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ACUMINATIN, A NEW *BIS*-PHENYLPROPIDE FROM *MAGNOLIA ACUMINATA* L.

R. W. DOSKOTCH and M. S. FLOM
Division of Natural Products Chemistry, College of Pharmacy, The Ohio State University, Columbus, Ohio 43210, USA

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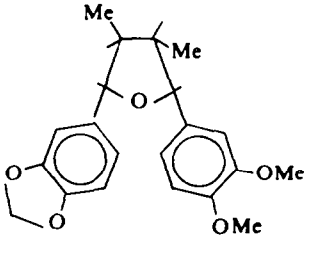
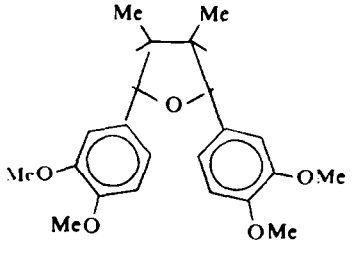
Abstract—Three uncommon lignans calopiptin (1), galgravin (2) and veraguensin (3) were isolated from *M. acuminata* root-bark, along with a novel *bis*-phenylpropide, acuminatin (4) which was characterized by physical and chemical methods.

MAGNOLIA ACUMINATA L. (family Magnoliaceae) commonly called the cucumber tree, because of its curious looking fruit, is a tall forest tree of the eastern and mainly southern parts of the United States, and is found predominantly on the mountain slopes. In addition to being an ornamental, it has been a source of lumber, and its bark was at one time an official drug,[1] used in the treatment of malaria and rheumatism, although the root is believed to be more efficient. We have examined the neutral fraction of the root bark and have identified three lignans; calopiptin (1), galgravin (2), veraguensin (3) and a new *bis*-phenylpropide for which the trivial name acuminatin (4) was chosen.

The four compounds were isolated by column chromatography on neutral alumina and on silicic acid. Acuminatin (4) was eluted first, followed by calopiptin (1), galgravin (2) and veraguensin (3). Identification of calopiptin (1) and galgravin (2) was by comparison of the physical properties with published data. The former was previously obtained from *Piptocalyx moorei* Oliv. (family Trimeniaceae),[2] and its absolute stereochemistry was established in 1968;[3] while the latter was isolated from *Himantandra belgraveana* F. Muell. (family Himantandraceae).[4] The identification of veraguensin (3) was made by direct comparison with an authentic sample* obtained from *Ocotea veraguensis* Mez. (family Lauraceae).[5] Veraguensin has also been isolated from *Trimenia papuana* (family Trimeniaceae).[3]



1



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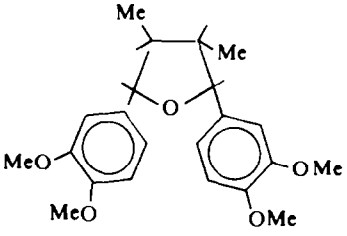
* We thank Professor C. Djerassi of Stanford Univeristy for the sample of veraguensin.



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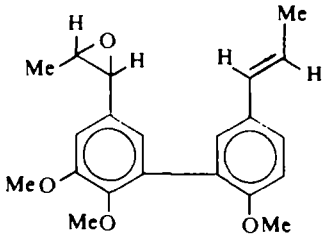

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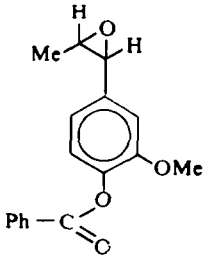
Acuminatin (**4**), mp 77·5°, analyzed for $C_{21}H_{24}O_4$ and showed a molecular ion in the high resolution mass spectrum in agreement with the formula. The UV spectrum indicated conjugated benzenoid absorption consistent with an β-methylstyrene system.[6] The NMR spectrum exhibited two Me doublets at δ 1·36 (J = 7·0 Hz, epoxide Me) and 1·84 (peak separation of 5·4 Hz is discussed below), sharp singlets at δ 3·86 and 3·83 integrating for one and two OMe groups, respectively, a one proton singlet at δ 5·08 (J = 9·5 Hz) for the benzylic and epoxide proton, and a five peak multiplet (two overlapping quartets) at δ 3·43 (J = 9·5 and 7·0 Hz) for the other epoxide proton. These and other assignments which follow were established by double-irradiation experiments. A deceptively simple pattern for the AB part of an ABX_3 system (J_{AB} = 15·5 Hz) was observed between δ 5·8 and 6·4, where the X_3 portion was the doublet at δ 1·84, with the line splitting $J_{AX} + J_{BX}$. A nearly identical pattern has been reported for *trans*-isoeugenol[7] and supports the presence of a *trans*-β-methylstyrene unit in acuminatin. The five aromatic protons are located as a complex pattern between δ 6·5 and 7·1.

Since the remaining oxygen function of acuminatin appeared unreactive, and the IR spectrum lacked OH and CO adsorption, an oxirane substituted by an aromatic ring and a Me group was suggested, for which the NMR spectrum was in agreement. The large coupling constant (J = 9·5) between the vicinal protons of the epoxide points to *cis* stereochemistry, although the value is higher than generally observed.[8] For example, the model compounds *cis*- and *trans*-epoxides **5** and **6**, prepared from *cis*- and *trans*-isoeugenol benzoate esters with *m*-chloroperbenzoic acid, showed vicinal coupling of J = 4·2 and 2·0 Hz, respectively. It appears that in acuminatin the unusually large coupling constant must result from the influence of the biphenyl system, since degradation products **7** and **10** have similarly large values.



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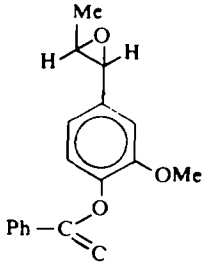

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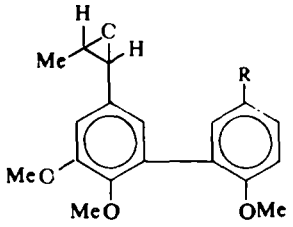
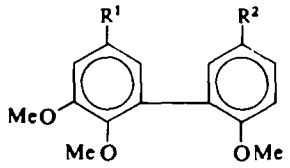
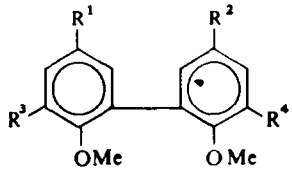


7: R = CHO
9: R = COOH
10: R = COOMe



8: R¹ = R² = COOH
11: R¹ = R² = COOMe

Oxidation of acuminatin (**4**) by the Lemieux-von Rudloff procedure[9] formed the epoxy-aldehyde **7** and the biphenyl dicarboxylic acid **8**. The epoxy-aldehyde **7** showed in the IR spectrum the aromatic aldehyde adsorption at 1685 cm^{-1}, and in the NMR spectrum the aldehydic proton peak at δ 9·87. The Me of the propylene oxide appeared as a doublet at δ 1·46 (J = 6·8 Hz) and the vicinal protons adsorbed at δ 5·29 (doublet, J = 9·2) and 3·58 (double quartet, J = 9·2 and 6·8). The corresponding epoxy-acid **9** was prepared by $KMnO_4$ oxidation of acuminatin and was characterized as the methyl ester **10**.

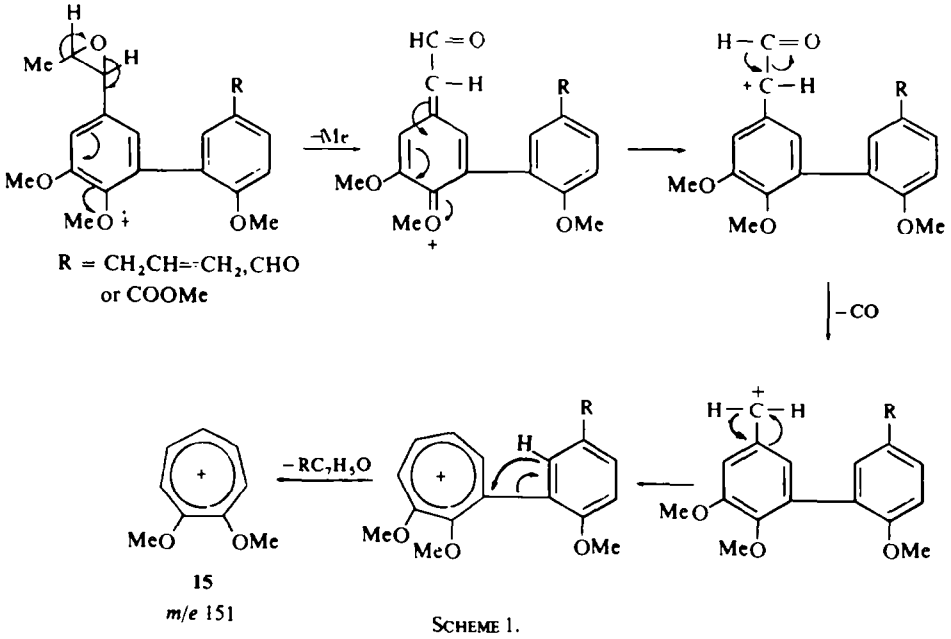


12: R¹ = R² = COOMe, R³ = R⁴ = H
13: R¹ = R² = CHO, R³ = R⁴ = OMe
14: R¹ = CHO, R² = COOMe,
R³ = OMe, R⁴ = H

The biphenyl dimethyl ester **11** prepared from the acid **8** was identified as 2,2',3-trimethoxy-5,5'-dimethoxycarbonylbiphenyl by comparison with an authentic sample prepared by synthesis via the Ullmann reaction from methyl 3-iodo-4-methoxybenzoate[10] and 5-iodoveratraldehyde.[11] The products of the reaction were the two symmetrical biphenyls, 2,2'-dimethoxy-5,5'-dimethoxycarbonylbiphenyl[12] (**12**) and 2,2',3,3'-tetramethoxy-5,5'-diformylbiphenyl[13] (**13**), and the unsymmetrical 2,2',3-trimethoxy-5-formyl-5'-methoxycarbonylbiphenyl (**14**). Permanganate oxidation of the unsymmetrical biphenyl **14** and methylation of the product with diazomethane gave 2,2',3-trimethoxy-5,5'-dimethoxycarbonylbiphenyl (**11**) identical with the product from acuminatin; thus establishing for it the substutution position of the methoxy groups and the side chains.

Evidence for placing the propylene oxide group on the phenyl ring bearing two OMe groups was obtained from mass spectral studies of acuminatin (**4**) and its degradation products, epoxy-aldehyde **7** and epoxy-ester **10**. All showed a peak at *m/e* 151 with intensities 11, 25 and 17%, respectively, corresponding to a $C_9H_{11}O_2$

fragment; the dimethoxytropylium ion **15** visualized as arising by the fragmentations shown in Scheme 1.



SCHEME 1.

EXPERIMENTAL

M.ps were taken in sealed evacuated capillaries and are corrected. IR spectra were taken in $CHCl_3$ or as stated otherwise on a Perkin–Elmer Infracord 237 or 257 spectrophotometer, and UV spectra were taken in EtOH on a Cary Model 15 recording spectrophotometer, NMR spectra were measured in $CDCl_3$ on a Varian A-60A or a HA-100 instrument with TMS as internal standard and chemical shifts reported in δ (ppm) units; singlets are not designated, d = doublet, t = triplet, q = quartet and m = multiplet. Double-irradiation studies were performed in the frequency sweep mode on the latter instrument. Optical rotations were taken on a Zeiss polarimeter. Mass spectra were obtained on an AEI MS-9 double focusing mass spectrometer via the direct inlet mode at 70 eV.

Extraction and initial fractionation. The dried and powdered root bark (1 kg) of *Magnolia acuminata* L.* was percolated at room temp with 25 l EtOH. The extract residue (190 g) after removal of alkaloids with 2% aqueous citric acid was partitioned between 10% aqueous MeOH and light petroleum (bp 60–70°). The light petroleum residue (31 g) was divided into two parts and each part was chromatographed on 600 g of activity I neutral alumina beginning with benzene as eluting solvent and proceeding through benzene–$CHCl_3$ in ratios of 9:1, 9:2 and 1:1, and then with $CHCl_3$ and $CHCl_3$–MeOH (1:1). The orange oil (6·31 g) eluted with $CHCl_3$:MeOH (1:1) was rechromatographed on a column (300 g) of silicic acid–diatomaceous earth (4:1) using benzene–$CHCl_3$ (1:9) as eluent. Column fractions (15 ml) were evaporated, the residue weighed and analyzed by TLC on silica gel G and $CHCl_3$ (System A) or $CHCl_3$–EtOAc (40:1) (System B) as solvent. Detection was by spraying with Et_2O–conc H_2SO_4 (4:1) to give reddish-purple zones.

Calopiptin (**1**). Silicic acid column fractions 88–101 (335 mg) containing material with R_f 0·21 (System A) were combined and crystallized from isopropyl ether and then hexane to give colorless rosettes of **1**: mp 94·5°; $[\alpha]_D^{26}$ + 45·8° (*c* 0·66, $CHCl_3$); UV max 282 nm (log ε 3·82) and 233 nm (4·16); IR 1612 m, 1596 m, 1520 vs, 1490 vs, 1444 vs, 1250 vs, 1234 vs, 1162 s, 1127 vs, 1027 vs and 930 s cm^{-1}; and NMR δ 0·67 (d, *J* 6·7 Hz, C-3 Me), 1·05 (d, 6·2, C-2 Me), 1·8 (m, H_2), 2·2 (m, H_3), 3·90 and 3·93 (2 OMe), 4·38 (d, 8·7, H_1), 5·11

* Obtained from the Secrest Arboretum, Ohio Agricultural Research and Development Center, Wooster, Ohio, through the courtesy of Mr. T. F. Wonderling.

(d, 8·2, H_4), 5·95 (OCH_2O) and 6·8–7·2 (m, ArH): [lit[2] mp 95·5°, $[\alpha]^{14}$ + 28° (*c* 2·086, $CHCl_3$), and the UV, IR and NMR data were in agreement].

Galgravin (**2**). Column fractions 106–111, (354 mg) were part of a single peak (fractions 106–123) containing both galgravin and veraguensin and were pooled after GLC (4 ft column of 3·8% silicone gum rubber UC W-98 adsorbed on Diatoport (80–100 mesh) at 230° using a flame ionization detector) indicated it was mainly one component. Crystallization several times from hexane gave pure **2**: mp 121°, $[\alpha]_D^{22}$ 0° (*c* 1·30, $CHCl_3$), UV max 278 nm (log ε 3·82) and 233 (4·31); IR 1612 m, 1595 m, 1515 vs, 1465 vs, 1260 vs, 1235 vs, 1160 vs, 1140 vs, 1025 vs and 885 m cm^{-1}; and NMR δ 1·05 (d, *J* 6·3 Hz, C-2 and -3 Me), 2·37 (m, H_2 and H_3), 4·61 (d, 6·6), 3·91 and 393 (4 OMe), and 6·9–7·3 (m, ArH): [lit[4] mp 121°, the NMR peaks were in agreement with reported values[5]].

Veraguensin (**3**). Fractions 119–123 of the single peak (fractions 106–123) were pooled, after GLC indicated them to contain mainly one component, and crystallized from Et_2O to give prisms of veraguensin: mp 128–129°; $[\alpha]_D^{25}$ + 41·7° (*c* 0·96, MeOH); UV max 278 nm (log ε 3·79) and 233 (4.28); IR 1613 m, 1595 m, 1315 vs, 1465 vs, 1260 vs, 1235 s, 1160 s, 1140 vs and 1025 vs; and NMR δ 0·66 (d, *J* 6·7 Hz, C-3 Me), 1·06 (d, 6·2, C-2 Me), 1·7 (m, H_2), 2·2 (m, H_3), 3·88 and 3·92 (4 OMe), 4·43 (d, 8·6, H_1), 5·16 (d, 8·2, H_4) and 6·8–7·2 (ArH): [lit[5] mp 128–129°; $[\alpha]_D^{25}$ + 34·2° (*c* 1·10, $CHCl_3$), and the NMR peaks are in accord with the literature values]. Admixture of our sample with authentic veraguensin did not show a mp depression, and the two gave identical IR spectra.

Acuminatin (**4**). Pooled column fractions 29–40 (67·8 mg) gave from isopropyl ether colorless needles of **4** mp 77·5° (Found: C, 73·94; H, 7·22. $C_{21}H_{24}O_4$ requires: C, 74·09; H, 7·11%); $[\alpha]_D^{27}$ + 43·3° (*c* 0·22, MeOH) UV max 275 nm (log ε 4·28) and shld at 312 (3·43); IR 1610, 1600 s, 1520 vs, 1495 s, 1465 s, 1455 s, 1335 s, 1260 vs, 1140 vs, 1025 s, 960 cm^{-1}; and mass spectrum *m/e* 340·1678 (M^+, 100%) with $C_{21}H_{24}O_4$ requiring 340·1674.

Isoeugenol cis-*epoxide benzoate* (**5**). *cis*-Isoeugenol benzoate[14] (1·61 g) in 30 ml $CHCl_3$ at 0° was treated dropwise (35 min) with 1·23 g *m*-chloroperbenzoic acid in 30 ml $CHCl_3$. After 31 hr at 5° the solution was extracted with dil $NaHCO_3$ aq and H_2O. The $CHCl_3$-soluble oil was chromatographed on activity V neutral alumina with benzene as solvent. Crystallization of the column fraction from benzene–light petroleum gave 267 mg of **5**: mp 83–84° (Found: C, 71·92; H, 5·89. $C_{17}H_{16}O_4$ requires: C, 71·82; H, 5·67%); UV max 282 nm (log ε 3·64), 275 (3·67) and 228 (4·32); IR 1738 (ester), 1260 and 830 cm^{-1} (epoxide); and NMR δ 1·13 (d, *J* 5·4, Me), 3·36 (m, β–H), 4·08 (d, 4·2, benzylic H) and 3·83 (OMe).

Isoeugenol trans-*epoxide benzoate* (**6**). *trans*-Isoeugenol benzoate[14] (1·61 g) was epoxidized as described for the *cis* isomer and the product crystallized, without prior chromatography, from benzene–light petroleum to give 857 mg of **6**: mp 79–80° (Found: C, 71·82; H, 5·69. $C_{17}H_{16}O_4$ requires: C, 71·83; H, 5·67%); IR 1738 (ester), 1255 and 842 cm^{-1} (epoxide); and NMR δ 1·45 (d, *J* 5·2, Me), 3·03 (m, β-H), 3·61 (d, 2·0, benzylic H and 3·81 (OMe).

Oxidation of acuminatin (**4**) *by the Lemieux–von Rudloff method.* Acumination (**4**, 186 mg) and anhyd Na_2CO_3 (42 mg) were dissolved in 67 ml t-BuOH and 111 ml H_2O, and treated with 928 mg $NaIO_4$ and 18 mg $KMnO_4$ in 45 ml H_2O for 48 hr with stirring. Solid $NaHSO_3$ was added to clear the soln which was then basified with solid Na_2CO_3. The solvent was removed by evaporation, H_2O was added and the mixture was extracted with $CHCl_3$. The $CHCl_3$-soluble oil (77 mg) was chromatographed on 5 g silicic acid eluting with solvents beginning with benzene and proceeding through increasing amounts of $CHCl_3$ to pure $CHCl_3$. The $CHCl_3$ fraction gave a homogeneous oil (**7**, 31 mg): $[\alpha]_D^{25}$ + 89° (*c* 2·2, MeOH); R_f 0·40 on TLC in silica gel G (benzene–$CHCl_3$): positive 2,4-dinotrophenylhydrazine reaction; mass spectrum *m/e* 328 (M^+, 100%), 313 (31), 253 (14), 164 (20) and 151 (41); IR 1685 vs, 1590 vs, 1377 vs, 1265 vs, 1140 vs, 1030 vs; uv max 304 nm (log ε 4·18), 288 (4·19) and 235 (4·39); and NMR δ 1·46 (d, *J* 6·8, Me), 3·58 (m, βH), 5·29 (d, 9·2), 3·89 (2 OMe), 3·97 (OMe), 6·9–7·1 (m, 3H, ArH), 7·3–7·5 (m, 2H, ArH) and 9·87 (CHO).

The Na_2CO_3 sol after removal of aldehyde **7** was acidified to pH 2 (HCl) and extracted with $CHCl_3$. The $CHCl_3$-soluble oil (20 mg) was treated with ethereal CH_2N_2 and the product purified on a short column of silicic acid eluting with $CHCl_3$. The one spot fraction (TLC, R_f 0·48 in benzene–$CHCl_3$ and R_f 0·82 in $CHCl_3$) weighed 9 mg and crystallized to give 4 mg of **11**, mp 107–108°, identical with (IR, NMR and mmp) an authentic synthetic sample.

Oxidation of acuminatin **4** *with* $KMnO_4$ *and methylation to product* **10**. Acuminatin (**4**, 200 mg) was dissolved in 30 ml Me_2CO and treated with 800 mg $KMnO_4$ over 0·5 hr at reflux temp. After another 0·5 hr of reflux the volume was reduced to 10 ml (40 ml) H_2O was added and the mixture boiled, then filtered to remove MnO_2. The filtrate at pH 9·0 was extracted with $CHCl_3$ then acidified to pH 2 (HCl) and extracted with $CHCl_3$. The $CHCl_3$-soluble amorphous material (**9**, 187 mg), one spot on TLC [R_f 0·73, $CHCl_3$–

HOAc (93:7)] and IR bands at 3500, 3320–3000, and 1685 cm^{-1} (COOH) had a D_2O exchangeable broad peak in the nmr at δ 8·80.

Methylation of 50 mg of acid **9** in Et_2O–MeOH (7:3) with ethereal CH_2N_2 gave a crude acid that was passed through a short silicic acid column in $CHCl_3$ to give **10** as an oil; IR 1710 vs, 1610 s, 1600 s, 1315 s, 1330 vs, 1250 vs and 1025 s: mass spectrum *m/e* 358·1417 (100%) [$C_{20}H_{22}O_6$ requires: 358·1416], 343 (8), 327 (8) and 151·0749 (15) [$C_9H_{11}O_2$ requires: 151·0759]; and NMR δ 1·44 (d, *J* 6·8, Me), 3·53 (m, β-H), 5·23 (d, 9·0), 3·89 (2 OMe), 3·91 and 3·94 (2 OMe), 6·8–7·0 (m, 3H, ArH), 7·5–7·6 (AB doublet, outer peaks too weak to designate, inner peaks at δ 7·53 and 7·55).

2,2',3-*Trimethoxy*-5-*formyl*-5'-*methoxycarbonylbiphenyl* (**14**). 5-Iodoveratraldehyde[11] (84·7 g) and methyl 3-iodo-4-methoxybenzoate[10] were dissolved in 700 ml dimethylformamide, then stirred under reflux with 140 g of copper bronze for 12 hr, at which time an additional 140 g of copper bronze was added and refluxing continued for 12 hr more. Cu salts were filtered from the cooled soln and the solvent evaporated at reduced pressure to give 105 g of a dark oil which when treated with 500 ml Et_2O deposited 22·5 g of **12**, mp 173–174° (from Et_2O) [lit[12] mp 174–175°]. (Found: C, 65·46; H, 5·60. $C_{18}H_{18}O_6$ requires: C, 65·44; H, 5·49%), IR 1715 cm^{-1} (ester), and NMR δ 3·81 (2 OMe, ether) and 3·88 (2 OMe, ester).

Concentration of the Et_2O soln to 200 ml deposited **13**, mp 137–138° (from Et_2O) [lit[13] mp 138–140°]. (Found: C, 65·46; H, 5·54. $C_{18}H_{18}O_6$ requires: C, 65·44; H, 5·49%), IR 1690 cm^{-1} (aldehyde), and NMR δ 3·78 and 3·98 (4 OMe), 7·41 and 7·53 (q, AB type, *J* 2, ArH) and 9·88 (CHO).

The oil from the Et_2O filtrate was dissolved in 175 ml benzene and extracted with 3–300 ml 1·35 M $NaHSO_3$. The $NaHSO_3$ extract was basified, extracted with $CHCl_3$ and the $CHCl_3$–soluble oil (22·8 g) yielded veratraldehyde mp 44–45° (from Et_2O) identical with an authentic sample.

The benzene–soluble oil (47·5 g) after removal of veratraldehyde was mixed with 100 ml sat $NaHSO_3$ sol and 70 ml EtOH. The mixture was filtered, diluted with H_2O to 400 ml, and extracted with ether. The ether residue crystallized from Et_2O to give 5·3 g of **14**. Acidification of the aqueous bisulfite soln, extraction with $CHCl_3$ and crystallization of the residue from Et_2O–light petroleum ether gave an additional 9·9 g of **14**: mp 91–92°. (Found: C, 65·42; H, 5·60. $C_{18}H_{18}O_6$ requires: C, 65·44; H, 5·49%); IR 1725 (ester) and 1695 cm^{-1} (aldehyde); UV max 258 nm (log ε 4·31) and 230 nm (4·81); and nmr δ 3·75, 3·85, 3·89 and 3·98 (OMe), 6·9–8·2 (AB and ABC spin systems, ArH), and 9·92 (CHO).

2,2',3-*Trimethoxy*-5,5'-*methoxycarbonylbiphenyl* (**11**). Compound **14** (1·5 g) was stirred in 75 ml 5% Na_2CO_3 soln and 6·0 g $KMnO_4$ added slowly. After stirring 21 hr, $NaHSO_3$ was added along with 5 ml conc HCl. The white ppt that formed was taken up in CH_2Cl_2 and after removal of solvent weighed 1·3 g, mp 274–277°. Without purification the acid was dissolved in 23 ml MeOH containing 1·8 ml acetyl chloride[15] and refluxed 21 hr. The solid remaining after evaporation of solvent crystallized from Et_2O–MeOH and then Et_2O to give 619 mg of **11**: mp 109–110°. (Found: C, 63·37; H, 5·65. $C_{19}H_{20}O_7$ requires: C, 63·33; H, 5·59%), IR 1710 cm^{-1}, UV max 258 nm (log ε 4·17) and 225 (4·29); NMR δ 3·90 (2 OMe, ester), 3.98, 3·85, 3·73 (OMe, ether), and 7·5–8.2 (AB and ABC spin systems, ArH).

Acknowledgments—This study was supported in part by Public Health Research Grant CA-08133 from the National Cancer Institute and FR-03328 from Special Research Resources for purchase of the nmr spectrometer (Varian A-60A) and accessories. We thank Dr. R. L. Folz of Battelle Memorial Institute, Columbus, Ohio, and Mr. R. Weisenberger of the Chemistry Department for the mass spectral determinations.

REFERENCES

1 *Pharmacopeia of the United States of America* (6th Decennial Revision) p. 215. William Wood, N.Y. (1883); *The Dispensatory of the United States of America* (20th Edition) p. 1479. (Edited by J. P. Remington and H. C. Wood) Lippincott, Philadelphia (1918)

2 N. V. Riggs and J. D. Stevens, *Aust. J. Chem.* **15**, 305 (1962)

3 J. B. McAlpine, N. V. Riggs and P. G. Gordon, *Ibid.* **21**, 2095 (1968)

4 G. K. Hughes and E. Ritchie, *Ibid.* **7**, 104 (1954)

5 N. S. Crossley and C. Djerassi, *J. Chem. Soc.* 1459 (1962)

6 A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products* p. 97. Macmillan, New York (1964).

7 H. Rottendorf, S. Sternhell and J. R. Wilmshurst, *Aust. J. Chem.* **18**, 1759 (1965)

8 L. M. Jackman and S. Sternhell, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* (2nd edition) p. 287. Pergamon Press, New York (1969)

[9] E. van Rudloff, *Canad. J. Chem.* **43**, 1784 (1965)
[10] F. G. Badder, L. S. El-Assal and V. B. Baghos, *J. Chem. Soc.* 1714 (1955)
[11] F. B. Wittmer and L. C. Raiford, *J. Org. Chem.* **10**, 527 (1945)
[12] J. Runeberg, *Acta Chem. Scand.* **12**, 188 (1958); Y. Sugi, *J. Pharm. Soc. Japan* **50**, 23 (1930)
[13] M. Nilsson, *Acta Chem. Scand.* **12**, 1830 (1958); K. Elbs and H. Lerch, *J. Prakt. Chem.* **93** [2], 1 (1916)
[14] F. Boedecker and H. Volk, *Ber. Dtsch Chem. Ges.* **64**, 61 (1931)
[15] J. Gmuender, *Helv. Chim. Acta* **36**, 2021 (1953)