

products from the two sources. Since our work was completed, Barnes and Gerber² have reported isolation of the stilbene from *Toxylum pomiferum* wood.

	Takaoka's compound	Phenol from <i>Artocarpus lakoocha</i>
Cryst. form	—	Plates
M. p.	199·5°	201°
Ammoniacal AgNO ₃	Reduces	Reduces
Fehling's soln.	Reduces	Reduces
Tetra-acetate	M. p. 142°	M. p. 142°
Tetra-benzoate	M. p. 193·5°	M. p. 193°
Me ₄ ether	Oil	M. p. 84°

EXPERIMENTAL

2 : 4 : 3' : 5'-Tetrahydroxystilbene.—Obtained by concentrating a hot aqueous extract of the powdered wood of *Artocarpus lakoocha*, the light brown powder contained small amounts of resin and gum. The ethereal extract of the crude product was treated with charcoal and evaporated, leaving a brown syrup which slowly crystallised and then on repeated crystallisation from hot water gave the dihydrate of the tetrahydroxystilbene in plates with a transient blue-green ferric reaction in alcohol, m. p. 201°, after softening at about 150° (depending on rate of heating) (Found, in a dried material : C, 60·2; H, 5·9; H₂O, by drying *in vacuo* at 100°, 12·5. Calc. for C₁₄H₁₂O₄·2H₂O : C, 59·9; H, 5·8; H₂O, 12·8. Found, in anhyd. compound, m. p. 201° without previous softening : C, 69·2; H, 5·2. Calc. for C₁₄H₁₂O₄ : C, 68·8; H, 5·0%).

The compound, which readily reduced Fehling's solution and ammoniacal silver nitrate, gave, by the methyl sulphate-potassium carbonate method, a tetramethyl ether forming needles, m. p. 84°, from a little methanol, readily soluble in alcohol or benzene and insoluble in aqueous sodium hydroxide [Found : C, 71·9; H, 6·7; OMe, 39·3%; *M* (Rast), 297. C₁₄H₈(OMe)₄ requires C, 72·0; H, 6·7; OMe, 41·3%; *M*, 300]. Prepared by the pyridine- or sodium acetate-acetic anhydride method, the tetra-acetate separated from alcohol in stout needles, m. p. 142° (Found : C, 63·9; H, 4·9; Ac, 40·4. Calc. for C₁₄H₈O₄Ac₄ : C, 64·1; H, 4·9; Ac, 41·8%). With benzoyl chloride and pyridine the phenol gave the tetrabenzoate, prisms, m. p. 193°, from benzene-light petroleum (b. p. 60–80°) and then aqueous acetic acid (Found : C, 75·8; H, 4·2. Calc. for C₂₄H₂₈O₈ : C, 76·4; H, 4·2%).

Oxidation of 2 : 4 : 3' : 5'-Tetramethoxystilbene.—(a) Powdered potassium permanganate (2·0 g.) was added in small portions to an agitated solution of the ether (1 g.) in acetone (100 ml.) and water (5 ml.) and after being kept for 1 hr. the mixture was clarified with sulphur dioxide, acidified with a little dilute sulphuric acid, and concentrated *in vacuo*. After isolation the semisolid was extracted with aqueous sodium hydrogen carbonate, the extract was acidified, and the solid, m. p. 160–177°, was repeatedly crystallised from hot aqueous methanol, giving *O*-dimethyl- α -resorcylic acid, plates, m. p. and mixed m. p. 182° [Found : C, 59·8; H, 5·5; OMe, 34·4. Calc. for C₇H₄O₂(OMe)₂ : C, 59·3; H, 5·5; OMe, 34·0%]. Evaporation of the aqueous-methanolic mother-liquors followed by extraction with ether gave 2 : 4-dimethoxybenzoic acid, needles, m. p. and mixed m. p. 109°, from dilute methanol and then light petroleum (b. p. 80–100°) (Found : C, 59·8; H, 5·4. Calc. for C₉H₁₀O₄ : C, 59·3; H, 5·5%).

(b) The ozonide from the stilbene tetramethyl ether was decomposed with water, and the product treated with an excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate. The resulting mixture of hydrazones, m. p. 240–248°, which could not be satisfactorily resolved by chromatography on aluminium oxide, was separated by fractionation from warm alcohol. The less soluble product was the 2 : 4-dinitrophenylhydrazone of 3 : 5-dimethoxybenzaldehyde, orange yellow needles, m. p. and mixed m. p. 260–261° (Found : N, 16·2. Calc. for C₁₅H₁₄O₈N₄ : N, 16·2%). The more soluble fraction consisted of the 2 : 4-dinitrophenylhydrazone of 2 : 4-dimethoxybenzaldehyde, scarlet needles, m. p. and mixed m. p. 258° (Found : N, 15·6%).

1-(2 : 4-Dihydroxyphenyl)-2-(3 : 5-dihydroxyphenyl)ethane.—(a) Hydrogenation of 2 : 4 : 3' : 5'-tetrahydroxystilbene (1 g.) in methanol (100 ml.) with hydrogen and palladium-charcoal gave the *diphenylethane* which separated from water as a *dihydrate* in rectangular plates, m. p. 94–96° (rapid heating) (Found : C, 59·4; H, 6·3; H₂O, 11·5. C₁₄H₁₄O₄·2H₂O requires C, 59·6; H, 6·4; H₂O, 12·8%). On further heating, the compound solidified and then melted at 160°; anhydrous material, m. p. 160°, was also obtained by heating the hydrate *in vacuo* at 80° (Found : C, 68·3; H, 5·8. Calc. for C₁₄H₁₄O₄ : C, 68·3; H, 5·7%).

² Barnes and Gerber, *J. Amer. Chem. Soc.*, 1955, **77**, 3259.

This compound gave a negative ferric reaction in alcohol and a blue reaction in water. Prepared by methyl sulphate-potassium carbonate method, the *tetramethyl ether* separated from 95% methanol (charcoal) in needles, m. p. 51—52° [Found: C, 71.4; H, 7.0; OMe, 40.6. $C_{14}H_{10}(OMe)_4$ requires C, 71.5; H, 7.5; OMe, 41.0%]. The *tetra-acetate* formed needles, m. p. 75°, identical with a specimen obtained by the hydrogenation of 2:4:3':5'-tetra-acetoxy-stilbene (Found: C, 64.2; H, 5.3. $C_{22}H_{22}O_8$ requires C, 63.8; H, 5.4%).

(b) 3:5-Dimethoxybenzyl cyanide (1.75 g.) was condensed with resorcinol (1.1 g.) in ether (75 ml.) by zinc chloride (1 g.) and an excess of hydrogen chloride, and the ketimine washed with much ether and hydrolysed with hot water. A solution of the resulting oil in ether (150 ml.) was washed with aqueous sodium hydrogen carbonate (10 ml. \times 3) to remove traces of acidic material and then extracted with 2% aqueous sodium hydroxide. Acidification of the extracts gave ω -(3:5-dimethoxyphenyl)resacetophenone, which separated from dilute methanol in rhombs (0.6 g.), m. p. 137°, with a red-brown ferric reaction [Found: C, 66.7; H, 5.2; OMe, 21.3. $C_{14}H_{10}O_3(OMe)_2$ requires C, 66.7; H, 5.6; OMe, 21.5%]. By the methyl sulphate-potassium carbonate method this was converted into 3:5-dimethoxybenzyl 2:4-dimethoxyphenyl ketone, m. p. 107° after purification from methanol (Found: C, 68.4; H, 6.4. $C_{18}H_{20}O_5$ requires C, 68.4; H, 6.4%).

Reduction of this ketone by Clemmensen's method furnished the diphenylmethane in needles, m. p. 50°, undepressed on admixture with a "natural" specimen, m. p. 51—52° (Found: C, 71.4; H, 7.5. Calc. for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3%).

In attempts to synthesise the tetramethyl ether of the hydroxystilbene, α -(3:5-dimethoxyphenyl)-2:4-dimethoxycinnamionitrile was prepared by the condensation of 2:4-dimethoxybenzaldehyde (1 g.) and 3:5-dimethoxybenzyl cyanide³ (1 g.) in alcohol (250 ml.) with sodium ethoxide (5 ml. of 5% alcoholic solution) at room temperature for 1 hr. In almost quantitative yield this *nitrile* crystallised from alcohol in yellow needles, m. p. 120° (Found: C, 69.6; H, 5.8; N, 4.4. $C_{19}H_{19}O_4N$ requires C, 70.1; H, 5.8; N, 4.3%). Attempts to hydrolyse this compound with acidic or alkaline reagent gave intractable products.

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Adams, McKenzie, and Lowe, *ibid.*, 1948, **70**, 664.
