699. *The Constitution of Chlorophorin, a Constituent of Iroko, the Timber of* Chlorophora excelsa. *Part I.*

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Ether-extraction of the timber of *Chlorophora excelsa* has given an amorphous compound, chlorophorin, $C_{24}H_{28}O_4$, containing four phenolic hydroxyl groups and three exocyclic double bonds, which readily undergoes catalytic reduction to tetrahydrochlorophorin. The action of hydrogen peroxide on tetrahydrochlorophorin destroys the phenolic nuclei, leaving 3 : 7-*dimethylnon-2-enoic acid*, $Me_2CH{\cdot}[CH_2]_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CO_2H$. The nature of the aromatic constituent is shown by permanganate oxidation of O-*tetramethylchlorophorin*, 2 : 4-dimethoxybenzoic acid, and 4-*carboxy*-2 : 6-*dimethoxyphenylacetic acid* being isolated. Chlorophorin is therefore a 3 : 5 : 2′ : 4′-tetrahydroxystilbene with a diolefinic side-chain, $-CH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}C_5H_9$ at position 4.

THE tree *Chlorophora excelsa* is the source of one of the principal commercial hardwoods of tropical Africa. The timber, generally know as iroko, is of good appearance, and on account of its valuable technical properties is used for a wide variety of purposes including the construction of laboratory benches. Iroko is resistant to fungus and insect attack, but its reputation for durability has not hitherto occasioned any chemical investigations of the timber, and there are few references to it in the scientific literature. Davidson (*Lancet*, 1941, **240**, 38) has commented on the marked irritant effects of the wood dust, but the observation clearly relates to an exceptional specimen, and there is no record of an attempted isolation of the irritant substance. Marmasse (" Contribution à l'étude analytique de quelques bois coloniaux," Paris, 1938) obtained a resinous material (4·46%) by extraction with acetone, but has recorded no further examination of the extract.

In the present investigation it was found that simple digestion of the powdered wood with boiling ether readily extracted a light-brown solid in amounts, varying with different samples, of 2—8%, which separated from toluene as a flocculent powder, m. p. 157—159°. The isolation and preliminary experiments concerning the structure of this compound, to which we have given the name *chlorophorin*, have already been reported (Grundon and King, *Nature*, 1949, **163**, 564). It has the properties of a phenol, being soluble in sodium hydroxide solution and insoluble in sodium hydrogen carbonate, but neither by precipitation from alkali nor by use of organic solvents has it been possible to obtain a crystalline specimen. The phenolic nature of the extract was confirmed by the preparation, in high yield, of a crystalline *tetra-acetate*, and of crystalline *tetramethyl* and *tetraethyl ethers* by the alkyl iodide–potassium carbonate–acetone method, and analyses of these derivatives indicated for chlorophorin a molecular formula of $C_{24}H_{28}O_4$ or $C_{25}H_{30}O_4$. Since chlorophorin is stable to boiling alcoholic potassium hydroxide, the repeatedly recrystallised tetra-acetate was submitted to mild alkaline hydrolysis in the hope of obtaining the phenol in a crystalline condition, but without success.

The existence in chlorophorin of two easily hydrogenated double bonds was demonstrated by the ready absorption of two molecules of hydrogen in presence of Raney nickel or palladised charcoal at room temperature. The resulting tetrahydrochlorophorin was also amorphous, but gave a crystalline *tetra-acetate* and *tetramethyl ether*, the latter being independently prepared by catalytic reduction of *O*-tetramethylchlorophorin. Further reduction did not readily occur, but the existence of a third and less reactive double bond was later detected by ozonolysis. The ultra-violet absorption of *O*-tetramethyltetrahydrochlorophorin was similar to that of resorcinol derivatives, and from a zinc dust distillation of chlorophorin a sublimate of resorcinol was obtained.

Ozonolysis of *O*-tetramethylchlorophorin gave a syrupy product, partly resinifying when heated at low pressure but yielding a crystalline distillate. This was recognised from its melting point and analysis as 2 : 4-dimethoxybenzaldehyde, the identification being confirmed by the preparation of its oxime and 2 : 4-*dinitrophenylhydrazone*. The action of ozone on *O*-tetramethyltetrahydrochlorophorin led to two carbonylic products of which the lower-boiling was shown by the iodoform reaction and by analysis of its *semicarbazone* to be a methylheptanone. Its exact constitution was established when this semicarbazone was found to be identical with that of 6-methyl-2-heptanone, $Me{\cdot}CO{\cdot}[CH_2]_3{\cdot}CHMe_2$, prepared by catalytic reduction of the methylheptanone derived from citral. Analyses of the *oxime* and 2 : 4-*dinitrophenylhydrazone* of the less volatile product of the ozonolysis corresponded to a molecular formula of $C_{20}H_{24}O_5$ or $C_{21}H_{26}O_5$.

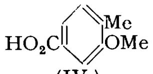
From the oxidation of tetrahydrochlorophorin with hydrogen peroxide in alkaline solution an unsaturated aliphatic *acid*, $C_{11}H_{20}O_2$, was isolated by steam-distillation. Ozonolysis of this acid gave 6-methyl-2-heptanone, thus limiting its constitution to the alternatives (I) and (II) :

(I.) $HO_2C{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$ $HO_2C{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$ (II.)

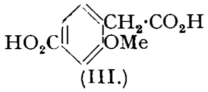
Of these two structures that in which the carbonyl and the ethylene bond occupy adjacent positions, *i.e.*, (I), was excluded in favour of (II) by a determination of the ultra-violet absorption of the acid which gave no evidence of conjugation.

Indications as to the nature of the aromatic constituent of chlorophorin were obtained from an oxidation of the tetramethyl ether with potassium permanganate in acetone. Trituration of the product with chloroform resolved it into two fractions, one readily soluble and consisting of 2 : 4-dimethoxybenzoic acid. The other component (III), m. p. 286—287°, had the composition $C_{11}H_{12}O_6$ and, from its formation of an ester $C_{13}H_{16}O_6$ on reaction with diazomethane, was evidently a dicarboxylic acid. In view of its derivation from the tetramethyl compound it could be assumed that the remaining two oxygen atoms of (III) were present in methoxyl groups and it therefore followed that this oxidation product was either a dimethoxymethylbenzenedicarboxylic or a carboxydimethoxyphenylacetic acid.

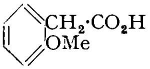
The relative position of the two methoxyl groups was determined by the fluorescein reaction which, though unsuccessful for the acid, gave a positive result with the dimethyl ester, thus establishing the compound as a resorcinol derivative. In an attempt to ascertain the orientation of the two carboxyl groups, the acid was heated with acetic anhydride, but the product failed to crystallise. It was evident, however, that it did not consist of an intramolecular *ortho*-dicarboxylic anhydride since, when it was subjected to distillation at low pressure, decomposition occurred and only a trifling amount of sublimate was obtained which on heating with water gave a monocarboxylic acid subsequently identified as (IV) (see below).



(IV.)



(III.)



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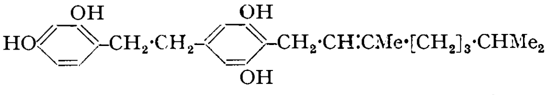

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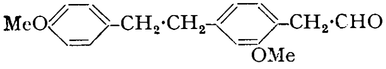
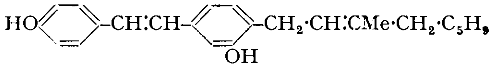


(VII.)



(VIII.)

The decarboxylation of (III) was more fully investigated by heating it in quinoline with a copper catalyst whereby two monocarboxylic acids, $C_{10}H_{12}O_4$, were obtained and were separated as a result of their different solubilities in water. Owing to the relative stability of phenylacetic acids the formation of two isomeric mono-acids under these conditions was at first believed to favour a methylbenzenedicarboxylic structure for the oxidation product (III) (see Grundon and King, *loc. cit.*). This view had later to be modified when Kuhn–Röth estimations indicated the absence of *C*-methyl groups in the dimethyl ester of (III) but gave values approximating to one *C*-Me for the ester of the less-soluble derived monocarboxylic acid, which was then recognised as 3 : 5-dimethoxy-4-methylbenzoic acid (IV) by direct comparison with a specimen synthesised by the method of Charlesworth and Robinson (*J.*, 1934, **1531**), and by the identity of the methyl esters of the synthetic and degradation products. It follows that the dicarboxylic acid (III) is 4-*carboxy*-2 : 6-*dimethoxyphenylacetic acid*, and hence its other decarboxylation product is 2 : 6-dimethoxyphenylacetic acid. As the more soluble isomer, this has proved difficult to purify, and the specimen of m. p. 119—120° to which reference has already been made (Grundon and King, *loc. cit.*) may not be homogeneous. We expect shortly to record the synthesis of the acid (V) which is the sole remaining dimethoxyphenylacetic acid to be described.

With the elucidation of the structure of (III) it became apparent that the substituent $-CH_2{\cdot}CO_2H$ resulted from the oxidation of the unsaturated aliphatic residue at the position corresponding to the $\beta\gamma$-double bond of the oxidation product (II). The alternative hypothesis, *viz.*, that it arose from the substituent carrying the second resorcinol nucleus, was excluded by the ultra-violet absorption of chlorophorin, which revealed a high degree of conjugation typical of a stilbene structure. This characteristic absorption vanished on reduction to the tetrahydro-derivative. The isolation from the permanganate oxidation of tetrahydrochlorophorin of succinic acid, which has not been detected as an oxidation product of the parent phenol, is a further indication of the nature of the linkage uniting the two aromatic nuclei. It is interesting to recall that pinosylvin, isolated from the heartwood of *Pinus sylvestris*, is 3 : 5-dihydroxystilbene (Erdtmann, *Annalen*, 1939, **539**, 116).

It was now clear that the molecular formula of chlorophorin was $C_{24}H_{28}O_4$, the alternative $C_{25}H_{30}O_4$ (*loc. cit.*) having been considered only while it appeared that the dicarboxylic acid contained a nuclear methyl group. On the basis of the foregoing evidence the tetrahydro-derivative, $C_{24}H_{32}O_4$, has the structure (VI), and the formerly unidentified ozonolysis product of its tetramethyl ether is therefore the aldehyde (VII). The constitution of chlorophorin can thus be represented by the expression (VIII), but the position of the remaining double bond in the residue C_5H_9 cannot yet be assigned with certainty. The oxidation of *O*-tetramethylchlorophorin with permanganate in dioxan has given acetone, isolated in the form of its 2 : 4-dinitrophenylhydrazone, but neither acetone nor formaldehyde has been detected among the ozonolysis products of the phenol tetramethyl ether. The group C_5H_9 does not therefore appear to terminate in the commonly occurring *iso*propenyl residue, but further information on this point is now being sought.

EXPERIMENTAL.

Chlorophorin.—The iroko used in this investigation, consisting of off-cuts from timber employed in the manufacture of laboratory furnishings, was kindly supplied by Messrs. Baird and Tatlock, Ltd. The wood, in the form of powder or fine shavings, was covered with ether which was heated under reflux for 15 minutes. The treatment was repeated with a further quantity of solvent, and the combined extracts were dried (Na_2SO_4). Evaporation of the solution gave the crude *chlorophorin* as a light-brown solid (yield, 2—8%) which separated from toluene as an amorphous powder, m. p. 157—159°. Colourless specimens were obtained from alcoholic solutions which had been shaken with charcoal for several hours. Chlorophorin is insoluble in water, chloroform, carbon tetrachloride, and light petroleum, but dissolves in hot acetic acid, benzene, and toluene, and in ether, methanol, ethanol, ethyl acetate, and pyridine. It is soluble in aqueous sodium carbonate or hydroxide, but not in sodium hydrogen carbonate solution, and gives no marked colour with alcoholic ferric chloride.

By heating the crude compound (4 g.) with anhydrous sodium acetate (1 g.) and acetic anhydride (25 c.c.) under reflux for 30 minutes, *tetra-acetylchlorophorin* was obtained. The product, isolated by pouring the solution into water, crystallised from ethanol in fine colourless needles (5·9 g.), m. p. 133—134° [Found : C, 70·2, 70·0; H, 6·4, 6·6; Ac, 32·3, 29·8. $C_{24}H_{24}(OAc)_4$ requires C, 70·1; H, 6·6; Ac, 31·4%. $C_{25}H_{26}(OAc)_4$ requires C, 70·5; H, 6·8; Ac, 30·6%].

Methylation of chlorophorin (15 g.) with methyl iodide (102 g., 12 mols.) and anhydrous potassium carbonate (110 g.) in refluxing acetone (200 c.c.) for 30 hours gave O-*tetramethylchlorophorin* (11·8 g., 66%), which separated from ethanol in faintly yellow elongated prisms, m. p. 73—74° [Found : C, 77·1; H, 8·5; OMe, 25·4; *C*-Me, 6·8. $C_{24}H_{24}(OMe)_4$ requires C, 77·1; H, 8·3; OMe, 28·4; 2*C*-Me, 6·9% $C_{25}H_{26}(OMe)_4$ requires C, 77·3; H, 8·4; OMe, 27·5; 2*C*-Me, 6·7%]. Ultra-violet light absorption in alcohol : $\lambda_{max.}$ 2200 and 3300 A., $\varepsilon_{max.}$ 15,300 and 18,600, respectively.

O-*Tetraethylchlorophorin* obtained in a similar way crystallised from ethanol in very pale yellow prisms, m. p. 78—79° [Found : C, 78·0, 77·8; H, 9·1, 8·9; OEt, 34·7. $C_{24}H_{24}(OEt)_4$ requires C, 78·0; H, 8·9; OEt, 36·6%].

Tetrahydrochlorophorin.—A solution of chlorophorin (10 g.) in ethanol (50 c.c.) was hydrogenated over Raney nickel at room temperature. Approximately 2 mols. of hydrogen were absorbed in 105 minutes and reduction then ceased. Pouring the solution into water gave a voluminous cream-coloured precipitate (9·7 g.) which was dried and dissolved in boiling benzene. The tetrahydro-compound, which separated in the cold, was an amorphous solid, m. p. 116—118°. A similar product was obtained on reduction in presence of a palladised charcoal catalyst. Heating in boiling acetic anhydride (5 c.c.) with sodium acetate (0·3 g.) converted the amorphous reduction product (1 g.) into *tetra-acetyltetrahydrochlorophorin* which was isolated by pouring the solution into water. The viscous oil slowly solidified, and crystallised from light petroleum in large colourless needles, m. p. 53—55° (Found : C, 69·6; H, 7·1. $C_{32}H_{40}O_8$ requires C, 69·6; H, 7·2%).

O-*Tetramethyltetrahydrochlorophorin* was obtained by refluxing a solution of the tetrahydro-compound (3 g.) in acetone (100 c.c.) containing methyl iodide (20 g.) and potassium carbonate (23 g.). It separated from methanol in colourless needles (2·8 g.), m. p. 52—53° (Found : C, 76·5; H, 8·7; OMe, 25·0. $C_{28}H_{40}O_4$ requires C, 76·4; H, 9·1; OMe, 28·2%). Ultra-violet light absorption in ethanol : $\lambda_{max.}$ 2800 A., $\varepsilon_{max.}$ 3388. This derivative was also obtained on catalytic reduction of *O*-tetramethylchlorophorin.

Chlorophorin–Zinc Dust Distillation.—A mixture of chlorophorin (0·5 g.) and zinc dust (8 g.) was heated at 200—220° in a hard-glass tube; a colourless sublimate (0·05 g.,), m. p. 104—108°, was collected. The product appeared to be resorcinol from its violet aqueous ferric chloride reaction and m. p. The identification was confirmed by dissolving the product in sulphuric acid and adding concentrated nitric acid; after 10 minutes the solution was poured into water, and when recrystallised from water the product was identified as styphnic acid by its m. p. and mixed m. p., 175—176°.

Ozonolysis of O-*Tetramethylchlorophorin.*—A solution of tetramethylchlorophorin (2 g.) in methyl acetate (15 c.c.) was subjected to the action of ozonised oxygen for 9 hours. The solvent was removed at room temperature, and to the residue ether (100 c.c.) and acetic acid (4 c.c.) containing a little water (0·5 c.c.) were added. Zinc dust (5 g.) was introduced in small portions while the mixture was gently refluxed until it no longer gave the starch–iodide reaction. The filtered solution was then evaporated and the brown residue heated at low pressure. Considerable resinification occurred, but an oil (0·2 g.) distilled at 85—90°/0·03 mm. which solidified on storage. Crystallisation from aqueous alcohol gave long needles, m. p. 65—67° undepressed when mixed with 2 : 4-dimethoxybenzaldehyde, m. p. 67—68°. The identity of the aldehyde was confirmed by the preparation of its oxime, m. p. 101—102° unaffected when mixed with an authentic specimen, m. p. 102—104°, and of the 2 : 4-*dinitrophenylhydrazone*, a microcrystalline orange-red powder from ethanol, m. p. 244—246° (Found : C, 52·3; H, 4·3. $C_{15}H_{14}O_6N_4$ requires C, 52·0; H, 4·1%).

Ozonolysis of O-*Tetramethyltetrahydrochlorophorin.*—Ozonised oxygen was passed into a solution of *O*-tetramethyltetrahydrochlorophorin (6 g.) in methyl acetate (25 c.c.) for 17 hours; the solvent was then evaporated under diminished pressure, and the residue dissolved in ether (100 c.c.) with acetic acid (7 c.c.) containing water (0·3 c.c.) and gradually treated with zinc dust (10 g.) until the starch–iodide test was negative. Evaporation of the filtered ethereal solution gave a yellow syrup (5·6 g.) from which a colourless oil (0·45 g.) distilled at a bath temperature of 145—155° (760 mm.). The distillate responded to the iodoform reaction and gave a semicarbazone as glistening plates from aqueous alcohol, m. p. 155—156° (Found : C, 58·2; H, 9·9; N, 23·4%) undepressed on mixing with 6-methyl-2-heptanone semicarbazone, m. p. 155—156° (Calc. for $C_9H_{19}ON_3$: C, 58·4; H, 10·3; N, 22·7%).

Heating of the yellow syrup mentioned above was continued at low pressure, whereupon a yellow oil (3·2 g.) distilled at 175—185° (bath temperature)/0·08 mm. It formed an *oxime*, crystallising in needles, m. p. 145—146° (Found : C, 66·7, 66·7; H, 7·1, 7·0; N, 4·0. $C_{20}H_{25}O_5N$ requires C, 66·8; H, 7·0; N, 3·9%. $C_{21}H_{27}O_5N$ requires C, 67·6; H, 7·3; N, 3·8%), and a 2 : 4-*dinitrophenylhydrazone*, a yellow-orange micro-crystalline powder, m.p. 134—136°, from alcohol (Found: C, 59·0, 58·9; H, 5·1, 5·5; N, 10·7, 11·0. $C_{26}H_{28}O_8N_4$ requires C, 59·5; H, 5·3; N, 10·7%. $C_{27}H_{30}O_8N_4$ requires C, 60·2; H, 5·6; N, 10·4%).

Hydrogen Peroxide Oxidation of Tetrahydrochlorophorin.—A solution of tetrahydrochlorophorin (8 g.) in aqueous sodium hydroxide (170 c.c.; 10%) was treated with hydrogen peroxide (450 c.c. of 6%) and set aside at room temperature for 12 hours; the mixture was then concentrated to 250 c.c., acidified with concentrated hydrochloric acid, and steam-distilled. Extraction of the condensate with ether gave a pale brown oil which was distilled at 10 mm. from a bath at 145—155°. The colourless product, 3 : 7-*dimethylnon-2-enoic acid* (1 g.), dissolved in aqueous sodium carbonate with effervescence and rapidly decolorised bromine water (Found: C, 71·6, 71·5; H, 10·9, 10·7; *C*-Me, 14·9. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·9; 2*C*-Me, 16·3%). Ultra-violet light absorption in alcohol : $\lambda_{max.} < 2200$ A.; $\varepsilon_{max.} > 645$. Heating the acid under reflux with methanolic hydrogen chloride for 3 hours gave the *methyl* ester which distilled as a colourless oil at 20 mm. (bath temperature, 125—135°) (Found : C, 72·2; H, 11·7. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%).

A solution of the acid (0·7 g.) in methyl acetate (20 c.c.) was treated with ozonised oxygen until a test portion no longer reacted with bromine (2 hours). The solvent was then removed and the residue shaken with water (25 c.c.). After 12 hours the liquid was made alkaline with sodium hydrogen carbonate and extracted with ether. The oil (0·45 g.) thus isolated was heated at 40 mm., and the distillate (0·07 g.) (bath at 85—95°) converted into a semicarbazone, glistening plates (from aqueous methanol), m. p. and mixed m. p. with 6-methyl-2-heptanone semicarbazone, 155—156°.

Potassium Permanganate Oxidation of O-*Tetramethylchlorophorin.*—A well-shaken solution of tetramethylchlorophorin (5 g.) in acetone (300 c.c.) was treated in the cold with powdered potassium permanganate added in small portions until no further oxidation occurred (total, 29 g. in 14 hours). Water (300 c.c.) was afterwards added and the mixture saturated with sulphur dioxide. The solution was then strongly acidified with hydrochloric acid and repeatedly extracted with ether (10 × 50 c.c.). The ether-soluble solid (4·52 g.) thus isolated was triturated with chloroform (25 c.c.), whereupon a colourless acid (0·61 g.), m. p. 253—260°, remained. A further quantity (0·23 g.) was obtained by evaporating the chloroform solution, treating the residue with benzene, and again triturating the benzene-insoluble solid with chloroform. Evaporation of the combined benzene–chloroform solution gave a product crystallising from aqueous ethanol in colourless needles (0·45 g.), m. p. 107—108° alone or mixed with 2 : 4-dimethoxybenzoic acid. The fraction of m. p. 253—260°, sparingly soluble in chloroform, on recrystallisation from aqueous ethanol gave colourless prisms, m. p. 286—287° with darkening, now regarded as 4-*carboxy*-2 : 6-*dimethoxyphenylacetic acid* (III) (Found: C, 55·1, 55·1; H, 5·1, 4·8; OMe, 26·1. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0; OMe, 25·8%). A specimen of the acid (0·45 g.), dissolved in ethereal diazomethane (5 c.c.), was converted into the *dimethyl* ester, crystallising from aqueous alcohol in colourless needles (0·29 g.), m. p. 106—108° (Found: C, 58·0; H, 6·2; *C*-Me, 1·47, 1·9. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0; 1*C*-Me, 5·6%).

The acid (III) (0·3 g.) was dissolved in acetic anhydride (1 c.c.) and heated on a steam-bath for 15 minutes. Evaporation left a gum (insoluble in aqueous sodium hydrogen carbonate), which was heated under low pressure. A colourless sublimate (0·07 g.), m. p. 184—189°, b. p. (bath temperature) 210—220°/1·5 mm., was thus obtained which was heated with water on a steam-bath for 15 minutes and then dissolved by adding ethanol. The solid which separated on cooling had m. p. 205—210°, raised by recrystallisation to 209—212°, undepressed when mixed with 3 : 5-dimethoxy-4-methylbenzoic acid.

3 : 5-*Dimethoxy*-4-*methylbenzoic Acid*.—A mixture of the dicarboxylic acid (III) (1·55 g.), copper powder (1·5 g.), and quinoline (3 g.) was heated at 220—230° for 40 minutes in an atmosphere of nitrogen. Concentrated hydrochloric acid (15 c.c.) was then added and the mixture extracted with ether (6 × 10 c.c.). After being washed with hydrochloric acid and water, the combined ether extracts were shaken with five 10-c.c. portions of aqueous sodium hydrogen carbonate which were then acidified to precipitate the crude product (0·6 g.), m. p. 210—230°. Unchanged dicarboxylic acid was removed by treatment with chloroform, and the chloroform-soluble portion crystallised from aqueous ethanol. The resulting acid (0·3 g.), m. p. 209—212°, was indistinguishable from a specimen of 3 : 5-dimethoxy-4-methylbenzoic acid (m. p. 213—215° and mixed m. p.) prepared by the method of Charlesworth and Robinson (*loc. cit.*) (Found: C, 61·1; H, 6·0. Calc. for $C_{10}H_{12}O_4$: C, 61·2; H, 6·1%). When this was heated under reflux with methyl iodide and potassium carbonate in acetone solution, the methyl ester was obtained, crystallising from methanol in clusters of colourless needles, m. p. 100—101° alone or mixed with the methyl ester of the synthetic acid, m. p. 101·5—102·5° (Found: C, 62·7; H, 6·6; *C*-Me, 8·4. Calc. for $C_{11}H_{14}O_4$: C, 62·9; H, 6·7; 1*C*-Me, 7·1%).

Ether-extraction of the acid solution from which the crude product, m. p. 210—230°, had separated yielded a further product, crystallising from water and having m. p. 119—120°, isomeric with the foregoing dimethoxytoluic acid (Found: C, 60·6; H, 6·3; *C*-Me, 4·3. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1; 1*C*-Me 7·6%)

Potassium Permanganate Oxidation of Tetrahydrochlorophorin.—Powdered permanganate (19 g.) was added in small portions to an acetone solution (30 c.c.) of tetrahydrochlorophorin (3 g.). When oxidation was complete, water (200 c.c.) was added and the mixture saturated with sulphur dioxide. The solution was further acidified with hydrochloric acid, the acetone evaporated, and the pale yellow solution extracted continuously with ether for 48 hours. Acid products were removed by washing the ethereal solution with aqueous sodium hydrogen carbonate, and the acidified alkaline washings also submitted to continuous ether-extraction for 48 hours. The semi-solid residue obtained on evaporation of the ether, and of other volatile material under reduced pressure at 100°, gave on trituration with chloroform colourless crystals (0·22 g.), m. p. 180—181°. The *p*-phenylphenacyl ester separated from acetone in colourless plates, m. p. 210° undepressed by admixture with an authentic specimen of di-*p*-phenylphenacyl succinate (Drake and Bronitsky, *J. Amer. Chem. Soc.*, 1930, **52**, 3715).

Potassium Permanganate Oxidation of O-*Tetramethylchlorophorin*.—An ice-cold solution of tetramethylchlorophorin (2 g.) in dioxan (150 c.c.) was treated with small quantities of aqueous permanganate (5%) until, after the addition of 95 c.c., a slight excess of the oxidising agent was present. The solution was filtered, treated with sulphur dioxide, and filtered again, and then made alkaline and distilled until 30 c.c. of solution had collected. Treatment of this distillate with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride gave a yellowish-orange precipitate which crystallised from aqueous ethanol in yellow needles, m. p. and mixed m. p. with acetone 2 : 4-dinitrophenylhydrazone, 123—124°. The distillate from the acidified oxidation mixture contained a negligible amount of steam-volatile acid as measured by titration with standard alkali.

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