[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF BUDAPEST]

DIMERIC PROPENYL PHENOL ETHERS. XV. THE SYNTHESIS OF 1-VERATRYL-2,3-DIMETHYL-6,7-DIMETHOXYTETRALIN

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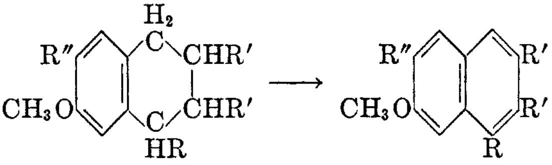
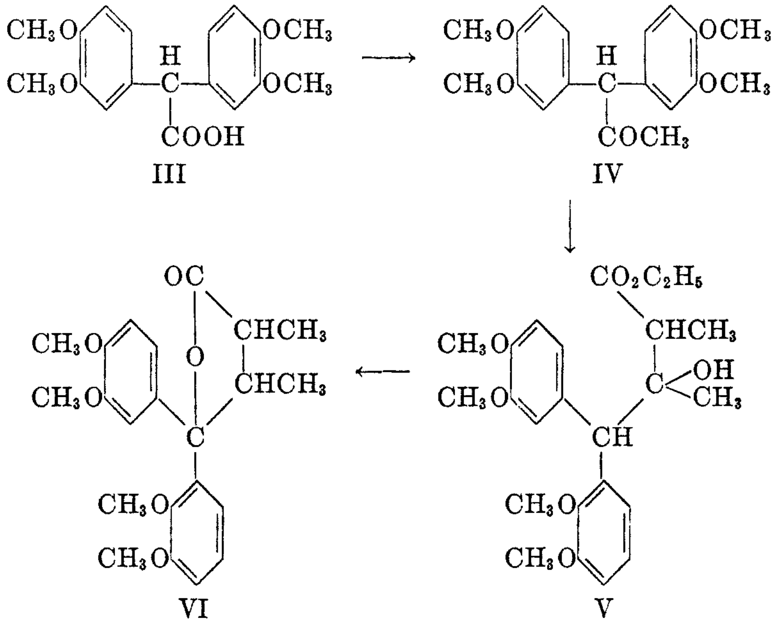
Chromic acid oxidation of diisohomogenol (diisoeugenol dimethyl ether) gave evidence that this compound is 1-veratryl-2-methyl-3-ethyl-5,6-dimethoxyindan, the primary product of the reaction having been found to be an α-substituted arylacetone (1) which Doering and Berson (2) later recognized as being α-(*o*-veratroylveratryl)propyl methyl ketone. The alternative of a 1-veratryl-2,3-dimethyl-6,7-dimethoxytetralin, which has been repeatedly suggested for diisohomogenol (3, 4) was thereby definitively ruled out. Cartwright and Haworth have shown that 1-veratryl-6,7-dimethoxytetralin (Ia) will, in sharp contradistinction to diisohomogenol, readily undergo dehydrogenation to the corresponding naphthalene (IIa), thus lending support to this argument. In connection with these studies we have now synthesized one of the racemic forms of 1-veratryl-2,3-dimethyl-6,7-dimethoxytetralin (Ib) and can state, experimentally, that dehydrogenation of this compound does, in fact, proceed as expected, in full analogy to the recently observed (6) similar behavior of 1-*p*-anisyl-2,3-dimethyl-7-methoxytetralin (Ic).



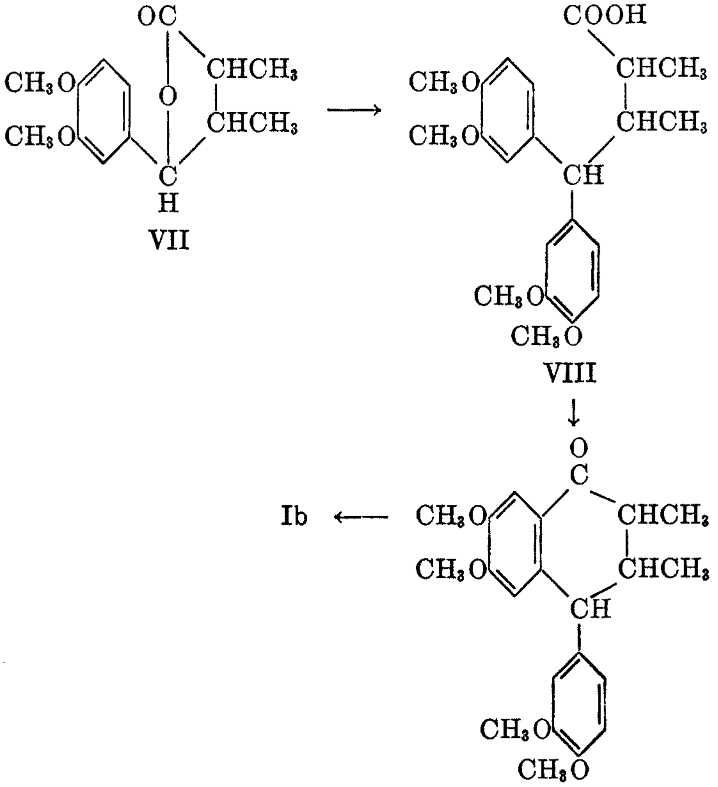
I II

a. R = $C_6H_3(OCH_3)_2$-*3*,*4*, R′ = H , R″ = OCH_3
b. R = $C_6H_3(OCH_3)_2$-*3*,*4*, R′ = CH_3, R″ = OCH_3
c. R = $C_6H_4(OCH_3)$ -*4* , R′ = CH_3, R″ = H

A synthesis of tetralin Ib has been reported (5) to be difficult, and our first attempt likewise failed to end satisfactorily. Diveratrylacetic acid (III) was prepared from veratraldehyde, following essentially the description given by Dreyfuss and Serra (7). Condensation of the methyl ester of III with ethyl acetate in the presence of finely dispersed sodium, followed by acid hydrolysis of the resulting intermediate, gave α,α-diveratrylacetone (IV), m.p. 109–110°. A compound of this structure has been obtained by Haworth, Mavin, and Sheldrick (8) by oxidation of α,α-diveratryl-Δ^1-propene with perbenzoic acid and subsequent dehydration of the resulting glycol; the final product had m.p. 123–124°. No doubt this is a crystalline modification of the ketone in our hands, since α,α-diphenylacetone also has been known to exhibit two modifications with respective melting points of 42° and 61° (9). Condensation of ketone IV with ethyl α-bromopropionate in the presence of zinc produced a crystalline ethyl α,β-dimethyl-β-hydroxy-γ,γ-diveratrylbutyrate (V). Dehydration of the latter invariably resulted in the formation of α,β-dimethyl-γ,γ-diveratrylbutyrolactone (VI), the α,β-unsaturated ester being unobtainable. The lactone proved to be highly stable to reductive cleavage by catalytic hydrogenation at atmospheric pressure, or under the conditions of a Clemmensen-Martin reduction. This circumstance prevented our further efforts to obtain the desired α,β-dimethyl-γ,γ-veratrylbutyric acid by the intended route. Since α,β-dimethyl-γ-*p*-anisylbutyrolactone offers no similar difficulties toward reduction to the corresponding acid (6), the enhanced stability of its γ,γ-diveratryl analog appears to be due to the quaternary character of the γ-carbon atom. Fittig (10), and also Willstätter and Hatt (11), have already observed and discussed the remarkable stability of γ,γ-dialkylated butyrolactones toward reduction.



In a more successful attempt, use was made of the procedure given by Arnold, Buckley, and Richter for the γ-phenylation of γ-methylvalerolactone in which 4,4-dimethyltetralone was found to be the end product. After converting veratrylacetone (13) to α,β-dimethyl-γ-veratrylbutyrolactone (VII) in the usual way, the latter was reacted with veratrole. This procedure gave, when conducted in the presence of the recommended excess of aluminum chloride, a non-crystalline α,β-dimethyl-γ,γ-diveratrylbutyric acid (VIII). This substance was cyclized by the phosphorus pentachloride-stannic chloride method. A Clemmensen-Martin reduction of the resulting tetralone (IX) yielded the expected tetralin Ib, which was found to crystallize from alcohol in slender needles, m.p. 117–118°, and to give color reactions that are distinctly different from those of diisohomogenol. Its dehydrogenation with palladized-charcoal at 280–320° readily gave 1-veratryl-2,3-dimethyl-6,7-dimethoxynaphthalene, m.p. 177–178°; this compound formed a picrate readily, and was identical with dehydroguaiaretic acid dimethyl ether (8, 14).



EXPERIMENTAL

3,4-Dimethoxymandelonitrile. A solution of 66 g. (0.4 mole) of veratraldehyde in 60 ml. of alcohol was mixed with a 10% aqueous solution of 28 g. of 70% sodium cyanide (0.4 mole). The mixture was then cooled by ice-water, and under vigorous stirring 60 ml. of conc'd hydrochloric acid was added in drops (three hours), until a thick mass of small colorless crystals was formed. This was collected and washed free of acid with water, then dissolved in chloroform and again washed with water. The extract was then concentrated under reduced pressure, benzene being added subsequently to the viscous concentrate until a slight turbidity was present. On cooling, a solid mass crystallized. The crude, m.p. 104–109°, yielded after one recrystallization from dry benzene, 60 g. (72%) of small colorless needles, m.p. 109° [reported by Fulton and Robinson (15), m.p. 104°, by Dreyfuss and Serra, m.p. 109.5°].

Bis(3,4-dimethoxyphenyl)acetonitrile. A suspension of 12 g. (0.06 mole) of finely powdered 3,4-dimethoxymandelonitrile in 15 ml. (0.09 mole) of veratrole was mixed with 45 ml. of 74% sulfuric acid, and warmed very gradually to 70° (not higher) in a water-bath, with occasional stirring, the temperature being maintained for 30–40 minutes after complete dissolution. After pouring the deep cherry-red solution into ice-water, the separated oil was repeatedly washed with water by decantation, and then freed from occluded veratrole by steam-distillation. The residual oil crystallized from alcohol in slender, flat, colorless needles (18 g.), melting at 106°, resolidifying at 113–115° and melting again at 142–146°. After recrystallization from alcohol the product also exhibits a double melting point of 106° and 147°. (Dreyfuss and Serra report the melting points 106° and 141°, respectively, and one single m.p. 147° for highly purified material.) No reaction was observed with methylmagnesium iodide, or with ethyl acetate in the presence of sodium.

Anal. Calc'd for $C_{18}H_{18}NO_4$: C, 68.9; H, 6.1; N, 4.5.

Found: C, 69.1, 68.9, 68.8; H, 6.3, 6.3, 6.2; N, 4.3, 4.3.

Bis(3,4-dimethoxyphenyl)acetic acid monohydrate. A solution of 20 g. of the above nitrile in 150 ml. of alcoholic 20% potassium hydroxide was refluxed on the steam-bath for two hours. Then the reflux condenser was removed and the evaporating alcohol was gradually replaced with water. After about ten hours on the steam-bath, no more ammonia was evolved. Acidification of the filtered solution with acetic acid precipitated an oil, which completely crystallized in one or two days. Recrystallization from 30% acetic acid (charcoal) gave 16–18 g. of slender, colorless needles, m.p. 118–120°. (Dreyfuss and Serra report m.p. 114°, and 5.1% loss of weight on drying.)

Ethyl bis(3,4-dimethoxyphenyl)acetate. A solution of 20 g. of the foregoing hydrate of III in 100 ml. of absolute alcohol was saturated with dry hydrogen chloride, with cooling with ice-water, and then refluxed on the steam-bath for 30 minutes, after which it was cooled and saturated with hydrogen chloride again. After the solution had stood overnight, the solvent was removed under reduced pressure and the solid residue was recrystallized from alcohol, 18 g. of colorless needles, m.p. 69–70°, being obtained.

Anal. Calc'd for $C_{21}H_{24}O_6$: C, 66.6; H, 6.7.

Found: C, 66.6, 66.7; H, 6.8, 6.8.

α,α-Bis(3,4-dimethoxyphenyl)acetone (IV). To 11.5 g. (0.5 g.-atom) of finely dispersed sodium in the usual apparatus was added 48.5 g. (0.115 mole) of ethyl diveratrylacetate and 20 ml. of ethyl acetate (dried and twice distilled over calcium chloride). After warming this mixture on the steam-bath with stirring, another 80 ml. of dry ethyl acetate was slowly added over 4–6 hours. While stirring and heating were continued for another six hours, a light brown paste formed gradually. After 12 hours at room temperature, the mixture was stirred with dilute acetic acid, crushed ice, and 200 ml. of benzene. The benzene layer was then separated, washed with water, and evaporated at 14 mm. The oily residue was refluxed subsequently with 300 ml. of 10% hydrochloric acid with stirring (16 hours). Extraction with benzene followed, the extract being washed subsequently 12 times with a total of 500 ml. of 10% sodium carbonate solution (until the last washings acquired only a light yellow color). From the alkaline extracts 15 g. of III was recovered. The remaining benzene solution, washed once with water, then dried over sodium sulfate, on being evaporated at 14 mm., left a light-brown spontaneously-crystallizing oil, which was dissolved subsequently in 20 ml. alcohol and 4 ml. ether. Recrystallization from alcohol gave 15 g. of stout colorless prisms, m.p. 109–110°.[Haworth, Mavin, and Sheldrick (8) claim to have obtained a modification of this substance, melting at 123–124°]. From the combined mother liquors by evaporation and subsequent distillation at 230–238°/0.1 mm. a viscous pale-yellow oil was obtained, that partly crystallized from 5 ml. of alcohol. From this product at times 1–2 g. of above ketone, m.p. 108°, was isolated by repeated recrystallizations, but more often the solid proved to be unreacted ethyl diveratrylacetate, m.p. 69–70° (2–3 g.).

Anal. Calc'd for $C_{19}H_{22}O_5$: C, 69.1; H, 6.7.

Found: C, 68.9, 69.0; H, 6.8, 6.9.

The *semicarbazone* crystallized from a lukewarm solution of IV in aqueous alcoholic semicarbazide acetate as long colorless needles, m.p. 153–155°, after a few hours at room temperature.

Anal. Calc'd for $C_{20}H_{25}N_3O_5$: N, 10.8. Found: N, 10.5, 10.6.

Ethyl α,β-dimethyl-β-hydroxy-γ,γ-bis(3,4-dimethoxyphenyl)butyrate (V). A mixture of 11.2 g. (0.033 mole) of IV, 7 g. (0.033 mole) of ethyl α-bromopropionate, and 25 ml. of dry benzene was refluxed with 2.4 g. (0.033 g.-atom) of zinc foil, previously activated by heating with a few crystals of iodine, until the metal dissolved (about 3 hours). After pouring the solution into 5% sulfuric acid mixed with crushed ice, the benzene layer was removed and the aqueous layer was extracted with the same solvent. The combined benzene solutions were washed repeatedly with 10% sulfuric acid, then with water, and dried with sodium sulfate. Removal of the solvent at 14 mm. left a slowly-crystallizing oily residue which, on being dissolved in 45 ml. of alcohol, yielded 8 g. of colorless plates, m.p. 134–136°. Recrystallization from alcohol raised the melting point to 137–138°. (The first mother liquor on standing deposited 1.2 g. of unreacted IV.) Upon adding conc'd sulfuric acid to the alcoholic solution, a deep red-violet coloration was observed.

Anal. Calc'd for $C_{24}H_{32}O_7$: C, 66.5; H, 7.4; OCH_3, 35.6.

Found: C, 66.5, 66.4; H, 7.4, 7.5; OCH_3, 35.0.

The substance is highly resistant toward reagents commonly used for the dehydration of β-hydroxy esters. Upon refluxing for 3 hours a solution of 1 g. of V in (a) 4 ml. of acetic anhydride, or (b) 25 ml. of glacial acetic acid containing 1 g. of anhydrous zinc chloride, or (c) a mixture of 5 ml. of dry pyridine and 0.5 ml. of acetic anhydride, and then pouring the mixture into ice-water, unchanged material, m.p. 136–137°, in yields of about 80%, was recovered. After heating V with an equal weight of freshly fused and finely powdered potassium hydrogen sulfate to 150° for two hours, and then pouring the mixture into ice-water, unchanged V, m.p. 137–138° alone or mixed, (80%) was obtained by isolation with ether.

α,β-Dimethyl-β-hydroxy-γ,γ-bis(3,4-dimethoxyphenyl)butyric acid. After refluxing 4 g. of V in 200 ml. of 20% alcoholic potassium hydroxide solution for six hours, and then warming the solution on the steam-bath for another six hours, with the condenser removed and the alcohol gradually being replaced by water, a clear aqueous solution was obtained. Addition of HCl gave an oil, which gradually solidified on standing to very small clusters and needles, m.p. 133–135° (3.0 g.). No adequate method was found for recrystallization. The substance was readily soluble in cold aqueous alkali. The solution in glacial acetic acid gave a deep red-violet coloration with conc'd sulfuric acid.

Anal. Calc'd for $C_{22}H_{28}O_7$: C, 65.2; H, 7.0; Neut. equiv., 404.

Found: C, 65.3, 65.3; H, 7.1, 7.0; Neut. equiv., 406, 408.

α,β-Dimethyl-γ,γ-bis(3,4-dimethoxyphenyl)butyrolactone (VI). (*a*) A solution of 1.0 g. of V in 5 ml. of glacial acetic acid was mixed with 0.1 g. of conc'd sulfuric acid and then warmed on the steam-bath for one hour, in which time the red-violet color of the solution changed to emerald-green. Upon pouring the mixture onto ice, a semisolid was obtained which crystallized readily from alcohol in long colorless needles, m.p. 160–162° (0.5 g.). One recrystallization from the same solvent gave m.p. 169–170°. The same product was obtained by refluxing the above quantity of V with 5 ml. of 80% formic acid for three hours.

(*b*) A mixture of 2 g. of the foregoing acid, 30 ml. of conc'd hydrochloric acid, and 25 ml. of toluene was refluxed with 7.5 g. of amalgamated zinc foil for 20 hours. The toluene layer, washed with 10% sodium carbonate solution, upon evaporation left an oily residue which crystallized from alcohol in needles (1.2 g.) of m.p. 169–170°. The same product was obtained by refluxing 1 g. of the acid with 20 ml. of conc'd hydrochloric acid for one hour.

The substance was insoluble in cold aqueous alkali, while complete hydrolysis required one hour of refluxing with 10% alcoholic alkali. The solution in glacial acetic acid (a) did not decolorize bromine and (b) developed a pink color on the addition of conc'd sulfuric acid. A 1% solution in alcohol on the presence of 10% palladium-charcoal catalyst did not absorb hydrogen at normal or at 10–12 atm. pressure.

Anal. Calc'd for $C_{22}H_{26}O_6$: C, 68.3; H, 6.8; OCH_3, 32.1; Neut. equiv., 386.

Found: C, 68.5, 68.4; H, 6.9, 6.9; OCH_3, 32.4; Neut. equiv., 378, 389.

α,β-Dimethyl-γ-(3,4-dimethoxyphenyl)butyrolactone (VII). Upon adding 52.2 g. (0.27 mole) of ethyl α-bromopropionate by drops to a refluxed and vigorously stirred mixture of 18.6 g. (0.35 g.-atom) of iodine-activated zinc foil and 50 g. (0.17 mole) of veratrylacetone in 150 ml. of dry benzene, the reaction suddenly set in, leading to almost complete dissolution of the metal in about one hour. The mixture was poured onto 500 g. of crushed ice and 100 ml. of conc'd sulfuric acid, the benzene layer was separated, and the aqueous layer was extracted twice with benzene. The combined benzene solutions, washed five times with 25% sulfuric acid and then with water and dried with sodium sulfate, left on evaporation an almost colorless oil of b.p. 168–176°/0.4 mm. (52 g.). Then 50 g. of this material was dissolved in 200 ml. of glacial acetic acid, with ice-cooling and vigorous stirring, and 50 ml. of conc'd sulfuric acid was added by drops over 60 minutes. The cherry-red mixture, warmed subsequently on the steam-bath for one hour, and then poured onto crushed ice, was extracted with ether. The extract was washed with water, and with sodium carbonate solution until the latter removed no more coloring matter, and then dried with sodium sulfate and evaporated. The residue crystallized from alcohol, yielding 10 g. of faintly colored needles, m.p. 107–108°. Two subsequent recrystallizations from alcohol, with the addition of charcoal, yielded an entirely colorless material, without further change of the melting point. Evaporation of the combined mother liquors, and distillation of the residue gave an orange colored oil of b.p. 180–190°/0.8 mm. which partially crystallized from alcohol, the solid (2 g.) being identical with the main product.

Anal. Calc'd for $C_{14}H_{18}O_4$: C, 67.2; H, 7.2; Neut. equiv., 250.

Found: C, 67.3, 67.4; H, 7.4, 7.3; Neut. equiv., 243.

1-(3,4-Dimethoxyphenyl)-2,3-dimethyl-6,7-dimethoxytetralone-4 (IX). To a suspension of 13.3 g. (0.1 mole) of aluminum chloride in 17 ml. of veratrole, 7.2 g. (0.02 mole) of VII in 18 ml. of veratrole was added by drops, with ice-cooling and energetic stirring. The mixture was warmed gradually up to 80° with the continued stirring and kept at this temperature for three hours. The aluminum chloride complex was then decomposed by dissolution in alcohol and by addition to a mixture of conc'd hydrochloric acid and crushed ice. After complete disappearance of solid particles, the mixture was extracted with ether. The ethereal layer was then washed with water, followed by repeated extractions with 8% sodium carbonate solution. (The residue of the evaporated and then steam-distilled neutral fraction crystallized from alcohol, yielding 0.1 g. of slender needles of IX, m.p. 165–168°.) Acidification of the sodium carbonate extract precipitated an oil, which was subsequently isolated by extraction with ether. Removal of the solvent left a brown resinous mass (13.5 g.) of Neut. equiv., 415, 418 (Calc'd for $C_{22}H_{28}O_5$, Neut. equiv., 388). This is readily soluble in the usual organic solvents, and gave no crystalline derivatives. After adding 5.1 g. of phosphorus pentachloride to 9.5 g. of this acid (VIII) in 25 ml. of dry benzene, the mixture was kept in ice for 15 minutes with occasional shaking, and then warmed to 40° until complete dissolution of the reactants took place. The mixture was then chilled, and mixed with 4.7 ml. of stannic chloride in 5 ml. of dry benzene. A red-brown semisolid complex soon separated, and, after ten minutes at +5°, was decomposed by the addition of conc'd hydrochloric acid and ice, and of some ether. In about ten minutes, dissolution was complete, the two layers being then almost colorless. After extracting the aqueous layer with benzene, the combined benzene solutions were washed with water and with an 8% sodium carbonate solution, until free of acid, then dried with sodium sulfate and evaporated under reduced pressure. The oily residue (7.5 g.) crystallized from alcohol, yielding 3 g. of a solid, m.p. 161–164°. After two recrystallizations from alcohol, 2.2 g. of colorless slender needles, m.p. 165–168°, were obtained. The solution in glacial acetic acid on addition of conc'd sulfuric acid took on a deep yellow coloration, which turned to orange-red on heating. No oxime or semicarbazone was obtained.

Anal. Calc'd for $C_{22}H_{26}O_5$: C, 71.3; H, 7.1.

Found: C, 71.5, 71.6; H, 7.1, 7.3.

1-(3,4-Dimethoxyphenyl)-2,3-dimethyl-6,7-dimethoxytetralin (Ib). After refluxing a mixture made up of 3 g. of IX, 7.6 g. of amalgamated zinc foil, 4.8 ml. of water, 11 ml. of conc'd hydrochloric acid, and 16 ml. of toluene mixed with 0.5 ml. of dioxane (24 hours), the liquid was cooled and then extracted with a generous quantity of ether. The extract, washed with a 3% sodium carbonate solution and dried over solid potassium carbonate, on evaporation left a residue which crystallized from alcohol in colorless, very slender, somewhat interlacing, needles (1.5 g., m.p. 112–114°). Two subsequent recrystallizations from the same solvent gave m.p. 117–118°. Upon adding conc'd sulfuric acid the glacial acetic acid solution became orange and turned slowly to eosin red.

Anal. Calc'd for $C_{22}H_{28}O_4$: C, 74.3; H, 7.9.

Found: C, 74.5, 74.4; H, 8.0, 8.1.

1-(3,4-Dimethoxyphenyl)-2,3-dimethyl-6,7-dimethoxynaphthalene, dehydroguaiaretic acid dimethyl ether (IIb). A mixture of 1.0 g. of Ib and 0.4 g. of 10% palladium-charcoal was brought very gradually in four hours to 320°, this temperature then being maintained for one hour, after which the pressure was lowered to 1 mm. Within a few minutes a pale yellow, resinous distillate was obtained, which readily crystallized from 3 ml. of alcohol and yielded 0.7 g. of colorless, small needles, m.p. 163–168°. Recrystallization from 12 ml. of alcohol, and then from 3 ml. of glacial acetic acid, gave 0.48 g. of small cubes or flat prisms, m.p. 177–178°. A sample of identical appearance, prepared according to Schroeter, *et al.*, (14), starting from guaiac resin, had m.p. 177–178° and gave the same color reaction. A mixture of the two substances had m.p. 177–178° [Reported (8, 14) m.p. 178–179°]. Upon adding conc'd nitric acid to the solution in glacial acetic acid, an intense deep orange coloration was observed.

Anal. Calc'd for $C_{22}H_{24}O_4$: C, 75.0; H, 6.8.
Found: C, 75.2, 74.8; H, 6.9, 7.0.

The *picrate* separated from an alcoholic solution of the components in small rosettes of interlacing, very fine, bright red-brown needles, m.p. 161–162°. From the sample prepared according to (14), an identical picrate, fiery red needles of m.p. 161–162°, was obtained. The mixture of the two picrates showed no depression in melting point.

Anal. Calc'd for $C_{22}H_{24}O_4 \cdot C_6H_3N_3O_7$: N, 7.2. Found: N, 7.0, 7.1.

Acknowledgment. We wish to express our indebtedness to Mrs. H. Medzihradszky-Schweiger for the microanalyses.

SUMMARY

α,β-Dimethyl-γ-veratrylbutyrolactone was converted to 1-veratryl-2,3-dimethyl-6,7-dimethoxytetralin, which readily yielded dehydroguaiaretic acid dimethyl ether on dehydrogenation.

α,β-Dimethyl-γ,γ-diveratrylbutyrolactone failed to serve as an intermediate in the synthesis of the above tetralin, being found to be stable to catalytic hydrogenation at pressures of 1–12 atmospheres, owing to the quaternary character of its γ-carbon atom.

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