19 g.), m. p. 241—242° (Found: C, 63·0; H, 5·5. $C_8H_8O_3$ requires C, 63·2; H, 5·3%), which gave a red ferric test.

Oxidation of β-*Methyltropolone with Potassium Persulphate.*—A solution of potassium persulphate (4 g.) in water (130 c.c.) was added with stirring during 4 hours to an ice-cooled suspension of the sodium salt obtained by adding β-methyltropolone (2 g.) to 10% sodium hydroxide solution (40 c.c.). After 12 hours at 0°, the solution was acidified to Congo-red, and extracted with ether which removed unchanged β-methyltropolone (0·55 g.) and a brown tar. The aqueous portion was acidified further with concentrated hydrochloric acid (10 c.c.), heated at 100° for 1 hour, and continuously extracted with ether. The product, triturated with a little ether (A), solidified. Sublimation at 190°/0·05 mm. and crystallisation from alcohol gave γ-hydroxy-β-methyltropolone as a mixture of stout and elongated prisms (0·44 g.), m. p. 232—233° (decomp.) (Found: C, 63·5; H, 5·6. Calc. for $C_8H_8O_3$, C, 63·2; H, 5·3%), identical with the material described in Part IV (*loc. cit.*). The *diacetate,* prepared by boiling acetic anhydride and a drop of pyridine and isolated with chloroform, sublimed at 120—130°/0·01 mm. and crystallised from carbon tetrachloride in colourless prisms, m. p. 129—130° (Found: C, 61·3; H, 4·9; Ac, 35·9. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1; Ac, 36·4%), giving a negative ferric test. Evaporation of the ethereal washings (A) gave an oil, which was extracted with hot carbon tetrachloride (2 × 30 c.c.); evaporation of this extract gave a crystalline residue of α(or α′-)-*hydroxy*-β-*methyltropolone* which sublimed at 100°/12 mm., and crystallised from carbon tetrachloride in cream-coloured needles (0·1 g.), m. p. 103—105° [Found: C, 62·9; H, 5·3% *M* (Rast), 165. $C_8H_8O_3$ requires C, 63·2; H, 5·3%; M, 152·1], readily soluble in dilute aqueous sodium hydroxide and giving a green ferric test.

Anhydride (X; R = CO_2H) *of* β-*Carboxymethyltropolone*-αβ′-*dicarboxylic Acid.*—The acid (II; R = CO_2H) (1 g.) was warmed at 60° for a few minutes with concentrated sulphuric acid (5 c.c.) and after 5 minutes the mixture was poured into water (200 c.c.). The crimson *anhydride* (X; R = CO_2H) was collected and separated from dioxan in lustrous plates (0·7 g.), m. p. 249—251° (decomp.) (rapid heating) (Found: C, 52·8; H, 2·6. $C_{11}H_6O_7$ requires C, 52·6; H, 2·4%), readily soluble in aqueous sodium hydrogen carbonate, giving an olive-green ferric test, and hydrolysed to the tricarboxylic acid (II; R = R′ = CO_2H) by boiling water, hydrochloric acid, or sodium hydroxide. The enol *acetate* (XI; R = CO_2H), prepared by heating the acid (II; R = CO_2H) (0·5 g.) with acetic anhydride (2—3 c.c.) under reflux for 10 minutes, crystallised from toluene in dark red needles (0·37 g.), m. p. 210—212° (decomp.) (Found: Ac, 14·2. $C_{13}H_8O_8$ requires Ac, 13·6%), soluble in cold sodium hydrogen carbonate solution from which it was recovered by acidification. With cold 10% sodium hydroxide solution it gave the anhydride (X; R = CO_2H), m. p. 249—251° (decomp.).

Anhydride (X; R = H) *of* β-*Carboxymethyltropolone*-α-*carboxylic Acid.*—Prepared similarly from the acid (II; R = H), this *anhydride* sublimed at 100°/0·01 mm. and crystallised from dioxan or anisole in dark red prisms, m. p. 205—208° (decomp.) (Found: C, 58·3; H, 3·3%; active H, 1·9, 2·0 atoms. $C_{10}H_6O_5$ requires C, 58·3; H, 2·9%; active H, 2·0 atoms). Light absorption in dioxan showed maxima at 275, 315, and 475 mμ (log ε 4·0, 4·0, 4·21, and 3·12 respectively). The colour of a chloroform solution was intensified by addition of ferric chloride. The *enol* acetate (XI; R = H), obtained from (II; R = H) by boiling acetic anhydride, crystallised from toluene or acetic acid as dark red monoclinic crystals, m. p. 192—193° (decomp.) [Found; C, 58·4; H, 3·3; acetyl, 17·0%; active H, 1·1, 1·1 atom; *M* (ebullioscopic in chloroform), 230, 235. $C_{12}H_8O_6$ requires C, 58·1; H, 3·3; acetyl, 17·3%; active H, 1·0 atom; M, 248]. Light absorption in dioxan showed maxima at 290, 350, 365, and 470 mμ (log ε 4·20, 4·21, 4·15, and 2·99 respectively). The enol acetate (XI; R = H) dissolved with effervescence in sodium hydrogen carbonate solution and gave a positive test, and hydrolysis to the anhydride (X; R = H) took place in sodium hydroxide·solution. No reaction took place when the enol acetate was heated with benzaldehyde at 160°.

β-3 : 4-*Methylenedioxystyryltropolone*-α-*carboxylic Acid* (XII; R = CO_2H).—The anhydride (X; R = H) (0·4 g.) was warmed at 100° with piperonaldehyde (2 g.); carbon dioxide was evolved. The excess of aldehyde was removed in benzene and the residual *derivative* crystallised from dioxan as yellow needles (0·55 g.), m. p. 212—214° (decomp.) (Found: C, 64·9; H, 4·1. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%), which effervesced and formed a sparingly soluble salt with sodium hydrogen carbonate solution and gave a red ferric test.

The *styryl* derivative, prepared similarly, separated from ethyl acetate or acetic acid in yellow prisms, m. p. 167—169° (decomp.) (Found: C, 71·7; H, 4·5. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

The 2-*nitrostyryl* derivative crystallised from acetic acid–dioxan in brown-yellow needles, m. p. 203—205° (decomp.) (Found: N, 4·4. $C_{16}H_{11}O_6N$ requires N, 4·5%).

β-3 : 4-*Methylenedioxystyryltropolone* (XII; R = H).—The above methylenedioxystyryl derivative (XII; R = CO_2H) (0·5 g.) was heated at 220—230° with a little copper bronze in dibutyl phthalate (4 c.c.) until gas evolution ceased. 3 : 4-*Methylenedioxystyryltropolone* (0·3 g.), precipitated with light petroleum (b.p. 60—80°) (10 c.c.), sublimed at 200—210°/0·5 mm., and crystallised from benzene as yellow needles, m. p. 191—192° (Found: C, 71·7; H, 4·4.

$C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%), which gave an insoluble sodium salt with sodium hydroxide solution.

Methyl β-*Carboxymethyltropolone-*α*-carboxylate* (XIII).—The anhydride (X; R = H) (0·22 g.) was boiled with methyl alcohol (10 c.c.) and dioxan (5 c.c.) for 1 hour. The residue, obtained by evaporation of the colourless solution, crystallised from methyl alcohol yielding methyl β-carboxymethyltropolone-α-carboxylate (XIII), m. p. 179—180° (decomp.), identical with a sample described in Part IV (*loc. cit.*). Identity was confirmed by decarboxylation to methyl β-methyltropolone-α-carboxylate (XIV; R = Me), m. p. 122—123° (Part IV, *loc. cit.*, and below).

β-*Methyltropolone-*α*-carboxylic Acid* (XIV; R = H) [with J. D. HOBSON].—In addition to the method outlined above and the methods described in Part IV (*loc. cit.*), this acid may be prepared by partial decarboxylation of β-carboxymethyltropolone-α-carboxylic acid (II; R = H). This acid (10 g.) was heated with nitrobenzene or dibutyl phthalate (50 c.c.) at 170° until evolution of gas ceased. The cooled solution was diluted with ether, filtered, and extracted with sodium hydrogen carbonate solution. Acidification of the extract yielded β-methyltropolone-α-carboxylic acid (XIV; R = H) which separated from hot water (charcoal) in colourless needles (5 g.), m. p. 190—191° (decomp.) (Found: C, 60·3; H, 4·8. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·5%). Methylation with methyl sulphate and sodium hydroxide gave methyl β-methyltropolone-α-carboxylate (XIV; R = Me), m. p. 122—123° (Part IV, *loc. cit.*, and above).

Alkaline Fusion of β-*Methyltropolone-*α*-carboxylic Acid.*—The acid (XIV; R = H) (1 g.) was fused with sodium hydroxide (7 g.) at 330—340° for 5 minutes. The product was dissolved in water, acidified, boiled with charcoal, and filtered whilst hot. The cooled filtrate was extracted with ether (4 × 50 c.c.), and the solvent evaporated. Impurities were removed from the crude product with hot *cyclo*hexane, and the residue, crystallised from 2N-hydrochloric acid, had m. p. 152—153°, undepressed by admixture with 3-methylphthalic acid (Jurgens, *Ber.*, 1907, **40**, 4409; Müller, *Ber.*, 1909, **42**, 430); sublimation gave the anhydride, m. p. 116—117° (Found: C, 66·8; H, 4·0. Calc. for $C_9H_6O_3$: C, 66·7; H, 3·7%) alone or mixed with 3-methylphthalic anhydride.

β-*Carbamylmethyltropolone-*α*-carboxylic Acid* (XV; R = CO_2H).—The anhydride (X; R = H) (0·15 g.) was shaken with ammonia (1 c.c.; *d* 0·88). When the colour had faded excess of ammonia was removed on the water-bath and the solution acidified to Congo-red. The *amic acid* (XV; R = CO_2H) (0·13 g.) which separated crystallised from water in cream-coloured prisms, m. p. 167—168° (decomp.) (Found: C, 53·8; H, 4·3; N, 6·3. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·1; N, 6·2%), which dissolved in sodium hydrogen carbonate solution and gave a green ferric test.

β-*Carbamylmethyltropolone* (XV; R = H).—The amic acid (XV; R = CO_2H) (1 g.) was heated at 130° in quinoline (2 c.c.) until gas evolution ceased (10 minutes). The cooled solution deposited crystals (0·5 g.) of the *amide* which were washed with dilute acid, sublimed at 200—210°/0·01 mm., and crystallised from water, forming cream-coloured prisms, m. p. 216—218° (Found: C, 59·9; H, 5·0; N, 7·7. $C_9H_9O_3N$ requires C, 60·3; H, 5·1; N, 7·85%), insoluble in aqueous sodium hydrogen carbonate and giving a red ferric test.

β-*Carboxymethyltropolone* (XVI; R = H).—The amide (XV; R = H) (0·4 g.) was heated under reflux with 2N-sodium hydroxide 10 c.c.) until evolution of ammonia ceased (30 minutes). Extraction of the acidified solution with ether gave the *acid* (XVI; R = H), which crystallised from alcohol or water in needles, m. p. 156—158° (decomp.) (Found: C, 59·9; H, 4·4. $C_9H_8O_4$ requires C, 60·0; H, 4·5%), soluble in sodium hydrogen carbonate, giving a green ferric test and decarboxylated to β-methyltropolone when heated above its m. p. The *methyl* ester, prepared with methyl-alcoholic hydrogen chloride, crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 67—68° (Found: C, 61·3; H, 5·5. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%), giving a green ferric reaction.

*Tropolone-*αβ*-dicarboxylic Anhydride* (XVII; R = O).—The ethereal liquors, from which β-carboxymethyltropolone-α-carboxylic acid had been isolated, from the oxidation of purpurogallin (120 g.) (Part IV, *loc. cit.*) were evaporated and the dark red residual oil was taken up in acetone–ether (1 : 3; 400 c.c.). The solid which gradually separated was periodically removed, and the solution was repeatedly made up to volume by addition of ether. The early crops consisted mainly of β-carboxymethyltropolone-α-carboxylic acid, but the last crops were mainly oxalic acid and intermediate fractions were mixtures containing the *anhydride* (XVII; R = O), which was isolated by washing with a little hot water and purified by sublimation and crystallisation from acetic acid or diethyl malonate; yellow plates (3·5 g.), m. p. 251—253° (Found: C, 55·9; H, 2·5%; equiv., 63·0. $C_9H_4O_5$ requires C, 56·3; H, 2·1%; equiv., 64·0), were obtained. The anhydride gave a red green ferric test, and a sparingly soluble orange salt with aqueous sodium hydrogen carbonate, but it was unaffected by boiling ethyl alcohol.

Tropolone-β-carboxylic Acid.—The anhydride (0·4 g.) was suspended in water (5 c.c.) and heated at 170—180° for 30 minutes. The cooled solution deposited tropolone-β-carboxylic acid (0·2 g.) which crystallised from dioxan in solvated prisms, m. p. (dioxan-free) 217° alone or mixed with a sample prepared as described in Part IV (*loc. cit.*). The *methyl* ester prepared (with J. D. Hobson) by methyl-alcoholic hydrogen chloride, crystallised from benzene in pale cream-coloured plates, m. p. 117—118° (Found : C, 60·3; H, 4·5. $C_9H_8O_4$ requires C, 60·0; H, 4·5%), which gave a red ferric test and slowly dissolved to a yellow solution in sodium hydrogen carbonate solution.

Methylation of tropolone-β-carboxylic acid with ethereal diazomethane gave a brown gum which gave a negative ferric test.

Alkaline Fusion of Tropolone-αβ-dicarboxylic Anhydride.—The anhydride (XVII; R = O) (0·3 g.), fused with sodium hydroxide (3 g.) at 170—180° for 3 minutes, gave an almost colourless melt, which was dissolved in water, acidified, and extracted continuously with ether. The product, after three crystallisations from dilute hydrochloric acid (1 : 4), had m. p. 195—197°, undepressed by a specimen of hemimellitic acid obtained from 1 : 8-naphthalic acid (Graebe and Leonhardt, *Annalen*, 1896, **290**, 218), and identity was confirmed by preparation of the trimethyl ester, m. p. 101—102° (Found : C, 57·2; H, 5·0. Calc. for $C_{12}H_{12}O_6$: C, 57·2; H, 4·8%) (Ruzicka, Goldberg, Huyser, and Seidel, *Helv. Chim. Acta*, 1931, **14**, 545, give m. p. 101°).

Condensation of Tropolone-αβ-dicarboxylic Anhydride with Amines.—(*a*) The anhydride (XVII; R = O) (0·01 g.) was heated in alcohol (2 c.c.) with *o*-phenylenediamine; the brown crystalline solid which quickly separated, could not be recrystallised and was recovered from solution in dilute mineral acid. (*b*) The anhydride (0·2 g.) was boiled with acetic acid (3 c.c.) and aniline (0·2 g.) for 1 minute, and the N-*phenylimide* (XVII; R = NPh) (0·15 g.), deposited on cooling, was washed with dilute acid and crystallised from acetic acid; yellow plates, m. p. 243—245° (Found : N, 5·4. $C_{15}H_9O_4N$ requires N, 5·2%), were obtained. Addition of sodium hydroxide to an alcoholic solution produced an orange colour, and the compound gave a red-brown ferric test. (*c*) The anhydride (0·08 g.), heated with aniline (0·5 g.) for 5 minutes on the water-bath, gave on dilution with ether the *compound* (XVIII), which crystallised from a large volume of acetic acid in scarlet plates (0·12 g.), m. p. 281—283° (Found : N, 8·0. $C_{21}H_{14}O_3N_2$ requires N, 8·2%). It was insoluble in dilute acids, gave a brown ferric test, and yielded the anhydride (XVII; R = O) when boiled with sodium hydroxide solution. The compound (XVIII) was also formed similarly from the *N*-phenylimide and aniline.

Our thanks are offered to the Commonwealth Scientific Research Organisation for Overseas Studenships (to W. D. C.), to the University of Western Australia for a Hackett Research Studentship (to P. R. J.), and to Imperial Chemical Industries Limited for a grant which has defrayed some of the expenses of the research.

The University, Sheffield, 10.

[*Received, May* 30*th*, 1952.]