## 43. *The Depside Esters of Dihydric Phenols and Some Polydepsides.*

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THESE compounds have been prepared, by methods employed in the synthesis of depsides (J., 1932, 2263), for comparison with certain fully methylated phlobotannins.

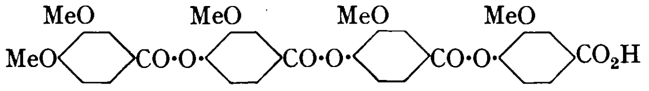
For the preparation of the didepside esters, the depside acid chloride was shaken for 3—16 hours with the requisite amount of the sodium phenoxide in acetone solution. As both didepside and phenol are soluble in alkali, that part of the reaction mixture insoluble in alkali, when all acid chloride had disappeared, was the ester required. Tridepsides are not, however, easily soluble in alkali, and the tridepside ester was isolated by washing the reaction product free from tridepside with boiling acetone.

The method for polydepsides was similar: the tridepsides resulted by coupling didepside chloride with the sodium salt of the hydroxy-aldehyde and oxidising the resulting aldehyde; for tetradepside the procedure was the same.

An improved method of oxidising aldehyde to didepside is given. This, with modifications, is applied to the oxidation of tri- and tetra-depside aldehydes to the corresponding tri- and tetra-depsides. The aldehyde of a decadepside, obtained by coupling 2 : 3 : 4-trihydroxybenzaldehyde with three molecules of 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzoyl chloride, is described. In all cases where atmospheric oxidation of the phenol in alkaline solution occurred, the experiments were done in an atmosphere of nitrogen.

All the depside esters and the polydepsides are crystalline; with increase in molecular weight there is an increase in m. p. and greater difficulty of crystallisation, but no loss of crystalline properties. Acid hydrolysis produces the parent substances without other decomposition.

The nomenclature previously used (*loc. cit.*) is extended, *ppp*-tetraprotocatechuic acid pentamethyl ether, *e.g.*, being named 3 : 3′ : 3″ : 3‴ : 4‴-pentamethoxy-*ppp*-tetrabenzoic acid.



3 : 3′ : 4′-*Trimethoxy*-p-*dibenzoic Acid* (Improved method).—A suspension of 3 : 3′ : 4′-trimethoxy-*p*-dibenzaldehyde (8 g.) in a solution of $KMnO_4$ (6 g.) in $H_2O$ (600 c.c.) was warmed at 70—80° till decomp. was complete. The depside separated when the cooled filtrate from the $MnO_2$ was acidified. Yield, 85%. 4′-Methoxy-*p*-dibenzoic acid was similarly prepared.

*Quinol Bis*-(3 : 3′ : 4′-*trimethoxy*-p-*dibenzoyl*) *Ether*.—Solutions of 0·5 g. (1 mol.) of quinol in acetone (20 c.c.) and *N*-NaOH (2 mols.) and of 3·5 g. (> 2 mols.) of 3 : 3′ : 4′-trimethoxy-*p*-dibenzoyl chloride in acetone (60 c.c.) were mixed and shaken for 6 hr. The product pptd. by $H_2O$ and insol. in alkali was recrystallised from $CHCl_3$; m. p. 229° (yield, 2 g.) (Found : C, 64·5; H, 4·6. $C_{40}H_{34}O_{14}$ requires C, 65·0; H, 4·6%).

*Quinol bis*-(3′ : 4′-*dimethoxy*-p-*dibenzoyl*) *ether*, m. p. 232° (Found : C, 66·7; H, 4·3. $C_{38}H_{30}O_{12}$ requires C, 67·3; H, 4·4%), also was recrystallised from $CHCl_3$. *Catechol bis*-(3′ : 4′-*dimethoxy*-p-*dibenzoyl*) *ether*, m. p. 175° (Found : C, 66·5; H, 4·3%), *resorcinol bis*-(3′ : 4′-*dimethoxy*-p-*dibenzoyl*) *ether*, m. p. 194° (Found : C, 66·8; H, 4·35%), *resorcinol bis*-(4′-*methoxy*-p-*dibenzoyl*) *ether*, m. p. 154° (Found : C, 69·3; H, 4·4. $C_{36}H_{26}O_{10}$ requires C, 70·0; H, 4·2%), and *quinol bis*-(4′-*methoxy*-p-*dibenzoyl*) *ether*, m. p. 230° (Found : C, 71·0; H, 4·25%), were recrystallised from $CHCl_3$–EtOH.

3 : 3′ : 3″ : 4″-*Tetramethoxy*-pp-*tribenzaldehyde* was similarly obtained from solutions of 3 g. (8 mols.) of vanillin in acetone (30 c.c.) and *N*-NaOH (20 c.c.; 1 mol.) and of 7·0 g. (1 mol.) of 3 : 3′ : 4′-trimethoxy-*p*-dibenzoyl chloride after 4 hrs.' shaking; recryst. from aq. acetone, it had m. p. 159° (yield, 8·3 g.) (Found : C, 61·7; H, 5·0. $C_{25}H_{22}O_9,H_2O$ requires C, 62·0; H, 5·0%).

3 : 3′ : 3″ : 4″-*Tetramethoxy*-pp-*tribenzoic Acid*.—3 : 3′ : 3″ : 4″-Tetramethoxy-*pp*-tribenzaldehyde (7 g.) was oxidised with 5 g. of $KMnO_4$ in 400 c.c. of warm $H_2O$ (24 hr.) and the cooled mixture decomposed with $SO_2$. The gelatinous *depside* was crystallised from aq. acetone; m. p. 251—252° (yield, 4 g.) (Found : C, 61·5; H, 4·7. $C_{25}H_{22}O_{10}$ requires C, 62·2; H, 4·6%).

3 : 3′ : 3″ : 4″-*Tetramethoxy*-pp-*tribenzoyl Chloride*.—3 : 3′ : 3″ : 4″-Tetramethoxy-*pp*-tribenzoic acid (3 g., dried at 100° for 24 hr.) was refluxed with $SOCl_2$ (10 c.c.) (3 hr.), the excess of this removed under reduced press., and the residue recrystallised from dry acetone; yellowish needles, m. p. 171° (evolution of gas) (yield, theoretical) (Found : Cl, 7·2. $C_{25}H_{21}O_9Cl$ requires Cl, 7·1%).

3 : 3′ : 3″ : 3‴ : 4‴-*Pentamethoxy*-ppp-*tetrabenzaldehyde*.—Solutions of 0·38 g. (1 mol.) of vanillin in acetone (30 c.c.) and *N*-NaOH (2·5 c.c.; 1 mol.) and of 1·16 g. (1 mol.) of 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzoyl chloride in acetone (150 c.c.) were shaken together for 20 hr. The solid product was washed with boiling acetone, dried at 100°, and recrystallised from AcOH; m. p. 249° (Found : C, 63·5; H, 4·7. $C_{33}H_{28}O_{12}$ requires C, 64·3; H, 4·55%).

3 : 3′ : 3″ : 3‴ : 4‴-*Pentamethoxy*-ppp-*tetrabenzoic Acid*.—3 : 3′ : 3″ : 3‴ : 4‴-Pentamethoxy-*ppp*-tetrabenzaldehyde (0·5 g.) was warmed with $KMnO_4$ (0·8 g. in 100 c.c. $H_2O$) for 36 hr., and the *depside* isolated by decomp. with $SO_2$ and recrystallised from $C_2H_2Cl_4$–EtOH; m. p. 327° (Found : C, 61·3; H, 4·5. $C_{33}H_{28}O_{13}$ requires C, 62·7; H, 4·4%).

3 : 4″-*Dimethoxy*-pp-*tribenzaldehyde* was prepared from 4′-methoxy-*p*-dibenzoyl chloride

and the sodium salt of vanillin (as for 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzaldehyde) and recrystallised from aq. acetone; m. p. 152° (Found: C, 67·7; H, 4·6. $C_{23}H_{18}O_7$ requires C, 68·0; H, 4·4%). Oxidation of the aldehyde (as for 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzoic acid) gave 3 : 4″-*dimethoxy*-pp-*tribenzoic acid*, which was recrystallised from acetone; m. p. 233° (Found: C, 64·6; H, 4·4. $C_{23}H_{18}O_8$ requires C, 65·4; H, 4·3%). The *chloride* (prepared as for 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzoyl chloride), cryst. from acetone, had m. p. 155° (Found: Cl, 8·25. $C_{23}H_{17}O_7Cl$ requires Cl, 8·05%).

*Quinol Bis-*(3 : 4″-*dimethoxy*-pp-*tribenzoyl*) *Ether*.—A solution of 0·5 g. (1 mol.) of quinol in acetone (20 c.c.) and *N*-NaOH (10 c.c.; 2 mols.) and a suspension of 3·4 g. (2 mols.) of 3 : 4″-dimethoxy-*pp*-tribenzoyl chloride in acetone (100 c.c.) were shaken together for 24 hr. The mixture was diluted to 500 c.c. with $H_2O$, and the ppt. collected, washed with boiling acetone, and recrystallised from $C_2H_2Cl_4$–EtOH; m. p. 278—279° (Found: C, 66·7; H, 4·3. $C_{52}H_{38}O_{16}$ requires C, 68·0; H, 4·1%).

*Tris-*(3 : 3′ : 3″ : 4″-*tetramethoxy*-pp-*tribenzoyl*)-2 : 3 : 4-*trihydroxybenzaldehyde*.—To 0·25 g. (1 mol.) of 2 : 3 : 4-trihydroxybenzaldehyde, dissolved in acetone (20 c.c.) and *N*-NaOH (5 c.c.; 3 mols.), were added 2·3 g. (3 mols.) of 3 : 3′ : 3″ : 4″-tetramethoxy-*pp*-tribenzoyl chloride in acetone (200 c.c.). The finely cryst. solid that separated after 36 hrs.' shaking was recrystallised from EtOH; small leaflets (0·22 g.), m. p. 263° (evolution of gas) (Found: C, 60·5; H, 4·3. $C_{82}H_{66}O_{31}$ requires C, 63·5; H, 4·3%).

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