1274. *Gallotannins. Part XI.*[1] *Synthesis of* m-*Digallic and* m-*Trigallic Acids and Their Derivatives*

By P. W. Crabtree, E. Haslam, R. D. Haworth, S. D. Mills, and J. E. Stangroom

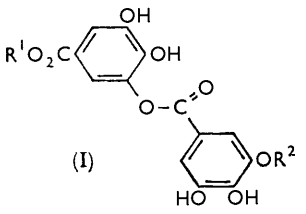
The synthesis of *m*-digallic and *m*-trigallic acids, methyl *m*-trigallate and cyclohexyl *m*-trigallate are reported.

Excepting tara tannin which is a polygalloylquinic acid [2,3] the gallotannins have been shown by previous work [4,5] to be polygalloyl-D-glucose derivatives the nature and complexity of which vary from plant to plant. In all the gallotannins a certain percentage of the galloyl groups are bound in the form of depsides but the disposition of these residues on the basic galloylglucose (or quinic acid) core is not proved. However, the view that they form part of a polygalloyl chain, of indeterminate length, attached at one or more positions to the gallotannin core is supported by a number of lines of evidence. Thus acid hydrolysis of Chinese gallotannin yields *m*-digallic (I; $R^1 = R^2 = H$) and *m*-trigallic (I; R = H, R^2 = 3,4,5-trihydroxybenzoyl) acids in significant amount [8] and interruption of the methanolysis of the tannin at an intermediate stage gives methyl *m*-digallate (I; R^1 = Me, $R^2 = H$).[4] Improved syntheses of these linear depsides and some of their derivatives which confirm their structures are reported here.

Fischer and Freudenberg [6,7] first reported rational syntheses of *m*-digallic acid (I; $R^1 = R^2 = H$) but although their general procedures have since been utilised in a successful synthesis of *m*-trigallic acid [8] (I; $R^1 = H$, R^2 = 3,4,5-trihydroxybenzoyl) these methods

[1] Part X, R. Biggins and E. Haslam, preceding Paper.
[2] E. Haslam, R. D. Haworth, and P. C. Keen, *J.*, 1962, 3814.
[3] D. F. Horler and H. E. Nursten, *J.*, 1961, 3786.
[4] R. Armitage, G. S. Bayliss, J. W. Gramshaw, E. Haslam, R. D. Haworth, K. Jones, H. J. Rogers, and T. Searle, *J.*, 1961, 1842.
[5] E. Haslam and R. D. Haworth, "Progress in Organic Chemistry," Butterworths, London, 1964, **6**, p. 1.
[6] E. Fischer, M. Bergmann, and W. Lipschitz, *Ber.*, 1918, **51**, 45.
[7] E. Fischer and K. Freudenberg, *Ber.*, 1913, **46**, 111.
[8] H. G. C. King and T. White, *J.*, 1961, 3231.

have been shown to be not entirely unambiguous,[9] owing in the main to rearrangement or hydrolysis of the depside linkages occurring during the removal of the acetyl or methoxycarbonyl groups from the final intermediates. Accordingly methods have been evolved using protecting groups removable under the mild conditions of hydrogenolysis. Diphenyldiazomethane gave with the acid (II; R^1 = ethoxycarbonyl, R^2 = H) the ester (II; R^1 = ethoxycarbonyl, R^2 = diphenylmethyl) which on deacylation gave the phenolic ester (II; R^1 = H, R^2 = diphenylmethyl). Condensation with tri-*O*-benzoylgalloyl chloride yielded the depside (II; R^1 = tri-*O*-benzylgalloyl, R^2 = diphenylmethyl) which when hydrogenated afforded *m*-digallic acid (I; $R^1 = R^2$ = H) identical with the product from the acid hydrolysis of Chinese gallotannin and which with diazomethane gave the known methyl penta-*O*-methyl-*m*-digallate.[6,7] *m*-Digallic acid had similar solubility characteristics to those of the product described by Fischer [6,7] but with aqueous potassium cyanide did not give a positive test for free gallic acid [10] and on methanolysis liberated equivalent amounts of gallic acid and methyl gallate.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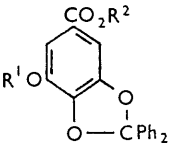
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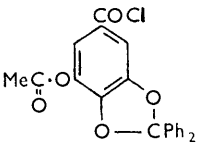
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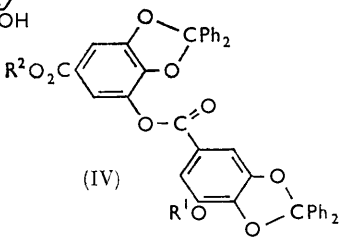
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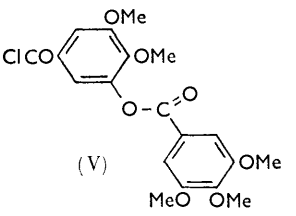
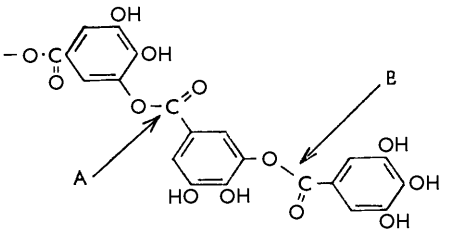

(V)

m-Trigallic acid (I; R^1 = H, R^2 = 3,4,5-trihydroxybenzoyl) and its methyl and cyclohexyl esters have also been prepared by extensions of the above methods. An important intermediate in these syntheses was 3-acetoxy-4,5-diphenylmethylenedioxybenzoyl chloride (III) prepared by standard procedures from the acid (II; $R^1 = R^2$ = H). Condensation with methyl 3,4-diphenylmethylenedioxy-5-hydroxybenzoate (II; R^1 = H, R^2 = Me) gave the depside (IV; R^1 = acetyl, R^2 = Me) which on deacetylation yielded the phenol (IV; R^1 = H, R^2 = Me). Hydrogenation of the latter gave methyl *m*-digallate, identical with a sample prepared as described previously.[9] Condensation of the phenol (IV; R^1 = H, R^2 = Me) with tri-*O*-benzylgalloyl chloride yielded the fully protected linear trigallate ester (IV; R^1 = tri-*O*-benzylgalloyl, R^2 = Me) which on hydrogenation gave methyl *m*-trigallate (I; R^1 = Me, R^2 = 3,4,5-trihydroxybenzoyl). Methyl *m*-trigallate was identical paper-chromatographically with the substance produced transiently during the initial stages of the methanolysis of Chinese gallotannin,[11] but since isolation of this material was not possible a more complete comparison of these two materials was not made. Analogous syntheses proceeding *via* the intermediates (IV; R^1 = H, R^2 = cyclohexyl) and (IV; R^1 = H, R^2 = diphenylmethyl) gave on subsequent hydrogenation cyclohexyl *m*-trigallate (I; R^1 = cyclohexyl, R^2 = 3,4,5-trihydroxybenzoyl) and *m*-trigallic acid (I; R^1 = H, R^2 = 3,4,5-trihydroxybenzoyl), respectively. Treated with diazomethane *m*-trigallic acid gave an octa-*O*-methyl derivative the structure of which was confirmed by a rational synthesis from methyl 3-hydroxy-4,5-dimethoxy-benzoate and compound (V).

[9] E. Haslam, R. D. Haworth, S. D. Mills, H. J. Rogers, R. Armitage, and T. Searle, *J.*, 1961, 1836.
[10] O. Th. Schmidt, " Moderne methoden der Pflanzenanalyse," III, Springer-Verlag, Berlin, 1955, 517.
[11] H. J. Rogers, Ph.D. Thesis, University of Sheffield, 1958.

m-Trigallic acid crystallised readily from water and was identical with the acid obtained from the partial acid hydrolysis of Chinese gallotannin. Its relationship with *m*-digallic and gallic acids was revealed by its relative mobility to these substances in paper-chromatographic and electrophoretic systems. Methanolysis of *m*-trigallic acid proceeded with the initial readily observed formation of *m*-digallic acid and methyl gallate indicating a greater ease of rupture of the terminal depside bond (VI,B). Under similar conditions the cyclohexyl and methyl esters of *m*-trigallic acid showed an opposite behaviour. The implication of these results and their understanding and application to the elucidation of the fine structure of the gallotannins will be discussed later.



(VI)

Experimental

3,4-*Diphenylmethylenedioxy*-5-*hydroxybenzoic Acid*.—Methyl 3,4-diphenylmethylenedioxy-5-hydroxybenzoate [12] (5·0 g.) was refluxed in sodium hydroxide solution (6N; 500 c.c.) containing methanol (20 c.c.) for 5 hr. The *acid*, obtained by ether extraction of the acidified solution, crystallised from ethyl acetate–light petroleum (b. p. 40—60°) as prisms (4·1 g.), m. p. 177—178° (Found: C, 71·7; H, 4·4. $C_{20}H_{14}O_5$ requires C, 71·8; H, 4·2%).

3,4-*Diphenylmethylenedioxy*-5-*ethoxycarbonylbenzoic Acid*.—To the foregoing acid (2 g.) dissolved in sodium hydroxide (N; 12 c.c.) and cooled to −5° ethyl chloroformate (0·6 c.c.) was added dropwise. After 10 min. the paste was diluted with water, acidified (2N–HCl), and extracted with ether (3 × 50 c.c.). Removal of the ether and crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave the *acid* as prisms (1·8 g.), m. p. 182—183° (Found: C, 67·9; H, 4·4. $C_{23}H_{18}O_7$ requires C, 68·1; H, 4·5%).

Diphenylmethyl **3,4-*Diphenylmethylenedioxy*-5-*ethoxycarbonylbenzoate*.**—A solution of 3,4-diphenylmethylenedioxy-5-ethoxycarbonylbenzoic acid (1 g.) in benzene (35 c.c.) containing diphenyldiazomethane (0·75 g.) was set aside for 1 hr. at 20°, warmed to 80° for ½ hr., and left overnight at 20°. Removal of the benzene and crystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave the *diphenylmethyl ester* as needles (1·1 g.), m. p. 117—118° (Found: C, 75·3; H, 5·1. $C_{36}H_{28}O_7$ requires C, 75·5; H, 4·9%).

Diphenylmethyl **3,4-*Diphenylmethylenedioxy*-5-*hydroxybenzoate*.**—A solution of the ethoxycarbonyl ester (2 g.) in dioxan–water (80 c.c.; 1 : 1) and containing sodium hydroxide solution (N; 18 c.c.) was maintained at 20° for 2 hr. before concentration at 20° and dilution with water (200 c.c.). Acidification (HCl) followed by ether extraction gave, on removal of the ether, an oil from which the *phenolic ester* crystallised [benzene–light petroleum (b. p. 60—80°)] as prisms (1·5 g.), m. p. 160° (Found: C, 79·4; H, 4·9. $C_{33}H_{24}O_5$ requires C, 79·2; H, 4·8%).

3-*Acetoxy*-4,5-*diphenylmethylenedioxybenzoic Acid*.—A mixture of 3,4-diphenylmethylenedioxy-5-hydroxybenzoic acid (20 g.), fused sodium acetate (0·5 g.), and acetic anhydride was refluxed for 15 min. before dilution with water (200 c.c.) and heating to 100° for 5 min. The supernatant aqueous layer was decanted and the residual gum washed several times with water (100 c.c.) before being dissolved in ether (300 c.c.) and dried ($MgSO_4$). Removal of the ether gave a gum which crystallised from benzene to give the *acid* as needles (14·5 g.), m. p. 172° (Found: C, 69·8; H, 4·5. $C_{22}H_{16}O_6$ requires C, 70·2; H, 4·3%).

3-*Acetoxy*-4,5-*diphenylmethylenedioxybenzoyl Chloride*.—The above acid (10 g.) was refluxed in benzene (50 c.c.) containing thionyl chloride (50 c.c.) for 1 hr. Removal of the solvent (30°) gave a clear oil from which the *acid chloride* crystallised [light petroleum (b. p. 60—80°)] as prisms (8·9 g.), m. p. 86° (Found: C, 66·9; H, 4·1; Cl, 9·3. $C_{22}H_{15}ClO_5$ requires C, 67·2; H, 3·8; Cl, 9·0%).

[12] L. Jurd, *J. Amer. Chem. Soc.*, 1959, **82**, 4606.

Diphenylmethyl 3,4-*Diphenylmethylenedioxy*-5-(3,4,5-*tri*-O-*benzylgalloyl*)*benzoate*.—A solution of tri-*O*-benzylgalloyl chloride (6·0 g.) and diphenylmethyl 3,4-diphenylmethylenedioxy-5-hydroxybenzoate (5·0 g.) in chloroform (100 c.c.) and pyridine (5 c.c.) was kept at 20° for 24 hr., diluted with chloroform (200 c.c.) and the chloroform layer washed with 2N-hydrochloric acid and water and dried ($MgSO_4$). Removal of the chloroform gave a gum which when dissolved in benzene (15 c.c.) slowly deposited tri-*O*-benzylgallic anhydride (1·1 g.), m. p. and mixed m. p. 166°. After filtration the filtrate was chromatographed in benzene on alumina (200 g.). Concentration of the eluate and crystallisation from ether gave the *depside* as fine needles, m. p. 136—137° (Found: C, 79·1; H, 5·0. $C_{61}H_{46}O_9$ requires C, 79·4; H, 5·0%).

m-*Digallic Acid*.—The above ester (1·0 g.) was hydrogenated over palladium–charcoal (10%, 0·2 g.) in ethyl acetate until uptake of hydrogen ceased. Removal of the catalyst and solvent and crystallisation from aqueous acetone then gave *m*-digallic acid as white cubes (0·3 g.), m. p. 260—261° (Fischer [6,7] gives m. p. 280°) (Found: C, 52·4; H, 3·6. Calc. for $C_{14}H_{10}O_9$: C, 52·2; H, 3·1%), R_F (6% acetic acid; 0·25), migration relative to gallic acid in 0·01M-acetate buffer, pH 5·9 at 1500v, 0·50. The acid was identical on paper-chromatographic and electrophoretic analysis with *m*-digallic acid from Chinese gallotannin.[8]

Diphenylmethyl 3-(3-*Acetoxy*-4,5-*diphenylmethylenedioxybenzoyl*)-4,5-*diphenylmethylenedioxybenzoate*.—Diphenylmethyl 3,4-diphenylmethylenedioxy-5-hydroxybenzoate (0·5 g.) and 3-acetoxy-4,5-diphenylmethylenedioxybenzoyl chloride (0·46 g.) were dissolved in chloroform (6 c.c.) and pyridine (0·3 c.c.) and kept at 20° for 72 hr. before dilution with chloroform (25 c.c.). The chloroform layer was washed with hydrochloric acid (N; 2 × 10 c.c.), saturated sodium hydrogen carbonate solution (2 × 10 c.c.), and water and dried ($MgSO_4$). Removal of the solvent and crystallisation of the residue from ethanol–chloroform gave the *depside* (0·52 g.) as fine needles, m. p. 203—204° (Found: C, 75·3; H, 4·5. $C_{55}H_{38}O_{10}\cdot C_2H_5OH$ requires C, 75·7; H, 4·9%); $\nu_{max.}$ (Nujol) at 1690, 1730, and 1760 cm.$^{-1}$.

Diphenylmethyl 3,4-*Diphenylmethylenedioxy*-5-(3,4-*diphenylmethylenedioxy*-5-*hydroxybenzoyl*)-*benzoate*.—Ethanolic ammonia (6·0 c.c.), obtained by adding liquid ammonia to ethanol and allowing the temperature to rise to 0°, was added to a solution of the above depside (0·6 g.) in chloroform (3·0 c.c.) at 0° and the solution kept at 0° for 2½ hr. Removal of the chloroform and chromatography on alumina (60 g.) in benzene gave the *phenolic depside*, after crystallisation from benzene–light petroleum (b. p. 40—60°), as small cubes (0·4 g.), m. p. 201—202° (Found: C, 77·8; H, 4·6. $C_{53}H_{36}O_9$ requires C, 77·9; H, 4·4%); $\nu_{max.}$ (Nujol) at 1690, 1730, and 3300 cm.$^{-1}$. Acetylation by the usual methods gave (IV; R^1 = Ac, R^2 = diphenylmethyl), m. p. and mixed m. p. 203—205°.

Diphenylmethyl 3,4-*Diphenylmethylenedioxy*-5-[3,4-*diphenylmethylenedioxy*-5-(3,4,5-*tri*-O-*benzylgalloyl*)]*benzoate*.—The foregoing phenolic depside (0·75 g.) and tri-*O*-benzylgalloyl chloride (0·7 g.) were dissolved in chloroform (3·0 c.c.) and pyridine (0·50 c.c.) and the solution kept at 20° for 4 days before dilution with chloroform (20 c.c.). After washing (hydrochloric acid, sodium hydrogen carbonate solution, and water) and removal of the chloroform a pale yellow oil was obtained and chromatographed in benzene over alumina (30 g.). Removal of the solvent from the eluate gave the *ester* as a gum (0·28 g.) which was freeze-dried from glacial acetic acid (Found: C, 78·0; H, 5·2. $C_{81}H_{58}O_{13}$ requires C, 78·5; H, 4·7%); $\nu_{max.}$ (Nujol) at 1690, 1720, and 1730 cm.$^{-1}$.

m-*Trigallic Acid*.—The above ester (0·25 g.) was hydrogenated in ethyl acetate (7·0 c.c.) containing acetic acid (0·5 c.c.) and over palladium–charcoal (10%, 0·2 g.) for 48 hr. Removal of the catalyst and solvent gave a gum which slowly crystallised from aqueous acetone to give *m*-trigallic acid (0·045 g.) as small needles, m. p. 228°, lit.,[8] 217° (Found: C, 53·6; H, 3·7. Calc. for $C_{21}H_{14}O_{13}$: C, 53·3; H, 3·1%); $\nu_{max.}$ (Nujol) at 1690, 1720, and 3300 cm.$^{-1}$, R_F (6% acetic acid) 0·15, migration relative to gallic acid in 0·01M-acetate buffer, pH 5·9, 1500v, 0·28. The product was identical on paper-chromatographic or electrophoretic analysis with *m*-trigallic acid from Chinese gallotannin.[8] *m*-Trigallic acid (0·01 g.) was dissolved in methanol (4 c.c.) containing sodium acetate (0·5N; pH 6·0, 0·3 c.c.) and kept at 37°. After ½ hr. paper-chromatographic analysis [4] showed the presence of *m*-trigallic acid, methyl gallate, R_F (6% acetic acid) 0·53 and *m*-digallic acid, R_F (6% acetic acid) 0·25.

Methyl Hepta-O-*methyl*-m-*trigallate*.—(*a*) *m*-Trigallic acid (0·2 g.) (above or from Chinese gallotannin [8]) in acetone (2 c.c.) was treated with ethereal diazomethane [prepared from nitrosomethylurea (5 g.)] for 24 hr. at 15° and the process repeated twice. Removal of the solvent gave a gum which was chromatographed over alumina (20 g.) in benzene. Crystallisation of the

residue, on removal of the solvent from the eluate, from chloroform–light petroleum (b. p. 40—60°) gave *methyl hepta-O-methyl*-m-*trigallate* (0·2 g.) as needles, m. p. 129° (Found: C, 59·3; H, 5·6. $C_{29}H_{30}O_{13}$ requires C, 59·3; H, 5·1%).

(*b*) A solution of 3,4-dimethoxy-5-*O*-(3,4,5-tri-*O*-methylgalloyl)benzoyl chloride [13] (0·55 g.) and methyl 3-hydroxy-4,5-dimethoxybenzoate (0·30 g.) in chloroform (1·0 c.c.) containing pyridine (0·3 c.c.) was kept at 20° for 100 hr. when it was diluted with chloroform (20 c.c.) and the chloroform layer washed with hydrochloric acid (N; 2 × 5 c.c.), sodium hydrogen carbonate solution (2 × 5 c.c.), and water (10 c.c.), and finally dried ($MgSO_4$). Removal of the solvent gave a gum which was dissolved in benzene (5 c.c.), set aside for 24 hr. at room temperature, filtered, and then evaporated to dryness. The residual gum was extracted with light petroleum (b. p. 60—80°; 30 c.c.) under reflux and on cooling the light petroleum extract gave rosettes of the methyl ether (0·3 g.), m. p. and mixed m. p., 129°.

Methyl 3-(3-*Acetoxy*-4,5-*diphenylmethylenedioxybenzoyl*)-4,5-*diphenylmethylenedioxybenzoate*.—Methyl 3,4-diphenylmethylenedioxy-5-hydroxybenzoate (4·7 g.) and 3-acetoxy-4,5-diphenylmethylenedioxybenzoyl chloride (6·0 g.) were dissolved in chloroform (50 c.c.) and pyridine (3·5 c.c.) and kept at 20° for 48 hr. when chloroform was added and the solution washed (N-hydrochloric acid, water) before drying ($MgSO_4$). Removal of the solvent and crystallisation of the residue from acetone gave the *depside* as prisms (7·0 g.), m. p. 111—113° (Found: C, 72·1; H, 4·7. $C_{43}H_{30}O_{10}$ requires C, 72·1; H, 4·4%).

Methyl 3,4-*Diphenylmethylenedioxy*-5-(3,4-*diphenylmethylenedioxy*-5-*hydroxybenzoyl*)*benzoate*.—The depside prepared as described above (2·0 g.) in tetrahydrofuran (30 c.c.) containing ammonium hydroxide (2N; 15 c.c.) was kept at 20° for 19 hr. when water (200 c.c.) was added and the mixture acidified with 2N-hydrochloric acid. Extraction with ether and crystallisation from benzene–light petroleum (b. p. 60—80°) gave the *phenolic depside* as needles (1·5 g.), m. p. 231—232° (Found: C, 74·6; H, 4·7. $C_{41}H_{28}O_9$ requires C, 74·2; H, 4·3%). Hydrogenation of a sample of this compound followed by crystallisation from acetone–water gave methyl *m*-digallate, m. p. and mixed m. p. 226°

Methyl 3,4-*Diphenylmethylenedioxy*-5[3,4-*diphenylmethylenedioxy*-5-(3,4,5-*tri*-O-*benzylgalloyl*)*benzoyl*]*benzoate*.—A solution of the phenol prepared as described above (0·8 g.) and tri-*O*-benzylgalloyl chloride (0·8 g.) was dissolved in chloroform (15 c.c.) containing pyridine (0·25 c.c.) and kept at 20° for 40 hr. when chloroform was added and the organic layer washed (2N-hydrochloric acid and water) and dried ($MgSO_4$). Removal of the solvent gave an oil which was chromatographed in benzene over alumina (25 g.) to give the *ester* as prisms (0·7 g.) (from acetone–ethanol), m. p. 157—158° (Found: C, 76·2; H, 4·8. $C_{69}H_{50}O_{13}$ requires C, 76·3; H, 4·6%).

Methyl m-*Trigallate*.—Hydrogenation of the foregoing ester (0·8 g.) in ethyl acetate (10 c.c.) over palladium–charcoal (10%, 0·07 g.) followed by removal of the catalyst and solvent gave an oil which crystallised from acetone–water to give *methyl* m-*trigallate* (0·2 g.) as fine needles, m. p. 253—255° (Found: C, 51·4; H, 3·8. $C_{22}H_{16}O_{13}\cdot H_2O$ requires C, 51·8; H, 3·6%); $\nu_{max.}$ (KBr) at 1708 cm.$^{-1}$, R_F (6% acetic acid), 0·22.

Cyclohexyl 3,4-*Diphenylmethylenedioxy*-5-*hydroxybenzoate*.—This was prepared from cyclohexyl gallate [14] and diphenyldichloromethane as described previously for the methyl ester and crystallised as prisms (from benzene), m. p. 172° (Found: C, 75·1; H, 6·07. $C_{26}H_{24}O_5$ requires C, 75·0; H, 5·8%); $\nu_{max.}$ (Nujol) at 1705 cm.$^{-1}$.

Cyclohexyl 3-(3-*Acetoxy*-4,5-*diphenylmethylenedioxybenzoyl*)-4,5-*diphenylmethylenedioxybenzoate*.—This was prepared as described above for the methyl ester; it crystallised from acetone–ethanol as small needles, m. p. 115° (Found: C, 74·1; H, 5·1. $C_{48}H_{38}O_{10}$ requires C, 74·4; H, 4·9%); $\nu_{max.}$ (Nujol) at 1790, 1750, and 1720 cm.$^{-1}$.

Cyclohexyl 3-O-(3-*Hydroxy*-4′,5′-*diphenylmethylenedioxybenzoyl*)-4,5-*diphenylmethylenedioxybenzoate*.—This was prepared as described above for the methyl ester and was isolated after chromatography in chloroform over alumina and crystallisation from benzene–light petroleum (b. p. 60—80°) as prisms, m. p. 206—208° (Found: C, 75·3; H, 5·0. $C_{46}H_{36}O_9$ requires C, 75·4; H, 4·9%); $\nu_{max.}$ (Nujol) at 3450, 1750, and 1720 cm.$^{-1}$.

Cyclohexyl 3,4-*Diphenylmethylenedioxy*-5-[3,4-*diphenylmethylenedioxy*-5-(3,4,5-*tri*-O-*benzylgalloyl*)*benzoyl*]*benzoate*.—The above phenol (2·0 g.) and tri-*O*-benzylgalloyl chloride were dissolved in pyridine (60 c.c.) and the solution maintained at 20° for 4 days when it was diluted with benzene (250 c.c.) and washed (2N-hydrochloric acid, saturated sodium hydrogen carbonate,

[13] E. Fischer and K. Freudenberg, *Ber.*, 1912, **45**, 2709.
[14] G. J. M. Van der Kerk, J. H. Verbeek, and J. C. F. Cleton, *Rec. Trav. chim.*, 1951, **70**, 277.

and water). The solution was concentrated (approximately 80 c.c.) and kept at 20° for 36 hr., whereafter tri-*O*-benzylgallic acid, m. p. and mixed m. p. 189—190°, was filtered off. The filtrate was chromatographed in benzene over alumina (80 g.) and the *product* isolated, after crystallisation from benzene–light petroleum (b. p. 80—100°), as microcrystals (1·6 g.) m. p. 173—175° (Found: C, 76·7; H, 5·1. $C_{74}H_{53}O_{13}$ requires C, 76·9; H, 5·0%); $\nu_{max.}$ (Nujol) at 1750, 1740, and 1710 cm.$^{-1}$.

Cyclohexyl m-*Trigallate*.—This was prepared from the above-named ester as described for the methyl analogue; it separated in small prisms (microscope) from acetone–benzene, m. p 210—215° (Found: C, 56·4, 56·1; H, 4·5, 4·2. $C_{27}H_{24}O_{13},H_2O$ requires C, 56·5; H, 4·9%).

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