NEW AND OLD PHENANTHRENE DERIVATIVES FROM *ONCIDIUM CEBOLLETA*, A PEYOTE-REPLACEMENT PLANT

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ABSTRACT.—A member of the family Orchidaceae, *Oncidium cebolleta* (Jacq.) Sw., is used by the Tarahumara Indians of northern Mexico as a temporary replacement for peyote. We have found it to contain the known compounds 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene (**2**), 2,7-dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene (**3**), 2,3-dihydroxy-4,7,8-trimethoxyphenanthrene (**1**), and the new compounds 2,7-dihydroxy-3,4-dimethoxyphenanthrene (**5**) and 2,7-dihydroxy-4,8-dimethoxyphenanthrene, (**6**).

The Tarahumara Indians of northern Mexico use a number of hallucinogenic plants in religious ceremonies and were one of the first peoples to gain publicity for their use of *Lophophora williamsii* (peyote) (1). Along with other plants, one important temporary replacement for peyote among the Tarahumara is *Oncidium cebolleta* (Jacq.) Sw. (Orchidaceae) (1). The whole, green leaf is said to be consumed after it is crushed in water. This member of the so-called "rat-tail" (Teretifolia or Cebolletae section) of *Oncidium* orchids was one of the first introduced from the Caribbean islands into Europe for culture. It was very early reported that "the natives use it externally . . . crushed with salt . . . wherein it has a great reputation [in treatment] of serious contusions, bone fractures, and other diseases" (2).[1] *Oncidium cebolleta* was listed as containing alkaloids (3), but no further work has been reported.

RESULTS

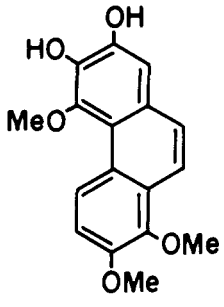
We obtained dried *O. cebolleta* from the Tarahumara country and found weak positive alkaloid tests in the methanol fraction from a small sample extracted successively with hexane, chloroform, and methanol. When the procedure was scaled up, no extracts positive for alkaloids were obtained. The chloroform fraction did, however, contain a number of isolable components, which were identified as follows.

TWO KNOWN PHENANTHRENES AND ONE KNOWN DIHYDROPHENANTHRENE.—A total of 114 g of dried *O. cebolleta* leaves yielded a chloroform extract, which was purified to give **1** (16 mg), **2** (7 mg), and **3** (4 mg). These structures were ensured by comparison with literature data on the compounds and their derived acetates (see Experimental section).

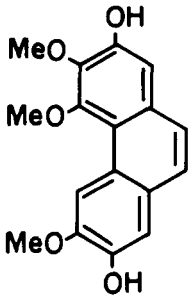
TWO NEW PHENANTHRENES.—The chloroform extract also yielded 8 mg of an unknown phenanthrene, which was obtained pure by plc and converted to a crystalline diacetate. Although spectral data could be interpreted in terms of a most likely structure for the unknown phenanthrene, an absolute proof could not be deduced. The structure of the diacetate was, therefore, determined by single crystal X-ray diffraction and found to be **4**. The phenanthrene could thus be assigned structure **5**. (Discussion of the X-ray crystal data is given in a following section.)

A second new phenanthrene (**6**), (10 mg), was also identified. It formed a diacetate

[1]Leaves are also used by indigenous peoples of Costa Rica for a variety of ailments (R. A. Ocampo, personal communication).



1



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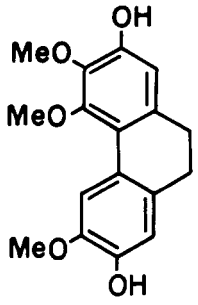

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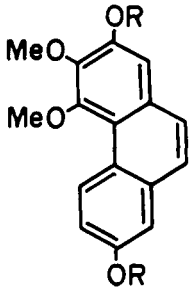
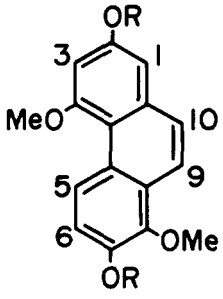
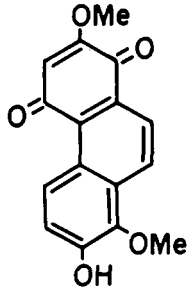


4: R=Ac
5: R=H



6: R=H
7: R=Ac



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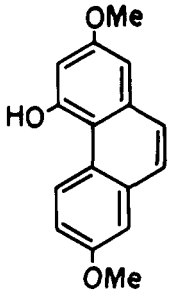

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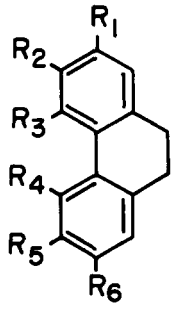

8: R_1=R_3=OMe; R_6=OH; R_2=R_4=R_5=H
9: R_3=OMe; R_1=R_6=OH; R_2=R_4=R_5=H
10: R_1=R_3=OMe; R_4=OH; R_2=R_5=R_6=H
13: R_1=OMe; R_3=R_5=OH; R_2=R_4=R_6=H

whose molecular formula was shown to be $C_{20}H_{18}O_6$ by high resolution mass spectrometry. The unknown itself, therefore, had the molecular formula $C_{16}H_{14}O_4$. It had a typical phenanthrene uv spectrum and two methoxy groups as established by the ^{1}H-nmr spectrum and the ^{13}C-nmr spectrum of the diacetate. The unknown was thus isomeric with **5**, differing only in substituent group placement.

The general substituent pattern could be determined by examination of the ^{1}H-nmr spectra of the unknown. One-half of an AB doublet was present at 9.17 ppm, indicating the presence of a proton at C-5. The doublet resonance was coupled to that of a one-proton absorbance at 7.20 ppm, which would mean that C-6 was unsubstituted. The occurrence of an absorption for only one proton in the downfield 9 ppm region showed that C-4 was substituted. The substituent at C-4 had to be a methoxy group because the C-5 proton absorption was at 9.47 ppm in the diacetate. Had there been an OH at C-4, acetylation would have shifted the C-5 proton *upfield* rather than downfield (4,5). One-proton doublets (J=2.4 Hz) occurred at 6.84 and 6.92 ppm. These col-

lapsed to singlets upon double irradiation. These data are characteristic of *meta*-coupled aromatic protons, which could only occur in ring A. A substituent must, therefore, be present at C-2. Protons at C-9 and C-10 appeared as an AB quartet (7.57 and 7.95 ppm, J=9.1 Hz), which is only the case when C-8 is substituted (5,6). The unknown was, therefore, a 2,4,7,8-tetrasubstituted phenanthrene, with a methoxy at the C-4 position.

The final structure proof as **6** was achieved by data from a series of nOe difference spectra obtained on the diacetate.[2] Irradiation of the C-4 methoxy methyl (4.18 ppm) gave an nOe difference spectrum showing enhancement only of the 7.15 ppm aromatic proton. Thus, the aromatic position next to the methoxy, that at C-3, must bear a proton. Irradiation at 7.15 ppm showed an enhancement only of the C-4 methoxy methyl. Irradiation of the second methoxy methyl, that at 4.00, gave an nOe difference spectrum that showed no enhancement of any proton resonances. There must be no aromatic protons on carbons neighboring the second methoxy group. Irradiation of each of the aromatic protons confirmed these data and also allowed assignments to be made.

Irradiation at 7.84 (the C-9 or C-10 proton) gave enhancements in the resonances at 8.21 and 7.41. Irradiation at 8.21 enhanced only the 7.84 resonance. We can, therefore, assign the 7.84 resonance to the proton at C-10 and the 8.21 resonace to the proton at C-9. The 7.41 resonance must be due to the proton at C-1. The doublet at 7.44 could be assigned to the proton at C-6, because irradiation at 7.44 gave enhancement only of the 9.47 ppm resonance. This also confirmed that the second methoxy could not be at C-7, inasmuch as no enhancement of the 4.00 methoxy methyl was observed. The only possible structure that can account for these data is **7**, and, hence, the isolated phenol must be **6**.

OTHER RESULTS.—We had only dried Mexican material for analysis, but it was important to investigate fresh plants, which is what are consumed directly (1). A number of "*Oncidium cebolleta*" plants were purchased from several commercial suppliers, but many of these bloomed out to be other species of the Teretifolia section of oncidiums. It is not possible to identify the species on the basis of vegetative growth alone. Several were, however, identified as authentic *O. cebolleta*, and enough fresh material was obtained for tlc analysis. Results with phenolic reagent sprays showed the crude chloroform extract from the fresh material to be very similar in phenolic content to that of the dried material, and nothing tractable could be identified from the methanol extract.

X-RAY STRUCTURE OF 4.—The structures of the two crystallographically independent molecules of **4** found in the asymmetric unit of the lattice are displayed in figure 1. Although the structures of molecules 1 and 2 of compound **4** are very similar in

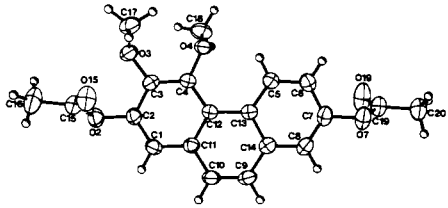

FIG. 1a. Final plot of the structure of molecule 1. Thermal elipsoids are drawn at the 40% probability level, and hydrogen atoms are shown with fixed, arbitrary radius for clarity.

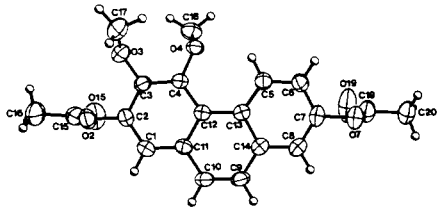

FIG. 1b. Final plot of the structure of molecule 2, drawn as described above.

[2]We are indebted to B. Hawkins an the NSF Regional NMR Center at Colorado State University for obtaining these series of data.

most respects, it can be seen from figure 1 that the acetyl substituent at C-2 occupies positions on opposite sides of the phenanthrene ring in these two cases. Interconversion of molecules 1 and 2 is presumably very easy, as rotation of this acetyl group about the C-2 O-2 bond should be relatively unhindered on the C-1 side. It is not clear from examination of packing diagrams which interactions cause these two different forms of **4** to co-crystallize.

TABLE 1. Bond lengths (Å) and Angles (deg).[a]

Molecule 1				Molecule 2			
C1-C2	1.351(4)	C1-C11	1,401(3)	C1-C2	1.358(3)	C1-C11	1.396(3)
C2-C3	1.400(3)	C2-O2	1.400(3)	C2-C3	1.392(3)	C2-O2	1.396(3)
C3-C4	1.375(3)	C3-O3	1.367(3)	C3-C4	1.384(3)	C3-O3	1.370(3)
C4-C12	1.416(3)	C4-O4	1.379(3)	C4-C12	1.428(3)	C4-O4	1.369(3)
C5-C6	1.377(4)	C5-C13	1.414(3)	C5-C6	1.367(4)	C5-C13	1.409(3)
C6-C7	1.385(4)	C7-C8	1.348(4)	C6-C7	1.385(4)	C7-C8	1.353(4)
C7-O7	1.404(3)	C8-C14	1.401(3)	C7-O7	1.405(3)	C8-C14	1.407(4)
C9-C10	1.341(4)	C9-C14	1.424(4)	C-9-C10	1.331(4)	C9-C14	1.414(3)
C10-C11	1.429(3)	C11-C12	1.424(3)	C10-C11	1.434(3)	C-11-C12	1.424(3)
C12-C13	1.464(3)	C13-C14	1.427(3)	C12-C13	1.453(3)	C13-C14	1.428(3)
C15-C16	1.487(4)	C15-O2	1.379(3)	C15-C16	1.482(4)	C15-O2	1.363(4)
C15-O15	1.179(3)	C17-O3	1.437(3)	C15-O15	1.179(4)	C17-O3	1.418(4)
C18-O4	1.429(3)	C19-C20	1.481(4)	C18-O4	1.427(3)	C19-C20	1.485(4)
C19-O7	1.351(3)	C19-O19	1.177(4)	C19-O7	1.337(4)	C19-O19	1.197(5)
C2-C1-C11	120.2(2)	C1-C2-C3	120.7(2)	C2-C1-C11	120.2(2)	C1-C2-C3	120.8(2)
C1-C2-O2	120.6(2)	C3-C2-O2	118.6(2)	C1-C2-O2	120.8(2)	C3-C2-O2	118.4(2)
C2-C3-C4	119.8(2)	C2-C3-O3	116.9(2)	C2-C3-C4	120.2(2)	C2-C3-O3	118.1(2)
C4-C3-O3	123.3(2)	C3-C4-C12	121.8(2)	C4-C3-O3	121.7(2)	C3-C4-C12	121.2(2)
C3-C4-O4	117.6(2)	C12-C4-O4	120.5(2)	C3-C4-O4	118.4(2)	C12-C4-O4	120.5(2)
C6-C5-C13	122.0(2)	C5-C6-C7	119.6(2)	C6-C5-C13	122.0(2)	C5-C6-C7	119.7(2)
C6-C7-C8	120.7(2)	C6-C7-O7	119.9(2)	C6-C7-C8	121.2(2)	C6-C7-O7	119.8(2)
C8-C7-O7	119.3(2)	C7-C8-C14	121.3(2)	C8-C7-O7	118.9(2)	C7-C8-C14	120.3(2)
C10-C9-C14	121.3(2)	C9-C10-C11	121.6(2)	C10-C9-C14	121.5(2)	C9-C10-C11	121.4(2)
C1-C11-C10	119.1(2)	C1-C11-C12	121.2(2)	C1-C11-C10	119.0(2)	C1-C11-C12	121.5(2)
C10-C11-C12	119.7(2)	C4-C12-C11	116.1(2)	C10-C11-C12	119.4(2)	C4-C12-C11	116.1(2)
C4-C12-C13	125.1(2)	C11-C12-C13	118.7(2)	C4-C12-C13	124.9(2)	C11-C12-C13	119.0(2)
C5-C13-C12	124.8(2)	C5-C13-C14	116.6(2)	C5-C13-C12	125.1(2)	C5-C13-C14	116.9(2)
C12-C13-C14	118.6(2)	C8-C14-C9	120.3(2)	C12-C13-C14	118.1(2)	C8-C14-C9	119.9(2)
C8-C14-C13	119.8(2)	C9-C14-C13	120.0(2)	C8-C14-C13	119.8(2)	C9-C14-C13	120.3(2)
C16-C15-O2	110.5(2)	C16-C15-O15	127.3(3)	C16-C15-O2	110.1(3)	C16-C15-O15	127.6(4)
O2-C15-O15	122.1(2)	C20-C19-O7	111.3(2)	O2-C15-O15	122.3(3)	C20-C19-O7	112.7(3)
C20-C19-O19	126.5(3)	O7-C19-O19	122.2(2)	C20-C19-O19	125.8(3)	O7-C19-O19	121.5(3)
C2-O2-C15	115.9(2)	C3-O3-C17	116.0(2)	C2-O2-C15	116.4(2)	C3-O3-C17	114.7(2)
C4-O4-C18	115.8(2)	C7-O7-C19	118.3(2)	C4-O4-C18	115.8(2)	C7-O7-C19	117.9(2)

[a]Estimated standard deviations in the least significant digits are reported in parentheses.

The planarity of the two phenanthrene rings, as well as the bond length patterns seen in these rings (see table 1), are very similar to those found in unsubstituted phenanthrene (7). In both mescaline hydrobromide (8) and reserpine (9), three methoxy groups are bound to consecutive carbon atoms of a phenyl ring. In both of these cases, the outer pair of methoxy substituents are approximately coplanar with the aromatic ring, while the central methoxy group is held approximately perpendicular to the ring. Such an arrangement is impossible for the O-4 methoxy group of **4**, due to steric clashes between the C-18 methyl group on O-4 and atoms H-5 and O-3. In **4**, the O-3 methoxy group is not nearly perpendicular to the phenanthrene ring, but makes a dihedral angle of only 57.9°, with the phenanthrene ring in molecule 1 and a similar, but larger, angle (67.6°) in molecule 2. This larger dihedral angle presumably is a result of the fact that the acetyl group at C-2 is on the opposite side of the ring in that molecule.

DISCUSSION

Phenanthrenes, dihydrophenanthrenes, and their related stilbenes and bibenzyls occur sporadically in botanically rather widely separated genera (10). Such compounds from the genera *Dioscorea, Tamus, Combretum,* and *Juncus*, for example, have been shown to have biological properties as diverse as dormancy inhibition in yam tubers, inhibition of termite and borer insects in wood, cytotoxicity, and antitumor activity. From the orchid family, the dihydrophenanthrenes orcinol (**8**), hircinol (**9**), and loroglossol (**10**) of the genera *Orchis* and *Loroglossum* are phytoalexins active against plant fungal diseases (11). The related phenanthrene quinone (**11**) is the active principle of the orchid *Cypripedium calceolus*, which causes contact dermatitis (12). Interesting in the present context is the fact that **12** and **13** have been found in the opium poppy (*Papaver somniferum*) (10) and in marihuana (*Cannabis sativa*) (13), respectively. No suggestions have been made that **12** or **13** contributes to the pharmacological activity of those entities, nor do we have evidence that the compounds we have isolated from *Oncidium cebolleta* account for its use as a peyote-replacement plant. In spite of several attempts, we have not been able to identify other secondary metabolites in this species. The question of biological activity for **1-3**, **5**, and **6** remains an open one at present.

EXPERIMENTAL

ISOLATION AND PURIFICATION.—Leaves of *Oncidium cebolleta* were collected in the Rio Chinipas region of northern Mexico in 1978, air dried, and cut into small pieces. The dried material (114 g) was extracted in a Soxhlet successively with 2.5 liters of hexane, chloroform, and methanol. The methanol was evaporated to dryness to leave 4.3 g of residue. This was dissolved in 150 ml of 2 N sufuric acid, extracted with chloroform, made basic to ph 9 with NH_4OH and extracted with two 100-ml portions of chloroform, followed by three 100-ml portions of butanol. The chloroform, methanol, and butanol extracts were evaporated to dryness and tested by tlc with iodoplatinic acid visualization. No alkaloid-positive spots were noted. An early test of 1 g of plant was weakly positive.

Evaporation of the chloroform extract of the plant material yielded 4.0 g of residue. A portion (3.0 g) was chromatographed in silica gel with a low pressure system (14) and eluted with 33, 50, and 67% EtOAc in hexane, followed by pure EtOAc. Residues from fractions 1-24 showed only alkane-type ^{1}H-nmr absorptions. Fractions 25 and 26 were combined to give 84 mg of residue showing aromatic proton nmr absorptions, as did the combination of fractions 27-29 (141 mg).

The 141 mg of fractions 27-29 were rechromatographed as above, eluting with pure chloroform. Fractions 4-7 were combined, evaporated, and purified by silica gel (chloroform-methanol 25:1) plc to yield 16 mg of **2**. Fractions 18-20 were combined, evaporated, and the residue purified by plc as above to yield 10 mg of **6**.

The 84 mg of fractions 25 and 26 from the original chromatography were rechromatographed at low pressure with pure chloroform as eluent. Fractions 8-12 were combined, evaporated, and purified by plc (chloroform-methanol 24:1) to yield 8 mg of **5**. Fractions 3-7 were combined and purified by plc to yield 4 mg of **1** (lower band) and 7 mg of **3** (upper band).

STRUCTURE IDENTIFICATION.—Compounds **1** and **2** both showed uv spectra typical of phenanthrenes and ^{1}H-nmr spectra indicating the presence of three methoxy groups. Both formed diacetates and, hence, were isomeric dihydroxytrimethoxyphenanthrenes. Letcher isolated and studied many pentasubstituted phenanthrenes from *Combretum* and *Tamus* species (15), but was able to furnish a standard sample only of 3,8-diacetoxy-2,4,7-trimethoxyphenanthrene.[3] This was not identical with either **1** or **2**; **2** could, however, be positively identified as 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene by comparison of its ^{1}H-nmr spectrum and that of its diacetate with values from the literature (16).

The second pentasubstituted phenanthrene, **1**, also had a methoxy group at C-4, because formation of the acetate derivative caused an upfield shift of the C-5 proton (from 9.18 to 9.44 ppm) (15). The C-5 proton was a doublet, and, hence, the C-6 carbon must bear a proton. The most likely structure was, therefore, a 2,3,4,7,8-pentasubstituted phenanthrene with a methoxy at C-4. Proof of the structure of **1** as 2,3-dihydroxy-4,7,8-trimethoxyphenanthrene was accomplished by comparison of the ^{1}H-nmr spectrum of its acetate with that of the known acetate prepared by Letcher (15).

The structure of the 9,10-dihydrophenanthrene derivative **3** was assured by comparison of the ^{1}H-

[3]We appreciate receiving this sample and useful correspondence from R. M. Letcher.

TABLE 2. Fractional Atomic Coordinates (x 10^4).[a]

Molecule 1				Molecule 2			
Atom	x	y	z	Atom	x	y	z
C1	11016(3)	823(1)	5671(3)	C1	13510(3)	1618(1)	481(3)
C2	9851(3)	695(1)	6356(3)	C2	14683(3)	1786(1)	955(3)
C3	8743(3)	835(1)	7173(3)	C3	16011(3)	1696(1)	1854(3)
C4	8840(3)	1106(1)	7287(3)	C4	16163(3)	1430(1)	2254(3)
C5	9373(3)	1708(1)	7685(3)	C5	16179(3)	840(1)	3214(3)
C6	9686(3)	1975(1)	7834(3)	C6	16176(3)	573(1)	3495(3)
C7	10956(3)	2080(1)	7122(3)	C7	14997(4)	418(1)	2763(3)
C8	11897(3)	1924(1)	6298(3)	C8	13799(3)	527(1)	1834(3)
C9	12642(3)	1490(1)	5265(3)	C9	12472(3)	915(1)	619(3)
C10	12430(3)	1228(1)	5130(3)	C10	12382(3)	1175(1)	342(3)
C11	11158(3)	1098(1)	5817(3)	C11	13617(3)	1350(1)	901(3)
C12	10075(3)	1250(1)	6659(3)	C12	14951(3)	1246(1)	1813(3)
C13	10320(3)	1535(1)	6832(3)	C13	14999(3)	965(1)	2210(3)
C14	11623(3)	1651(1)	6129(3)	C14	13759(3)	802(1)	1541(3)
C15	9914(3)	277(1)	7639(4)	C15	15269(4)	2143(1)	−732(4)
C16	9403(5)	−2(1)	7372(4)	C16	15196(5)	2436(1)	−832(5)
C17	7454(4)	706(1)	9523(4)	C17	17354(5)	1928(1)	4011(4)
C18	6232(3)	1260(1)	7227(4)	C18	18875(3)	1358(1)	2249(4)
C19	10365(3)	2531(1)	6523(4)	C19	15841(4)	−13(1)	2208(4)
C20	10896(4)	2803(1)	7041(4)	C20	15755(4)	−295(1)	2702(4)
O2	9691(2)	420(1)	6202(2)	O2	14562(2)	2057(1)	607(2)
O3	7572(2)	691(1)	7777(2)	O3	17154(2)	1875(1)	2301(3)
O4	7720(2)	1236(1)	8104(2)	O4	17500(2)	1348(1)	3115(2)
O7	11330(2)	2348(1)	7349(3)	O7	14972(2)	145(1)	3084(2)
O15	10450(2)	372(1)	8873(2)	O15	15821(3)	1996(1)	−1649(4)
O19	9279(3)	2472(1)	5740(3)	O19	16594(4)	73(1)	1157(4)

[a]Estimated standard deviations in the least significant digits are reported in parentheses.

nmr data for **3** and its diacetate with the data reported for 2,7-dihydroxy-3,4,5-trimethoxy-9,10-dihydrophenanthrene isolated by Letcher (16).

The structure of **5** was determined by X-ray diffraction on the diacetate **4**. Because both **5** and its diacetate are new compounds, their spectral data are given here.

5: $C_{16}H_{14}O_4$ (found by high resolution ms: 270.0920; calcd for $C_{16}H_{14}O_4$: 270.0912); uv (EtOH) 365, 347, 330, 304, 293sh, 284, 259, 232, and 211 nm; uv (EtOH, OH^-) 393, 376, 320, 307, 270, and 217 nm; ms *m/z* 270(100%), 255(42), 212(40); ^{1}H-nmr (60 MHz, $CDCl_3$) 3.97 (s, 3H), 4.10 (s, 3H), 7.17 (s, 1H), 7.17 (dd, 1H, *J*=10 and 1 Hz), 7.26 (d, 1H, *J*=1 Hz), 7.50 (s, 2H), 9.35 ppm (d, 1H, *J*=10 Hz); ^{1}H-nmr of **5** diacetate mp 159° (360 nmr $CDCl_3$); 2.39 (s, 3H), 2.42 (s, 3H), 4.02 (s, 3H), 4.05 (s, 3H), 7.38 (s, 1H), 7.38 (dd, 1H, *J*=10 and 1 Hz), 7.58 (d, 1 H, *J*=1 Hz), 7.60 (s, 2H), 9.59 ppm (d, 1H, *J*=10 Hz).

The new phenol **6**, whose structure assignment was discussed in the results section, gave the following data: ^{1}H-nmr (60 MHz $CDCl_3$): 3.92 (s, 3H), 4.09 (s, 3H), 6.84 (d, 1H, *J*=2 Hz), 6.92 (d, 1H, *J*=2 Hz), 7.20 (d, 1H, *J*=9 Hz), 7.57 (d, 1H, *J*=9 Hz), 7.95 (d, 1H, *J*=9 Hz), 9.17 ppm (d, 1H, *J*=9 Hz); uv (EtOH): 327 sh, 309, 295 sh, 285 sh, 263, 228 sh, 210 nm; uv (EtOH, OH^-): 309 sh, 299 sh, 283, 269, 220 nm. Acetylation gave a diacetate **7**, $C_{20}H_{18}O_6$ (exact mass found 354.1096, calcd. 354.1104); ^{1}H-nmr (360 MHz d_6-acetone) 2.35 (s, 3H), 2.39 (s, 3H), 4.00 (s, 3H), 4.18 (s, 3H), 7.15 (d, 1H, *J*=2.4 Hz), 7.41 (d, 1H, *J*=2.4 Hz), 7.44 (d, 1H, *J*=9.4 Hz), 7.84 (d, 1H, *J*=9.1 Hz), 8.21 (d, 1H, *J*=9.1 Hz), 9.47 ppm (d, 1H, 9.4 Hz).

X-RAY STRUCTURE DETERMINATION FOR **4**.—Crystals of **4** were grown by slow evaporation from ethanol. A colorless, single crystal measuring 0.20([10$\bar{1}$]) x 0.21([010]) x 0.34([101])mm^3 was carefully centered on the Nicolet *R*3 diffractomer. Least squares treatment of the setting angles for 20 reflections yielded cell constants as follows: a=8.637(1) Å, b=50.511(6) Å, c=8.158(1) Å, β=94.30(1) Å, V=3549 Å^3. Systematic absences ($h0\ell$, $\ell=2n+1$; $0k0$, $k=2n+1$) indicated the space group $P2_1/c$ (No. 14) (17), which with Z=8 ($\rho_{calcd.}$ = 1.33 g cm^{-3}) demanded two molecules of **4** per asymmetric unit. All accessible data for which 3.6° <2θ<135°, $h\geq0$, and $k\geq0$ were collected using CuK_α radiation (graphite

monochromator). The θ-2θ scan mode was employed, with a scan range of $[2.0° + (2\theta_{K_{\alpha_1}} - 2\theta_{K_{\alpha_1}})]$, a variable scan speed (2.02-29.30 deg min^{-1}), and background counted for one-half the total scan time. The intensities of three control reflections were measured every 100 reflections, and no significant change in these intensities was noted during the course of data collection. *Lp* corrections were applied to the data, but no absorption correction was applied due to the small crystal size and low absorption coefficient ($\mu = 7.78$ cm^{-1}). Of the 4983 unique reflection intensities measured, 3564 exhibited $I > 2\sigma(I)$ and were included in further calculations.

Structure solution and refinement were carried out by use of the SHELXTL program package written by G. M. Sheldrick and supplied by Nicolet XRD, Inc., for the Data General Eclipse S/140 computer in our laboratory. Solution of the structure was accomplished by the direct-methods routine SOLV from this package. Least squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms, with hydrogen atoms in idealized positions 0.96 Å from carbon, and with reflection weights calculated as $[\sigma^2(F) + gF^2]^{-1}$, where $g = 5.5 \times 10^{-4}$. Convergence of the 493 least squares parameters was indicated by an average shift/standard deviation < 0.1, with the maximum shift/estimated standard deviation < 0.5. Final values for the residual indices were: $R = 0.047$, $R_w = 0.055$, and the error in an observation of unit weight $= 2.08$. The highest peak in the final difference Fourier synthesis showed a density of 0.29e $Å^{-3}$. The final atomic coordinates for the two independent molecules of **4** are listed in table 2, while bond lengths and angles derived from these coordinates are listed in table 1. The following tables have been submitted for deposition[4]: table 3, the anisotropic thermal parameters for the non-hydrogen atoms; table 4, hydrogen atom positions and isotropic thermal parameters; table 5, equations for and displacements from least squares planes; table 6, a listing of F_o and F_c. The numbering scheme used in these tables is depicted for both of the crystallographically independent molecules of **4** figure 1.

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[4]These tables are available from O. P. Anderson.