Synthetic Experiments in the cyclo*Heptatrienone Series. Part IV.** 3-*Hydroxytropone.*

By R. B. Johns, A. W. Johnson, and M. Tišler.

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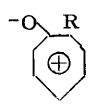
3-Hydroxytropone has been synthesised by three methods, and its physical and chemical properties have been compared with those of tropone and tropolone. A previous claim to have prepared *iso*stipitatic acid has been disproved and the preparation of the authentic compound is described.

Considerable experimental evidence has now accumulated to substantiate Dewar's prediction (*Nature*, 1945, **155**, 50) that tropolone would have aromatic character (review: Johnson, *J.*, 1954, 1331). This feature has been associated with the *cyclo*heptatrienylium cation as expressed in the resonance hybrid (I; R = OH), which as it contains 6π-electrons in the ring fulfils an important condition required by theory for aromatic rings (cf. Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203). Tropone (*cyclo*heptatrienone) (I; R = H) has also been prepared (Dauben and Ringold, *J. Amer. Chem. Soc.*, 1951, **73**, 876; Doering and Detert, *ibid.*, p. 876; Nozoe, Kitahara, Ando, Masumune, and Abe, *Sci. Rep. Tôhoku Univ.*, 1952, **36**, 166; see also Büchi, Yang, Emerman, and Meinwald, *Chem. and Ind.*, 1953, 1063; Van Tamalen and Hildahl, *J. Amer. Chem. Soc.*, 1953, **75**, 5451) and, as the *cyclo*heptatrienylium cation is also present in this simplified structure, a comparison of the aromatic character of tropone and tropolone is of theoretical interest. Tropone can be readily brominated and aminated (by hydroxylamine) in position 2 but it is less stable than tropolone towards heat and alkali. It thus appears that in tropolone the five-membered hydrogen-bonded ring involving the carbonyl and the 2-hydroxyl group makes a significant contribution to its stability.

The isomers of tropolone, *i.e.*, 3- and 4-hydroxytropone, are as yet unknown and their properties would clearly be of importance for a discussion of the degree of aromatic character in seven-membered ring systems. The present paper deals with the preparation of 3-hydroxytropone (II), for which the ring expansion of resorcinol dimethyl ether with diazoacetic ester, known to give 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid (III, or a double bond isomer) (Johns, Johnson, and Murray, *J.*, 1954, 198), provided a starting point. Bromination of the acid (III) in acetic acid caused replacement of the carboxyl group as well as nuclear substitution, and 2 : 5 : 7-tribromo-3-hydroxytropone (IV; R = Br) was obtained in 73% yield. The structure of this compound was proved by the following sequence: reaction with sodium methoxide replaced the 5- and the 7-bromine atom by methoxyl to give the ether (IV; R = OMe), the 2-bromine atom being more resistant to substitution because of steric hindrance although this was not sufficient to prevent hydro-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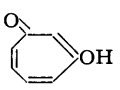
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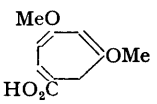
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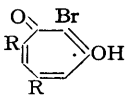
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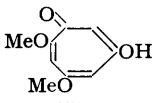

(V)

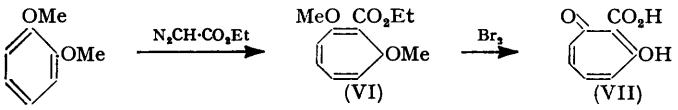
genolysis which gave 6-hydroxy-2 : 4-dimethoxytropone (V). Acid hydrolysis of (V) gave 4 : 6-dihydroxytropolone and alkaline rearrangement yielded 3 : 5-dihydroxybenzoic acid, thus confirming the structure of (V) and providing strong support for the orientation of the bromine atoms in the tribromo-3-hydroxytropone.

Hydrogenolysis of 2 : 5 : 7-tribromo-3-hydroxytropone (IV; R = Br) proved very difficult to regulate without causing simultaneous reduction of the tropone ring, but by use of a palladium catalyst partly poisoned by the addition of lead acetate a small yield of 3-hydroxytropone (II) (isolated as its crystalline picrate) was obtained, together with a little bromo-3-hydroxytropone. The bromine in this compound is probably in the 5-position as it differed from the possible isomeric bromo-compounds, which were also prepared in

* Part III, *J.*, 1954, 198.

this work. Regeneration of 3-hydroxytropone from its picrate was effected conveniently with Dowex 2 ion-exchange resin. A more convenient synthesis of 3-hydroxytropone from 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid (III) involved decarboxylation and subsequent bromine oxidation of the 3 : 5-dimethoxy*cyclo*heptatriene to 3-methoxytropone which was also purified through its crystalline picrate. Hydrolysis of 3-methoxytropone with hydrogen bromide gave 3-hydroxytropone in overall yields of up to 75% from 3 : 5-dimethoxy*cyclo*heptatriene. A small quantity of 2-bromo-5-hydroxytropone was also isolated from the product, the orientation of the bromine atom being proved by *X*-ray analysis (Mr. T. R. MacDonald, personal communication).

In another investigation, a third route to 3-hydroxytropone was discovered. The crude ester from the reaction of veratrole with diazoacetic ester (Bartels-Keith, Johnson, and Taylor, *J.*, 1951, 337), on treatment with bromine, gave tropolone-4-carboxylic ester together with an acid, m. p. 149°, isomeric but not identical with any of the tropolonecarboxylic acids. It has now been proved that this acid is a 3-hydroxytroponecarboxylic acid and the only isomer which can be obtained from veratrole by a logical sequence is the 2-carboxylic acid (VII), presumably with the intermediate formation of a dimethoxy-*cyclo*heptatrienecarboxylic ester such as (VI) or a double-bond isomer.



(VI) (VII)

The reaction of diazoacetic ester at two substituted positions in a benzenoid compound seems to be peculiar to veratrole among the *o*-disubstituted benzenes which have been studied. Normally diazoacetic ester reacts with an unsubstituted double bond in the aromatic nucleus although a few cases of ring expansion of benzenoid compounds containing no unsubstituted *o*-positions by means of this reagent have been reported (*e.g.*, Buchner, *Ber.*, 1920, **53**, 869; Plattner *et al.*, *Helv. Chim. Acta*, 1949, **32**, 2137, 2452, 2464). Fractionation of the crude reaction mixture from veratrole and diazoacetic ester gave the crystalline ester (VI) which yielded the corresponding acid and, on oxidation with bromine, 3-hydroxytropone-2-carboxylic acid, identical with the product obtained earlier. Hydrogenation of the ester (VI) gave ethyl 2 : 7-dimethoxy*cyclo*heptanecarboxylate, and decarboxylation of the acid corresponding to (VI) gave 1 : 3-dimethoxy*cyclo*heptatriene, identified by oxidation with bromine to 3-methoxytropone.

3-Hydroxytropone is an almost colourless crystalline solid. When it is compared with tropolone many of the marked differences in its physical properties (cf. Table) can be

Comparison of physical properties of tropolone, tropone, and 3-hydroxytropone.

	Tropolone [1]	Tropone [2]	3-Hydroxytropone
M. p.	49°	−8° to −5°	179—180°
pK_a	6·7	—	5·4
Colour of anion	Intense yellow	—	Colourless
Volatility	Sublimes at 100°/150 mm.	B. p. 113°/15 mm.	Sublimes slowly at 140°/0·1 mm.
Ferric reaction	Green	—	—
Solubility in non-polar solvents	Soluble	Moderately soluble	Insoluble
Max. (mμ) in u.v. spectrum	228, 237, 303 (infl.), 320, 351 (EtOH)	225, 228, 231, 239, 312 (H_2O)	247, 255, 298, 309 (EtOH)
Max. (mμ) in u.v. spectrum (0·1N-NaOH)	234, 330, 393	—	257, 267, 295, 304
Principal max. in i.r. spectrum (1650—1150 cm.$^{-1}$)	1615, 1553, 1475, 1440, 1255	1638, 1582, 1524, 1475, 1225, 1217	1647, 1587, 1550, 1515, 1477, 1443, 1258, 1230, 1196

[1] Doering and Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 828; Koch, *J.*, 1951, 513. [2] Dauben and Ringold; Doering and Detert, *locc. cit.*

ascribed to the lack of hydrogen bonding. The pK_a value of 5·4 for 3-hydroxytropone recalls that of dihydroresorcinol (pK_a 5·25; Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1162), and both compounds could be regarded as monoenolic forms of cyclic β-diketones. Phenol on the other hand has pK_a 10·0. The intensity of absorption of the

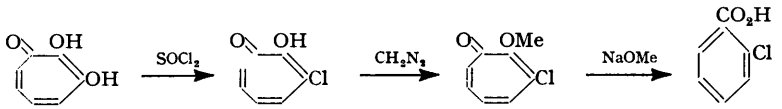
principal band in the ultra-violet spectrum of 3-hydroxytropone (log ε 4·51 at 247 mμ, 4·41 at 255 mμ) is even greater than that of tropolone log ε 4·33 at 225 mμ) and it appears that introduction of a β-hydroxy-group into the tropone molecule has a greater effect on the ultra-violet absorption spectrum than does an α-hydroxyl group. A similar effect has been noted with the carboxylic acids:

Tropone-4-carboxylic acid [1]	233 mμ; log ε 4·41
2-Hydroxytropone-4-carboxylic acid [2]	244—246 mμ; log ε 4·49
6-Hydroxytropone-4-carboxylic acid [3]	254 mμ; log ε 4·40

[1] Bartels-Keith, Johnson, and Langemann, *J.*, 1952, 4461. [2] Bartels-Keith, Johnson, and Taylor, *loc. cit.* [3] This paper.

The infra-red spectrum of 3-hydroxytropone, when determined on a mull in Nujol, provides evidence for strong intermolecular bonding in the solid state. Thus there is no distinct absorption in the hydroxyl region and the intensity of the band at 1647 cm.$^{-1}$, ascribed to the carbonyl group, greatly increases when the spectrum is measured on a solution in chloroform.

Apart from the methods of preparation from resorcinol dimethyl ether and from veratrole the evidence for the structure of 3-hydroxytropone has been derived from consideration of its physical and chemical properties. Like tropolone and tropone it exhibits basic properties and forms a crystalline hydrobromide and picrate. The presence of the hydroxyl group is substantiated by the formation of methyl ethers produced with diazomethane from both 3-hydroxytropone and its tribromo-derivative (IV; R = Br). However an examination of the bromination of 3-hydroxytropone has placed its structure on a secure basis. Even in the presence of excess of bromine the main product is a monobromo-derivative which is the 2-bromo-compound because of the combined directive influence of the two oxygen atoms. 2-Bromo-3-hydroxytropone has been prepared by another method by Seto (*Sci. Rep. Tôhoku Univ.*, 1953, **37**, 377). Its *X*-ray analysis confirmed conclusively the relative positions of the bromine and two oxygen atoms in the seven-membered ring (T. R. MacDonald, personal communication) and showed that the two carbon–oxygen bonds can be differentiated. Acid hydrolysis yields 3-hydroxytropolone, m. p. 136—137°, which gives salicylic acid on fusion with potassium hydroxide. 3-Hydroxytropolone has been reported as having m. p. 136—137° (Nozoe, Seto, Ito, Sato, and Katono, *ibid.*, p. 191) and 244° (Abadir, Cook, Loudon, and Steel, *J.*, 1952, 2350). The compound of m. p. 136—137° was prepared by Nozoe *et al.* (*loc. cit.*) together with the known 5-hydroxytropolone, also of m. p. 244°, by the persulphate oxidation of tropolone, and the following transformations leading to *o*-chlorobenzoic acid were adduced in support of the structure:



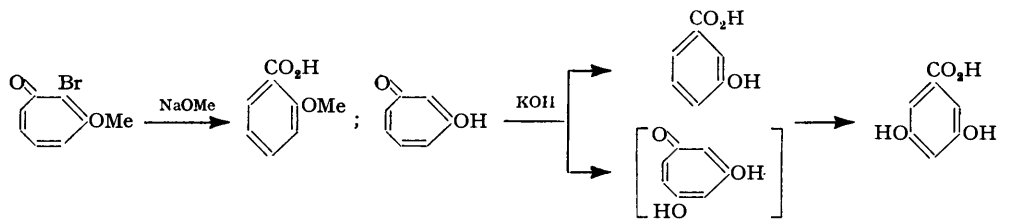
The British claim to have prepared 3-hydroxytropolone involved the interaction of potassium hydroxide and 3-bromotropolone, the structure of which is in no doubt. Nozoe, Kitahara, and Masumune (*Proc. Japan Acad.*, 1951, **27**, 649) had already studied this reaction and obtained a hydroxytropolone of m. p. 226—227° which was originally thought to be the 3-hydroxy-compound but later (Nozoe, Seto, Ito, Sato, and Katono, *loc. cit.*; Nozoe and Kitahara, *Proc. Japan Acad.*, 1954, **30**, 204) was shown to be 4-hydroxytropolone, *i.e.*, the decarboxylation product of stipitatic acid for which Birkinshaw, Chambers, and Raistrick (*Biochem. J.*, 1942, **36**, 242) give m. p. 227—228°. A minute amount of the authentic 3-hydroxytropolone has been isolated from the potassium hydroxide–3-bromotropolone reaction by Nozoe and Kitahara (*loc. cit.*).

The formation of 4-hydroxytropolone from 3-bromotropolone recalls the commercial production of *m*-cresol from *o*- or *p*-chlorotoluene with sodium hydroxide (Shreve and Marsel, *Ind. Eng. Chem.*, 1946, **38**, 254) and is an example of the so-called aromatic cine-substitutions (*e.g.*, Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 273; Roberts, Simmons, Carlsmith, and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 3290). The ease of formation

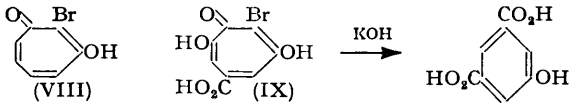
of the postulated " acetylenic " intermediates may be greater in the tropone series because of the decreased steric strain.

The nature of the yellow product, m. p. 244°, which gives salicylic acid on alkaline rearrangement as reported by Abadir *et al.* is still unknown. From the hydrolysis of 3-bromotropolone with hydrochloric acid–acetic acid we have obtained 3-hydroxytropolone, m. p. 136—137°, identical with the product obtained from 2-bromo-3-hydroxytropone by acid hydrolysis. Hydrolysis of 3-bromotropolone with hydrogen bromide in aqueous acetic acid gave tropolone (cf. Doering and Knox, Abs. 123rd Meeting Amer. Chem. Soc., 1953, p. 8M).

The alkaline rearrangement of 3-hydroxytropone and its 2-bromo-derivative presented some interesting features. Treatment of 2-bromo-3-methoxytropone with sodium methoxide gave *o*-methoxybenzoic acid as expected but 2-bromo-3-hydroxytropone and 3-methoxytropone were unchanged after similar reactions. As with tropone itself, considerable decomposition of 3-hydroxytropone occurred during fusion with potassium hydroxide but reaction at 300° gave α-resorcylic acid, oxalic acid, and a very small quantity of (probably) *m*-hydroxybenzoic acid, but no salicylic acid. The hydroxybenzoic acids are not hydroxylated when fused with potassium hydroxide at 300°, and to explain the formation of α-resorcylic acid an initial hydroxylation of the seven-membered ring at the 5-position must be postulated. Such hydroxylations during potassium hydroxide fusions are well-known with benzenoid compounds, especially those containing electron-attracting groups (cf., *e.g.*, Bradley, *Chem. and Ind.*, 1954, 631). Further oxidation involving ring fission could account for the formation of oxalic acid. Attack by hydroxyl at $C_{(1)}$ and expulsion of a hydride ion from $C_{(7)}$ from the presumed 3 : 5-dihydroxytropone intermediate in the usual manner lead to α-resorcylic acid although the possibility of a tropolone intermediate (*i.e.*, hydroxylation at $C_{(7)}$ as well as $C_{(5)}$) must not be overlooked.



As in the tropolone series the ease of alkaline rearrangement of tropones is largely dependent on the nature of the substituents. The resistance of 3-hydroxytropone to rearrangement should be contrasted with the ease of formation of terephthalic acid from tropone-4-carboxylic acid in alkali at room temperature (Bartels-Keith, Johnson, and Langemann, *loc. cit.*). In the alkaline rearrangement of a tropone, the hydride ion can be expelled either from $C_{(2)}$ (with $C_{(1)}$–$C_{(7)}$ fission) or from $C_{(7)}$ (with $C_{(1)}$–$C_{(2)}$ fission). In the examples studied so far it is the hydrogen attached to the more positive (or less negative) centre which is expelled, *i.e.*, that from $C_{(7)}$ in both 3-hydroxytropone and tropone-4-carboxylic acid. When the effects of hydroxy- and carboxy-substituents are opposed, *e.g.*, in 3-hydroxytropone-5-carboxylic acid (3-hydroxy-4-oxo*cyclo*heptatriene-carboxylic acid; XII, see below) the effect of the hydroxy-group predominates and the product of rearrangement is 5-hydroxy*iso*phthalic acid.

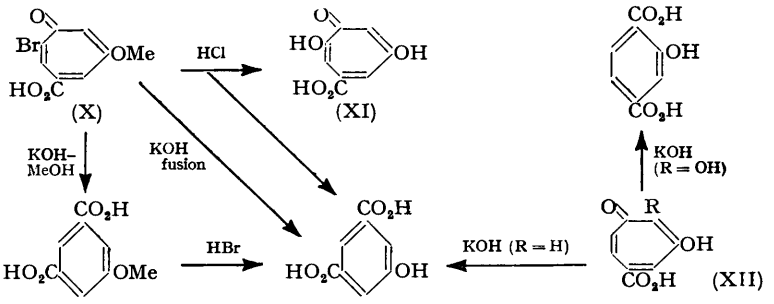


Fusion of 2-bromo-3-hydroxytropone (VIII) with potassium hydroxide at 300° also gave α-resorcylic acid and oxalic acid, as well as a little 3-hydroxytropolone and (probably) *m*-hydroxybenzoic acid. A closely related case is the rearrangement of bromostipitatic acid (IX) to 5-hydroxy*iso*phthalic acid on fusion with alkali (Birkinshaw, Chambers, and Raistrick, *loc. cit.*) although under slightly milder conditions puberulic acid is obtained

(Johns, Johnson, and Murray, *loc. cit.*). It is probable that with 2-bromo-3-hydroxytropone initial dehalogenation occurs and that the reaction then proceeds as outlined above for 3-hydroxytropone. *p*-Chlorophenol, for example, gives appreciable amounts of phenol by vigorous reaction with sodium hydroxide, and the resorcinol which is also obtained may well be derived by hydroxylation of phenol (Fierz-David and Stamm, *Helv. Chim. Acta*, 1942, **25**, 364).

Substitution reactions of 3-hydroxytropone other than bromination will be reported in a later paper.

iso*Stipitatic Acid. A Correction.*—The widespread use of the benzilic acid type of alkaline rearrangement of tropolones and their derivatives to benzenoid compounds for assignment of structure (Johnson, *J.*, 1954, 1331) necessitates the assumption that substituent groups retain their relative positions in the ring during the reaction. Apart from nucleophilic substitutions (including cine-substitutions), no exceptions to this rule have been substantiated (cf., *e.g.*, Doering and Sayigh, *J. Amer. Chem. Soc.*, 1954, **76**, 39); one apparent anomaly is the rearrangement of derivatives of *iso*stipitatic acid to 5-hydroxy-*iso*phthalic acid (Johns, Johnson, and Murray, *loc. cit.*). Re-examination of the reactions leading to the alleged *iso*stipitatic acid has shown that certain of the intermediates were orientated incorrectly. The compound believed to be 4-bromo-3-methoxy-5-oxo*cyclo*heptatrienecarboxylic acid, prepared by the bromination of 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid in chloroform, is the 6-bromo-compound (X) as hydrolysis with hydrochloric acid and acetic acid gives stipitatic acid (XI). The course of this nucleophilic displacement depends on the experimental conditions, for the intermediate carbonium ion can either react with hydroxyl to give stipitatic acid or (when a rather greater concentration of acid is used) can rearrange to a benzenoid intermediate before recombination, the product being 5-hydroxy*iso*phthalic acid. This type of ring contraction under acid conditions recalls the formation of salicylic acids on decomposition of diazonium salts of 3-aminotropolones (Haworth and Jefferies, *J.*, 1951, 2067; Nozoe *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 1895; *Proc. Japan Acad.*, 1951, **27**, 282, 565). Rearrangement of the acid (X) or its ester with methanolic potassium hydroxide (Part III; *loc. cit.*) gives 5-methoxy*iso*phthalic acid with a little of the isomeric *O*-methylstipitatic acid, and rearrangement of (X) by fusion with potassium hydroxide gives 5-hydroxy*iso*phthalic acid. In common with all other troponecarboxylic acids which we have prepared, and unlike the tropolonecarboxylic acids (*e.g.*, Haworth and Hobson, *J.*, 1951, 561), the acid (X) was resistant to decarboxylation.



Bromination of 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid in acetic acid gave 3-hydroxy-5-oxo*cyclo*heptatrienecarboxylic acid (XII; R = H) in good yield and this on further bromination yielded 4-bromo-3-hydroxy-5-oxo*cyclo*heptatrienecarboxylic acid (XII; R = Br) (cf. the bromination of 3-hydroxytropone). Acid hydrolysis of (XII; R = Br) gave authentic *iso*stipitatic acid (XII; R = OH), m. p. 282°, which yielded 2-hydroxyterephthalic acid with potassium hydroxide at 300°. *iso*Stipitatic acid gave a green ferric derivative and with sodium hydroxide a yellow colour which, although more intense than that of solutions of the stipitatic acid anion, was not so marked as that of the salts of puberulic acid. In the 300—400 mμ region the acid showed the sharp

bands considered characteristic of 3-hydroxytropolones (Nozoe, Seto, Sato, and Katono, *Sci. Rep. Tôhoku Univ.*, 1953, **37**, 191) but otherwise the ultra-violet and the infra-red spectrum of *iso*stipitatic acid strongly resembled those of stipitatic acid and tropolone-4-carboxylic acid (Bartels-Keith, Johnson, and Taylor, *loc. cit.*) (see Table).

	*iso*Stipitatic acid	Stipitatic acid	Tropolone-4-carboxylic acid
Max. ($cm.^{-1}$) in i.r. spectrum (Nujol mull)	1287, 1506, 1534, 1623, 1704	1285, 1480, 1570, 1615, 1700	1272, 1468, 1530, 1605, 1770
Max. ($m\mu$) in u.v. spectrum (95% ethanol)	252, 340, 373, 385	261—264, 361—362 (infl., 368—369, 388—390)	244—246, 324—325, 367—369

Experimental

Unless otherwise stated, ultra-violet spectra were determined in 95% EtOH, and infra-red spectra on Nujol mulls.

2 : 5 : 7-*Tribromo*-3-*hydroxytropone*.—To a solution of 3 : 5-dimethoxy*cyclo*heptatriene-carboxylic acid (1 g.; Johns, Johnson, and Murray, *loc. cit.*) in glacial acetic acid (10 c.c.) and water (2 c.c.) at 0° bromine (1 c.c.) was added dropwise and, after slight warming to dissolve any bromine complex precipitated, the solution was set aside at room temperature for 15 min., then diluted to 50 c.c. with water and kept at 0° for 24 hr. The aqueous layer was decanted from any precipitated material (*A*) and concentrated under reduced pressure, any solid material being collected as it was formed. More water was added to the residue and the process repeated. Meanwhile the precipitate (*A*) was dissolved in aqueous acetone, and the acetone slowly evaporated on the steam-bath. Hydrogen bromide was evolved and needles of 2 : 5 : 7-*tribromo*-3-*hydroxytropone* were obtained. All the solid fractions were then combined and crystallised from methanol, to give the product as pale yellow needles (1·35 g.), m. p. 222° (decomp.). In another experiment the material (*A*) was not separated, but the mixture was concentrated and cooled as before. Any solid material which was now obtained was separated and the process repeated twice. The combined precipitates were crystallised from methanol as before (Found, on a sample sublimed at 140—150°/0·1 mm.: C, 23·3; H, 1·0. $C_7H_3O_2Br_3$ requires C, 23·4; H, 0·85%). The compound was slightly soluble in methanol and ethanol and insoluble in water. It gave no ferric reaction. The yellow potassium salt was obtained by addition of potassium acetate to a solution of the tribromo-3-hydroxytropone in methanol. Light absorption: max. at 374, 337, 323, 290, 278, and 238 $m\mu$ (log ε 3·52, 3·61, 3·63, 4·20, 4·28 and 4·10 respectively). Infra-red max.: 1605, 1541, 1513, 1406, 1333, 1280, 1235, 1101, 1070, 1040, 939, 912, 884, 866, 778, 741, 729, 724, 701, and 666 $cm.^{-1}$.

2 : 5 : 7-*Tribromo*-3-*methoxytropone*, obtained by treatment of a solution of the 3-hydroxy-compound (0·5 g.) in methanol (50 c.c.) with an excess of ethereal diazomethane at room temperature overnight, crystallised from methanol as yellow needles, m. p. 198—199° (decomp.). For analysis, it was sublimed at 160°/0·3 mm. (Found: C, 25·5; H, 1·6. $C_8H_5O_2Br_3$ requires C, 25·7; H, 1·3%). Light absorption: max. at 373—375, 331, 320, 278, and 238 $m\mu$ (log ε, 3·58, 3·71, 3·70, 4·35 and 4·15 respectively). Infra-red max.: 1610, 1550, 1408, 1339, 1271, 1235, 1149, 1104, 1042, 966, 943, 910, 885, 866, 775, 740, 724, 701, and 666 $cm.^{-1}$.

2-*Bromo*-3-*hydroxy*-5 : 7-*dimethoxytropone*.—2 : 5 : 7-Tribromo-3-hydroxytropone (1·98 g.) was added to a solution prepared from sodium (1·5 g.) and dry methanol (100 c.c.), then heated under reflux for 2 hr., diluted with water (10 c.c.), and kept for a further hour. The solid obtained after removal of the solvent was dissolved in water (30 c.c.) and the solution acidified with 3N-hydrochloric acid. After cooling at 0° for 2 hr. the cream-coloured precipitate was separated, washed with water, and dried (1·36 g., 94%). It crystallised from methanol (charcoal) in pale yellow needles, m. p. 221° (decomp. with previous darkening), which did not sublime (Found: C, 41·7; H, 3·5. $C_9H_9O_4Br$ requires C, 41·4; H, 3·4%). The *compound* was soluble in aqueous alkali, slightly soluble in cold methanol and insoluble in water. Light absorption: max. at 338 and 262 $m\mu$ (log ε 3·89 and 4·42 respectively).

6-*Hydroxy*-2 : 4-*dimethoxytropone*.—The foregoing bromo-compound (1·36 g.) was suspended in methanol and the minimum quantity of 10% aqueous sodium hydroxide added to effect dissolution. Potassium acetate (0·4 g.) was added and a little charcoal (0·1 g.), which after agitation for 1 min., was separated by filtration. The filtrate was then hydrogenated with a 10% palladium–charcoal catalyst (0·2 g.), and the reaction discontinued after absorption of 1 mol. of hydrogen (120 c.c. at N.T.P.). The catalyst was separated, and the solvent removed

from the acidified filtrate. Water (20 c.c.) was added to the residue, the suspension cooled (ice), and the precipitate (0·57 g.) separated and dried. A further quantity (76 mg.) was obtained by continuous ether-extraction of the mother-liquor for 2 days. The product crystallised from water and for analysis was sublimed at 155°/0·3 mm., being obtained as colourless needles, m. p. 210° (decomp.) (Found: C, 59·0; H, 5·6. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%). Light absorption: max. at 329 and 252 mμ (log ε 3·92 and 4·58 respectively). Infra-red max.: 2924, 2564, 1639, 1613, 1539, 1508, 1460, 1443, 1431, 1387, 1335, 1287, 1267, 1220, 1198, 1181, 1159, 1067, 1032, 1001, 948, 917, 855, 842, 830, 769, 754, 697, and 659 cm.$^{-1}$.

Alkaline Rearrangement of 6-*Hydroxy*-2 : 4-*dimethoxytropone*.—6-Hydroxy-2 : 4-dimethoxytropone (0·51 g.) was fused in a nickel crucible with potassium hydroxide (5 g.) and water (1·5 c.c.). The temperature was raised slowly and at 160° a further quantity of potassium hydroxide (2 g.) was added. At 190° considerable effervescence occurred and a pale yellow suspension was obtained which became colourless at 290°. The melt was kept at 300° for 10 min., then cooled, dissolved in water (10 c.c.), and acidified with hydrochloric acid. The colourless solution was extracted with ether (5 × 20 c.c.), and the solvent removed from the washed and dried ethereal extracts to give a residue (40 mg.) which was purified by sublimation at 0·1 mm. The product was a colourless solid which gave no ferric reaction and had m. p. 225—227° and m. p. 226—228° when mixed with α-resorcylic acid, m. p. 227—229°. A further quantity (81 mg.) was obtained by continuous ether-extraction of the aqueous layer for 36 hr.

2 : 4 : 6-*Trihydroxytropone*.—6-Hydroxy-2 : 4-dimethoxytropone was heated for 12 hr. at 110° with 48% hydrobromic acid. The solution was evaporated to dryness and water (0·5 c.c.) added to the residue, together with potassium acetate to give pH 6. After cooling (ice), the precipitate of 2 : 4 : 6-trihydroxytropone was separated and crystallised from water, as needles, m. p. 222° (decomp.). For analysis it was sublimed at 170°/0·5 mm. (Found: C, 54·5; H, 4·0. $C_7H_6O_4$ requires C, 54·6; H, 3·9%). The compound gave a blood-red ferric reaction and formed a yellow solution in 10% aqueous sodium hydroxide. Light absorption: max. at 334 and 254 mμ (log ε 3·93 and 4·42 respectively). Infra-red max.: 3559, 3333, 2915, 2584, 1647, 1605, 1541, 1408, 1366, 1294, 1258, 1209, 1190, 1047, 995, 889, 869, 846, 784, 760, 735, 727, and 667 cm.$^{-1}$

1 : 3-*Dimethoxy*cyclo*heptatriene*.—(i) A mixture of 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid (1 g.) (Johns, Johnson, and Murray, *loc. cit.*) and copper bronze (10 g.) was heated and the distillate was collected. The distillates from three such experiments were combined and redistilled; the fraction, b. p. 80—81°/3 mm. (0·73 g.), was collected as an almost colourless oil (Found: C, 71·0; H, 7·8. $C_9H_{12}O_2$ requires C, 71·0; H, 7·95%). Light absorption: max. at 279 mμ (log ε 3·70). The infra-red spectrum, determined on a film of the liquid, showed max. at 2994, 2941, 2825, 1724, 1631, 1600, 1553, 1511, 1495, 1464, 1456, 1439, 1416, 1383, 1357, 1339, 1287, 1261, 1224, 1200, 1178, 1163, 1148, 1133, 1093, 1037, 1013, 993, 957, 920, 900 862, 844, 823, 800, 767, 749, 728, and 704 cm.$^{-1}$. The product slowly resinified in air but was stable in a sealed tube in the dark.

(ii) A similar experiment on 2 : 7-dimethoxy*cyclo*heptatrienecarboxylic acid (see below) gave a dimethoxy*cyclo*heptatriene (38%), b. p. 82—84°/2 mm., n_D^{20} 1·5374 (Found: C, 71·5; H, 8·0%). The ultra-violet and infra-red spectra were very similar to those of the preceding product.

3-*Hydroxytropone*.—(i) *From* 1 : 3-*dimethoxy*cyclo*heptatriene*. A solution of this triene (1·35 g.) in chloroform (15 c.c.) was cooled (ice), and a solution of bromine (1·4 g., 1 mol.) in carbon tetrachloride (5 c.c.) was added dropwise at <5°. The cooled red solution was kept at 0° for a further 10 min. and the solvent then removed under reduced pressure. A little chloroform was added to the residue and the solution evaporated once more. The solid residue was triturated with cooled chloroform–carbon tetrachloride (1 : 1), and the insoluble material consisting largely of the hydrobromide of 3-methoxytropone (1·05 g.) was hydrolysed by 48% aqueous hydrogen bromide (7 c.c.) and water (7 c.c.) at 110° for 3 hr. Any solid material was separated, and the solvent removed from the filtrate. The residue was taken up in water (6 c.c.), and filtered if necessary, and the cooled filtrate neutralised with 10% aqueous sodium hydroxide and then made faintly acid with 2N-hydrochloric acid. After 30 min. at 0°, the pale brown precipitate of 3-hydroxytropone was separated and dried (0·57 g.). The filtrate was evaporated under reduced pressure to 3 c.c. and treated with an excess of aqueous picric acid, the 3-*hydroxytropone picrate* (0·49 g.) being obtained which recrystallised from water as yellow needles, m. p. 165° (decomp.) (Found: C, 44·7; H, 2·8; N, 12·2. $C_{13}H_9O_9N_3$ requires C, 44·45; H, 2·6; N, 12·0%).

When 3-*hydroxytropone* crystallised from ethyl acetate–methanol (1 : 1) or from water it

formed almost colourless needles, m. p. 179—180° (decomp. with previous darkening) (Found: C, 69·0; H, 5·15. $C_7H_6O_2$ requires C, 68·85; H, 4·95%). Light absorption: (i) in 95% ethanol: max. at 309, 298, 255, and 247 mμ (log ε 3·52, 3·65, 4·41, and 4·51 respectively); (ii) in 0·1N-sodium hydroxide: max. at 304, 295, 267, and 257 mμ (log ε 3·85, 3·84, 4·55, and 4·59 respectively). Infra-red max.: 1647, 1587, 1550, 1515, 1504, 1477, 1443, 1399, 1348, 1330, 1312, 1285, 1258, 1230, 1196, 996, 985, 881, 872, 826, 819, 786, 763, and 722 cm.$^{-1}$.

3-Hydroxytropone was readily soluble in methanol and ethanol, soluble in water, slightly soluble in ethyl acetate, and almost insoluble in cold chloroform, carbon tetrachloride, and carbon disulphide. It gave no colour with 10% aqueous sodium hydroxide or methanolic ferric chloride. The compound sublimed slowly at 140°/0·1 mm. but considerable decomposition occurred. Its pK in water at 16·5° was 5·4.

3-Hydroxytropone was regenerated by shaking a solution of its picrate (0·35 g.) in warm methanol (10 c.c.) with a slight excess of Dowex 2 resin in the hydroxide form, the solution becoming colourless. The resin was separated and after removal of the methanol there was obtained 3-hydroxytropone (0·12 g.) which was purified by crystallisation as before.

From some of the bromine oxidations of 1 : 3-dimethoxy*cyclo*heptatriene, small amounts of 2-*bromo*-6-*hydroxytropone*, m. p. 208° (with previous darkening), which crystallised from water in pale yellow needles, were isolated (Found: C, 41·9; H, 2·8. $C_7H_5O_2Br$ requires C, 41·8; H, 2·5%). The compound gave no ferric reaction and no colour with 10% aqueous sodium hydroxide. It decomposed on prolonged heating at 150° and could not be sublimed. Light absorption (i) in 95% ethanol: max. at 323, 311, 265, and 256 mμ (log ε 3·52, 3·54, 4·52, and 4·50 respectively); (ii) in 0·1N-sodium hydroxide: max. at 304, 276, 267, and 223 mμ (log ε 3·72, 4·65, 4·65, and 3·83 respectively). Infra-red max.: 2632, 1634, 1585, 1541, 1527, 1418, 1300, 1289, 1274, 1258, 1222, 1211, 1047, 1016, 975, 939, 916, 897, 878, 848, 816, 789, 734, 722, and 651 cm.$^{-1}$.

(ii) *Hydrogenolysis of* 2 : 5 : 7-*tribromo*-3-*hydroxytropone*. Anhydrous potassium acetate (1 g.) was added to a solution of 2 : 5 : 7-tribromo-3-hydroxytropone (1 g.) in ethanol (100 c.c.), and the precipitated potassium salt redissolved by the addition of water (30 c.c.). The solution was then hydrogenated in the presence of 10% palladium–barium sulphate poisoned with lead acetate; the reaction stopped after the uptake of 2·9 mols. of hydrogen. The catalyst was separated, the filtrate evaporated under reduced pressure, the residue dissolved in N-hydrochloric acid (5 c.c.), and any solid material removed. The filtrate was extracted with ether (4 × 5 c.c.) and then ethyl acetate (4 × 5 c.c.), and the combined extracts were dried and the solvent removed. The residue was extracted with dry ether (5 × 40 c.c.), and hydrogen chloride was bubbled through the cooled ethereal extract. The flocculent precipitate was separated, dissolved in a small volume of water, and treated with an excess of picric acid; 3-hydroxytropone picrate (50 mg.) was obtained and purified as before. In one experiment a small amount of a *monobromo*-3-*hydroxytropone* was obtained as colourless needles, m. p. 207°, from water (Found: C, 41·8; H, 2·3. $C_7H_5O_2Br$ requires C, 41·8; H, 2·5%) and did not form a picrate. When mixed with 7-bromo-hydroxytropone, it had m. p. 180°.

3-*Methoxytropone*.—(i) *From* 3-*hydroxytropone*. A methanolic solution of 3-hydroxytropone was treated with excess of ethereal diazomethane at room temperature for 20 min. The solvent was then removed and the residue treated with a slight excess of aqueous picric acid, to give 3-*methoxytropone picrate* as yellow needles, m. p. 128° (decomp.) after recrystallisation from water (Found: C, 45·9; H, 2·95. $C_{14}H_{11}O_9N_3$ requires C, 46·0; H, 3·0%). Treatment of this (0·17 g.) with Dowex 2 resin as before gave the free base as an almost colourless oil (43 mg.), b. p. 60—70° (bath-temp.)/0·5 mm.

(ii) *From* 1 : 3-*dimethoxy*cyclo*heptatriene*. A solution of 1 : 3-dimethoxy*cyclo*heptatriene (0·6 g.; from 2 : 7-dimethoxy*cyclo*heptatrienecarboxylic acid) in chloroform (10 c.c.) was treated with bromine (0·6 g., 1 mol.) in chloroform (5 c.c.) as described for 3-hydroxytropone. The solvent was removed under reduced pressure and the residual red oil triturated with absolute ethanol (2 c.c.). The resulting white crystalline solid 3-*methoxytropone hydrobromide* (80 mg., 17%) was separated; after sublimation during which extensive evolution of hydrogen bromide occurred it had m. p. 121—122° (decomp.), and gave no ferric reaction or 2 : 4-dinitrophenylhydrazone. A solution of the hydrobromide in water was neutralised with aqueous sodium hydroxide and treated with aqueous picric acid, 3-methoxytropone picrate being obtained as yellow needles, m. p. 146° after rapid crystallisation from water. Slow crystallisation of this picrate from water gave the other form, m. p. 128°, identical with that prepared in the previous experiment.

2 : 7-*Dimethoxy*cyclo*heptatrienecarboxylic Acid and Ethyl Ester*.—Veratrole (200 g.) and

ethyl diazoacetate (40 g.) were heated at 150° as described by Bartels-Keith, Johnson, and Taylor (*loc. cit.*), and the excess of veratrole was removed under reduced pressure. The residual esters from six such experiments were fractionated at 3×10^{-3} mm. and the following fractions collected: (i) b. p. 70—90° (3·5 g.), (ii) b. p. 90—105° (23·3 g.), (iii) b. p. 105—110° (23·2 g.), (iv) residue (34·5 g.). After 7 days at 0°, the crystalline product (2·5 g.) which had separated from fractions (ii) and (iii) and a second crop (0·6 g.) from the filtrate was collected and recrystallised from ethanol, giving *ethyl* 2 : 7-*dimethoxy*cyclo*heptatrienecarboxylate* as colourless needles, m. p. 98° (Found: C, 64·3; H, 6·9. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%). Light absorption: max. at 279 mμ (log ε 3·80). Infra-red max.: 1742, 1628, 1547, 1360, 1288, 1250, 1194, 1166, 1141, 1097, 1038, 1010, 1000, 970, 948, 854, 784, and 746 cm.$^{-1}$.

Hydrolysis of the ester (2 g.) with boiling alcoholic potassium hydroxide (10 c.c. of 2%) for 3 hr. gave the *acid*, which formed colourless plates (1·6 g.), m. p. 188—189° (decomp.), from methanol (Found: C, 61·0; H, 6·3. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). Light absorption: max. at 278 mμ (log ε 3·81), min. at 238—239 mμ (log ε 3·34). Infra-red max.: 2666, 1709, 1639, 1552, 1428, 1360, 1303, 1288, 1228, 1199, 1168, 1144, 1023, 1015, 1001, 965, 937, 920, 843, 780, and 740 cm.$^{-1}$.

The derived *hydrazide* (120 mg.) was obtained from the ester (0·15 g.) in boiling ethanol (5 c.c.) and aqueous hydrazine (1 c.c. of 30%) under reflux (1 hr.) and crystallised from ethanol as needles, m. p. 162—163° (decomp.) (Found: C, 57·3: H, 6·7; N, 13·3. $C_{10}H_{14}O_3N_2$ requires C, 57·1; H, 6·7; N, 13·3%). Light absorption: max. at 282 and 212 mμ (log ε 3·79 and 4·30 respectively). Infra-red max. (Nujol mull): 3226,1675, 1631, 1618, 1552, 1492, 1360, 1285, 1236, 1199, 1168, 1153, 1138, 1038, 1019, 1000, 990, 950, 921, 889, 869, 851, 845, 784, and 746 cm.$^{-1}$.

Hydrogenation. The ester (1·78 g.) in 95% ethanol was hydrogenated in the presence of Adams platinum catalyst. After saturation of the three double bonds (H_2, 507 c.c.; theor., 512 c.c.), the catalyst and solvent were removed. The residue was distilled and *ethyl* 2 : 7-*dimethoxy*cyclo*heptanecarboxylate* was collected as a fraction, b. p. 125—130°/20 mm. (1·6 g.), n_D^{15} 1·4662 (Found: C, 62·75; H, 9·2. $C_{12}H_{22}O_4$ requires C, 62·6; H, 9·6%).

3-*Hydroxytropone*-2-*carboxylic Acid.*—Ethyl 2 : 7-dimethoxy*cyclo*heptatrienecarboxylate (425 mg.) was dissolved in chloroform (10 c.c.), cooled to −20°, and treated dropwise with bromine (0·1 c.c.) in chloroform (5 c.c.). The product was kept for a further 15 min. and the chloroform then removed under reduced pressure. The residue, a thick reddish paste, was triturated with acetone and the solid residue sublimed at 90—95°/10^{-2} mm. The colourless crystalline product decomposed rapidly at 150°; with slow heating it had m. p. 149° (decomp.) (cf. Bartels-Keith, Johnson, and Taylor, *loc. cit.*) but with rapid heating m. p. up to 161° (Found: C, 57·8; H, 3·5. Calc. for $C_8H_6O_4$: C, 57·8; H, 3·6%). Infra-red max.: 1666, 1250, 1069, 1007, 975, 892, 836, and 778 cm.$^{-1}$.

2-*Bromo*-3-*hydroxytropone.*—A cooled solution of 3-hydroxytropone (0·24 g.) in glacial acetic acid (15 c.c.) was treated dropwise with 1·1 c.c. (1 mol.) of a solution of bromine (1 c.c.) in acetic acid (10 c.c.). Reaction was very rapid. The precipitated monobromo-derivative was separated, dried (0·26 g.), and crystallised from aqueous ethanol (charcoal) as buff-coloured needles, m. p. 214° (decomp.). Evaporation of the filtrate yielded a further quantity (54 mg.) of the product (Found: C, 41·5; H, 2·8. Calc. for $C_7H_5O_2Br$: C, 41·8; H, 2·5%). Light absorption: max. at 307, 261, 254, and 218 mμ (log ε 4·69, 4·37, 4·36, and 4·17 respectively). Infra-red max.: 2912, 2532, 1639, 1595, 1538, 1520, 1460, 1416, 1370, 1325, 1304, 1274, 1256, 1220, 1042, 1026, 985, 888, 868, 837, 794, 763, and 689 cm.$^{-1}$. Seto (*Sci. Rep. Tôhoku Univ.*, 1953, **37**, 377) gives m. p. 205—210° (decomp.).

The *methyl ether*, obtained by the action of diazomethane, formed colourless needles, m. p. 118—119°, from ethanol (Found: C, 44·7; H, 3·5. $C_8H_7O_2Br$ requires C, 44·7; H, 3·3%). The ultra-violet spectrum showed max. at 325, 312, 266, 251, and 223 mμ (log ε, 3·67, 3·70, 4·33, 4·35, and 4·20 respectively) with an inflection at 340—347 mμ (log ε 3·60). Infra-red max. (Nujol mull): 1639, 1562, 1481, 1438, 1410, 1315, 1282, 1242, 1219, 1176, 1075, 1015, 935, 882, 866, 824, 790, 684, and 666 cm.$^{-1}$.

Acid Hydrolysis of 2-*Bromo*-3-*hydroxytropone.*—The bromo-compound (0·15 g.) was heated in concentrated hydrochloric acid (12 c.c.), glacial acetic acid (10 c.c.), and water (1·5 c.c.) at 180° for 15 hr. The product was evaporated to dryness, the residue dissolved in water (6 c.c.), and the acidity of the solution adjusted to pH 6. A small amount (10 mg.) of insoluble material was separated and the filtrate extracted with ether (4 × 12 c.c.) and then ethyl acetate (4 × 12 c.c.). The solvent was removed from the combined dried extracts, and the residue sublimed at 110—120°/0·2 mm. to give colourless needles of 3-hydroxytropolone, m. p. 128—130° with previous softening [mixed m. p. with the hydrolysate of 3-bromotropolone (see below), 129—131°].

Alkaline Rearrangement of 2-Bromo-3-hydroxytropone.—The bromo-compound (0·46 g.) was thoroughly mixed with potassium hydroxide (5 g.), water (1 c.c.) was added, and the mixture heated in a nickel crucible. Effervescence was marked between 160° and 240°, but above 240° a dark brown melt was obtained which was kept at 300° for 10 min. The product was cooled, dissolved in water (10 c.c.), acidified with hydrochloric acid, and extracted with ether (5 × 30 c.c.). The solvent was removed from the combined dried extracts, and the syrupy residue (0·21 g.) sublimed at 120°/0·2 mm., the main portion of the sublimate forming a colourless solid (24 mg.), m. p. 132—133° alone and when mixed with 3-hydroxytropolone (see below). The ultra-violet absorption spectrum was also identical with that of authentic 3-hydroxytropolone (below): max. at 375, 365, 324, and 246 mμ (log ε 3·98, 3·93, 3·82, and 4·57 respectively).

The residue from the sublimation was subjected to further sublimation at 160°/0·2 mm., another colourless solid (30 mg.) being obtained. After crystallisation from benzene–acetone and re-sublimation, it had m. p. 225—226° (Found: C, 54·3; H, 4·0. Calc. for $C_7H_6O_4$: C, 54·5; H, 3·9%). Light absorption: max. at 309 and 250 mμ (log ε 3·46 and 3·82). The infra-red spectrum was that of α-resorcylic acid.

The colourless intermediate fraction (*ca.* 10 mg.) which was obtained between the 3-hydroxytropolone and α-resorcylic acid fractions had m. p. 176—180° and gave no ferric reaction. The ultra-violet absorption spectrum showed a max. at 297—298 mμ with an inflection at 230—235 mμ. Authentic *m*-hydroxybenzoic acid shows max. at 299 and 233 mμ and has m. p. 200°. Lack of material prevented complete purification.

The aqueous mother-liquors from the ethereal extraction were further extracted with ether continuously for 2½ days. Removal of the solvent gave a colourless crystalline residue (85 mg.) which sublimed at 120°/0·2 mm. and recrystallised from a little water as thick needles, m. p. 188° (after sublimation) alone or mixed with anhydrous oxalic acid.

Rearrangement of 2-Bromo-3-methoxytropone with Sodium Methoxide.—A solution of sodium methoxide (0·5 g.) in methanol was added to 2-bromo-3-methoxytropone (50 mg.) in methanol (2 c.c.) and the mixture heated under reflux for 2 hr. 3N-Sodium hydroxide (1 c.c.) was added and heating continued for a further 30 min. The methanol was evaporated and the residue then acidified with 3N-sulphuric acid and continuously extracted with ether for 3 hr. After removal of the solvent from the washed and dried extract the residue sublimed as a colourless solid, m. p. 101° alone and mixed with *o*-methoxybenzoic acid.

Alkaline Rearrangement of 3-Hydroxytropone.—3-Hydroxytropone (0·4 g.) was mixed with potassium hydroxide (5 g.) and water (1·5 c.c.) and fused as described above for 2-bromo-3-hydroxytropone. The temperature was kept at 300° for 5 min. but considerable charring occurred. The product was cooled, dissolved in water, and acidified as before, and then extracted first with ether (4 × 12 c.c.) and then with ethyl acetate (4 × 12 c.c.). The combined extracts were dried and the solvent was removed. The residual syrup was sublimed and the fraction obtained at 100—160°/0·2 mm. (6 mg.) was separated. This had m. p. *ca.* 180° (not sharp) and gave no ferric reaction, and the ultra-violet absorption showed a max. at 297 mμ and an inflection at 233—234 mμ (identical with that of the similar product from 2-bromo-3-hydroxytropone). A further fraction which sublimed at 180—190°/0·2 mm. (5 mg.) had m. p. 215° although its ultra-violet absorption was identical with that of α-resorcylic acid.

The aqueous mother-liquors were continuously extracted with ether for 3 days and after removal of the solvent the residue was sublimed at 120°/0·2 mm. The colourless sublimate was crystallised from water as before to yield oxalic acid dihydrate (28 mg.), m. p. and mixed m. p. 98°.

3-Hydroxytropolone.—3-Bromotropolone (0·49 g.) (Cook, Gibb, Raphael, and Somerville, *J.*, 1951, 503) was heated in acetic acid (5 c.c.), concentrated hydrochloric acid (5 c.c.), and water (2 c.c.) at 160—180° for 12 hr. The brown solution was continuously extracted with ether for 6 hr. and the solvent removed from the extract. The solid residue sublimed at 90°/0·05 mm. as a colourless solid which crystallised from ethanol. The 3-hydroxytropolone so obtained formed colourless needles (222 mg., 66%), m. p. 136° (Nozoe, Seto, Ito, Sato, and Katone, *Sci. Reports Tôhoku Univ.*, 1953, **37**, 191, give m. p. 136—137°) (Found: C, 60·8; H, 4·5. Calc. for $C_7H_6O_3$: C, 60·8; H, 4·4%). The yield of 3-hydroxytropolone was reduced to 47% when the hydrolysis was conducted for 24 hr.

Alkaline Rearrangement of 3-Hydroxytropolone.—3-Hydroxytropolone (0·15 g.) was heated with potassium hydroxide (2 g.) at 280—300° as described for 2-bromo-3-hydroxytropone. The cooled melt was dissolved in water and acidified with 11N-hydrochloric acid, and the resulting solution extracted with ether for 4 hr. After removal of the solvent and sublimation

at 90—100°/0·5 mm. the residue gave salicylic acid, m. p. and mixed m.p. 155—156°. The ultra-violet absorption spectrum was also that of salicylic acid.

3-*Hydroxy*-5-*oxo*cyclo*heptatrienecarboxylic Acid.*—Bromine (0·3 c.c.) in glacial acetic acid (3 c.c.) was added dropwise to 3 : 5-dimethoxy*cyclo*heptatrienecarboxylic acid (1 g.) (Johns, Johnson, and Murray, *J.*, 1954, 198) in cold acetic acid (15 c.c.) with stirring. The temperature was controlled so that the acetic acid remained liquid and after 3 min. sufficient water was added to redissolve any precipitate which had formed. The solution was cooled (ice) for a further 15 min. the solvent removed under reduced pressure, and water (5 c.c.) again added to the residue. The solvent was once more removed, the residue cooled in ice, and water (5 c.c.) again added, causing the oily residue to solidify. The suspension was set aside at 0° for ½ hr. and the dark grey solid separated, washed with water, and crystallised from methanol to give slightly impure 3-methoxy-5-oxo*cyclo*heptatrienecarboxylic acid (0·58 g.) (Johns, Johnson, and Murray, *loc. cit.*). This crude acid (0·39 g.) was heated with aqueous hydrobromic acid (20 c.c. of 48%) at 110° for 5 hr. and the product reduced to dryness. The residue was washed with a little cold water and then crystallised from water (charcoal) to give 3-*hydroxy*-5-*oxo*cyclo*heptatriene-carboxylic acid* as colourless needles (0·24 g.), m. p. 201—203° (decomp.) (Found : C, 54·7; H, 4·3. $C_8H_6O_4,\frac{1}{2}H_2O$ requires C, 54·9; H, 4·0%). The acid did not sublime. It was very soluble in methanol, soluble in hot water, and slightly soluble in acetone. Light absorption : max. at 306, 254 and 218 mμ (log ε 3·60, 4·40 and 4·17 respectively); inflection at 336—337 mμ (log ε 3·37). Infra-red max. : 3390, 3165, 3058, 2907, 1887, 1695, 1645, 1600, 1550, 1515, 1479, 1372, 1339, 1282, 1263, 1205, 1093, 990, 948, 893, 881, 775, 767, 688, and 680 cm.$^{-1}$.

Alkaline Rearrangement of 3-*Hydroxy*-5-*oxo*cyclo*heptatrienecarboxylic Acid.*—The acid (0·2 g.) was fused with potassium hydroxide (5 g.) and water (2 c.c.) at 300° for 10 min. After cooling and acidification with hydrochloric acid the solution was extracted with ether (6 × 25 c.c.), the extract dried, and the solvent removed. The fraction of the residue subliming at 160°/0·3 mm. (36 hr.) crystallised from water; the product (10 mg.) had m. p. 285—286° not depressed when mixed with 5-hydroxy*iso*phthalic acid (ultra-violet spectra identical).

4-*Bromo*-3-*hydroxy*-5-*oxo*cyclo*heptatrienecarboxylic acid.*—Bromine (0·14 c.c.) in acetic acid (1 c.c.) was added to a solution of 3-hydroxy-5-oxo*cyclo*heptatrienecarboxylic acid (0·42 g.) in acetic acid (20 c.c.) with stirring. After 5 min., water (4 c.c.) was added and after a further 15 min. the solution was evaporated to dryness under reduced pressure. The residual *mono-bromo-acid* crystallised from aqueous ethanol as pale yellow needles (0·53 g.). After sublimation at 170°/0·2 mm. they had m. p. 224° (previous charring) (Found : C, 39·2; H, 2·3. $C_8H_5O_4Br$ requires C, 39·2; H, 2·05%). Light absorption : max. at 358—360, 328, 316, 263, and 224 mμ (log ε 3·60, 3·61, 3·62, 4·24 and 4·16 respectively). Infra-red max. : 3165—3077 (broad), 2985—2703 (broad), 1862, 1695, 1639, 1587, 1546, 1522, 1445, 1412, 1385, 1351, 1292, 1242, 1221, 1031, 1006, 967, 889, 867, 847, 775, 754, and 669 cm.$^{-1}$.

iso*Stipitatic Acid.*—The foregoing bromo-compound (0·34 g.) was heated in acetic acid (7 c.c.), water (2 c.c.), and 11N-hydrochloric acid (10 c.c.) at 180° for 16 hr. The precipitated charred material was removed, the solvent removed under reduced pressure, and the residue diluted with water (8 c.c.). The suspension was again evaporated to dryness and the residue mixed with cooled water (5 c.c.). The suspended solid was separated, dried (0·13 g.), and crystallised from water or aqueous ethanol (charcoal). iso*Stipitatic acid* was thus obtained as small cream-coloured needles and was sublimed at 160°/0·2 mm.; it then had m. p. 282° (Found : C, 52·5; H, 3·6. $C_8H_6O_5$ requires C, 52·7; H, 3·3%). The acid gave an intense deep green colour with ferric chloride and a deep yellow colour with aqueous sodium hydroxide. Light absorption : max. at 385, 373, 340, and 252 mμ (log ε 4·02, 3·97, 3·93 and 4·58 respectively). Infra-red max. (Nujol mull) : 3030, 2899, 1704, 1623, 1582, 1534, 1506, 1379, 1307, 1287, 1225, 1183, 1064, 943, 833, 784, 757, and 735 cm.$^{-1}$.

*Alkaline rearrangement. iso*Stipitatic acid (0·16 g.) was intimately mixed with potassium hydroxide (5 g.), water (1·5 c.c.) added, and the bright yellow solution carefully heated to 300° in a nickel crucible. Considerable effervescence occurred about 240° and the colour of the melt changed to light brown at 280°. The temperature was held at 300° for 10 min., then the melt was cooled and dissolved in water (10 c.c.). The solution was treated with 2N-hydrochloric acid (20 c.c.) and finally acidified with 11N-hydrochloric acid. The pale brown solution was extracted with ether (8 × 25 c.c.), the combined ethereal extracts were dried, and the solvent was removed to leave an almost colourless residue (85 mg.) which crystallised from water (charcoal) and sublimed at 170°/0·2 mm. (24 hr.). The non-volatile residue was crystallised from water, then having m. p. 328°. Kuhn, Zilliken, and Trischmann (*Ber.*, 1950, **83**, 204) give m. p. 325° for 2-hydroxyterephthalic acid. The product gave a cherry-red ferric reaction.

The sublimate (20 mg.) also recrystallised from water but the m. p. could not be raised above 314°. It was probably impure 2-hydroxyterephthalic acid and gave a large m. p. depression on admixture with 4-hydroxy*iso*phthalic acid.

Stipitatic Acid.—6-Bromo-3-methoxy-5-oxo*cyclo*heptatrienecarboxylic acid (0·4 g.) (Johns, Johnson, and Murray, *loc. cit.*, where it is incorrectly described as the 4-bromo-compound) was heated with acetic acid (7 c.c.), water (3 c.c.) and concentrated hydrochloric acid (11 c.c.) at 180° for 11 hr. The solvent was removed under reduced pressure from the product, and water (3 c.c.) was added to the residue and again removed. The residue was treated with water (5 c.c.) and cooled in ice, and the precipitate was separated (0·12 g.). When crystallised from water (charcoal) this had m. p. 280—283°, not depressed on admixture with stipitatic acid. The product gave an intense green ferric reaction and had an ultra-violet spectrum identical with that of stipitatic acid. Bromination in 80% acetic acid (Johns, Johnson, and Murray, *loc. cit.*) gave monobromostipitatic acid.

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