278. *Dunnione. Part II.*

By J. R. Price and Sir Robert Robinson.

The formula (I) proposed in Part I (J., 1939, 1522) for dunnione, a β-naphthaquinone colouring matter obtained from *Streptocarpus Dunnii*, is now supported by the isolation of methyl *iso*propyl ketone after oxidation by chromic acid. The results of oxidation experiments also indicate that the *gem*-dimethyl group in the isomerides of the *iso*dunnione series is directly attached to the oxygen atom of the dihydrofuran ring. Further data concerning the structure of *allo*dunnione do not support, though they do not definitely exclude, the formula previously suggested.

It was shown in Part I (*loc. cit.*) that dunnione, a β-naphthaquinone derivative resembling β-lapachone, can be converted into four isomerides, the changes involving at least one rearrangement not paralleled in the lapachol group. The structure of these isomerides has not yet been determined conclusively, but as further work may be postponed, we think it desirable to place the following data on record. The three distinct but related problems to be examined are (1) the structures of dunnione and α-dunnione, (2) the structure and mechanism of formation of the *iso*dunnione series, and (3) the structure and mechanism of formation of *allo*dunnione.

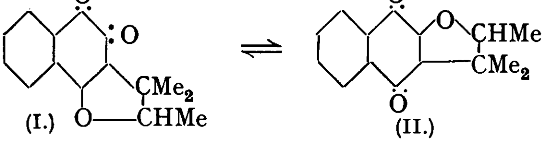
The structure of dunnione as a 1 : 2-naphthaquinone is already firmly established; that of α-dunnione as the corresponding 1 : 4-quinone follows from the ready interconversion of the two substances by standard methods. They constitute a pair which differs from α- and β-lapachone only in the arrangement of the heterocyclic ring. In Part I it was suggested that this portion of the molecule is an ααβ-trimethyldihydrofurano-group. This is now supported by the isolation of methyl *iso*propyl ketone after careful oxidation of dunnione with chromic acid. Dunnione and α-dunnione are therefore represented by formulæ (I) and (II) respectively.

1·3 Molecules of acetic acid were obtained from dunnione by the Kuhn–Roth oxidation. This is approximately the amount to be expected from one side-methyl group and a *gem*-dimethyl group. α-Dunnione should give the same result as dunnione, but the amount of acetic acid produced was smaller, *viz.*, 1·04 molecules. Dr. F. B. Strauss, who carried out the Kuhn–Roth estimations, found concordant results difficult to obtain with these substances. The fluctuations probably depend to some extent on the ease of isomerisation in acid solutions, as already suggested in Part I (*loc. cit.*, p. 1524), and on the volatility of 1 : 4-quinones. Evidently the significance which can be attached to the figures is not sufficient for them to constitute an objection to the proposed formulæ. The results of individual analyses are set out for comparison in Table I.

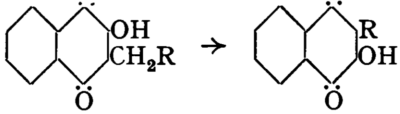
Table I.

Substance.	CH_3·C–, %.	Average, %.	Mols. HOAc.
Dunnione	10·0, 7·2, 7·0	8·07	1·30
α-Dunnione	6·5, 6·36	6·43	1·04
β-*iso*Dunnione	6·5, 4·7	5·6	0·90
α-*iso*Dunnione	5·36	5·36	0·86
β-Lapachone	3·67, 4·4	4·03	0·65
*allo*Dunnione	8·5, 6·9, 7·43	7·6	1·23
The acid $C_{12}H_{12}O_4$	3·52	3·52	0·52

The change from the dunnione to the *iso*dunnione series is brought about by heating α-dunnione with concentrated sulphuric acid. We have now found that some β-*iso*-dunnione is obtained when dunnione is used as the starting material, but the extent of the conversion is small even after treatment for several hours. The structures of α- and β-*iso*dunnione have been established as 1 : 4- and 1 : 2-quinones respectively by their properties, by the preparation of characteristic derivatives, and by their easy interconversion analogous to that of α- and β-lapachones. In fact the *iso*dunniones resemble the lapachones more closely than they do dunnione and α-dunnione, because they react with alkali to give a stable *hydroxyhydro*iso*dunniol* * similar to hydroxyhydrolapachol. The corresponding hydroxyhydrodunniol could not be isolated because of its marked sensitivity to alkalis (which transform it into *allo*dunnione) and to acids, which bring about ring closure. Hydroxyhydro*iso*dunniol has been characterised by the *tetra-acetyldihydro*-compound and by its condensation *product* with *o*-phenylenediamine. The latter derivative was deep red, similar to methylhydroxyhydrolapeurhodone (Hooker, J., 1893, **63**, 1376), and was converted into the yellow azine of β-*iso*dunnione by treatment with sulphuric acid. Hooker (*J. Amer. Chem. Soc.*, 1936, **58**, 1174) has shown that alkylhydroxynaphthaquinones of the type (III) can be oxidised by alkaline permanganate to (IV) with elimination of the methylene group next to the nucleus.



(I.) (II.)



(III.) (IV.)

When hydroxyhydro*iso*dunniol was treated in this way, no oxidation product could be detected and most of the starting material was recovered. This behaviour resembles that of 3-hydroxy-2-β-hydroxy*iso*butyl-1 : 4-naphthaquinone (Hooker, *loc. cit.*). However, Fieser, Hartwell, and Seligmann (*ibid.*, p. 1223) oxidised 3-hydroxy-2-*iso*butyl-1 : 4-naphthaquinone to the *iso*propyl compound, which on further oxidation gave phthalonic and *iso*butyric acids. Hence the inactivity of hydroxyhydro*iso*dunniol in this process does not help in determining its structure. Oxidations of β-*iso*dunnione with chromic acid and with alkaline peroxide (*i.e.*, oxidation of hydroxyhydro*iso*dunniol) both gave acetone. Therefore the *iso*propyl group must be at the end of the alkyl chain instead of being directly attached to the nucleus as it is in dunnione. There are, then, three possible formulæ for β-*iso*dunnione: αββ-trimethyldihydrofurano-1 : 2-naphthaquinone (V), β-lapachone, and *iso*-β-lapachone (VI).

The lapachone structure can be eliminated at once because the melting points of α- and β-lapachone and certain of their derivatives differ from those of α- and β-*iso*dunnione and their corresponding derivatives. The recorded melting point of *iso*-β-lapachone (Hooker, *J. Amer. Chem. Soc.*, 1936, **58**, 1181) is 124·5—125·5°, only 6° lower than that of β-*iso*dunnione, but the hydroxyhydro-compound, hydro*iso*lomatiol, melts 10° higher than hydroxyhydro*iso*dunniol. No other derivatives of *iso*-β-lapachone have been recorded. When hydro*iso*lomatiol is treated with concentrated sulphuric acid at room temperature, the principal product is β-lapachone (Hooker, *loc. cit.*). We have experienced no difficulty in obtaining pure β-*iso*dunnione under conditions which should have favoured its conversion into β-lapachone had it actually been *iso*-β-lapachone. The preparation of β-*iso*dunnione from α-dunnione is a sufficient example of such conditions. Finally, it is unlikely that *iso*-β-lapachone would give acetone on oxidation with alkaline peroxide.

These points enable us to eliminate (VI) and to infer that β-*iso*dunnione is αββ-trimethyldihydrofurano-1 : 2-naphthaquinone (V). Its formation evidently involves the migration of a methyl group, and we hope to deal with the course of the rearrangement in a later paper. Bromination of β-*iso*dunnione in chloroform solution at room temperature gave a *bromo*-β-iso*dunnione*, whereas dunnione did not react when kept with bromine in chloroform at 55° for four days. By analogy with bromo-β-lapachone, which can be

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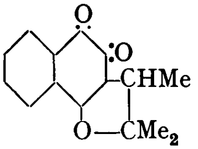
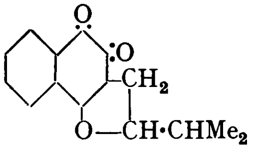
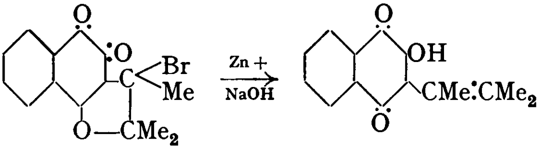
* Nomenclature based on that used by Hooker for the lapachol compounds.

brominated in the nucleus only in the presence of excess of hydrobromic acid, there can be no doubt that the bromine of bromo-β-*iso*dunnione is in the side chain. This is supported by the ease with which the bromine is removed by zinc dust and sodium hydroxide to give iso*dunniol*. Assuming that β-*iso*dunnione is αββ-trimethyldihydrofurano-1 : 2-naphthaquinone, bromo-β-*iso*dunnione and *iso*dunniol are best represented by (VII) and (VIII) respectively.


(V.)


(VI.)



(VII.) (VIII.)

However, *iso*dunniol is yellow and dissolves in alkali, giving a red solution, whereas Hooker showed (*J. Amer. Chem. Soc.*, 1936, **58**, 1163) that 2-hydroxy-3-alkylene-1 : 4-naphthaquinones with a double bond in the αβ-position are usually red or orange-red and give a violet solution in alkalis. Those with a saturated side chain or with a double bond in a position other than αβ are yellow and their alkaline solutions are red. Some modification of these colours results from substitution, as shown in Table II, but until further data become available the colour of *iso*dunniol, alone and with alkalis, remains difficult of explanation in terms of formula (VIII). It is possible that the double bond is in a different position in the side chain.

TABLE II.

Side chain.	Colour of substance.	Colour in alkaline solution.
$\cdot\mathrm{CH{:}CH\cdot CHMe_2}$	Brick-red	Purple
$\cdot\mathrm{CH{:}CMe_2}$	Orange-red	Reddish-purple
$\cdot\mathrm{CH{:}CMe\cdot CH_2\cdot OH}$	Orange	?
$\cdot\mathrm{CH{:}CMe\cdot CHO}$	Orange	Crimson
$\cdot\mathrm{CH{:}CH\cdot C(OH)Me_2}$	?	Crimson

In any case it is evident that the formation of the *iso*dunnione series is not so straightforward as was suggested in Part I, and there is no analogy to it in the chemistry of the lapachol derivatives.

Little progress has been made in determining the structure of *allo*dunnione, and the new data do not support the formula previously suggested. When *allo*dunnione was reduced by tin and hydrochloric acid, or by zinc and acetic acid, a *dihydro*-compound was formed. This substance is weakly acidic and contains two hydroxyl groups, as shown by the preparation of a *diacetyl* derivative. However, there is evidence confirming the presence of a ring system which undergoes fission in alkaline solution. When *allo*dunnione was treated with zinc dust and sodium hydroxide, the elements of water, together with two hydrogen atoms, were added, presumably owing to the opening of a lactone, coumaran or chroman ring. We also know that the isoprene chain is intact, because chromic acid oxidation gave acetone and (as shown in Part I) alkaline oxidation gave acetaldehyde. The formation of acetone shows that the point of attack on treatment with chromic acid is not the carbon next to the oxygen atom, as it is with alkaline reagents. That is, the heterocyclic ring does not open readily in acid solution. When *allo*dunnione was heated at 100° in solution in concentrated sulphuric acid, substitution took place with the formation of a *sulphonic acid*.

If it were not for the difficulty of the anomalous absorption spectrum (Part I), we should conclude that *allo*dunnione is a quinone. On the basis previously suggested, it is just possible that diacetyldihydro*allo*dunnione is a derivative of an enolic form of a ketolactone analogous to the enolic modification of glutaconic anhydride.

EXPERIMENTAL.

Dunnione.—The following method of isolation was found to be more satisfactory than that described in Part I.

Fresh leaves of *Streptocarpus Dunnii* were immersed in benzene and kept overnight. The benzene was poured off, and the leaves extracted a second time. By this treatment the dunnione was completely removed, together with only a small amount of chlorophyll. The benzene was distilled, and the residue dissolved in boiling alcohol; after filtration and cooling, a colourless crystalline wax separated. This substance is being investigated in collaboration with Dr. J. C. Smith. After filtration the alcoholic solution was concentrated to a small volume and poured into half-saturated aqueous sodium bisulphite as described in Part I (Found for dunnione : CH_3·C–, 7·0%). It was reported previously that dunnione is recovered unchanged after a solution in concentrated sulphuric acid has been heated for 1 hour. But after standing for 72 hours at room temperature and then heating at 100° for 3 hours, some change took place. The recovered quinone, after one crystallisation from light petroleum, was appreciably darker in colour than dunnione and melted below 90°. It was kept with 5% caustic soda solution for 2 hours and then boiled for ½ hour. The red solution was treated with excess of concentrated hydrochloric acid, boiled, and filtered from *allo*dunnione. The filtrate was extracted with the minimum amount of benzene, and the extract shaken with saturated sodium bisulphite solution. The bisulphite layer was then shaken with sodium hydroxide and benzene, and the resulting quinone crystallised from light petroleum. It had m. p. and mixed m. p. with β-*iso*dunnione, 129—131°. The amount obtained was less than 5%.

Further attempts were made to isolate hydroxyhydrodunniol from both dunnione and α-dunnione, but no stable product was obtained. Dunnione was recovered unchanged after attempted bromination under a variety of conditions.

Oxidation of Dunnione with Chromic Acid.—2·4 G. of dunnione were dissolved in concentrated sulphuric acid (32 c.c.) and water (48 c.c.), and the mixture boiled while 90 c.c. of 10% aqueous potassium dichromate were added dropwise in 10 c.c. portions with intervals of a few minutes between each addition to ensure the removal of volatile products. The distillate was carried into a solution of 2 : 4-dinitrophenylhydrazine in 5% sulphuric acid; the yellow precipitate, crystallised four times from alcohol, had m. p. 119—121°, mixed m. p. with acetone-2 : 4-dinitrophenylhydrazone *ca.* 95°, and with methyl *iso*propyl ketone 2 : 4-dinitrophenylhydrazone 120—122° (Found : C, 48·9; H, 5·3; N, 21·1. Calc. for $C_{11}H_{14}O_4N_4$: C, 49·6; H, 5·3; N, 21·05%).

[Methyl *iso*propyl ketone was prepared by dry distillation of the mixed calcium salts of acetic and *iso*butyric acids. The 2 : 4-dinitrophenylhydrazone had m. p. 122—123° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955, gives m. p. 117°) (Found : C, 49·7; H, 5·2%)].

Dunnione phenyleneazine. The condensation product of dunnione with *o*-phenylenediamine (see Part I) has $[\alpha]_D^{16^\circ}$ + 237° (*c*, 1·86 in chloroform).

αDunnione has $[\alpha]_D^{19^\circ}$ + 104° (*c*, 0·772 in chloroform) (Found : CH_3·C–, 6·5, 6·36%).

Diacetyldihydro-α-dunnione forms colourless prisms from methyl alcohol, m. p. 119—121° (Found : C, 69·0; H, 6·05. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%). $[\alpha]_D^{18^\circ}$ + 80·4° (*c*, 4·428 in chloroform).

β-iso*Dunnione* (Found : CH_3·C–, 6·5, 4·7%).—The oxidation of this substance by means of chromic acid was carried out in the same way as with dunnione. The 2 : 4-dinitrophenylhydrazone obtained melted at 123—124° after four crystallisations from alcohol. The mixed m. p. with acetone-2 : 4-dinitrophenylhydrazone was 124—125°, and that with methyl *iso*propyl ketone 2 : 4-dinitrophenylhydrazone was below 100°.

Diacetyldihydro-β-iso*dunnione* separated from aqueous methyl alcohol in colourless, rectangular prisms, m. p. 119—121° (mixed m. p. with diacetyldihydro-α-dunnione *ca.* 95°) (Found : C, 69·2; H, 6·1. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

β-iso*Dunnione semicarbazone* formed orange-yellow needles from aqueous alcohol, m. p. 218—219° (decomp.) (Found : N, 14·1. $C_{16}H_{17}O_3N_3$ requires N, 14·0%).

β-iso*Dunnione phenyleneazine* formed yellow, silky needles from alcohol, m. p. 118—120° (Found : N, 8·7. $C_{21}H_{18}ON_2$ requires N, 8·9%).

α-iso*Dunnione.*—Steam-distillation was found to be the only satisfactory method of purification for large-scale preparations. The product then melted sharply at 118—119° after crystallisation from aqueous alcohol (Found : CH_3·C–, 5·36%).

A solution of α-*iso*dunnione in concentrated sulphuric acid was kept at room temperature for an hour and then poured into water. The product crystallised from light petroleum in orange-red needles, m. p. and mixed m. p. with β-*iso*dunnione, 130—131°.

Diacetyldihydro-α-iso*dunnione* formed colourless prisms from methyl alcohol, m. p. 135—136° (Found : C, 69·8; H, 6·0. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

α-iso*Dunnione semicarbazone* crystallised in pale yellow needles from alcohol, m. p. 222—223° (Found : N, 14·4. $C_{16}H_{17}O_3N_3$ requires N, 14·0%).

*Hydroxyhydro*iso*dunniol.*—When β-*iso*dunnione was heated with 1—5% aqueous sodium hydroxide, it dissolved, giving an intense red solution which remained unaltered for a fortnight. Acidification with excess of concentrated hydrochloric acid produced a yellow emulsion, which soon changed to a suspension of orange needles of β-*iso*dunnione, m. p. and mixed m. p. 130—131°. When the alkaline solution was made only faintly acid and kept at 0° for 2—3 hours, a yellow solid separated. This was crystallised twice from aqueous alcohol and twice from benzene–light petroleum and melted at 112—113° (Found : C, 68·6 ; H, 6·2. $C_{15}H_{16}O_4$ requires C, 69·2 ; H, 6·15%).

*Tetra-acetyldihydrohydroxyhydro*iso*dunniol.*—Several attempts to acetylate directly hydroxyhydro*iso*dunniol were unsuccessful. Evidently ring closure took place to some extent, and the mixture obtained was a viscous oil which could not be crystallised. Reductive acetylation gave a gummy product, which on treatment with cold alcohol yielded a clean white solid. After two crystallisations from alcohol, colourless, hexagonal plates were obtained, m. p. 183—184° [Found : C, 64·0 ; H, 6·2. $C_{15}H_{14}(OAc)_4$ requires C, 64·2 ; H, 6·0%].

*Condensation of Hydroxyhydro*iso*dunniol with* o-*Phenylenediamine.*—When hydroxyhydro*iso*dunniol (0·5 g.), *o*-phenylenediamine (0·3 g.), and acetic acid (10 c.c.) were boiled for 1½ hours, the product was a mixture of β-*iso*dunnione and β-*iso*dunnione phenyleneazine (identified by their m. p.'s and mixed m. p.'s). The process was then repeated in a less acid medium, alcohol (20 c.c.) being used as solvent in place of the acetic acid. No reaction took place, so acetic acid was added in 0·5 c.c. portions and the solution refluxed for ½ hour after each addition. When 3 c.c. of acetic acid were present, the reaction proceeded as expected. After being heated for a further 2 hours, the mixture was poured into an excess of 2% aqueous sodium hydroxide. This was shaken with benzene, which extracted a small amount of β-*iso*dunnione phenyleneazine (m. p. and mixed m. p.). Acidification of the alkaline solution with 4% acetic acid gave a crimson gelatinous precipitate, which separated from aqueous alcohol as a deep red, micro-crystalline powder, m. p. 193—194° (Found : N, 8·5. $C_{21}H_{20}O_2N_2$ requires N, 8·4%). The substance gave in concentrated sulphuric acid a deep green solution. After ½ hour this was poured into water. The product was identified by the m. p. and mixed m. p. as β-*iso*dunnione phenyleneazine.

Attempts were made to prepare chlorohydro*iso*dunniol from hydroxyhydro*iso*dunniol by treatment with hydrochloric acid, both alone and in acetic acid solution (cf. Hooker, J., 1892, **61**, 611). In each case the only product isolated was α-*iso*dunnione (m. p. and mixed m. p. 117—119°).

*Oxidation Experiments with Hydroxyhydro*iso*dunniol.*—(a) Starting with β-*iso*dunnione, the oxidation with alkaline peroxide was carried out as described in Part I for dunnione. The products were phthalic acid, which was identified as phthalanil (m. p. and mixed m. p. 206—208°), and acetone. The acetone-2 : 4-dinitrophenylhydrazone had m. p. 124—126° after four crystallisations from alcohol, and the mixture with an authentic specimen melted at 125—127° (Found : N, 23·0. Calc. for $C_9H_{10}O_4N_4$: N, 23·5%).

(b) 1 G. of hydroxyhydro*iso*dunniol was dissolved in 100 c.c. of 10% aqueous sodium hydroxide, and a solution of 1 g. of potassium permanganate in 100 c.c. of water added at room temperature. The mixture was kept for 24 hours; the red solution was then filtered from manganese dioxide and acidified with excess of concentrated hydrochloric acid; after 2 hours, orange-red needles had separated. Extraction with benzene yielded β-*iso*dunnione (m. p. and mixed m. p. 129—131°) in amount representing the greater part of the starting material. In a second experiment, solutions of 1 g. of hydroxyhydro*iso*dunniol in 10 c.c. of 5% aqueous sodium hydroxide, 20 g. of sodium hydroxide in 100 c.c. of water, and 1 g. of potassium permanganate in 100 c.c. of water were cooled to 0°, mixed, and kept at 0° for 3 hours. The mixture was then kept at room temperature for a further 21 hours. The result was the same as in the first experiment. No acid oxidation product was obtained in amount sufficiently large to identify.

Bromo-β-iso*dunnione.*—3·5 G. of β-*iso*dunnione were dissolved in 70 c.c. of chloroform and added to a solution of 0·81 c.c. of bromine in 50 c.c. of chloroform. The mixture was then kept for 4—6 days at room temperature. In some experiments a few crystals separated towards the end of the reaction. These did not dissolve in chloroform or benzene unless first treated with water, which converted them into β-*iso*dunnione. The substance was evidently β-*iso*dunnione hydrobromide (cf. bromo-β-lapachone; Hooker, J., 1892, **61**, 611). The chloroform solution was shaken with water and evaporated to dryness, and the residue extracted with a small amount of light petroleum, which removed a dark-coloured resinous impurity. The *bromo*-β-iso*dunnione* remaining was twice crystallised from aqueous alcohol and twice from light petroleum. It was obtained as silky reddish-orange needles, m. p. 141—143°, which darkened in sunlight, though not as rapidly as β-*iso*dunnione (Found: C, 56·0; H, 4·05; Br, 24·9. $C_{15}H_{13}O_3Br$ requires C, 56·1; H, 4·05; Br, 24·9%).

In a small-scale experiment bromo-β-*iso*dunnione was boiled with 5% aqueous sodium hydroxide. After 1 hour the red solution was cooled and neutralised. The colour changed to pale yellow, but no solid separated after keeping at 0° for 24 hours. The product, which should be dihydroxyhydro*iso*dunniol, was not obtained pure. It evidently had a high solubility in water, as it could only be completely extracted by ether after the solution had been saturated with sodium chloride.

iso*Dunniol*.—0·6 G. of bromo-β-*iso*dunnione was ground with a little 10% aqueous sodium hydroxide until thoroughly wetted. The volume of 10% sodium hydroxide was made up to 14 c.c., 0·6 g. of zinc dust added, and the mixture kept for 2 hours, with occasional shaking; 100 c.c. of water were then added, the liquid filtered, and air drawn through it for 2 hours. The red solution was boiled for ½ hour, cooled, and neutralised with hydrochloric acid. After 24 hours, yellow needles had separated from the yellow emulsion. These were twice crystallised from aqueous alcohol and had m. p. 118—119° (Found: C, 73·9; H, 5·7. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

The substance dissolved readily in aqueous sodium carbonate and was immediately extracted from a benzene solution by this reagent, giving a red solution. A solution of iso*dunniol* in concentrated sulphuric acid was left overnight and then poured into water. The product crystallised from light petroleum in red needles, m. p. and mixed m. p. with β-*iso*dunnione, 129—130°.

allo*Dunnione* (Found: $CH_3{\cdot}C^-$, 7·43%); $[\alpha]_D^{18^\circ} + 10{\cdot}2^\circ$ (*c*, 5·47 in chloroform). allo*Dunnione* was recovered unchanged (m. p. and mixed m. p.) after an alkaline solution had been refluxed with *p*-phenylphenacyl bromide in alcohol.

Oxidation of allo*Dunnione with Chromic Acid*.—This process, carried out in the same way as with dunnione, yielded acetone. The 2 : 4-dinitrophenylhydrazone was difficult to obtain pure, and melted at 121—123° after five crystallisations from alcohol. The mixed m. p. with acetone-2 : 4-dinitrophenylhydrazone was 122—124° and with the methyl *iso*propyl ketone derivative was *ca.* 105°.

*Dihydro*allo*dunnione*.—Reduction of *allo*dunnione by zinc dust and acetic acid, or by tin and hydrochloric acid, gave the *dihydro*-compound. This crystallised in colourless needles, m. p. 141—142°, from light petroleum or from 25% aqueous alcohol (Found: C, 73·9; H, 6·85. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%). The substance was slightly soluble in water, but dissolved easily in concentrated hydrochloric acid. It did not react with Brady's reagent over a period of 5 days, and an alcoholic solution gave no coloration with ferric chloride. It dissolved extremely slowly in cold half-saturated aqueous sodium carbonate, but more readily in aqueous sodium hydroxide, giving a colourless solution which soon became pale yellow. On the other hand it was extracted from a benzene solution by sodium hydroxide only with considerable difficulty. When a drop of aqueous sodium hydroxide was added to an alcoholic solution of dihydro*allo*dunnione, an intense red coloration was produced which faded to yellow in 1—2 minutes. This red colour appeared only in the presence of alcohol and if the solution was acidified while still red it became colourless. But if the alkaline solution was yellow, then it remained pale yellow after acidification and some *allo*dunnione (m. p. and mixed m. p.), together with unchanged dihydro*allo*dunnione, was isolated from it.

*Diacetyldihydro*allo*dunnione* was obtained by acetylation of dihydro*allo*dunnione with acetic anhydride and anhydrous sodium acetate. It could not be prepared by direct reductive acetylation of *allo*dunnione. It crystallised from aqueous alcohol in colourless prisms, m. p. 191—193° [Found: C, 69·0; H, 6·2; $CH_3{\cdot}CO$, 24·6; *M* (Rast in camphor), 313. $C_{15}H_{14}O(OAc)_2$ requires C, 69·5; H, 6·1; $CH_3{\cdot}CO$, 26·2%; *M*, 328].

Reduction of allo*Dunnione in Alkaline Solution*.—A solution of *allo*dunnione in 10% aqueous sodium hydroxide was boiled with zinc dust. It changed rapidly from deep yellow to pale yellow and then during ½ hour became colourless. The cooled solution was neutralised with hydrochloric acid, saturated with salt, and extracted three times with ether. The residue after evaporation of the ethereal solution was crystallised from 25% aqueous alcohol and finally from water. The substance, evidently *dihydrohydroxyhydro*allo*dunnione*, separated in rosettes of colourless needles, m. p. 160—161° (Found: C, 68·6; H, 7·0. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

allo*Dunnionesulphonic Acid*.—A solution of *allo*dunnione in concentrated sulphuric acid was heated at 100° for ½ hour in order to determine whether isomerisation would take place.

The solution, which became green, was poured into water, and the product extracted by amyl alcohol after saturation with salt. The amyl-alcoholic solution was shaken with aqueous sodium hydroxide, and the alkaline solution acidified with excess of concentrated hydrochloric acid. The precipitate was twice crystallised from 15% hydrochloric acid and was obtained as an orange, micro-crystalline powder. It did not melt below 230° and did not contain chlorine (Found: C, 56·4; H, 4·65; S, 9·0. $C_{15}H_{14}O_6S$ requires C, 55·9; H, 4·35; S, 9·9%). The sulphur content was somewhat low, but the analysis was not repeated, as the compound was of no further interest. It gave an orange-yellow lead salt which was insoluble in water.

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