oxide at 90° for 2.5 hours. The impure material obtained after cooling and filtering was extracted with hot dioxane. The insoluble material melted at 349–353° and amounted to 2.2 g. (61%).

(B) From **2,8-Diaminophenoxathiin-10-dioxide**.—To 1.25 g. (0.005 mole) of 2,8-diaminophenoxathiin-10-dioxide in 10 ml. of dry benzene was added 1.25 g. (0.012 mole) of acetic anhydride. The resulting mixture was refluxed for three hours and filtered hot. The white crystals of 2,8-diacetaminophenoxathiin-10-dioxide that were obtained melted at 328–333°. The yield was 1.2 g. or 61%. Recrystallization from dioxane, acetone and glacial acetic acid raised the melting point to 338–341°. A mixed melting point with the material prepared by method (A) melted at 345–350°.

Anal. Calcd. for $C_{16}H_{14}O_4N_2S$: S, 9.32. Found: S, 9.17.

2,8-Dinitrophenoxathiin-10-dioxide.—To 10 g. (0.05 mole) of phenoxathiin were added 50 ml. of glacial acetic acid, 20 ml. of concentrated sulfuric acid and 30 ml. of fuming nitric acid. The reaction mixture was refluxed for 3.5 hours, cooled and poured into water. The crude yellow product was purified by extracting the mononitro compound with hot acetone. The insoluble residue amounted to 4.8 g. (30%) and melted at 283–286°.

Anal. Calcd. for $C_{12}H_6O_7N_2S$: S, 10.25. Found: S, 10.20.

Nitration of 20 g. (0.086 mole) of phenoxathiin-10-dioxide in 80 ml. of concd. sulfuric acid by the addition of 30 ml. of fuming nitric acid over a period of 15 minutes gave 11 g. (41%) of 2,8-dinitrophenoxathiin-10-dioxide melting at 277–280°.

2,8-Diaminophenoxathiin-10-dioxide.—To a mixture of 17 g. (0.052 mole) of 2,8-dinitrophenoxathiin-10-dioxide, 200 ml. of ethanol and 225 ml. of concd. hydrochloric acid was added 80 g. of zinc dust in portions over a period of 1.5 hours. After refluxing for two hours an additional 50 ml. of hydrochloric acid and 25 g. of zinc dust were added. Refluxing was continued for one hour and the reaction mixture allowed to stand overnight. The insoluble product was removed by filtration, suspended in water and neutralized with sodium hydroxide. The desired diamine was removed by solution in hot acetone and the acetone extracts evaporated nearly to dryness. There was obtained 9.7 g. (81%) of 2,8-diaminophenoxathiin-10-dioxide melting at 244–247.5°.

Anal. Calcd. for $C_{12}H_{10}O_3N_2S$: S, 12.20. Found: S, 12.05.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

Synthesis of 3′,4′-Dimethoxyphenylindanones and Tetralones

BY GORDON N. WALKER

RECEIVED AUGUST 14, 1952

Both stereoisomers of 2-methyl-3-(3′,4′-dimethoxyphenyl)-5,6-dimethoxy-1-indanone have been synthesized, the first by reduction of the corresponding indenone and the second by cyclization of the required acid. The polyphosphoric acid cyclization of β-carbethoxy-γ,γ-di-(3,4-dimethoxyphenyl)-butyric acid to 3-carbethoxy-4-(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone is described, and evidence is presented favoring a *trans* configuration for this product.

An earlier report[1] established the fact that simple benzylsuccinic acids and acid esters cyclize exclusively to tetralone derivatives in the presence of polyphosphoric acid. This reaction has now been extended (Chart II) to include substituted benzhydryl succinic acid esters, as IX, as a means of preparing compounds having a ring system such as that which occurs in the tumor-damaging compound, podophyllotoxin. At the same time, the related indanone, VI, was studied (Chart I) in an attempt to clarify questions of isomerism. The ketone, I, was employed as starting material in each case, for the sake of simplicity, since ring closures of compounds in the symmetrical tetramethoxydiphenylmethane series are not subject to the difficulty that two structural isomers can be formed.

A Stobbe reaction of I with ethyl succinate furnished an acid ester, VII, in high yield when potassium *t*-butoxide was used as the condensing agent. The product, VII, was hydrogenated in acetic acid at 80° in the presence of a palladium catalyst. Cyclization of the reduced material, IX, in polyphosphoric acid at 100° afforded a crystalline carbethoxytetralone, X, the only product which could be isolated from this reaction. Present evidence indicates that X was the *trans* isomer with respect to the 3-carbethoxy group and the 4-(3′,4′-dimethoxyphenyl) group. Alkaline hydrolysis of X led to a ketoacid, XI. Inversion of the carboxy function did not occur under these conditions since material identical with X was obtained when XI was esterified in ethanol. Catalytic hydrogenolysis of the tetralone, X, gave the corresponding tetralin derivative, XII. Saponification of XII in turn yielded an acid, XIII, which was dehydrogenated at 255° in the presence of 5% palladium–charcoal. This aromatization established the fact that X, XI, XII and XIII were compounds of the tetralin rather than of the indane, series. No dehydrogenation was observed at a lower temperature (175°), although 2-carboxy-6,7-dimethoxytetralin loses hydrogen readily at 175° in the presence of the same catalyst.[1] A possible explanation for the difficulty experienced in aromatizing XIII is that the hydrogen atoms at positions 3- and 4- in the latter are disposed *trans* to one another.

The indanone, VI, was synthesized by two different methods, first by hydrogenation of indenone III, which led to a glassy ketone, VIa, and secondly by polyphosphoric acid cyclization of the acid V, which led to a crystalline ketone, VIb. The properties of V and VIb indicated that they were the same compounds, acid and ketone, respectively, obtained by Müller and Gal[2] by different methods. The two ketones, VIa and VIb, were very probably stereoisomers, *cis* and *trans*, respectively. Evidence in favor of this conclusion was furnished by

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[1] E. C. Horning and G. N. Walker, THIS JOURNAL, **74**, 5147 (1952).

[2] A. Müller and E. Gal, *Ber.*, **77**, 343 (1944).

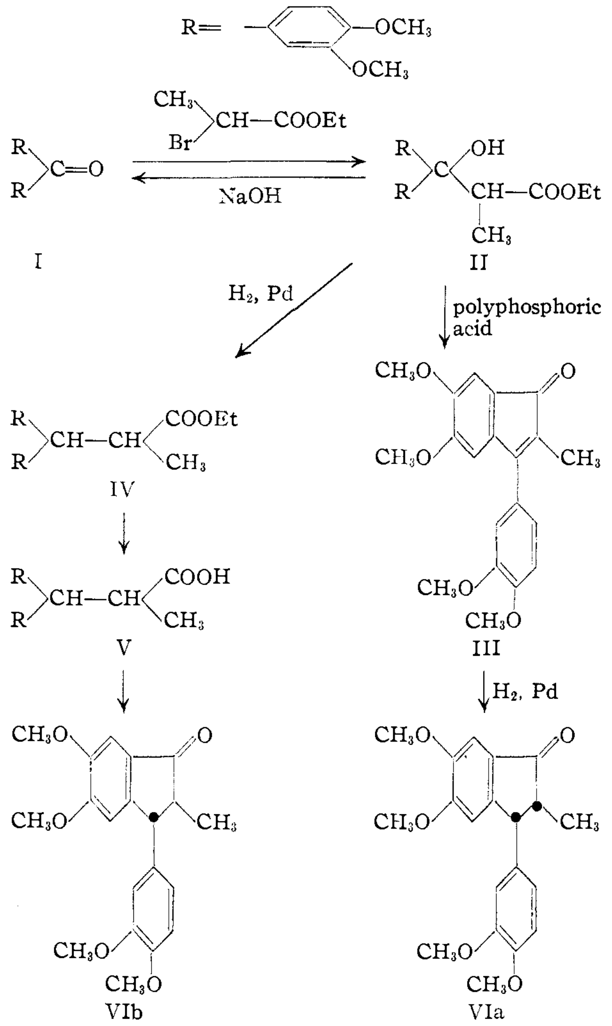

CHART I

the infrared spectra,[3] which were similar but not identical, and by the difference in melting points of the 2,4-dinitrophenylhydrazones obtained from the two ketones.

The cyclizations V → VIb and IX → X are not entirely analogous. Both, however, may proceed along courses involving the lesser degree of steric interaction of groups present in the respective molecules, and in each case a *trans* product appears to be more likely than a *cis* product. An anhydride, VIII, corresponding to the unsaturated acid ester, VII, was obtained when VII was allowed to react with polyphosphoric acid. Anhydride formation under these conditions parallels that observed with simpler arylitaconic acids.[1] Alkaline treatment of VIII resulted in cleavage and the return of I. The hydroxy ester, II, underwent a similar degradation in the presence of alkali.

Modifications of X leading to several analogs of compounds in the podophyllotoxin series will be reported in a following paper.

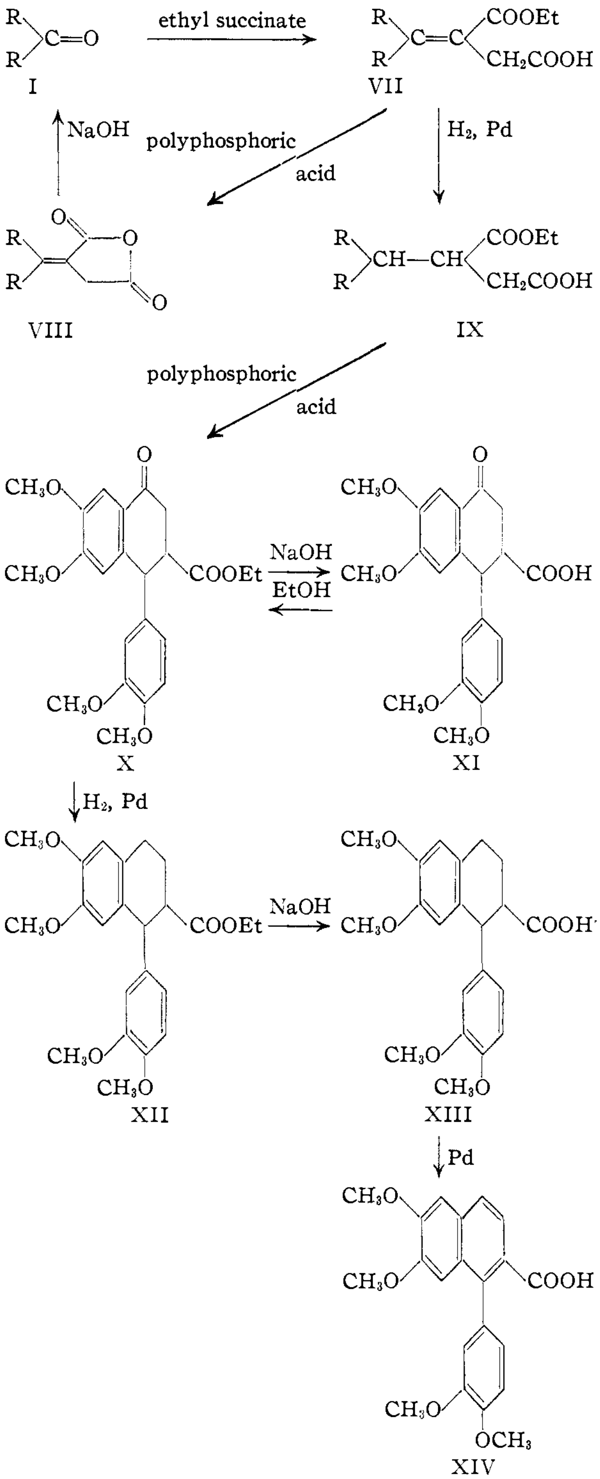

CHART II

Acknowledgment.—We are indebted to Mrs. Iris Siewers and Miss Alice Bernardi of our Instrumental Laboratory for the infrared and ultraviolet spectra, and to Dr. William Alford and his staff for the analytical data.

Experimental[4]

Ethyl α-Methyl-β-hydroxy-β,β-di-(3,4-dimethoxyphenyl)-propionate (II).—The Reformatsky reaction leading to this

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[3] Copies of the full infrared spectra discussed in this paper can be obtained as Document 3909 from American Documentation Institute Auxiliary Publications, Photoduplication Service, Library of Congress, Washington 25, D. C., remitting $1.25 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.25 for photostat readable without optical aid.

[4] Melting points are corrected.

compound was carried out in 97% yield.[5] The infrared spectrum showed peaks at 2.9 and 5.84 μ (bonded ester carbonyl). When the material was refluxed with 20% sodium hydroxide solution for four hours, ketone I was obtained (75% yield).

2-Methyl-3-(3',4'-dimethoxyphenyl)-5,6-dimethoxyindenone (III).—This indenone was prepared according to Horning and Parker[5] with the exception that heat was not applied in the cyclization. Recrystallization of the crude, neutral product from benzene gave red crystals, m.p. 202.5–204° (reported[5] m.p. 196–198°).

The infrared spectrum of this indenone ($CHCl_3$) showed absorption at 5.88 and 6.27 μ.

***cis*-2-Methyl-3-(3',4'-dimethoxyphenyl)-5,6-dimethoxy-1-indanone (VIa).**—A mixture of 1.4 g. of the indenone (III), 2 g. of 5% palladium–charcoal catalyst and 200 ml. of ethyl acetate was shaken under hydrogen (40 lb.) for 1.5 hours. The catalyst was removed by filtration, and the filtrate was evaporated. There was obtained 1.1 g. of yellow oil which, on standing, became a very viscous glass.

The infrared spectrum of the crude ketone ($CHCl_3$) had an absorption band at 5.90 μ and a second (double) peak at 6.20–6.26 μ.

The **2,4-dinitrophenylhydrazone** crystallized slowly; recrystallization from ethyl acetate gave red crystals, m.p. 212.5–214.5°.

Anal. Calcd. for $C_{26}H_{26}O_8N_4$: C, 59.76; H, 5.02. Found: C, 59.88; H, 5.22.

α-Methyl-β,β-di-(3,4-dimethoxyphenyl)-propionic Acid (V). (A) Reduction.—A solution of 5.3 g. of crude ethyl α-methyl-β-hydroxy-β,β-di-(3,4-dimethoxyphenyl)-propionate in 100 ml. of glacial acetic acid containing 2.5 g. of 5% palladium–charcoal catalyst was hydrogenated at 40 lb. and 80° for three hours. The catalyst was separated, and the solvent was evaporated; there remained 2.5 g. of yellow, viscous oil. The infrared spectrum of this crude product ($CHCl_3$) showed no appreciable absorption at 2.9 μ, but included a band at 5.78 μ (non-bonded ester carbonyl).

(B) Hydrolysis.—The crude ester from (A) was refluxed in 25% sodium hydroxide solution for three hours. The product, after acidification and trituration with ether, was a colorless powder, m.p. 174–177.5°. Recrystallization from ethyl acetate gave colorless crystals, m.p. 177–178.5° (reported[2] m.p. 176°).

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.62; H, 6.71.

***trans*-2-Methyl-3-(3',4'-dimethoxyphenyl)-5,6-dimethoxy-1-indanone (VIb).**—A mixture of 3.9 g. (0.0011 mole) of the acid (V) and 125 g. of polyphosphoric acid was heated on a steam-cone for 1.25 hours with steady stirring. The solid material dissolved slowly, and a carmine solution was formed. The solution was cooled and hydrolyzed with ice and water. The product was extracted with ether. The ether solution was washed with sodium bicarbonate solution and water, and was dried (magnesium sulfate). Evaporation of the ether gave 3.8 g. of oil. This material was dissolved in a small amount of ether, and the solution was chilled overnight. The crystals were collected; 2.9 g., m.p. 57–60°. One recrystallization from methanol–ether afforded 1.0 g., m.p. 110–112°. Further recrystallization from the same solvent mixture and from ether gave colorless crystals, m.p. 117.5–118.5° (reported[2] m.p. 120°).

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.22; H, 6.67.

The infrared absorption spectrum of this ketone ($CHCl_3$) showed a carbonyl absorption band at 5.88 μ, and a second peak at 6.24 μ (shoulder at 6.20 μ).

The **2,4-dinitrophenylhydrazone** was prepared from crude material and was fractionally crystallized and recrystallized from methanol; dark red needles, m.p. 182.5–184.5°.

Anal. Calcd. for $C_{26}H_{26}O_8N_4$: C, 59.76; H, 5.02. Found: C, 59.87; H, 5.26.

The mixed m.p. with the 2,4-dinitrophenylhydrazone of VIa was 176–183° (depressed).

Acid Ester of α,α-Di-(3,4-dimethoxyphenyl)-itaconic Acid (VII). Stobbe Condensation.—To a solution of 8.1 g. (0.208 g. atom) of potassium in 600 ml. of *t*-butyl alcohol was added 55 g. (0.182 mole) of 3,4,3',4'-tetramethoxybenzophenone and 46.5 g. (0.268 mole) of ethyl succinate. The mixture was refluxed with stirring for three hours. A clear solution was obtained initially; after 20 minutes a precipitate began to appear. Excess *t*-butyl alcohol (500 ml.) was removed by distillation, with continued stirring, over a period of one-half hour. The thick suspension was cooled, treated with one liter of water, and stirred for a half hour. Filtration afforded 11.4 g. of unreacted ketone, after washing with water and air-drying; m.p. 143–146°. The filtrate was washed with ethyl acetate, acidified strongly with hydrochloric acid, and chilled. The oil was extracted with ether. The ether solution was washed with water and was dried over magnesium sulfate. Evaporation of the ether afforded 58 g. (94%, based on ketone consumed) of red, viscous oil which crystallized very slowly on standing.

α,α-Di-(3,4-dimethoxyphenyl)-itaconic Anhydride (VIII).—A mixture of 7.9 g. of crude acid ester (VII) and 63.5 g. of polyphosphoric acid was stirred vigorously. A deep purple solution formed rapidly. The solution was warmed for one minute on the steam-cone, was cooled, and was treated with cold water. The gummy product was extracted with ethyl acetate. The ethyl acetate solution was washed with sodium bicarbonate solution and water; acidification of the bicarbonate solutions afforded 2.7 g. of unchanged material. The ethyl acetate solution was washed with successive portions of 5% sodium hydroxide solution, water, dilute acetic acid, sodium bicarbonate solution and water, and was dried (magnesium sulfate). Evaporation of the solvent gave 3.5 g. of gummy crystals. Trituration with ether and recrystallization from ethyl acetate afforded colorless crystals, m.p. 148.5–150°.

Anal. Calcd. for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24. Found: C, 65.41; H, 5.42.

The infrared absorption spectrum of this compound ($CHCl_3$) showed that the characteristic twin peaks of a cyclic anhydride, at 5.60 and 5.83 μ, respectively.

Hydrolysis of the material in water at 100° for several hours led to material, m.p. 115.5–117.5° (from methanol), the infrared spectrum of which indicated that a cyclic anhydride was still present. Further treatment of this material with 30% sodium hydroxide solution at 100° for three hours gave 3,4,3',4'-tetramethoxybenzophenone, m.p. 145–146° (from methanol); mixed m.p. with an authentic sample, 145.5–146.5°

Treatment of VII with polyphosphoric acid at 100° led, after hydrolysis, to highly refractory brown material.

***trans*-3-Carbethoxy-4-(3',4'-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone (X). (A). Reduction (IX).**—A mixture of 58 g. (0.135 mole) of crude Stobbe condensation product, 5.0 g. of 5% palladium–charcoal catalyst and 200 ml. of glacial acetic acid was shaken under hydrogen (initially at 40 lb.) at 80° for 2.5 hours. The hot solution was filtered to remove the catalyst. The acetic acid was evaporated. There remained 56.8 g. of viscous oil sufficiently pure for cyclization.

(B) **Cyclization.**—A mixture of 56.8 g. of the crude product from (A) and 240 g. of polyphosphoric acid was heated on a steam-cone for one-half hour with good stirring. The resulting red-brown solution was cooled and was treated with ice and water. The product was extracted with ethyl acetate. The organic solution was washed with three portions of sodium bicarbonate solution and one portion of water, and was dried over magnesium sulfate. Evaporation of the solvent gave a red, viscous oil. This material was dissolved in a small amount of ethyl acetate, and the solution was diluted with 20 volumes of dry ether. This solution was chilled overnight after seeding. The product was collected, washed with a small amount of dry ether, and air dried. There was obtained 28.8 g. (53%) of colorless crystals, m.p. 129–130.5°. Recrystallization from methanol–ether gave colorless, cottony crystals, m.p. 132–134°.

Anal. Calcd. for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.88; H, 6.47.

The **2,4-dinitrophenylhydrazone** was recrystallized from ethanol; red crystals, m.p. 164–166°.

Anal. Calcd. for $C_{29}H_{30}O_{10}N_4$: C, 58.58; H, 5.09. Found: C, 58.63; H, 5.22.

The infrared absorption spectrum of this ketoester ($CHCl_3$) showed bands at 5.77 μ (ester carbonyl), 5.97 μ (ketone) and 6.23 μ.

3-Carboxy-4-(3',4'-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone (XI).—A solution of 2.0 g. of 3-carbethoxy-4-

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[5] E. C. Horning and J. A. Parker, THIS JOURNAL, **74**, 3870 (1952).

(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone and 10 g. of sodium hydroxide in 20 ml. of ethanol and 40 ml. of water was refluxed for two hours. The acid was isolated in the usual way and was recrystallized from methanol. The product (1.4 g.) consisted of colorless cotton, m.p. 210.5–212°.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.27; H, 5.74. Found: C, 65.44; H, 5.81.

The infrared spectrum of this ketoacid ($CHCl_3$) included bands at 5.83 μ (acid carbonyl), 5.96 μ (ketone) and 6.22 μ.

This acid was esterified by refluxing it in a 3% solution of concentrated sulfuric acid in absolute ethanol for four hours. Recrystallization of the neutral product from ether–methanol provided colorless crystals, m.p. 132–133.5°. The mixed m.p. with *trans*-3-carbethoxy-4-(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone was 132–133.5° (undepressed).

1-(3′,4′-Dimethoxyphenyl)-2-carbethoxy-6,7-dimethoxytetralin (XII).—A solution of 2.1 g. of 3-carbethoxy-4-(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone in 150 ml. of glacial acetic acid containing 1.0 g. of 5% palladium–charcoal catalyst was shaken at 60° under hydrogen (40 lb.) for two hours. Filtration of the catalyst and evaporation of the acetic acid gave a quantitative yield of crystalline material. Purification was effected by recrystallization from cyclohexane–ether; colorless, cottony crystals, m.p. 97–98°.

Anal. Calcd. for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.07; H, 6.90. The infrared spectrum ($CHCl_3$) showed a band at 5.79 μ.

1-(3′,4′-Dimethoxyphenyl)-6,7-dimethoxy-2-carboxytetralin (XIII).—A mixture of 2.7 g. of the ester, XII, and 15 g. of sodium hydroxide in 45 ml. of water and 5 ml. of ethanol was refluxed for two hours. The salt suspension was diluted with 250 ml. of water and was warmed to provide a solution, which was filtered, acidified with hydrochloric acid, and chilled. The crystals were collected, washed with two portions of water, and air dried. Trituration with ether–methanol gave 2.3 g. (85%) of colorless crystals, m.p. 181–183°. Recrystallization from methanol afforded an analytical sample; colorless, fluffy crystals, m.p. 184.5-186.5°.

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.95; H, 6.54.

The infrared spectrum of this acid was characterized by a sharp peak at 5.77 μ.

1-(3′,4′-Dimethoxyphenyl)-2-carboxy-6,7-dimethoxynaphthalene (XIV).—A mixture of 0.6 g. of the acid, XIII, 25 ml. of biphenyl, and 1.5 g. of 5% palladium–charcoal catalyst was refluxed vigorously for three hours. Ethyl acetate (500 ml.) was added, after cooling the suspension, and the mixture was filtered to remove the catalyst. The filtrate was extracted with two portions of 5% sodium hydroxide solution. The alkaline extract was acidified with hydrochloric acid, and was chilled. The crystals were collected, washed with water, and air dried. The yield of crude acid was 0.4 g. (66%). Recrystallization from methanol (Norit) gave colorless crystals, m.p. 207.5–210°.

Anal. Calcd. for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.53; H, 5.44.

The ultraviolet absorption spectrum of this naphthalene was measured in ethanol solution. Maxima were observed at 220 mμ (log ε 4.77), 255 mμ (log ε 4.03) and 291 mμ (log ε 3.53). The ultraviolet absorption spectrum of 6,7-dimethoxy-2-carboxynaphthalene[1] in the same solvent had maxima at 215 mμ (log ε 4.20), 247 mμ (log ε 4.78), and 294 mμ (log ε 4.03).

The infrared spectrum ($CHCl_3$) showed broad absorption in the region of 3.0 μ and a band at 5.89 μ.

When *p*-cymene was substituted for biphenyl in the above reaction the starting material was recovered quantitatively.

BETHESDA, MARYLAND

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

Podophyllotoxin Studies. A Synthesis of the Carbon–Oxygen Skeleton

BY GORDON N. WALKER

RECEIVED JANUARY 23, 1953

Dieckmann cyclization of the required triester gave 2-carbomethoxy-3-carbethoxy-4-(3′,4′,5′-trimethoxyphenyl)-6,7-methylenedioxy-1-tetralone (III). This compound was converted *via* catalytic hydrogenolysis and hydrolysis to a tetralin anhydride, V, and *via* mild hydrolysis and acetylation to an unsaturated acetoxyanhydride, VI. Hydrolysis and decarboxylation of III gave the tetralone-acid, IVa, esterification of which led to the ester, IVb.

Derivatives of 1-(3′,4′,5′-trimethoxyphenyl)-6,7-methylenedioxytetralin, I, have not been obtained frequently by synthetic routes. Haworth and coworkers[1,2] prepared several closely related naphthalenes, and a dihydronaphthalene,[1] and Tarbell[3] reported a product of the reaction of isosafrole with 3,4,5-trimethoxycinnamic acid which was probably a compound having this ring system. This report deals with a new synthesis of compounds derived from I, in particular the ketodiester, III, and with several reactions of III which led to compounds closely related to podophyllotoxin.

The general approach in this synthesis was similar to that followed in obtaining 3-carbethoxy-4-(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone.[4] A Stobbe condensation of the ketoester, II,[5] with ethyl succinate and potassium *t*-butoxide gave an acid ester. The acid group appeared to be sterically hindered, since an attempt to esterify the material by the Fischer method was not successful. Esterification was effected with diazomethane. The neutral product was hydrogenated in glacial acetic acid at 80° in the presence of a palladium–charcoal catalyst. In this medium little hydrolytic cleavage of the methylenedioxy group occurred, although the absorption of hydrogen was very slow. The neutral material remaining after hydrogenation was subjected to Dieckmann cyclization. The reaction appeared to be accompanied by decomposition, and led to III in low yield. No other compounds were isolated from the crude product of this cyclization, and the stereochemical structure of III was not determined. Structure III was confirmed by the infrared spectrum,[6] in which

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(1) R. D. Haworth and T. Richardson, *J. Chem. Soc.*, 348 (1936).

(2) R. D. Haworth, T. Richardson and G. Sheldrick, *ibid.*, 1576 (1935).

(3) R. G. Nelb and D. S. Tarbell, THIS JOURNAL, **71**, 2936 (1949).

(4) G. N. Walker, *ibid.*, **75**, 3387 (1953).

(5) W. J. Gensler and C. H. Samour, *ibid.*, **73**, 5555 (1951).

(6) For complete infrared spectra for the substances referred to in this article order Document 3924 from ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., remitting $1.25 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.25 for photoprints readable without optical aid.