was warmed gradually to the boiling point. Reaction began immediately, and the solution boiled for 10–15 minutes without application of heat externally. During this time the solution became deep red, and carbon dioxide was evolved. When spontaneous reaction subsided, the solution was refluxed for 2.5 hours longer. Most of the excess reagent was distilled at atmospheric pressure (1 hour), and the residue was distilled *in vacuo*. There was obtained 19.2 g. (49%) of viscous, yellow oil, b.p. 119–127° (3.5 mm.), which crystallized immediately. Recrystallization from dry ether afforded 16.1 g. (41%) of pale yellow crystals, m.p. 76–78°. Further recrystallization raised the m.p. to 80–81°.

Anal. Calcd. for $C_9H_7O_2N$: C, 67.07; H, 4.38; N, 8.69. Found: C, 67.36; H, 4.56; N, 8.92.

The mixed m.p. with a sample of acetylanthranil prepared from anthranilic acid[2] (reported[1] m.p. 80–81°), was 80–81°. The infrared spectra (chf.) of the two samples were identical, having characteristic peaks at 5.69–5.72, 6.08 and 6.23 μ. The odor of the pure compound was as described previously.[1]

2-Acetylaminobenzoic Acid (IIIa).—Material obtained in the preceding experiment was treated with water, and the product was recrystallized from ethyl acetate. There was obtained colorless crystals, m.p. 182–184° (reported[2] m.p. 185°), which were soluble in sodium bicarbonate solution and which did not depress the m.p. of an authentic specimen of acetylanthranilic acid when admixed with it. The infrared spectra of the two samples in chloroform and Nujol were identical in each case; bands at 3.1–3.2, 5.92, 6.04–6.10, 6.23 and 6.32 μ (Nujol) were observed.

6,7-Dimethoxy-2-methyl-3,1,4-benzoxazine (R. I. 947) (IIb).—A mixture of 30.2 g. (0.125 mole) of 2-nitro-4,5-dimethoxyphenylacetic acid and 200 ml. of acetic anhydride was refluxed for 2 hours. An exothermic reaction resulting in a deep red color was observed during the first 10 minutes of this period. The excess reagent was evaporated at 100°. The residue crystallized, and was triturated with ethyl acetate. There was obtained 14.4 g. (52%) of orange crystals, m.p. 183–185°. Recrystallization from ethyl acetate (Norit) gave yellow crystals, m.p. 185–186.5°. The infrared spectrum (chf.) had intense peaks at 5.74, 6.07 and 6.19 μ.

Anal. Calcd. for $C_{11}H_{11}O_4N$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.64; H, 4.97; N, 6.32.

2-Acetylamino-4,5-dimethoxybenzoic Acid (IIIb).—A sample of IIb was warmed with water on a steam-cone for 1.5 hours. Recrystallization from methanol–ethyl acetate (Norit) afforded colorless crystals, m.p. 223.5–224.5° dec. (reported[12] m.p. 228°). The infrared spectrum (Nujol) had a band at 3.1–3.2 μ and intense peaks at 5.94, 6.09, 6.20 and 6.27 μ. The compound was soluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{11}H_{13}O_5N$: C, 55.22; H, 5.48; N, 5.86. Found: C, 55.37; H, 5.55; N, 5.73.

2-Methyl-6,7-dimethoxy-4-quinazolone (IVb).—A sample (0.2 g.) of IIb was warmed with 20 ml. of concd. ammonium hydroxide solution on a steam-cone for a half-hour. Evaporation of the excess reagent and recrystallization of the residue from ethyl acetate gave slightly yellow crystals, m.p. 297–300° dec. The infrared spectrum (Nujol) had peaks at 3.17 and 6.05–6.08 μ.

Anal. Calcd. for $C_{11}H_{12}O_3N_2$: C, 59.99; H, 5.49; N, 12.7. Found: C, 60.05; H, 5.64; N, 12.5.

2-Acetylaminobenzyl Alcohol.—A solution of 2.8 g. of IIa in 150 ml. of ethyl acetate containing 2 g. of 10% palladium-charcoal catalyst was shaken under hydrogen (40 lb.) at 80° for an hour. Filtration of the catalyst and evaporation of the solvent gave 2.8 g. of colorless crystals, m.p. 111–113°. Recrystallization from methanol raised the m.p. to 114–115° (reported[13] m.p. 115–116°). The compound was very soluble in dilute mineral acids and moderately soluble in water. The infrared spectrum (chf.) had peaks at 2.77, 2.97 and 5.95–5.98 μ.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.41; H, 6.53; N, 8.37.

Acetylation with acetic anhydride at 100° for 15 minutes gave the **O,N-diacetate** of *o*-aminobenzyl alcohol, m.p. 91–93°, after recrystallization from ether (lit.[14] m.p. 91°). The infrared spectrum of this compound (chf.) had peaks at 3.02, 5.80 and 5.93–5.96 μ.

4-Nitrophenylacetic Anhydride.—A mixture of 5 g. of 4-nitrophenylacetic acid and 50 ml. of acetic anhydride was refluxed for 2 hours. Evaporation of the excess reagent and trituration of the residue with ether gave 3.5 g. of crystals, m.p. 131–137°. Recrystallization from ethyl acetate (Norit) gave pale yellow crystals, m.p. 141–143°, the infrared spectrum of which (chf.) had a characteristic twin peak, 5.48 and 5.70 μ.

Anal. Calcd. for $C_{16}H_{12}O_7N_2$: C, 55.81; H, 3.51; N, 8.14. Found: C, 55.93; H, 3.76; N, 7.92.

(12) J. L. Simonsen and M. G. Rau, *J. Chem. Soc.*, 26 (1918).

(13) K. Auwers, *Ber.*, **37**, 2249 (1904).

(14) H. G. Soderbaum and O. Widman, *ibid.*, **22**, 1667 (1889).

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Hydrogenation of Purpurogallin and Its Derivatives

BY GORDON N. WALKER

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Since the structure of purpurogallin (I) was established by Haworth and his collaborators,[1-4] few reports of further work with this interesting and easily-prepared benztropolone have appeared. A three-step reduction of tetramethylpurpurogallin to 2,3,4-trimethoxybenzsuber-6-one has been reported.[5] This method requires that purpurogallin be methylated completely at the outset, which process is unattractive from a practical point of view, since methylation of purpurogallin beyond the trimethyl ether stage is not achieved easily.[1a] Catalytic hydrogenation of purpurogallin and its methyl ethers also has appeared unattractive because mixtures of products were obtained from such reactions in earlier work[1a] when platinum catalysts were used.

The use of 10% palladium–charcoal catalyst now has been found to give better results than were obtained previously in hydrogenation of compounds in this series. Purpurogallin is reduced to tetrahydropurpurogallin(II) in 75% yield in the presence of this catalyst. That hydrogen enters the tropolone ring rather than the benzene ring in this reaction follows from the fact that II is converted by diazomethane in two stages to the trimethyl derivative III, indicating that three phenolic groups are present in II. Conclusive evidence for structures II and III was obtained from further experiments. Compound III is an acyloin and as such is susceptible to oxidation under mild conditions. Thus with bismuth oxide in acetic acid,[6] III was converted to diketone IV,[2,3] identified as the 2,4-dinitrophenylhydrazone,[3] m.p. 179–181°. The carbonyl group of III can be reduced, and this was accomplished in two stages. Hydrogenation in ethyl acetate at 80° in the presence of 10% pal-

(1) R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, (a) 1045 (1948); (b) 3271 (1949).

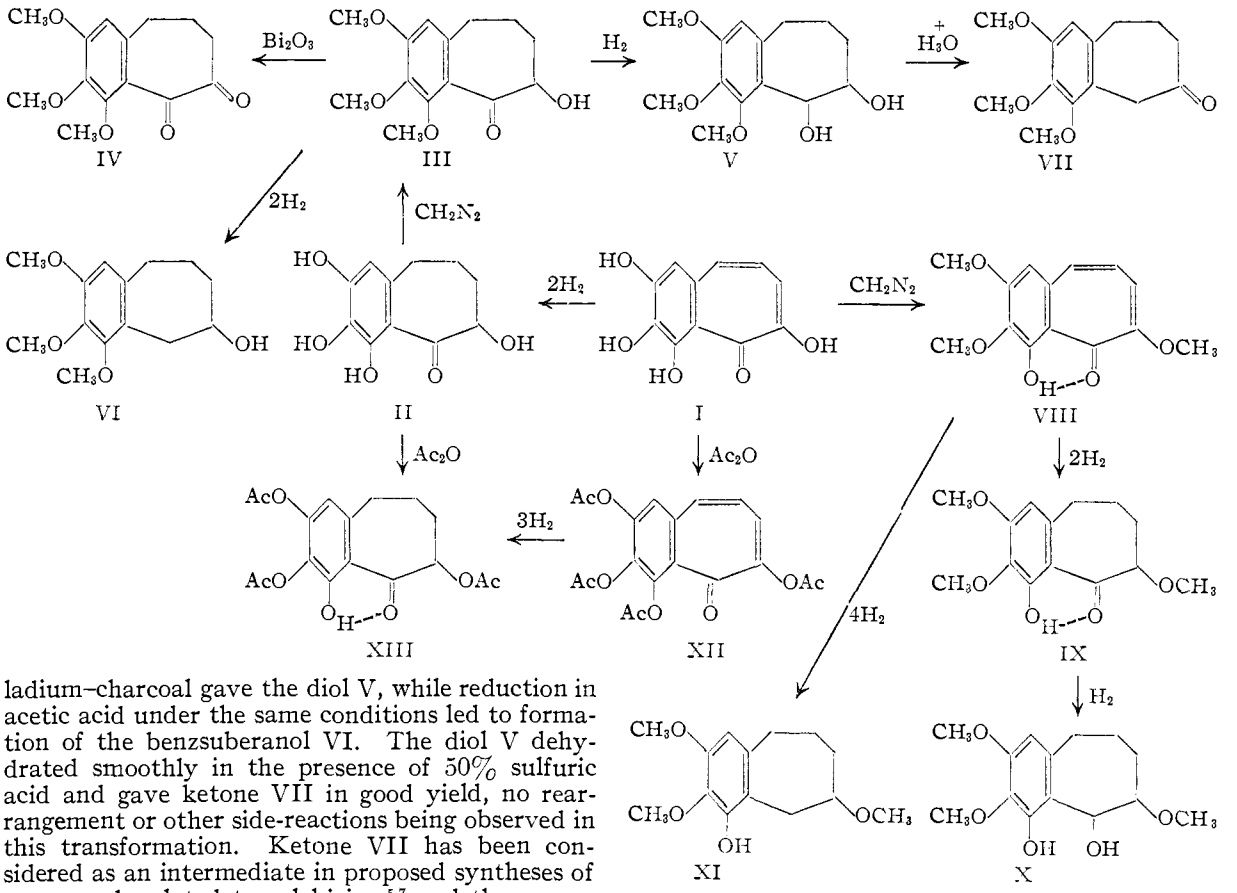
(2) D. Caunt, W. D. Crow, R. D. Haworth and C. A. Vodoz, *ibid.*, 1631 (1950).

(3) D. Caunt, W. D. Crow and R. D. Haworth, *ibid.*, 1313 (1951).

(4) A. Critchlow, R. D. Haworth and P. L. Pauson, *ibid.*, 1318 (1951).

(5) A. Eschenmoser and H. H. Rennhard, *Helv. Chim. Acta*, **36**, 290 (1953).

(6) W. Rigby, *J. Chem. Soc.*, 793 (1951).



ladium–charcoal gave the diol V, while reduction in acetic acid under the same conditions led to formation of the benzsuberanol VI. The diol V dehydrated smoothly in the presence of 50% sulfuric acid and gave ketone VII in good yield, no rearrangement or other side-reactions being observed in this transformation. Ketone VII has been considered as an intermediate in proposed syntheses of compounds related to colchicine,[5,7] and thus preparation of VII by the new method described here is of special interest. The preparation of VII from I by way of II, III, and V can be carried out in 20% over-all yield with no inconvenience other than that involved in securing diazomethane.

In contrast with earlier reported results,[1a] it has been found that methyl ethers of purpurogallin also may be hydrogenated smoothly in the presence of 10% palladium–charcoal. From experiments of this kind some new information concerning trimethylpurpurogallin has been obtained, and the structure VIII earlier advanced[1-3] for this compound has been substantiated further. By varying solvent and temperature, VIII was reduced in *three* distinct stages. From reduction of VIII in ethyl acetate at room temperature, trimethyltetrahydropurpurogallin IX was gotten quantitatively. Formerly this compound was obtained mixed with other products.[1a] When reduction of VIII was carried out in the same solvent at 80°, an additional molecule of hydrogen was absorbed, as in the case of reduction of III to V, and diol X was produced. Finally, reduction of VIII in acetic acid at 80° resulted in complete hydrogenolysis of the carbonyl group and gave XI, a reaction analogous to III → VI. Compounds IX (m.p. 85.5–88°), X (m.p. 129–131°) and XI (m.p. 91–93°) were *not* identical with the similarly-constituted compounds III (m.p. 109–111°), V (m.p. 178–180°) and VI (m.p. 98.5–99.5°), as was evident from comparison of spectra, solubilities and melting points. In the new trimethyl derivatives III, V and VI, all three methoxy groups of necessity are attached to the benzene ring, while the lone hydroxy group is attached to the seven-membered ring. Clearly then the hydroxy group must be located in the benzene ring in the different series of compounds VIII, IX, X and XI. The fourth, and singularly unreactive, hydroxy group has been assigned to the 4-position (*cf.* VIII) on the basis of other evidence.[1] This assignment is reasonable inasmuch as the 4-position is *a priori* the most highly hindered locality in the benzene nucleus, and also because a hydroxy group in this position can chelate strongly with the carbonyl group and thus be prevented from behaving normally. That this reasoning is correct is indicated by some additional findings. The infrared spectrum of VIII exhibits virtually no hydroxy absorption near 3.0 μ and no carbonyl band in the 6.0 to 6.1 μ region, but rather an intense doublet at 6.25–6.32 μ, in contrast with the spectrum of tetramethylpurpurogallin, which has a strong multiple conjugated carbonyl band at 6.05–6.16 μ. This effect must be due to chelation which is well-known to result in marked changes of this kind in hydroxy and carbonyl group vibrations. More indicative is the fact that while the spectrum of non-chelated III displays a strong carbonyl peak at 5.95 μ and a hydroxy band at 2.89 μ, the spectrum of the similarly-constituted compound IX has neither of these bands. Phenolic hydroxy absorption in the infra-

(7) H. Rapoport and J. E. Campion, THIS JOURNAL, **73**, 2239 (1951).

red becomes strong, however, in X and XI when the carbonyl group is reduced. The same effect of chelation upon carbonyl vibration is observed also in acetyl derivatives; a strong carbonyl band (6.04–6.12 μ) appears only when all four hydroxy groups of purpurogallin are acetylated.

Additional, and rather striking, evidence for the presence of an abnormal hydroxy group in compounds of this series was obtained from reduction experiments with acetyl derivatives. When tetraacetylpurpurogallin (XII)[8,9] was hydrogenated in the presence of 10% palladium–charcoal in ethyl acetate at 80°, acetic acid was formed by hydrogenolysis of the hindered acetoxy group, and *tri*acetyltetrahydropurpurogallin (XIII) was isolated. This compound was identical with material prepared by acetylation of tetrahydropurpurogallin with acetic anhydride. Structure XIII for the triacetate was confirmed by the infrared spectrum, in which hydroxyl and conjugated carbonyl bands were absent, as in other 4-hydroxy compounds. Evidently the 4-hydroxy group resists reaction strongly in derivatives of tetrahydropurpurogallin as it does in those of purpurogallin itself, for compounds IX and XIII cannot be methylated or acetylated further under ordinary conditions. However, it is also apparent that the nature of the 6-substituent plays an important part in influencing the degree to which the 4-hydroxy group is hindered in the tetrahydro-series. Thus when a hydroxy group is present at position 6, the 4-hydroxy group can undergo transformations, as in II → III, but when an acetoxy or methoxy group is attached at position 6, as in IX and XIII, reactions at position 4 are blocked completely.

Experimental[10,11]

Tetrahydropurpurogallin (II).—A mixture of 10 g. of purpurogallin,[12] 5 g. of 10% palladium-charcoal catalyst,[13] 200 ml. of ethyl acetate and 200 ml. of absolute ethanol was shaken under hydrogen (40 lb.) at 80° for 3 hours. Two moles of hydrogen were absorbed, most of this amount being consumed in a half-hour. The mixture was filtered while still boiling hot, and the catalyst was triturated with several portions of boiling ethanol. Crystalline product began to separate immediately as the filtrate cooled. The filtrate was evaporated to a small volume. The product was collected and was triturated with ethyl acetate. There was obtained 7.6 g. (75%) of yellow crystals, m.p. 222–226° dec. Recrystallization from ethyl acetate raised the m.p. to 230–232° dec. (lit.[1] m.p. 232–233° dec.). The compound gave a deep red-green dichroic test with ferric chloride, and dissolved in 5% sodium hydroxide solution with formation of a greenish-yellow solution which discolored slowly in the presence of air. The infrared spectrum (Nujol mull) had distinct peaks at 2.88 and 3.15 μ (unbonded and bonded hydroxyl), and a multiple peak at 6.14–6.28 μ, in contrast with the spectrum of purpurogallin which displays bands at 2.95–3.08, 6.17 and 6.29 μ, and which has an entirely different "fingerprint" pattern.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40. Found: C, 58.94; H, 5.32.

Hydrogenation of I in acetic acid under the same conditions as described above gave II in 51% yield.

(8) M. Nierenstein and C. W. Spiers, *Ber.*, **46**, 3151 (1913).

(9) A. G. Perkin and F. M. Perkin, *J. Chem. Soc.*, **85**, 243 (1904).

(10) Melting points are corrected.

(11) I am indebted to Dr. William C. Alford and his staff for microanalytical data and to Mrs. Iris Siewers and Mrs. H. F. Byers for infrared and ultraviolet spectra.

(12) T. W. Evans and W. M. Dehn, THIS JOURNAL, **52**, 3647 (1930).

(13) Obtained from Matheson, Coleman and Bell Co., Inc.

2,3,4-Trimethoxybenzsuber-5-one-6-ol (III).—Methylation of tetrahydropurpurogallin was accomplished in two stages. A suspension of 8.8 g. of II in 300 ml. of methanol was treated with a dry solution of 5 g. of diazomethane (from 31 g. of N-methyl-N-nitroso-N'-nitroguanidine) in 900 ml. of ether. Brisk nitrogen evolution took place and the solid material dissolved. After the mixture had stood 4 days, crystals were deposited again. Most of the solvent was evaporated. The crystals were collected and were triturated with methanol. This first product (6.0 g.) was largely a *monomethyl ether*, and had m.p. 187–195°. By repeated recrystallization (ethyl acetate) a pure sample of monomethyl ether, m.p. 202–204°, was obtained. The methoxy group is assigned tentatively to the 3-position in this compound.

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92; CH_3O, 13.03. Found: C, 60.71; H, 6.09; CH_3O, 13.20.

The monomethyl ether (6.0 g.) was dissolved in 300 ml. of methanol, and the solution was treated with 7 g. of diazomethane in 1 l. of ether. Nitrogen evolution again occurred. After standing 5 days, the solution was evaporated and the residual oil was taken up in ether. The ether solution was washed with two portions of 5% sodium hydroxide solution and two portions of water, and was dried (magnesium sulfate). Evaporation of the solvent afforded oily crystals, trituration of which with cyclohexane gave 2.8 g. (27%) of product, m.p. 105–109°. Recrystallization from cyclohexane gave colorless, dense crystals, m.p. 109–111°. The infrared spectrum (chf) had peaks at 2.89 and 5.95 μ. The compound gave no color with ferric chloride. It reacted readily with acetic anhydride, and the resulting acetate (a glass) showed strong absorption at 5.76 and 5.87 μ in the infrared spectrum. Compound III also reacted very slowly with 2,4-dinitrophenylhydrazine, but the derivative could not be obtained in a satisfactory condition.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81; CH_3O, 34.96. Found: C, 63.07; H, 7.07; CH_3O, 34.99.

Methylation of II with methyl sulfate in the presence of potassium hydroxide solution gave very poor yields of III.

2,3,4-Trimethoxybenzsuber-5,6-dione (IV).—A solution of 0.2 g. of III in 5 ml. of acetic acid was warmed on a steam-cone and was treated with 1 g. of bismuth oxide[6] in several portions (10 minutes). The cooled mixture was diluted with water and the product was extracted with ether. The organic solution was washed with water and was dried over magnesium sulfate. Evaporation of the solvent gave bright yellow, viscous oil (0.1 g.). **The 2,4-dinitrophenylhydrazone** was prepared in 65% yield from the crude ketone. Recrystallization from ethanol–ethyl acetate gave yellow-orange crystals, m.p. 179–181° (lit.[3] m.p. 180–181°).

2,3,4-Trimethoxybenzsuber-5,6-diol (V).—A solution of 1.0 g. of III in 200 ml. of ethyl acetate containing 1.0 g. of 10% palladium–charcoal[13] was shaken under hydrogen (40 lb.) at 80° for 2 hours. Filtration of the catalyst and evaporation of the solvent gave 0.95 g. of crystalline diol, m.p. 172–177°. Recrystallization (ethyl acetate) raised the m.p. to 178–181°. Apparently this product consisted almost entirely of one isomer, probably the *cis* form. The infrared spectrum (Nujol) had peaks at 2.96 and 3.10 μ.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51; CH_3O, 34.70. Found: C, 62.78; H, 7.56; CH_3O, 34.87.

2,3,4-Trimethoxybenzsuber-6-one (VII).—A mixture of 0.80 g. of V and 20 ml. of 50% sulfuric acid was warmed on a steam-cone until the crystals dissolved and oil separated (half-hour). The cooled mixture was diluted with water, and 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 solvent gave 0.75 g. of yellowish oil, the infrared spectrum of which had an intense peak at 5.89 μ. **The 2,4-dinitrophenylhydrazone** was prepared in 95% yield from the crude ketone. Recrystallization from ethanol–ethyl acetate gave yellow crystals, m.p. 176.5–177.5° (lit. m.p. 177°,[5] m.p. 177–178°[7]).

Anal. Calcd. for $C_{20}H_{22}O_7N_4$: C, 55.81; H, 5.15. Found: C, 56.03; H, 5.33.

2,3,4-Trimethoxybenzsuberan-6-ol (VI).—Hydrogenation of 0.3 g. of III in 80 ml. of glacial acetic acid at 80° in the presence of 0.7 g. of 10% palladium–charcoal[13] for 1.8 hours gave, after filtration of the catalyst and evaporation of the solvent, colorless oil which crystallized slowly. Recrystallization from cyclohexane afforded colorless crystals, m.p.

98.5–99.5°. The infrared spectrum (chf) had a rather weak band at 2.8–2.9 μ.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.47; H, 8.05.

Trimethylpurpurogallin (VIII).—Purpurogallin (22 g.) was treated with a solution of 15 g. of diazomethane in 1500 ml. of ether. Nitrogen was evolved copiously. The mixture was allowed to stand overnight, and the solvent was evaporated. Recrystallization of the residue from methanol afforded 18 g. (69%) of orange crystals, m.p. 172–177°, raised to 175.5–178° by further recrystallization (reported[1a] m.p. 176°). The infrared spectrum (chf) had a doublet at 6.25–6.32 μ (shoulder at 6.14 μ) and did not show any appreciable absorption in the region of 3.0 μ.

Tetramethylpurpurogallin.—Complete methylation of purpurogallin and VIII with methyl sulfate in the presence of 20% potassium hydroxide gave in each case the tetramethyl derivative, in low yield. Recrystallization of the neutral product from ether–cyclohexane afforded material, m.p. 92–93° (reported[1a] m.p. 94°). The infrared spectrum (chf) had a doublet at 6.10–6.16 μ (shoulder at 6.05 μ).

2,3,6-Trimethoxy-4-hydroxybenzsuber-5-one (IX).—Hydrogenation of 2.3 g. of VIII in ethyl acetate at 25° in the presence of 1.0 g. of 5% (or 0.5 g. of 10%) palladium–charcoal for an hour in the usual way afforded 2.3 g. of product, m.p. 82.5–85°. Recrystallization from cyclohexane or water gave pale yellow crystals, m.p. 86–88° (lit.[1a] m.p. 86–87°). The infrared spectrum (chf) had a peak at 6.15–6.18 μ, and did not display any absorption near 3.0 μ. The compound was soluble in 5% sodium hydroxide solution and gave a deep purple ferric chloride test.

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol; yellow crystals, m.p. 156–158°. The reported[1a] m.p. of this derivative is 204°. The reason for this large discrepancy is not clear at present.

Anal. Calcd. for $C_{20}H_{22}O_8N_4$: C, 53.81; H, 4.97. Found: C, 53.54; H, 4.93.

2,3,6-Trimethoxy-4,5-dihydroxybenzsuberan (X).—Hydrogenation of 1.0 g. of VIII in ethyl acetate at 80° in the presence of 2 g. of 10% palladium–charcoal[13] for 1.5 hours gave, after filtration of the catalyst and evaporation of the solvent, a mixture of glass and crystals. Trituration with ether afforded 0.4 g. of crystals, m.p. 119–123.5°. Recrystallization from cyclohexane gave colorless crystals, m.p. 129–131°. The infrared spectrum (chf) had an intense peak at 2.86 μ. The compound gave a very weak green color with ferric chloride on standing.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51; Found: C, 62.87; H, 7.76.

2,3-Trimethoxy-4-hydroxybenzsuberan (XI).—Hydrogenation of 2.7 g. of VIII in 100 ml. of glacial acetic acid in the presence of 1.8 g. of 10% palladium–charcoal[13] at 80° for 2 hours afforded viscous brown oil, after filtration of the catalyst and evaporation of the solvent. The crude material was dissolved in ether–ethyl acetate; the solution was washed with sodium bicarbonate solution and water, and was dried over magnesium sulfate. Evaporation of the solvents and distillation of the material *in vacuo* gave 1.4 g. of yellow, viscous oil, b.p. 150–165° (0.65 mm.), which material crystallized. Recrystallization from cyclohexane–ethyl acetate afforded 1.2 g. of very pale yellow crystals, m.p. 91–93.5° (reported[1a] m.p. 82°). The compound did not give a noticeable color with ferric chloride, but was readily soluble in 5% sodium hydroxide solution. The infrared spectrum (chf) had a strong, sharp peak at 2.85 μ. The mixed m.p. with compound VI was depressed (76–80°).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.83; H, 7.97.

Tetraacetylpurpurogallin (XII).—Purpurogallin (4.2 g.) was refluxed with acetic anhydride (50 ml.) for 2.5 hours. Evaporation of the excess reagent and trituration of the residue with ethyl acetate gave 4.4 g. of yellow crystals, m.p. 186–188°, raised to 188–190° after recrystallization from the same solvent (reported[9] m.p. 184–186°). The infrared spectrum (chf) had a very intense peak at 5.61–5.65 μ and a strong band at 6.04–6.12 μ.

Anal. Calcd. for $C_{15}H_{16}O_9$: C, 58.76; H, 4.15; Ac, 44.3. Found: C, 58.83; H, 4.17; Ac, 44.8.

Acetylation of purpurogallin (1.7 g.) with a mixture of 30 ml. of acetic anhydride and 2 ml. of methanol (refluxed 1 hour) gave **triacetylpurpurogallin** (1.3 g.), m.p. 156–160°. Recrystallization from ethyl acetate afforded orange crystals, m.p. 160–162°. The infrared spectrum (chf) had an intense peak at 5.62–5.66 μ and a weak band at 6.08–6.11 μ.

Anal. Calcd. for $C_{17}H_{14}O_8$: C, 58.97; H, 4.08; Ac, 37.3. Found: C, 59.13; H, 4.48; Ac, 36.6.

Triacetyltetrahydropurpurogallin (XIII).—A solution of 2.2 g. of XII in 200 ml. of ethyl acetate containing 2 g. of 10% palladium–charcoal[13] was shaken under hydrogen (40 lb.) at 80° for a half-hour. Filtration of the mixture and evaporation of the solvent gave glassy material which contained acetic acid. The material crystallized in the presence of methanol. Trituration with methanol gave 0.6 g. of product, m.p. 159–165°. Recrystallization from the same solvent afforded colorless crystals, m.p. 169.5–171°. The infrared spectrum (chf) had a triplet at 5.60 (intense), 5.73 and 5.81 μ, and did not show absorption in the 3.0 or 6.0 μ regions. The compound did not give a ferric chloride test, but was soluble in 5% sodium hydroxide solution.

Anal. Calcd. for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18; Ac, 36.8. Found: C, 58.19; H, 5.22; Ac, 41.0.

When the hydrogenation was allowed to proceed for longer periods at 80°, additional hydrogen was absorbed slowly, and no crystalline products were obtained.

Acetylation of tetrahydropurpurogallin (II) in refluxing acetic anhydride for an hour gave colorless crystals, m.p. 170–171°, after recrystallization from ethyl acetate. The mixed m.p. with material prepared as described above was not depressed, and the infrared spectra (chf and Nujol) were identical.

Compound XIII was recovered unchanged after treatment with bismuth oxide in warm acetic acid, and after attempted methylation with diazomethane.

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The Preparation of Some Alkyl Fumaric Acids and Maleic Anhydrides

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Two general methods for the preparation of alkylfumaric acids and/or maleic anhydrides have been reported: one involves the conversion of paraconic esters to citraconic anhydrides by way of the itaconic acids,[2] with subsequent conversion to the mesaconic acids by prolonged heating in aqueous alkali[3] or by the action of bromine in carbon tetrachloride in the presence of sunlight.[4] Several unsuccessful attempts to prepare cyclohexylmaleic anhydride by this method[5] led to the abandonment of this route, and though the alternative route was no more successful for this compound,[5] it proved to be very convenient for most of the desired substances. The new route, which involved dibromination of 2-alkylacetoacetic esters followed by alkali induced rearrangement to the alkylfumaric acids, was first reported by Demarcay[6] in 1880, and was subsequently modified by Walden and others.[7,8] Table I lists the new 2-alkylacetoacetic esters prepared for this purpose,

(1) Abstracted from a portion of the Ph.D. Dissertation of Kathryn G. Spackman, University of Michigan, 1954.

(2) J. Houben, "Die Methoden der Organischen Chemie," Vol. III, G. Thieme, Leipzig, 1930, p. 886.

(3) G. K. Almström, *Ber.*, **48**, 2009 (1915).

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