THE POLYOXYPHENOLS OF WESTERN RED CEDAR (THUJA PLICATA DONN)

II. DEGRADATION STUDIES ON PLICATIC ACID, A POSSIBLE LIGNAN ACID[1]

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ABSTRACT

Plicatic acid, $C_{20}H_{22}O_{10}$, a polyoxyphenol from western red cedar heartwood, described in a previous paper, has been further characterized by preparation and analysis of additional crystalline derivatives. Crystalline trimethyl and triethyl ethers have been oxidized by alkaline permanganate. The trimethyl ether yielded 3,4,5-trimethoxybenzioc acid, 4,5-dimethoxyphthalic acid (*m*-hemipinic acid), a pentamethoxy anthraquinone, and a pentamethoxy *o*-benzoylbenzoic acid which decarboxylated to 3,4,5,3′,4′-pentamethoxy benzophenone. Correspondingly, the triethyl ether gave 3,4-diethoxy-5-methoxybenzoic and 4-ethoxy-5-methoxyphthalic acids, a mixture of pentaalkoxy anthraquinones and a pentaalkoxy *o*-benzoylbenzoic acid which decarboxylated to 3,3′,4-triethoxy-4′,5-dimethoxy benzophenone identified by cleavage to 3-ethoxy-4-methoxybenzoic and 3,4-diethoxy-5-methoxybenzoic acids. These results fix the positions of the two methoxyl, three phenolic hydroxyls, and mode of linkage of the two benzene rings. Further evidence is provided indicating plicatic acid is probably a lignan of the 4-aryltetrahydronaphthalene series.

In a previous paper (1), the isolation and properties of plicatic acid, a reactive polyoxyphenolic amorphous acid, occurring in the aqueous extractive of western red cedar, were described. Analysis of crystalline derivatives, methylation results, color tests, and spectra indicated it to be an *n*-propylphenol dimer, $C_{20}H_{22}O_{10}$, probably a lignan acid, in which one phenyl ring was 4-hydroxy-3-methoxyphenyl and the other was 3,4-dihydroxy-5-methoxyphenyl, but the mode of linkage was unknown. Thus the formula was given provisionally as $C_6H_3(OH)(OCH_3).C_5H_4(OH)_3(COOH).C_6H_2(OH)_2(OCH_3)$. This paper describes the alkaline permanganate oxidation of the crystalline trimethyl and triethyl ethers which establishes the aromatic substitution and indicates that plicatic acid is a lignan of the aryltetrahydronaphthalene series.

Alkaline permanganate oxidation of plicatic acid trimethyl ether (II*a*) gave a 15% yield of a crystalline colorless pentamethoxy keto-acid, $C_{19}H_{20}O_8$, m.p. 225.5–226°; smaller quantities of a neutral brilliant yellow crystalline substance, $C_{19}H_{18}O_7$, m.p. 209–210°, which gave qualitative tests and had spectral characteristics of an anthraquinone; 3,4,5-trimethoxybenzoic acid (V*a*); and 4,5-dimethoxyphthalic acid (IV*a*). The latter two acids were not isolated but their presence in the oxidation mixture was shown by paper chromatographic comparison with synthetic samples.

The pentamethoxy keto-acid decarboxylated to a benzophenone shown to be 3,4,5,3′,4′-pentamethoxybenzophenone by comparison with a synthetic sample. With concentrated sulphuric acid, the keto-acid readily gave a yellow anthraquinone. The infrared absorption spectrum of the acid was typical of the lactol form of a γ keto-acid (2) showing an alcoholic, but no acidic, hydroxyl band. These results indicate it to be an *o*-benzoylbenzoic acid, either 2,3,4-trimethoxy-6-(3′,4′-dimethoxybenzoyl)-benzoic acid or 3,4-dimethoxy-6-(3′,4′,5′-trimethoxybenzoyl)-benzoic acid (III*a*), either of which would give the same benzophenone (VIII*a*) on decarboxylation. Since Chatterjee and Chakravarti (3) had reported the isolation of an *o*-benzoylbenzoic acid of formula III*a* of much lower melting

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point, 210–211°, by the permanganate oxidation of the lignan, sikkimotoxin, and since plicatic acid gave some vanillin on alkaline nitrobenzene oxidation, the former was considered first. However, this possibility was eliminated when neither veratric acid nor 3,4,5-trimethoxyphthalic could be detected in the other oxidation products. The presence of 3,4,5-trimethoxybenzoic acid (V*a*) and 4,5-dimethoxyphthalic acid (IV*a*) as shown by paper chromatography required formula III*a*. It was concluded that Chatterjee and Chakravarti's compound, m.p. 210–211° from boiling water and dilute ethanol, must have been a mixture of the keto-acid (III*a*) and its lactol form (III*c*).

In the present work, the acid when purified by repeated recrystallization, was obtained in the lactol form (III*c*), m.p. 225.5–226°, as shown by the infrared absorption spectra. However, acidification of a dilute alkaline solution of the lactol gave a crystalline product, m.p. 180–185° depending on the rate of heating, which on the basis of its infrared absorption was the keto-acid (III*a*), i.e., a strong acidic hydroxyl band, no alcoholic hydroxyl band, and a shift of the carbonyl band to the benzoic acid region. This material was rapidly transformed on the melting point stage to the lactol form. The lactol nature was confirmed by the formation of a neutral crystalline acetate whose infrared absorption spectrum was clearly characteristic of a pseudoacetate, showing one broad enhanced carbonyl absorption band at 1758 cm^{-1} (2).

The anthraquinone obtained in nearly quantitative yield from the *o*-benzoylbenzoic acid by ring closure with concentrated sulphuric acid was found to be identical with that obtained as one of the permanganate oxidation products of plicatic acid trimethyl ether. Inspection of formula III*a* shows that ring closure of this substituted *o*-benzoylbenzoic acid, at either the 2′ or 6′ position, would give only one anthraquinone, namely, 1,2,3,6,7-pentamethoxy anthraquinone (VI).

Formation of the products III*a*, IV*a*, and V*a* proves that the position of aromatic substitutions in plicatic acid is as shown in formula I. To confirm the relative positions of the phenolic hydroxyl and methoxyl groups, which had been indicated by color tests and vanillin formation (1), the permanganate oxidation products at 100° of plicatic acid triethyl ether were examined. A crystalline monomeric acid was obtained which was shown to be 3,4-diethoxy-5-methoxybenzoic acid (V*b*) by comparison with a synthetic sample. The presence in the oxidation products of 4-ethoxy-5-methoxyphthalic acid (IV*b*) was demonstrated by paper chromatography in three solvent systems using a synthetic reference sample.

A neutral brilliant yellow crystalline product, giving qualitative tests for an anthraquinone, was also obtained in small yield. In contrast to the readily purified sharply melting anthraquinone obtained in the oxidation of plicatic acid trimethyl ether, the product in this case appeared to be a mixture since, after repeated recrystallizations, it melted over a wide range. This result was to be expected since, in the case of the ethylated derivatives, two anthraquinones, VII*a* and VII*b*, should result in approximately equal yield from ortho ring closure of the triethoxy-dimethoxy-*o*-benzoylbenzoic acid (III*b*).

The formation of 3,4-diethoxy-5-methoxybenzoic proves ring C to be 3,4-dihydroxy-5-methoxyphenyl and the formation of the 4-ethoxy-5-methoxyphthalic acid indicates the substitution pattern on ring A as shown in formula I for plicatic acid. Alkaline permanganate oxidation of the triethyl ether at lower temperature yielded mainly the ethylated keto-acid 4-ethoxy-3-methoxy-6-(3′,4′-diethoxy-5′-methoxybenzoyl)-benzoic acid (III*b*) which underwent conversion from its keto form III*b* to the lactol form III*d* near the melting point similar to the methylated derivative previously obtained. Decarboxylation gave the corresponding benzophenone, 3,3′,4-triethoxy-4′,5-dimethoxy benzo-

phenone, which on cleavage with potassium *t*-butoxide yielded 3-ethoxy-4-methoxybenzoic acid (IX) and 3,4-diethoxy-5-methoxybenzoic acid (V*b*). The formation of these latter products fixes with certainty the position of the hydroxyl group on ring A, as shown in Fig. 1, formula I.

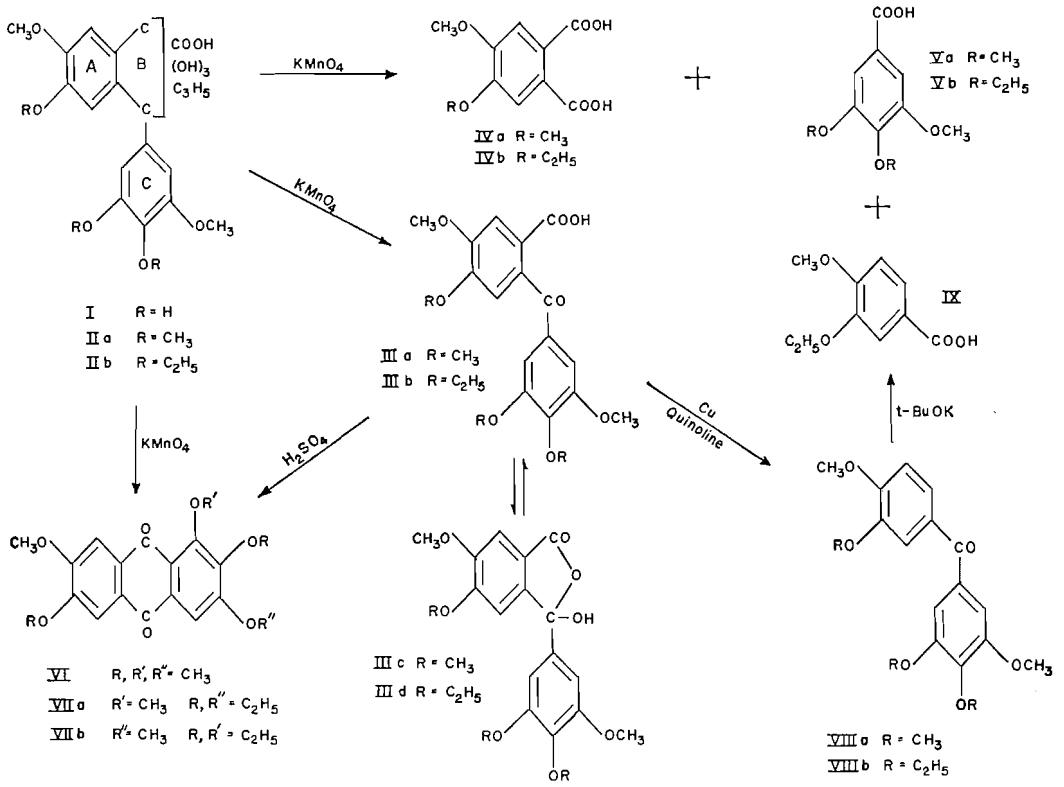

FIG. 1. Oxidation of methyl and ethyl ethers of plicatic acid.

The yield of vanillin (4%) obtained by alkaline nitrobenzene oxidation of plicatic acid (I) is in the same low range as that obtained from two other lignans, conidendrin and iso-olivil, 1 and 3% respectively (4). In the case of plicatic acid, since the C ring is a pyrogallol derivative, the vanillin formed must arise from the A ring via cleavage of an ortho-formylbenzophenone or decarboxylation of 6-carboxyvanillin. The vanillin from conidendrin and iso-olivil is probably derived similarly. This mode of vanillin formation is of interest in connection with alkaline nitrobenzene oxidation studies on lignins since a part of the vanillin formed could be so derived. While there is no evidence for the presence in lignin *in situ* of 3-methoxy-4-hydroxyphenylpropane structural units linked to the next through the 6-position, Richtzenhain (5) suggested the presence of such linkages in lignins isolated by acidic procedures to explain the formation of *m*-hemipinic acid by oxidation after methylation.

The presence of a monomethylated pyrogallol nucleus in plicatic acid explains the positive Mäule test, although this test is usually considered indicative of the dimethylated (syringyl) derivative. In contrast to the dimethylated (syringyl) derivatives, which occur widely in deciduous extractives and lignin, monomethylated derivatives of pyrogallol

are very rare in all plant products, none having been reported in wood components heretofore. It will be of considerable interest to determine whether products of additional methylation, i.e., syringyl derivatives, are also present in the western red cedar phenols.

In view of the easy formation of the tropolone derivative purpurogallin from pyrogallol, the occurrence of pyrogallol derivatives as well as tropolones in western red cedar is of interest in considering possible modes of biogenesis of the latter substances.

The oxidation products obtained herein together with the formation of γ lactones by plicatic acid and its trimethyl ether (1) are consistent with plicatic acid being a lignan of the 4-aryltetrahydronaphthalene series. Experimental proof of this and the pattern of hydroxylation on the saturated ring is in progress.

EXPERIMENTAL

Plicatic Acid Trimethyl Ether (IIa)

Plicatic acid (20 g) in water (40 ml) was treated with dimethyl sulphate (28 ml) and 20% sodium hydroxide dropwise at reflux for 2 hours under nitrogen while maintaining the pH at 9–10. After addition of the dimethyl sulphate, sodium hydroxide (50%) was added to raise the pH to 14. On cooling of the solution, the sodium salt precipitated and was separated on the centrifuge. The precipitated salt was dissolved in a minimum of distilled water, the solution acidified to pH 7 with sulphuric acid, extracted with chloroform to remove tarry residues, filtered, and further acidified to pH 2 to precipitate the free acid product. After filtration an additional crop was obtained by partial evaporation of the filtrate. Crude yield, 14.79 g (74%). The product was recrystallized from boiling water using decolorizing charcoal. Yield, 10.52 g (53%). Anal. Calc. for $C_{23}H_{28}O_{10}$: neutral equivalent, 464; OCH_3, 33.4. Found: neutral equivalent, 467; OCH_3, 32.7.

On rapid heating, the product melted with foaming between 210° and 218° depending on the rate of heating. It slowly recrystallized on the melting point stage and remelted at 253–255°. On slow heating, the product underwent a change in crystal structure between 220° and 245° and melted at 253–255°. The gas evolved during this conversion was shown to be water vapor and the new product proved to be plicatic acid trimethyl ether lactone, previously prepared from plicatic acid trimethyl ether methyl ester through loss of methanol (1), by mixed fusion and comparison of infrared spectra.

3,4-Dimethoxy-6-(3′,4′,5′-trimethoxybenzoyl)-benzoic Acid (IIIa)

Plicatic acid trimethyl ether (IIa) (4.56 g) was dissolved in 4% sodium hydroxide (100 ml) on a steam bath and 4% potassium permanganate (511 ml) slowly added with stirring in 10-ml portions until 400 ml had been added, and then in smaller portions to a 15-minute end point. The manganese dioxide together with the small yellowish precipitate which floated on the reaction mixture was filtered out (precipitate A) and washed with hot water (200 ml). After the pink filtrate had been decolorized with a few drops of bisulphite solution and acidified to pH 2 with hydrochloric acid, cooling precipitated pale yellow crystals. Filtration (filtrate B) and recrystallization from methanol–water (1:2) gave colorless needles. Yield, 0.679 g (15%). Anal. Calc. for $C_{19}H_{20}O_8$: C, 60.78; H, 5.10; OCH_3, 41.28; neutral equivalent, 375.4; mol. wt., 375.4. Found: C, 60.86; H, 5.09; OCH_3, 41.00; neutral equivalent, 371.3; mol. wt. (isothermal distillation), 388. The product gave a positive test with 2,4-dinitrophenylhydrazine. Heating rapidly gave partial melting at 180–185° followed by recrystallization and remelting at 218–220°, m.p. after five recrystallizations 225.5–226°. Infrared absorption spectrum was characteristic of the lactol of a keto-acid. ν_{max}^{KBr} 3340, 1702, 1668, 1582, 1322, 1128, 997, 765.

Acidification of a dilute alkaline solution and vacuum drying at room temperature produced the pure keto-acid form (III*a*), m.p. 184–185°. ν_{max}^{KBr} no hydroxyl band, 2600, 1668, 1648, 1580, 1502, 1460, 1410, 1322, 1280, 1120, 1003, 772.

When treated with concentrated sulphuric acid, the product gave a brilliant purple color transformed in a few minutes warming to brown. Dilution of the brown mixture with water and neutralization precipitated a bright yellow crystalline substance, m.p. 207–208° from methanol, showing no mixed melting point depression with 1,2,3,6,7-pentamethoxy anthraquinone (VI) (see below).

Treatment with diazomethane in methanol–ether gave a crystalline monomethyl ester, m.p. 147–147.5°, showing no absorption bands for the hydroxyl group in the infrared spectrum. Anal. Calc. for $C_{20}H_{22}O_8$: OCH_3, 47.64; mol. wt., 390. Found: OCH_3, 46.87; mol. wt. (Rast), 390.

Refluxing with acetic anhydride in pyridine gave a crystalline acetate, insoluble in bicarbonate solution, m.p. 118–119° from methanol. The infrared absorption spectrum showed no hydroxyl band and had one broad intense carbonyl band at 1758 cm^{-1} typical of a lactol acetate (2).

1,2,3,6,7-Pentamethoxy Anthraquinone (VI)

"Precipitate A" after drying was triturated with chloroform (4×50 ml). The solution was then dried over sodium sulphate and evaporated to yield a brilliant yellow powder (0.154 g, 3% yield), melting point after two recrystallizations from methanol, 209–210°. This compound when heated with sodium hydrosulphite in alkali gave a red solution which precipitated the yellow starting material on air oxidation. The red solution on further reduction with zinc and alkali gave a pale yellow precipitate. These positive qualitative tests for anthraquinone structure were supported by formation of the same substance by ring closure of the keto-acid (III*a*) and by the absorption spectra. The ultraviolet absorption in methanol exhibited an intense maximum at 285 mμ ($\log \epsilon = 4.81$). The infrared absorption (KBr pellet) showed one weak and one very strong band attributable to the carbonyls at 1740 cm^{-1} and 1662 cm^{-1}, respectively, comparable to those of anthraquinone at 1740 cm^{-1} and 1665 cm^{-1}. Anal. Calc. for 1,2,3,6,7-pentamethoxy anthraquinone, $C_{19}H_{18}O_7$: C, 63.67; H, 5.06; OCH_3, 43.24; mol. wt., 358. Found: C, 63.56; H, 4.97; OCH_3, 42.80; mol. wt. (Rast), 360.

Identification of 3,4,5-Trimethoxybenzoic Acid (Va) and 4,5-Dimethoxyphthalic Acid (IVa)

"Filtrate B" was extracted with ether (3×100 ml) and the ether solution extracted with sodium bicarbonate (3×25 ml). The mixed acids were isolated by acidification of the bicarbonate solution, extraction into ether, and solvent removal to yield a light tan solid (135 mg, 3% yield). This material was compared by descending paper chromatography on Whatman No. 1 using two solvents, *n*-propanol:26% ammonia (3:2) (6) and *n*-butanol:2% ammonia (1:1) using reference samples of 3,4,5-trimethoxybenzoic acid and 4,5-dimethoxyphthalic acid (7). Spots at R_f's 0.79 and 0.29 and at 0.30 and 0.036 in the two solvents systems respectively, identical with those of the reference samples, were present. Detection was made first with short ultraviolet light which shows the acids as dark spots, then by spraying with universal indicator (B.D.H.). Since 4,5-dimethoxyphthalic acid (*m*-hemipinic acid) and 3,4-dimethoxyphthalic acid (hemipinic acid) (7) have very similar R_f's in these solvents, the oxidation product was also run in benzene:acetic acid:water (125:72:3) over a period of 16 hours, the solvent being allowed to run off the paper. The synthetic 4,5-dimethoxyphthalic and the oxidation product ran $15\frac{1}{4}$ inches while the 3,4-dimethoxyphthalic acid ran 17 inches. These acids

were detected with short ultraviolet light as dark spots. No spots corresponding to synthetic veratric and 3,4,5-trimethoxyphthalic acid (8) were detected.

3,4,5,3′,4′-Pentamethoxy Benzophenone (VIIIa)

3,4,5,3′,4′-Pentamethoxy benzophenone was prepared by dissolving the keto-acid (III*a*) (275 mg) and its copper salt (25 mg) as catalyst (9) in quinoline (7 ml) and refluxing for ½ hour. Metallic copper settled out on cooling. The reaction mixture was diluted with ether (20 ml) and filtered. The filtrate was washed with 2 *N* hydrochloric acid (5×10 ml) until nearly colorless, then with 5% sodium hydroxide (2×10 ml) to remove the trace yellow color, dried over sodium sulphate, and evaporated to colorless crystals. Yield, 123 mg (45%). Recrystallization from methanol:water gave colorless platelets, m.p. 120.5–121°, oxime, m.p. 149.5–150°. Mixed melting point with synthetic samples (10, 11) 123.5° and 148.5–149.5°, respectively, showed no depression and the infrared absorption spectra of the benzophenones were identical. ν_{max}^{KBr} 1632, 1582, 1518, 1466, 1415, 1326, 1268, 1125, 770.

Plicatic Acid Triethyl Ether (IIb)

Plicatic acid (28.1 g) in water (25 ml) was treated with diethyl sulphate (30 ml) and 20% sodium hydroxide dropwise at reflux for 3 hours under nitrogen while maintaining the pH at 9–10. After addition of the diethyl sulphate, sodium hydroxide (10 ml, 20%) was added and the reaction mixture refluxed for an additional hour. On cooling, the reaction mixture solidified. After stirring and centrifuging several times, the supernatant liquor was decanted, the precipitated sodium salt acidified, and the free acid taken up in chloroform. The chloroform solution was extracted with sodium bicarbonate solution, the bicarbonate solution acidified, and the precipitated product recrystallized from methanol:water (1:1), m.p. 113–114°. Yield, 10.74 g (38%). As this compound lactonized very readily at 140°, excessive heating during recrystallization and drying was avoided. Stable gels were formed by cooling benzene solutions. Calc. for $C_{26}H_{34}O_{10}$: alkoxyl as methoxyl, 30.6%; neutral equivalent, 506. Found: alkoxyl as methoxyl, 30.2%; neutral equivalent, 509.

Permanganate Oxidation of Plicatic Acid Triethyl Ether (IIb) at 100°

Oxidation of this ether (6.2 g) was similar to that of the trimethyl ether with the exception that 5% potassium hydroxide and 5% potassium permanganate were used and the solution kept boiling throughout the addition of the potassium permanganate (864 ml). Due to the more drastic oxidation conditions no ethyl-substituted *o*-benzoyl-benzoic acid was obtained. The monomeric acids were obtained as a yellow plastic solid. Yield, 0.334 g (5.4%).

As in the case of oxidation of the trimethyl ether, brilliant yellow crystals precipitated from the boiling alkaline reaction mixture. Yield, 0.143 g (2%). Qualitative tests for anthraquinone structure were positive. A mixture of anthraquinones was suspected since two recrystallizations gave no change in the melting point range of 150–167°.

Isolation of 3,4-Diethoxy-5-methoxybenzoic Acid (Vb)

A portion of the mixed acids (0.09 g) was fractionated by column chromatography on silicic acid using the technique of Hathaway (6). Evaporation of the first fraction gave a crystalline product, m.p. 112–113°, from ethanol:water (1:1) identical with, by mixed melting point and infrared absorption spectrum, a reference sample synthesized from 5-hydroxy vanillin (12) by ethylation with diethyl sulphate followed by oxidation with cold 1% permanganate (13).

Detection of 4-Ethoxy-5-methoxyphthalic Acid (IVb)

A sample of the mixed acids was examined by descending paper chromatography in three solvent systems, *n*-propanol:26% ammonia (3:2), *n*-butanol:2% ammonia (1:1) and benzene:acetic acid:water (125:72:3). In each case, spots at R_f's identical with those of a synthetic sample of 4-ethoxy-5-methoxyphthalic acid were obtained. In the first two, the spots (R_f's 0.51 and 0.045 respectively) were detected first by short ultraviolet light and then by spraying with universal indicator (B.D.H.). In the last, the solvent was allowed to run off the paper to give 14 inches of migration by the acid and detection was by short ultraviolet light.

The reference sample of 4-ethoxy-5-methoxyphthalic acid (melting point of ethylimide, 204°) was obtained by the permanganate oxidation (13) of 4-ethoxy-5-methoxyphthalide synthesized from the ethyl ether of vanillic acid using the method of King and King (14).

4-Ethoxy-3-methoxy-6-(3',4'-diethoxy-5'-methoxybenzoyl)-benzoic Acid (IIIb)

Permanganate oxidation of plicatic acid triethyl ether (II*b*) at 50–55° was analogous to the previous oxidation for the trimethyl ether (II*a*). At this temperature only a trivial amount of the corresponding anthraquinones (VII*a* and VII*b*) was obtained. The main product was similarly a keto-acid, 4-ethoxy-3-methoxy-6-(3',4'-diethoxy-5'-methoxybenzoyl)-benzoic acid (III*b*) (8% yield). Anal. Calc. for $C_{22}H_{26}O_8$: neutral equivalent, 418. Found: 416. Heating rapidly gave a partial melting at 120–124° followed by recrystallization and remelting at 136–137°. Infrared absorption spectrum of the original material before melting was that of the keto-acid (III*b*). ν_{max}^{KBr} no hydroxyl band, 2600, 1670–1660 (doublet), 1580, 1500, 1418, 1320, 1270. After melting at 136–137° the spectrum was mainly that of the lactol (III*d*) contaminated with some of the keto-acid. ν_{max}^{KBr} 3250, 2600, 1705, 1680, 1580, 1500, 1418, 1320, 1270, 1120, 766.

3,3',4-Triethoxy-4',5-dimethoxy Benzophenone (VIIIb)

3,3',4-Triethoxy-4',5-dimethoxy benzophenone was prepared from the keto-acid (III*b*) in an analogous manner to the fully methylated benzophenone (VIII*a*). Yield, 68% of theoretical. Recrystallization from methanol:water (2:1) gave colorless needles, m.p. 96–96.5°. The infrared spectrogram was free of acid hydroxyl and acid carbonyl bands showing only the expected diaryl ketone carbonyl. ν_{max}^{KBr} 1640, 1580, 1518, 1420, 1322, 1262, 1122, 1023, 776.

Cleavage of 3,3',4-Triethoxy-4',5-dimethoxy Benzophenone (VIIIb)

In accordance with the procedure of Swan (15), potassium wire (30 mg, 0.00075 mole) was converted to potassium tertiary butoxide. A solution of the benzophenone (90.3 mg, 0.000242 mole) and water (4.8 microliters, 0.000265 mole) in anhydrous dioxane (5 ml) was added and refluxed at 90° for 18 hours under anhydrous conditions. The solvent was evaporated under reduced pressure, the residue dissolved in water, and extracted with ether (2×10 ml) to remove unreacted benzophenone and the neutral products. On acidification with HCl, the acids precipitated as colorless solids (36 mg, 80% yield). The mixed acids (30 mg) were separated by dissolving in acetone and streaking across a 9-in. wide No. 17 Whatman chromatographic paper. Development was with butanol – 2% ammonia (1:1) solvent and detection by short ultraviolet light. The spots were excised and Soxhlet extracted with acetone. After removal of the acetone under reduced pressure, the separated acids were taken up in bicarbonate, filtered, and precipitated with HCl. Yields were 3-ethoxy-4-methoxybenzoic acid (IX), 13 mg, m.p. 167.5–168° (R_f = 0.32

in butanol – 2% ammonia), and 3,4-diethoxy-5-methoxybenzoic acid (V*b*), 9 mg, m.p. 113–114° (R_f = 0.51 in butanol – 2% ammonia), identical with authentic samples by mixed melting point and infrared spectrogram.

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