Studies on the Chemical Constituents of Rutaceous Plants. Part 45.[1] Novel Phenyl Propanoids: Cuspidiol, Boninenal, and Methyl Boninenalate

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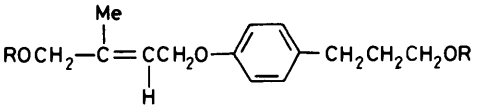
Cuspidiol, boninenal, and methyl boninenalate were established as having the structures 3-{4-[(*E*)-4-hydroxy-3-methylbut-2-enyloxy]phenyl}propanol (1), (*E*)-3-{4-[(*E*)-4-hydroxy-3-methylbut-2-enyloxy]phenyl}propenal (2), and (*E*)-3-{4-[(*E*)-4-methoxycarbonyl-3-methylbut-2-enyloxy]phenyl}propenal (3) respectively. The three compounds were also independently synthesized.

In the course of studies on the chemical constituents of Rutaceous plants, we have isolated three new phenyl propanoids, cuspidiol[2] (1), boninenal[3] (2), and methyl boninenalate[3] (3) from the plants of *Xanthoxylum* (*Fagara*) species. In a preliminary communication,[4] we showed that cuspidiol (1) belongs in a new class of phenyl propanoid having an isoprenoid moiety in the molecule. In this report, we give full details of the evidence for the structural establishment of these three naturally occurring products, involving their total syntheses.

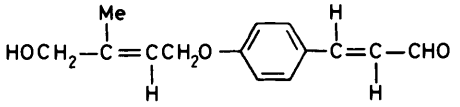
Cuspidiol (1) was obtained from the xylem and bark of *X. cuspidatum* Champ.[2] (*F. cuspidata* Engl.), a Formosan plant, as colourless needles, m.p. 65—67 °C [$C_{14}H_{20}O_3$ (M^+ 236)], while boninenal (2) and methyl boninenalate (3) were isolated from the xylem of the root of *X. inerme* Koidz. (*F. boninensis* Koidz.) as colourless prisms [the former, m.p. 95—97.5 °C, $C_{14}H_{16}O_3$ (M^+ 232) and the latter, m.p. 180 °C (softened at 107 °C), M^+ corresponding to $C_{15}H_{16}O_4$ at *m/z* 260]. Their n.m.r. spectra (see Experimental section) disclosed that a *p*-disubstituted phenyl ring is commonly present in each molecule. Moreover, the presence of the partial structure $-CH_2CH{=}CMe-$ as a common unit in each case was confirmed by decoupling experiments on irradiation of the methylene proton and the olefinic proton signals.

In its i.r. spectrum, cuspidiol (1) shows hydroxy- ($\nu_{max.}$ 3 330 and 3 270 cm^{-1}) but no carbonyl absorption. The presence of two hydroxy-groups in the cuspidiol molecule (1) was demonstrated by formation of the diacetate (4), $C_{18}H_{24}O_5$, which shows acetate ($\nu_{max.}$ 1 734 cm^{-1}) but no hydroxy-absorption in its i.r. spectrum. These facts led us to conclude that cuspidiol (1) should have an ether linkage. Irradiation at either δ 2.62 or 3.61 changed the 2 H multiplet at δ 1.86 to a triplet having *J* 7.5 Hz or 7.0 Hz, and irradiation at δ 1.86 changed both 2 H triplets at δ 2.62 and 3.61 to singlets, demonstrating that the three methylene groups are present as a sequential chain [$-CH_2CH_2CH_2-$]. In its n.m.r. spectrum, the diacetate (4) shows a 2 H triplet and a 2 H singlet at δ 4.07 and 4.53 which were shifted to lower field by 46—47 Hz, when compared with the corresponding signals (δ 3.61 and 4.06) of the original cuspidiol (1), indicating that the two partial formulae could be expanded to $HOCH_2CH_2CH_2-$ and $-CH_2CH{=}C(Me)CH_2OH$. This spectral evidence allows only two possible formulae [(1) and (1a)] for cuspidiol.

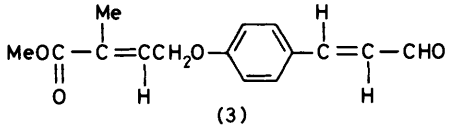
Oxidation of cuspidiol (1) with active manganese



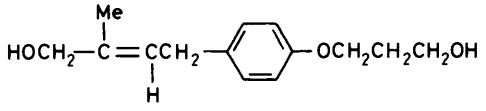
(1) R = H
(4) R = Ac



(2)



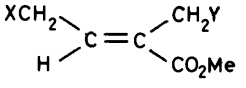
(3)



(1a)

dioxide in chloroform gave dehydrocuspidiol (5), an αβ-unsaturated aldehyde, $C_{14}H_{18}O_3$, which shows hydroxy- and carbonyl bands in its i.r. spectrum. Treatment of dehydrocuspidiol (5) with zinc dust in acetic acid gave dihydro-*p*-coumaryl alcohol[5] (6). Such a degradative result could be rationalized only by supposing that cuspidiol (1) is a vinylogous derivative of an α-aryloxyaldehyde. In other words, this experimental result clearly showed that cuspidiol should be depicted by formula (1). The *E*-configuration of cuspidiol (1) was demonstrated by the observation of a nuclear Overhauser effect: the intensity of the olefinic proton (at δ 5.74) increases (15%) on irradiation at δ 4.06, corresponding to the chemical shift of the allylic methylene, but not at δ 1.76, the chemical shift of the vinyl methyl.

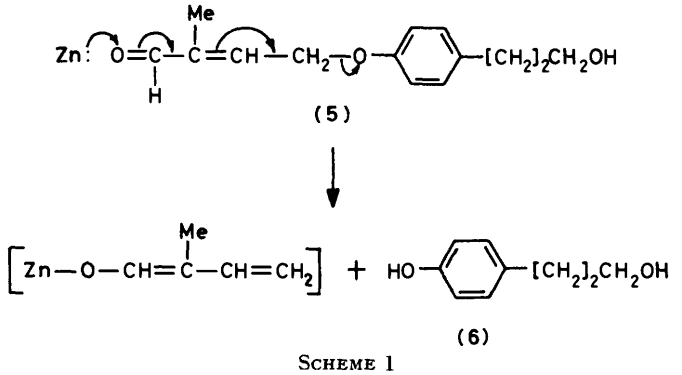
In the cases of boninenal (2) and methyl boninenalate (3), the presence of a common structural portion of a 2,3-disubstituted αβ-unsaturated aldehyde group was verified by decoupling experiments on the three signals at δ 7.40/7.39, 6.57, and 9.59. These facts allow us to formulate structures (2) and (3) for boninenal and methyl boninenalate respectively. These assumptions were also supported by the facts that, in the mass spectra of boninenal (2) and methyl boninenalate (3), the base peaks appear at *m/z* 148, corresponding to a cinnamyl aldehyde unit, instead of *m/z* 152, corresponding to a dihydrocinnamyl alcohol unit which was observed as the base peak in the case of cuspidiol (1). These ions could be easily formed by the fragmentation of an allylic ether unit. The configuration of the αβ-unsaturated aldehyde parts in boninenal (2) and methyl boninenalate (3) could be assigned as *E* from the *J* values of their olefinic protons (16.0 Hz).



(7) X = Br, Y = H
(8) X = Y = H
(9) X = H, Y = Br

Subsequently, the total syntheses of these compounds were undertaken. Methyl (*E*)-4-bromo-2-methylcrotonate [6] (7) was needed as a common starting material for our synthetic approach. In 1953, Inhoffen *et al.*[6a] brominated methyl 2-methylcrotonate (8) with *N*-bromosuccinimide. The brominated material was used in syntheses of naturally occurring crocetin dimethyl ether [6a] and zeatin,[6b] demonstrating the presence of the desired 4-bromo-derivative (7) in Inhoffen's brominated product. Later, Löffler *et al.*[6c] showed that an undesired methyl (*Z*)-2-bromomethylcrotonate (9) co-exists in the reaction mixture. Actually, in the n.m.r. spectrum of the reaction mixture in the presence of 0.2 equiv. of tris-(dipivalolylmethanate)europium(III) [Eu(dpm)$_3$], the relative intensities of the vinyl methyl signals at δ 2.81 (d, *J* 1.0 Hz) and 2.32 (d, *J* 7.0 Hz) were 2 : 1. Although this spectral evidence clearly showed that the reaction product is a mixture of two brominated compounds, the mixture * was usable for our synthetic approach as a starting material, because the desired 4-bromo-derivative (7) was expected to be more reactive.

First, we aimed at synthesizing cuspidiol (1). For this purpose, dihydro-*p*-coumaryl alcohol (6) was



(5)

(6)

SCHEME 1

required. When treated with thionyl chloride, *p*-benzyloxybenzyl alcohol (10) gave the corresponding chloride [7,†] (11) quantitatively. Treatment of the benzyl chloride (11) with diethyl malonate using sodium hydride as a catalyst afforded crude diethyl (*p*-benzyloxybenzyl)malonate (12), which was easily hydrolysed with potassium hydroxide to give *p*-benzyloxybenzylmalonic acid (13). Thermal decomposition of the dicarboxylic acid (13) gave smoothly the decarboxylated product, 3-(*p*-benzyloxyphenyl)propionic acid (14), which was converted into 3-(*p*-benzyloxyphenyl)propan-1-ol (16) by treatment with diazomethane followed by reduction with lithium aluminium hydride. Finally, catalytic hydrogenation of the phenylpropanol (16) on 10% palladium–charcoal gave dihydro-*p*-coumaryl alcohol [5] (6).

As expected, condensation of the alcohol (6) with the brominated mixture [(7) and (9)] gave the aryloxy-ester (17) in good yield. Reduction of the aryloxy-ester (17) with lithium aluminium hydride gave cuspidiol (1) which was identical with the specimen obtained from the natural source (i.r. spectrum and mixed m.p.).

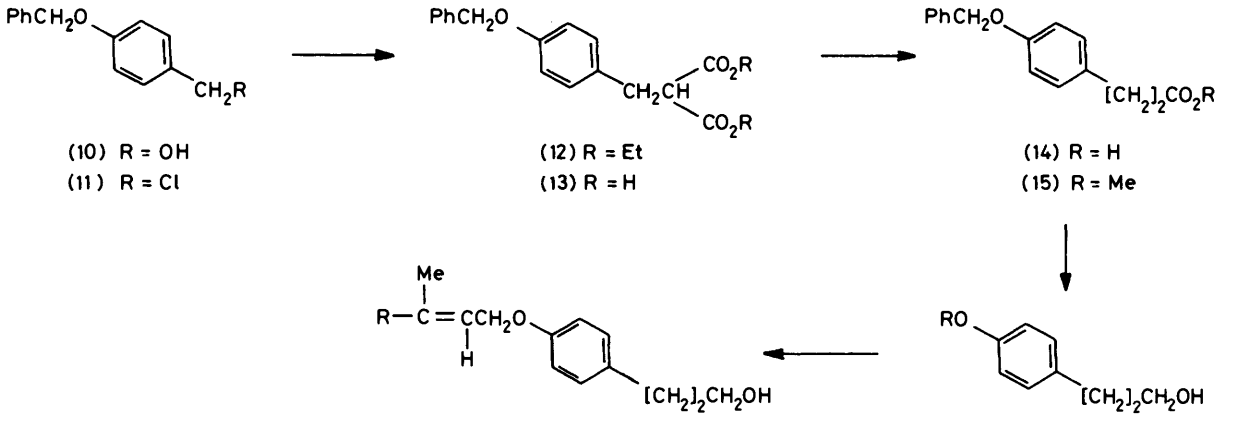
Subsequently, in order to synthesize methyl boninenalate (3) and boninenal (2), we attempted to prepare *p*-hydroxycinnamaldehyde [5,8] (18) from *p*-hydroxycinnamic acid by protecting the phenolic group as a benzyl ether. Thus, *p*-benzyloxycinnamic acid [9] (19) was esterified with methanol containing a small amount

* Löffler *et al.*[6c] described that the desired 4-bromo-product (7) was formed in the highest yield when the bromination was performed under irradiation with light. However, we found that their method provided a mixture contaminated with 4-bromo-2-methylbut-2-en-4-olide and an undefined dibromo-product, $C_6H_{10}Br_2O_2$. Details on this problem will be published elsewhere.

† In the preliminary report,[4] this material (11) was prepared by treatment of the alcohol (10) with hydrogen chloride according to the reported method.[7] However, on a large scale this method occasionally provided a product hardly contaminated with a debenzyl product.

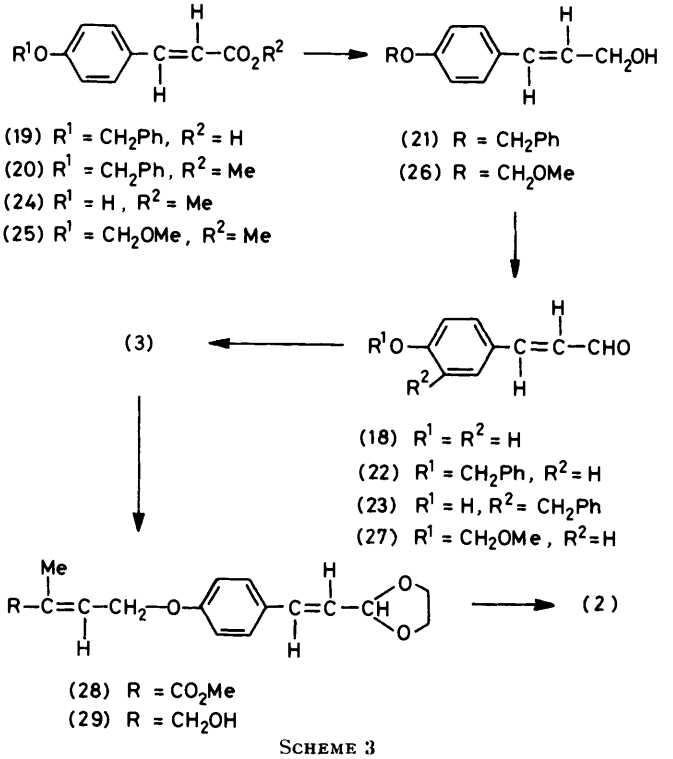
of hydrogen chloride to give methyl *p*-benzyloxycinnamate (20). Reduction of the ester (20) with lithium ethoxyaluminium trihydride [10] followed by oxidation with active manganese dioxide produced *p*-benzyloxycinnamaldehyde (22) in good yield. Unfortunately, aldehyde (22) failed, the protecting group of *p*-hydroxycinnamic acid was changed to a methoxymethyl ether.

From methyl methoxymethoxycinnamate (25), obtained by treatment of methyl *p*-hydroxycinnamate [11] (24) with chloromethyl methyl ether,[12] the desired *p*-



SCHEME 2

treatment of the benzyloxy-aldehyde (22) with trifluoroacetic acid gave a rearrangement product, *m*-benzyl-*p*-hydroxycinnamaldehyde (23), as the main product together with a small amount of the desired compound (18). Since all other attempts at preparing *p*-hydroxycinnamaldehyde (18) from the benzyloxy-methoxymethoxycinnamaldehyde [8b] (27) was prepared through the same reaction sequence [from (24) to (27) in Scheme 3] as used in the case of methyl *p*-benzyloxycinnamate (20). Treatment of the methoxymethyl ether (27) with sulphuric and acetic acids gave smoothly *p*-hydroxycinnamaldehyde (18). When treated with



SCHEME 3

the mixture of the brominated products [(7) and (9)], the aldehyde (18) provided methyl boninenalate (3) in good yield. The synthetic sample was identical with the specimen obtained from the natural source (i.r. spectrum and mixed m.p.).

For transforming methyl boninenalate (3) into boninenal (2), the aldehyde group of the former (3) must be protected as an ethylene acetal without fission of the allyl ether. This process was carried out by refluxing a solution of methyl boninenalate (3) with ethylene glycol in dry benzene in the presence of anhydrous copper(II) sulphate. Reduction of the acetal (28) followed by hydrolysis with water gave boninenal (3), identical with the specimen obtained from the natural source (i.r. spectrum and mixed m.p.).

EXPERIMENTAL

All m.p.s were measured on micro melting-point hot stage (Yanagimoto). I.r. spectra were recorded for Nujol mulls on a Hitachi EPI-G3 spectrometer. U.v. spectra were recorded on a Hitachi EPS-3T instrument for solutions in 95% ethanol. ^{1}H N.m.r. spectra were recorded on a JEOL JNM-4H-100 spectrometer in deuteriochloroform, with tetramethylsilane as internal reference. All NH and OH signals were confirmed by disappearance of their signals after addition of deuterium oxide. Mass spectra were measured with a Hitachi RMU-6E spectrometer using a direct inlet system. For column chromatography, silicic acid (100 mesh; Mallinckrodt Chemical Works), silica gel 60 (70—230 mesh ASTM; Merck), and aluminium oxide (neutral, grade I; Woelm) were used, while for preparative t.l.c., silica gel GF_{254} (Merck) was used. Products were identified by i.r., mixed m.p., and t.l.c.

Cuspidiol (1).—As reported previously,[2] cuspidiol (1) was isolated in 0.023% yield from the wood of *X. cuspidatum* Champ. (*F. cuspidata* Engl.) along with six alkaloids (nitidine, dictamnine, γ-fagarine, skimmianine, robustine, and haplopine) and β-sitosterol, and in 0.004% yield from the bark along with eleven alkaloids (nitidine, oxynitidine, de-*N*-methylchelerythrine, de-*N*-methylavicine, decarine, γ-fagarine, skimmianine, liriodenine, 4-methoxy-1-methyl-2-quinolone, arnottianamide, and isoarnottianamide), β-sitosterol, and dihydro-*p*-coumaryl alcohol. Recrystallization of crude cuspidiol from benzene–n-hexane gave colourless needles, m.p. 65—67 °C (Found: C, 70.95; H, 8.65. Calc. for $C_{14}H_{20}O_3$: C, 71.15; H, 8.55%); $\nu_{max.}$ 3 330 and 3 270 cm^{-1}; $\lambda_{max.}$ 278.5 and 286 nm (log ε 3.42 and 3.35); δ 1.76 (3 H, d, *J ca.* 1 Hz, vinyl Me), 1.80 (2 H, s, OH), 1.86 (2 H, m, $CH_2CH_2CH_2$), 2.62 (2 H, t, *J* 7.5 Hz, $ArCH_2CH_2$), 3.61 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 4.06 (2 H, s, CCH_2O), 4.54 (2 H, d, *J* 6.0 Hz, OCH_2CH), 5.74 (1 H, diffuse t, *J* 6.0 Hz, CH_2CH=C), 6.79 (2 H, d, *J* 8.5 Hz, 2- and 6-H), and 7.09 (2 H, d, *J* 8.5 Hz, 3- and 5-H).

Boninenal (2).—As reported previously,[3] boninenal (2) was isolated in 0.0023% yield from the xylem of the root of *X. inerme* Koidz. (*F. boninensis* Koidz.) along with three alkaloids (nitidine, oxynitidine, and dictamnine), two coumarins (aesculetin dimethyl ether and 6,7,8-trimethoxycoumarin), and five other chemical components [*N*-benzoyltyramine methyl ether, (±)-tembamide, (±)-syringaresinol, β-sitosterol, and methyl boninenalate (3)]. Recrystallization of crude boninenal from ether gave colourless *prisms*, m.p. 95—97.5 °C (Found: C, 72.0; H, 6.95. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.95%); $\nu_{max.}$ 3 400, 3 300, 1 680, and 1 665 cm^{-1}; $\lambda_{max.}$ 235 and 322.5 nm (log ε 4.06 and 4.48); δ 1.77 (3 H, s, vinyl Me), 1.93 (1 H, s, OH), 4.08 (2 H, s, CCH_2O), 4.63 (2 H, d, *J* 6.0 Hz, OCH_2CH), 5.75 (1 H, diffuse t, *J* 6.0 Hz, CH_2CH=C), 6.57 (1 H, dd, *J* 16.0 and 7.5 Hz, CH=C*H*CHO), 6.92 (2 H, d, *J* 9.0 Hz, 2- and 6-H), 7.40 (1 H, d, *J* 16.0 Hz, ArC*H*=CH), 7.49 (2 H, d, *J* 9.0 Hz, 3- and 5-H), and 9.59 (1 H, d, *J* 7.5 Hz, CHC*H*O); *m/z* 232 (M^+, 7.8%) and 148 (100).

Methyl Boninenalate (3).—Methyl boninenalate [3] (3) was obtained in 0.0002% yield from the xylem of the root of *X. inerme* Koidz. (*F. boninensis* Koidz.). Recrystallization of the crude material from methanol gave colourless prisms,* m.p. 180 °C (softened at 107 °C); $\nu_{max.}$ 1 715 and 1 665 cm^{-1}; δ 1.93 (3 H, s, vinyl Me), 3.75 (3 H, s, OMe), 4.74 (2 H, d, *J* 5.5 Hz, OCH_2CH), 6.57 (1 H, dd, *J* 16.0 and 7.5 Hz, CH=C*H*CHO), 6.87 (1 H, t, *J* 5 5 Hz, CH_2CH=C), 6.90 (2 H, d, *J* 8.5 Hz, 2- and 6-H), 7.39 (1 H, d, *J* 16.0 Hz, ArC*H*=CH), 7.49 (2 H, d, *J* 8.5 Hz, 3- and 5-H), and 9.59 (1 H, d, *J* 7.5 Hz, CHC*H*O); *m/z* 260 (M^+, 37.8%) and 148 (100).

Diacetylcuspidiol (4).—A mixture of cuspidiol (1) (0.075 g), acetic anhydride (1 ml), and pyridine (1 ml) was kept to stand at room temperature for 24 h, poured into water, and extracted with ether. The organic layer was washed with saturated copper(II) sulphate solution, dried over potassium carbonate, and evaporated to dryness *in vacuo*. Distillation of the residue at 150—160 °C (2×10^{-4} mmHg) afforded a colourless *oil* (0.094 g) (Found: C, 67.15; H, 7.7. $C_{18}H_{24}O_5$ requires C, 67.5; H, 7.55%); $\nu_{max.}$ ($CHCl_3$) 1 734 cm^{-1}; δ 1.77 (3 H, s, vinyl Me), 1.90 (2 H, m, $CH_2CH_2CH_2$), 2.05 (3 H, s, COMe), 2.08 (3 H, s, COMe), 2.63 (2 H, t, *J* 7.5 Hz, $ArCH_2CH_2$), 4.07 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 4.53 (2 H, s, CCH_2O), 4.55 (2 H, d, *J* 6.0 Hz, OCH_2CH), 5.77 (1 H, t, *J* 6.0 Hz, olefinic H), 6.81 (2 H, d, *J* 8.5 Hz, 3- and 5-H), and 7.08 (2 H, d, *J* 8.5 Hz, 2- and 6-H).

Dehydrocuspidiol (5).—To a solution of cuspidiol (1) (0.118 g) in dry chloroform (12 ml) was added active manganese dioxide (1.2 g) at room temperature. After the mixture was stirred at room temperature for 2.5 h, additional manganese dioxide (0.6 g) was added to the mixture and stirred at room temperature for further 1.5 h. The catalyst was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. Column chromatography of the residue on silicic acid with chloroform gave the oil (0.090 g), which was purified by distillation at 120—140 °C (1.9×10^{-4} mmHg) to give a colourless oil (0.088 g); $\nu_{max.}$ ($CHCl_3$) 3 620 and 1 693 cm^{-1}; δ 1.43br (1 H, s, OH), 1.83 (3 H, d, *J* 1.0 Hz, vinyl Me), 1.86 (2 H, m, $CH_2CH_2CH_2$), 2.65 (2 H, t, *J* 7.5 Hz, $ArCH_2CH_2$), 3.65 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 4.45 (2 H, d, *J* 6.0 Hz, OCH_2CH), 6.66 (1 H, dt, *J* 6.0 and 1.0 Hz, olefinic H), 6.84 (2 H, d, *J* 8.0 Hz, 3- and 5-H), 7.14 (2 H, d, *J* 8.0 Hz, 2- and 6-H), and 9.47 (1 H, s, CHO).

A mixed solution of dehydrocuspidiol (5) (0.030 g) and *p*-nitrobenzoyl chloride (0.040 g) in pyridine (0.5 ml) was stirred at 60 °C for 15 min, poured into water, and extracted with chloroform. After washing with saturated copper(II) sulphate solution and 5% sodium hydrogen carbonate solution, the organic layer was dried over potassium carbonate and evaporated to dryness *in vacuo*. Recrystallization of the residue from ethanol gave the p-*nitrobenzoate* as

* The amount of methyl boninenalate isolated (3) was too small to enable elemental analysis to be carried out.

pale yellow *prisms* (0.019 g), m.p. 102—104 °C (Found: C, 65.9; H, 5.6; N, 3.6. $C_{21}H_{21}NO_6$ requires C, 65.8; H, 5.5; N, 3.65%); $\nu_{max.}$ 1 730, 1 683, and 1 525 cm^{-1}.

Reduction of Dehydrocuspidiol (5) *with Zinc Dust in Acetic Acid*.—A mixture of the aldehyde (5) (0.117 g) and zinc dust (0.163 g) in acetic acid (2 ml) was refluxed for 1 h. The mixture was poured into water and extracted with ether. The ethereal solution was dried over magnesium sulphate and evaporated. Preparative t.l.c. of the residue [R_F 0.10—0.20 (chloroform–ethyl acetate, 3 : 1)] followed by distillation at 125—135 °C (1 mmHg) gave a colourless oil (0.004 g), identical with a synthetic specimen of 3-(*p*-hydroxyphenyl)propan-1-ol [5] (dihydro-*p*-coumaryl alcohol) (6).

Bromination of Methyl 2-Methylcrotonate (8) [*a Mixture of Methyl* (E)-4-*Bromo*-2-*methylcrotonate* [6] (7) *and Methyl* (Z)-2-*Bromomethylcrotonate* [6] (9)].—A mixture of methyl 2-methylcrotonate (5.24 g) and *N*-bromosuccinimide (9.05 g) in carbon tetrachloride (30 ml) was refluxed for 3 h. The reaction mixture was allowed to stand in a refrigerator and the precipitate formed was removed by filtration. After the filtrate had been evaporated, distillation of the residue at 63—65 °C (2 mmHg) gave a pale yellow liquid (5.14 g); δ [CCl_4 + 0.2 mol equiv. Eu(dpm)$_3$] 2.32 (3/3 H, d, *J* 7.0 Hz, CH*Me*), 2.81 (6/3 H, d, *J* 1.0 Hz, CMe), 4.27 (4/3 H, d, *J* 8.0 Hz, CHCH_2Br), 5.00 (11/3 H, s, OMe + CCH_2Br), 8.06 (2/3 H, dt, *J* 8.0 and 1.0 Hz, olefinic H), and 8.36 (1/3 H, q, *J* 7.0 Hz, olefinic H).

p-*Benzyloxybenzyl Chloride* (11).—A solution of *p*-benzyloxybenzyl alcohol [5] (10) (2.822 g) in dry benzene (30 ml) was added dropwise to a stirred solution of thionyl chloride (2.355 g) in absolute benzene (2 ml) containing pyridine (0.1 ml) at room temperature. The mixture was stirred at room temperature for 1 h, diluted with benzene, and poured into water. The aqueous layer was separated from the organic layer and extracted with benzene. The organic layers were combined, dried over potassium carbonate, and evaporated to dryness *in vacuo*. Recrystallization of the residue from n-hexane gave colourless plates (2.840 g), m.p. 80—82 °C (lit.,[7] 79—80 °C).

Diethyl p-*Benzyloxybenzylmalonate* (12).—A mixture of diethyl malonate (0.326 g) and sodium hydride * (0.092 g; 52.9% in mineral oil) in dry dimethylformamide (7.5 ml) was stirred at room temperature for 30 min. After a solution of the benzyl chloride (11) (0.376 g) in dry dimethylformamide (7.5 ml) had been added, the mixture was stirred at room temperature for further 3 h, poured into water, and extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, and evaporated to give a colourless oil (0.603 g); δ 1.20 (6 H, t, *J* 7.0 Hz, CH_2Me × 2), 3.15 (2 H, d, *J* 7.5 Hz, ArCH_2CH), 3.60 (1 H, dd, *J* 8.0 and 7.5 Hz, CH_2CH), 4.15 (4 H, q, *J* 7.0 Hz, OCH_2Me × 2), 6.86 (2 H, d, *J* 9.0 Hz, 3- and 5-H), 7.12 (2 H, d, *J* 9.0 Hz, 2- and 6-H), and 7.38 (5 H, s, ArH).

p-*Benzyloxybenzylmalonic Acid* (13).—A solution of the whole amount of the above oil (12) in ethanol (4.5 ml) involving potassium hydroxide (1.904 g) and water (4.4 ml) was refluxed for 3 h. The reaction mixture was poured into a large amount of water and extracted with ether. The ethereal solution was washed with 5% sodium hydroxide solution. The aqueous layer and washings were combined, acidified with 10% hydrochloric acid solution, and extracted with ether. The organic layer was dried over magnesium sulphate and evaporated to dryness. Recrystallization of the residue (0.447 g) from ether–n-hexane afforded colourless *prisms* (0.370 g), m.p. 156—158 °C (Found: C, 68.15; H, 5.45. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.35%); $\nu_{max.}$ 3 250 and 1 764 cm^{-1}; δ (CD_3SOCD_3) 2.96 (2 H, d, *J* 7.0 Hz, ArCH_2CH), 3.47 (1 H, t, *J* 7.0 Hz, CH_2CH), 5.04 (2 H, s, $PhCH_2O$), 6.89 (2 H, d, *J* 8.0 Hz, 3- and 5-H), 7.12 (2 H, d, *J* 8.0 Hz, 2- and 6-H), and 7.37 (5 H, m, ArH); *m/z* 300 (M^+, 3.8%) and 91 (100).

3-(p-*Benzyloxyphenyl*)*propionic Acid* (14).—The dicarboxylic acid (13) (0.316 g) was heated on an oil-bath (150—160 °C) under reduced pressure (15—20 mmHg) until evolution of gas had ceased. Recrystallization of the residue from benzene–n-hexane afforded colourless *needles* (0.249 g), m.p. 122—123 °C (Found: C, 75.05; H, 6.45. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); $\nu_{max.}$ 1 694 cm^{-1}; δ 2.76 (4 H, m, ArCH_2CH_2C), 5.03 (2 H, s, $PhCH_2O$), 6.87 (2 H, d, *J* 8.0 Hz, 3- and 5-H), 7.11 (2 H, d, *J* 8.0 Hz, 2- and 6-H), and 7.37 (5 H, m, ArH); *m/z* 256 (M^+, 22.9%) and 91 (100).

Methyl 3-(p-*Benzyloxyphenyl*)*propionate* (15).—A solution of the carboxylic acid (14) (1.770 g) in ether (60 ml) was treated with diazomethane prepared from nitrosomethylurea (20.6 g) at room temperature for 2 h. The mixture was evaporated to dryness *in vacuo*. Recrystallization of the residue from ether–n-hexane afforded colourless *leaflets* (1.663 g), m.p. 78—79 °C (Found: C, 75.45; H, 6.8. $C_{17}H_{18}O_3$ requires C, 75.55; H, 6.7%); $\nu_{max.}$ 1 730 cm^{-1}; δ 2.73 (4 H, m, ArCH_2CH_2C), 3.67 (3 H, s, OMe), 5.03 (2 H, s, $PhCH_2O$), 6.88 (2 H, d, *J* 8.0 Hz, 3- and 5-H), 7.09 (2 H, d, *J* 8.0 Hz, 2- and 6-H), and 7.37 (5 H, m, ArH); *m/z* 270 (M^+, 18.3%) and 91 (100).

3-(p-*Benzyloxyphenyl*)*propan*-1-*ol* (16).—To a stirred suspension of lithium aluminium hydride (0.347 g) in dry ether (38 ml) was gradually added a solution of the ester (15) (1.663 g) in dry tetrahydrofuran (19 ml) at room temperature. After the mixture had been stirred at room temperature for 1 h and refluxed for 1 h, the excess of lithium aluminium hydride was decomposed with ethyl acetate and wet ether followed by addition of a large amount of ice. The mixture was made acidic with 10% aqueous sulphuric acid and the aqueous solution was separated from the organic layer and extracted with ether. The ethereal solutions were combined, dried over potassium carbonate, and evaporated. Recrystallization of the residue from benzene–n-hexane gave colourless *leaflets* (1.305 g), m.p. 64—65 °C (Found: C, 79.1; H, 7.5. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%); $\nu_{max.}$ 3 320 cm^{-1}; δ 1.45 (1 H, s, OH), 1.85 (2 H, dt, *J* 7.5 and 7.0 Hz, CH_2CH_2-CH_2), 2.14 (2 H, t, *J* 7.5 Hz, ArCH_2CH_2), 3.68 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 5.04 (2 H, s, $PhCH_2O$), 6.98 (2 H, d, *J* 9.0 Hz, 3- and 5-H), 7.11 (2 H, d, *J* 9.0 Hz, 2- and 6-H), and 7.38 (5 H, m, ArH); *m/z* 242 (M^+, 3.2%) and 91 (100).

3-(p-*Hydroxyphenyl*)*propan*-1-*ol* (*Dihydro*-p-*coumaryl Alcohol*) (6).—A solution of the benzyl ether (16) (0.246 g) in ethanol (20 ml) was hydrogenated over 10% palladium–charcoal which was prepared from Norit (0.270 g) and 1% aqueous $PdCl_2$ (3 ml) at atmospheric pressure and room temperature. After removal of the catalyst by filtration, the filtrate was evaporated to dryness *in vacuo*. Sub-

* When sodium ethoxide instead of sodium hydride was used, a mixture of the desired compound and *p*-benzyloxybenzyl ethyl ether [b.p. 110—120 °C at 1 mmHg; $\nu_{max.}$ (neat) 1 620 cm^{-1}; δ 1.14 (3 H, t, *J* 6.5 Hz, CH_2Me), 3.39 (2 H, q, *J* 6.5 Hz, OCH_2Me), 4.30 (2 H, s, $ArCH_2O$), 4.93 (2 H, s, $PhCH_2O$), 6.78 (2 H, d, *J* 8.5 Hz, 3- and 5-H), 7.12 (2 H, d, *J* 8.5 Hz, 2- and 6-H), and 7.28br (5 H, s, ArH); *m/z* 242 (M^+, 14.8%) and 91 (100)] was obtained.

limation of the residue at 125—135 °C and 1 mmHg gave a colourless solid (0.149 g), m.p. 45—47 °C (lit.,[5] 54—55 °C) (Found: C, 70.75; H, 7.8. Calc. for $C_9H_{12}O_2$: C, 71.0; H, 7.95%); $\nu_{max.}$ 3 400 and 3 220 cm^{-1}; δ 1.60 (1 H, s, OH), 1.88 (2 H, m, $CH_2CH_2CH_2$), 2.63 (2 H, t, *J* 8.0 Hz, $ArCH_2CH_2$), 3.67 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 5.24br (1 H, s, OH), 6.72 (2 H, d, *J* 7.0 Hz, 3- and 5-H), and 7.03 (2 H, d, *J* 7.0 Hz, 2- and 6-H); *m/z* 152 (M^+, 32.8%) and 107 (100).

Methyl (E)-[p-(3-*Hydroxypropyl*)*phenoxy*]-2-*methylcrotonate* (17).—The mixture of the brominated products (7) and (9) (0.493 g) and the phenylpropanol (6) (0.259 g) were dissolved in acetone (12 ml) containing anhydrous potassium carbonate (0.354 g). The mixture was refluxed for 8.5 h, poured into water, and extracted with ether. The ethereal solution was washed with 10% sodium hydroxide solution, dried over potassium carbonate, and evaporated to dryness. The residue was chromatographed on silicic acid. After removal of the eluants with benzene and with chloroform, elution with ethyl acetate gave the crude material which was purified by sublimation at 130—135 °C (1.9×10^{-4} mmHg). Recrystallization of the crude product from ether–n-hexane afforded colourless *needles* (0.318 g), m.p. 43—48 °C (Found: C, 68.05; H, 7.7. $C_{15}H_{20}O_4$, requires C, 68.15; H, 7.65%); $\nu_{max.}$ ($CHCl_3$) 3 680, 3 615, and 1 718 cm^{-1}; δ 1.59 (1 H, s, OH), 1.85 (2 H, m, $CH_2CH_2CH_2$), 1.92 (3 H, d, *J* 1.0 Hz, CMe), 2.66 (2 H, t, *J* 7.5 Hz, $ArCH_2CH_2$), 3.66 (2 H, t, *J* 7.0 Hz, CH_2CH_2O), 3.77 (3 H, s, OMe), 4.68 (2 H, d, *J* 5.5 Hz, OCH_2CH), 6.78 (2 H, d, *J* 8.0 Hz, 3- and 5-H), 6.91 (1 H, fine t, *J* 5.5 and 1.0 Hz, olefinic H), and 7.15 (2 H, d, *J* 8.0 Hz, 2- and 6-H).

Synthetic Cuspidiol (1).—A solution of the ester (17) (0.132 g) in dry tetrahydrofuran (2 ml) was added to a stirred suspension of lithium aluminium hydride (0.085 g) in dry ether (3 ml). After the mixture had been stirred at room temperature for 1 h and refluxed for 2 h, the excess of the reagent was decomposed by addition of ethyl acetate and wet ether. The mixture was poured into ice–water, acidified with 10% aqueous sulphuric acid, and extracted with ether. The ethereal solution was dried over potassium carbonate and evaporated to dryness *in vacuo*. The residue was purified by column chromatography on silicic acid with a mixed solvent (chloroform–ether, 10 : 1). Recrystallization of the crude material from benzene–ether gave colourless fine needles (0.077 g), m.p. 68—70 °C, identical with a sample of cuspidiol obtained from the natural source.

Methyl p-*Benzyloxycinnamate* (20).—A suspension of *p*-benzyloxycinnamic acid [8] (19) (5.592 g) in methanol (223 ml) involving concentrated hydrochloric acid (1.15 ml) was refluxed for 9 h. After cooling, the precipitate was collected by filtration. The filtrate was made alkaline with saturated sodium hydrogen carbonate solution and extracted with ethyl acetate. The organic layer was dried over magnesium sulphate and evaporated to dryness *in vacuo*. The residue was combined with the precipitate and recrystallized from chloroform–methanol to give colourless *prisms* (5.047 g), m.p. 138—139.5 °C (Found: C, 76.55; H, 6.05. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%); $\nu_{max.}$ 1 725 cm^{-1}; δ 3.77 (3 H, s, OMe), 5.06 (2 H, s, $PhCH_2O$), 6.29 (1 H, d, *J* 15.8 Hz, CH=CHC), 6.96 (2 H, d, *J* 8.8 Hz, 3- and 5-H), 7.10—7.54 (7 H, m, ArH and 2- and 6-H), and 7.64 (1 H, d, *J* 15.8 Hz, ArCH=CH).

p-*Benzyloxycinnamyl Alcohol* (21).—A solution of dry ethanol (0.538 g) and dry ether (7 ml) was added to an ice-cooled suspension of lithium aluminium hydride (0.442 g) in dry ether (6 ml). After the mixture had been made up to 20 ml by addition of further dry ether, the suspension was stirred at room temperature for 20 min. A portion (0.2 ml) of this reagent was added to a stirred solution of the ester (20) (0.097 g) in dry ether (40 ml) at room temperature. This process was repeated every hour until a total of 1 ml of the reagent had been added. The reaction mixture was kept at room temperature for a further 30 min after the final addition of the reagent. The excess of the reagent was decomposed by cautious addition of water and the precipitate was removed by filtration and washed with ether. After the washings had been combined with the filtrate, the ethereal solution was separated from the aqueous layer which was repeatedly extracted with ether. The ethereal solution was dried over magnesium sulphate and evaporated to dryness *in vacuo*. The residue was purified by preparative t.l.c. on silicic acid using chloroform as solvent to give a colourless solid showing an R_F value of 0.17 on silicic acid (benzene–ethyl acetate, 10 : 1). Recrystallization of the solid from benzene–n-hexane gave colourless *scales* (0.058 g), m.p. 116—118 °C (Found: C 79.9; H, 6.7. $C_{16}H_{16}O_2$ requires C, 79.95; H, 6.7%); $\nu_{max.}$ 3 350 cm^{-1}; δ 1.59 (1 H, s, OH), 4.25 (2 H, d, *J* 5.0 Hz, $CHCH_2O$), 5.00 (2 H, s, $PhCH_2O$), 6.16 (1 H, dt, *J* 15.5 and 5.0 Hz, CH=CHCH$_2$), 6.52 (1 H, d, *J* 15.5 Hz, ArCH=CH), 6.89 (2 H, d, *J* 8.4 Hz, 3- and 5-H), 7.28 (2 H, d, *J* 8.4 Hz, 2- and 6-H), and 7.35 (5 H, s, ArH).

p-*Benzyloxycinnamaldehyde* (22).—To a solution of the αβ-unsaturated alcohol (21) (2.123 g) in carbon tetrachloride (450 ml) was added active manganese dioxide (11.837 g). The suspension was stirred at room temperature for 1 h and filtered. The manganese dioxide was washed with chloroform. The filtrate and the washings were combined and evaporated to dryness *in vacuo*. Recrystallization of the residue from ether–n-hexane gave pale yellow *prisms* (1.701 g), m.p. 72—74 °C (Found: C, 80.65; H, 5.95. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.9%); $\nu_{max.}$ 1 665 cm^{-1}; δ 5.07 (2 H, s, $PhCH_2O$), 6.54 (1 H, dd, *J* 15.4 and 7.6 Hz, CH=CHCH), 6.97 (2 H, d, *J* 8.9 Hz, 3- and 5-H), 7.37 (1 H, d, *J* 15.4 Hz, ArCH=CH), 7.36 (5 H, s, ArH), 7.47 (2 H, d, *J* 8.9 Hz, 2- and 6-H), and 9.58 (1 H, d, *J* 7.6 Hz, CHCHO).

Debenzylation of p-*Benzyloxycinnamaldehyde* (22) *with Trifluoroacetic Acid*.—A solution of *p*-benzyloxycinnamaldehyde (22) (0.099 g) in trifluoroacetic acid (1.26 ml) was allowed to stand at room temperature for 69 h and then evaporated to dryness *in vacuo*. The residue was dissolved in ether (20 ml) and extracted with 5% sodium hydroxide solution. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The ethereal solution was washed with saturated sodium hydrogen carbonate solution, dried over magnesium sulphate, and evaporated to dryness *in vacuo*. Preparative t.l.c. of the residue on silicic acid using a mixed solvent (chloroform–methanol, 20 : 1) gave two fractions.

m-*Benzyl*-p-*hydroxycinnamaldehyde* (23).—Recrystallization of the fraction showing the larger R_F value (0.66) on silicic acid (chloroform–methanol, 10 : 1) from benzene–n-hexane gave fine pale yellow *needles* (0.051 g), m.p. 155—157 °C (Found: C, 80.7; H, 5.9. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.9%); $\nu_{max.}$ 3 320 and 1 655 cm^{-1}; δ (CD_3SOCD_3) 3.90 (2 H, s, $PhCH_2Ar$), 6.56 (1 H, dd, *J* 15.6 and 7.8 Hz, CH=CHCH), 6.87 (1 H, d, *J* 8.3 Hz, 5-H), 7.21 (5 H, s, ArH), 7.44 (2 H, m, 2- and 6-H), 7.50 (1 H, d, *J* 15.6 Hz, ArCH=CH), 9.51 (1 H, d, *J* 7.8 Hz, CHCHO), and 10.16 (1 H, s, OH); *m/z* 238 (M^+, 68.3%), 147 (100), and 91 (29.3).

p-*Hydroxycinnamaldehyde* (18).—Recrystallization of the fraction showing the smaller R_F value (0.48) on silicic acid (chloroform–methanol, 10 : 1) from benzene–n-hexane gave pale yellow needles (0.025 g), m.p. 143—144 °C (lit.,[8a] 138—140 °C) (Found: C, 73.15; H, 5.5. Calc. for $C_9H_8O_2$: C, 72.95; H, 5.45%); $\nu_{max.}$ 3 125 and 1 640 cm^{-1}; δ (CD_3SOCD_3) 6.62 (1 H, dd, *J* 15.4 and 7.6 Hz, CH=C*H*CH), 6.84 (2 H, d, *J* 8.4 Hz, 3- and 5-H), 7.58 (2 H, d, *J* 8.4 Hz, 2- and 6-H), 7.59 (1 H, d, *J* 15.4 Hz, ArC*H*=CH), 9.55 (1 H, d, *J* 7.6 Hz, CHC*H*O), and 10.13 (1 H, s, OH).

Methyl p-*Methoxymethoxycinnamate* (25).—A solution of methyl *p*-hydroxycinnamate [11] (24) (19.451 g) in acetone (400 ml) containing potassium carbonate (42.642 g) was stirred at room temperature for 1 h and then chloromethyl methyl ether [12] (22.6 ml) was added during 30 min. After removal of the potassium carbonate by filtration, the filtrate was evaporated. Distillation of the residue at 163—164 °C (3 mmHg) gave a colourless *oil* (21.446 g) (Found: C, 64.6; H, 6.2. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35%); $\nu_{max.}$ (neat) 1 720 cm^{-1}; δ 3.46 (3 H, s, OMe), 3.78 (3 H, s, CO_2Me), 5.15 (2 H, s, OCH_2O), 6.28 (1 H, d, *J* 16.6 Hz, CH=C*H*C), 6.98 (2 H, dd, *J* 8.1 and 2.0 Hz, 3- and 5-H), 7.43 (2 H, dd, *J* 8.1 and 2.0 Hz, 2- and 6-H), and 7.62 (1 H, d, *J* 16.6 Hz, ArC*H*=CH).

p-*Methoxymethoxycinnamyl Alcohol* (26).—A mixed solution of dry ethanol (5.320 g) and dry ether (25 ml) was gradually added to a suspension of lithium aluminium hydride (4.403 g) in dry ether (100 ml). After the total volume had been made up to 200 ml by addition of further dry ether, the suspension was stirred at room temperature for 20 min. A portion (50 ml) of the reagent was added to a stirred solution of methyl *p*-methoxymethoxycinnamate (25) (20.349 g) in dry ether (200 ml) at room temperature every 1 h. After all the reagent (200 ml) had been added, the mixture was stirred for a further 40 min. The excess of the reagent was cautiously decomposed by addition of water and the precipitate was removed by filtration and then washed with ether. After the washings had been combined with the filtrate, the ethereal solution was separated from the aqueous layer which was repeatedly extracted with ether. The ethereal solution was combined, dried over potassium carbonate, and evaporated. The residue was purified by column chromatography on silicic acid and distilled at 190—193 °C (10 mmHg) to give a colourless *oil* (12.235 g) (Found: C, 67.3; H, 7.25. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.25%); $\nu_{max.}$ (neat) 3 400 cm^{-1}; δ 1.98 (1 H, s, OH), 3.46 (1 H, s, OMe), 4.25 (2 H, d, *J* 5.2 Hz, CHCH_2O), 5.13 (2 H, s, OCH_2O), 6.17 (1 H, dt, *J* 16.0 and 5.2 Hz, CH=C*H*CH_2), 6.53 (1 H, d, *J* 16.0 Hz, ArC*H*=CH), 6.95 (2 H, dd, *J* 8.4 and 2.0 Hz, 3- and 5-H), and 7.28 (2 H, dd, *J* 8.4 and 2.0 Hz, 2- and 6-H).

p-*Methoxymethoxycinnamaldehyde* (27).—To a solution of the αβ-unsaturated alcohol (26) (4.002 g) in carbon tetrachloride (400 ml) was added active manganese dioxide (20.123 g). The suspension was stirred at room temperature for 10 h and then filtered. The filtrate was evaporated. Distillation of the residue at 158 °C and 7 mmHg (lit.,[8b] b.p. 158—160 °C at 3 mmHg) gave a colourless oil (3.528 g); $\nu_{max.}$ (neat) 1 680 cm^{-1}; δ (CCl_4) 3.45 (3 H, s, OMe), 5.14 (2 H, s, OCH_2O), 6.50 (1 H, dd, *J* 16.0 and 7.4 Hz, CH=C*H*CH), 7.00 (2 H, d, *J* 8.2 Hz, 3- and 5-H), 7.29 (1 H, d, *J* 16.0 Hz, ArC*H*=CH), 7.45 (2 H, d, *J* 8.2 Hz, 2- and 6-H), and 9.55 (1 H, d, *J* 7.4 Hz, CHC*H*O).

p-*Hydroxycinnamaldehyde* (18).—To a mixed solution of water (10.3 ml) and acetic acid (9.7 ml) involving concentrated sulphuric acid (0.03 ml) was added the αβ-unsaturated aldehyde (27) (3.272 g). The mixture was heated at 80 °C for 2 h while nitrogen was bubbled through, poured into water, and extracted with ether. The ethereal solution was washed with saturated sodium hydrogen carbonate solution, dried over magnesium sulphate, and evaporated to dryness *in vacuo*. Recrystallization of the residue from methanol–benzene–n-hexane gave fine pale yellow *needles* (2.353 g), m.p. 139—142 °C (lit.,[8a] 138—140 °C). This material was identical with the sample prepared by debenzylation of *p*-benzyloxycinnamaldehyde (22).

Synthetic Methyl Boninenalate (3).—To a solution of a mixture of the brominated products (7) and (9) (0.956 g) and *p*-hydroxycinnamaldehyde (18) (0.249 g) in acetone (12 ml) was added anhydrous potassium carbonate (0.347 g). After having been stirred at room temperature for 15 min, the mixture was refluxed for 2 h and filtered. The filtrate was evaporated to dryness *in vacuo*. The residue was chromatographed on silicic acid with mixed solvent (benzene–ethyl acetate, 10 : 1) to give colourless *prisms* (0.331 g), m.p. 174 °C (softened at 100—101 °C), which was recrystallized from benzene (Found: C, 69.15; H, 6.15. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2%). The material was identical with a sample of methyl boninenalate obtained from the natural source.

Methyl Boninenalate Ethylene Acetal (28).—Ethylene glycol (2.5 ml) was added to a vigorously stirred solution of methyl boninenalate (3) (0.502 g) in dry benzene (200 ml) containing anhydrous copper(II) sulphate (5.012 g). The mixture was refluxed for 10 h and filtered. During the reaction, the refluxed benzene was dehydrated using a Soxhlet apparatus equipped with anhydrous copper(II) sulphate. The filtrate was evaporated and the excess of ethylene glycol was distilled off under reduced pressure. Recrystallization of the residue from dry benzene–n-hexane gave pale yellow *prisms* (0.567 g), m.p. 73—75 °C (Found: C, 66.9; H, 6.55. $C_{17}H_{20}O_5$ requires C, 67.1; H, 6.6%); $\nu_{max.}$ 1 710 and 1 662 cm^{-1}; δ 1.92 (3 H, s, CMe), 3.76 (3 H, s, OMe), 4.00 (4 H, diffuse d, *J* 4.1 Hz, OCH_2CH_2O), 4.70 (2 H, d, *J* 5.2 Hz, OCH_2CH), 5.39 (1 H, d, *J* 6.0 Hz, *H*CCH), 6.02 (1 H, dd, *J* 15.9 and 6.0 Hz, CH=C*H*CH), 6.72 (1 H, d, *J* 15.9 Hz, ArC*H*=CH), 6.84 (2 H, d, *J* 8.6 Hz, 3- and 5-H), and 7.35 (2 H, d, *J* 8.6 Hz, 2- and 6-H).

Boninenal Ethylene Acetal (29).—A mixed solution of absolute ethanol (0.539 g) in dry ether (5 ml) was gradually added to an ice-cooled stirred suspension of lithium aluminium hydride (0.442 g) in dry ether (10 ml). When the addition was complete, the total volume of the suspension was made up to 20 ml by further addition of dry ether. A portion (0.6 ml) of the suspension was added to a stirred solution of methyl boninenalate ethylene acetal (28) (0.300 g) in dry ether (60 ml) at room temperature every hour (four times; total amount of reagent used, 2.4 ml). After the final addition of the reagent, the reaction mixture was stirred for a further 1 h, decomposed by addition of saturated Rochelle salt solution (20 ml), and extracted with ether. The ethereal solution was dried over magnesium sulphate and evaporated to dryness *in vacuo*. Column chromatography of the residue on aluminium oxide with mixed solvent (benzene–ethyl acetate, 15 : 1) gave colourless prisms (0.151 g), m.p. 74—75 °C; ν_{max} 3 450 and 1 660 cm^{-1}; δ 1.65 (1 H, s, OH), 1.75 (3 H, s, CMe), 3.96—4.05 (6 H, m, CCH_2O and OCH_2CH_2O), 4.56 (2 H, d, *J* 6.2 Hz, OCH_2CH), 5.37 (1 H, d, *J* 6.2 Hz, CC*H*CH), 5.72 (1 H, t, *J* 6.2 Hz, CH_2CH=C), 5.98 (1 H, dd, *J* 15.6 and 6.2 Hz, CHC*H*=CH),

6.70 (1 H, d, *J* 15.6 Hz, ArC*H*=CH), 6.82 (2 H, d, *J* 8.0 Hz, 3- and 5-H), and 7.32 (2 H, d, *J* 8.0 Hz, 2- and 6-H); *m/z* 276 (M^+, 7.9%) and 120 (100). This material was so labile that it gave gradually boninenal when left in air.

Synthetic Boninenal (2).—A solution of boninenal ethylene acetal (0.130 g) in dioxan (10 ml) containing water (5 ml) was refluxed for 10 h, poured into a large quantity of water, and extracted with ether. The ethereal solution was dried over potassium carbonate and evaporated to dryness *in vacuo*. Recrystallization of the residue from ether gave pale yellow prisms (0.084 g), m.p. 94—95.5 °C, identical with a sample obtained from the natural source.

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