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CERATIOLIN AND OTHER FLAVONOIDS FROM *CERATIOLA ERICOIDES*

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Key Word Index—*Ceratiola ericoides*; Empetraceae; ceratiolin; chalcone; dihydrochalcones; flavanones; catechins; proanthocyanidins.

Abstract Chemical analysis of ground aerial parts of *Ceratiola ericoides* yielded the two known dihydrochalcones angoletin and 2',6'-dihydroxy-4-methoxy-3',5'-dimethyldihydrochalcone, as well as 2',4'-dihydroxychalcone. Furthermore, the known flavanones 7-hydroxyflavanone, 8-methylpinocembrin and 6,8-dimethylpinocembrin were isolated. Methanol extracts of ground leaves provided catechin, epicatechin and epicatechin-(4$\beta \rightarrow 8$; 2$\beta \rightarrow O \rightarrow 7$)-epicatechin. From water washes of freshly harvested leaves a novel dihydrochalcone, ceratiolin, was isolated. The structures were inferred from NMR, mass spectral and chemical data, and the molecular structure of 6,8-dimethylpinocembrin was determined by single crystal X-ray analysis.

INTRODUCTION

Ceratiola ericoides is a monotypic genus, which is one of only three genera in the Empetraceae. An endemic of the Florida scrub community, *Ceratiola* is locally dominant on disturbed sites. The absence of herbaceous growth around *Ceratiola* plants has prompted investigation of its allelopathic potential. Preliminary results from extensive bioassays and field transplants showed that water soluble litter extracts strongly inhibited germination and radicle growth of native grasses of the adjacent sandhill community; however, water soluble extracts of fresh leaves were only mildly allelopathic [1]. Although chromatographic patterns of the flavonoids of *Ceratiola* had been previously carried out in connection with a biochemical system study of the Empetraceae [2], an extensive re-investigation of this species was performed in a search for the allelopathic constituent(s).

RESULTS AND DISCUSSION

Crude dichloromethane extracts of *C. ericoides* leaves were chromatographed on a Sephadex LH20 column using a mixture of chloroform methanol (1:1). Early fractions contained a mixture of ursolic acid and erythrodiol in a 4:1 ratio. Intermediate fractions, which contained mixtures of flavonoids, were re-chromatographed over silica gel yielding pure compounds **1**–**6**.

The structures of the dihydrochalcones **1** and **2** were established by comparison of their ^{1}H NMR and MS spectral data with literature values [3–5]. The ^{13}C NMR spectrum of **2** (Table 1) was assigned by correlation with values reported for compound **1** [5]. Also, by comparison with the data for compound **2**, the interchangeable ^{13}C values reported for **1** could be unambiguously assigned.

The structure of flavanone **3** was assigned by comparison of its ^{1}H NMR data with values reported in the literature [6]. The ^{1}H NMR spectrum of compound **4** was nearly identical with that of **3** except for the appearance of a singlet at δ6.0 and the lack of a three-proton singlet. The UV spectrum showed a shift, as with pinocembrin [7], to longer wavelength when treated with $AlCl_3$, MeOH, indicating that there is no alkyl substitution at C-6 [8] leaving position 8 as the only possible site for the methyl substituent. Compound **5** [9] had a ^{1}H NMR spectral pattern similar to those of compounds **3** and **4** except for the following hydrogen absorptions of the A-ring: the doublet at δ6.48 (J = 2 Hz) was assigned to H-8, the doublet of a doublet at δ6.56 (J = 8.5; 2 Hz) to H-6, and the doublet at δ7.87 (J = 8.5 Hz) to H-5. Compound **6** [10] exhibited a ^{1}H NMR spectrum with a complex coupling pattern in the aromatic region. Therefore, the coupling constants were derived from a two-dimensional J-resolved ^{1}H NMR spectrum and are presented in the Experimental.

Partitioning of the methanol wash of ground aerial parts of *C. ericoides* between water and ethyl acetate yielded catechin, epicatechin, epicatechin-(4$\beta \rightarrow 8$; 2$\beta \rightarrow O \rightarrow 7$)-epicatechin (A-2 dimer) (**7**) and other unidentified proanthocyanidins. Silica gel column chromatography provided fractions which were acetylated to better facilitate the separation and identifications of the relatively polar phenolic constituents. The structures of the acetates of catechin and epicatechin were established on the basis of their ^{1}H NMR data, and in the case of epicatechin acetate, its ^{13}C NMR spectrum. The structures were confirmed by TLC and NMR comparisons with known standards.

The ^{1}H NMR spectrum of the acetate of **7** exhibited sharp peaks indicating a rigid oligomer of the A-type, in contrast to the B-type dimers where rotation around the 4u-8l bond is possible [11]. The chemical shifts were very similar to the ones described by Jacques and Haslam [12] but since the coupling constants were not obtainable at lower field [12], the 200 MHz ^{1}H NMR data are included in the Experimental. The presence of nine acetyl carbonyls and the shift of the C-2 signal from around δ77 to near

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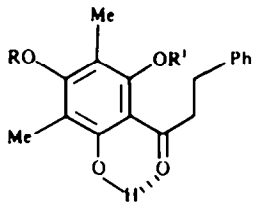
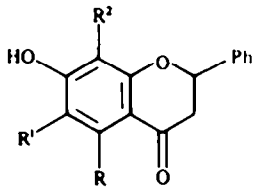
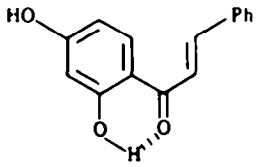


1 R = H, R' = Me
2 R = Me, R' = H



	R	R'	R²
3	OH	Me	Me
4	OH	H	Me
5	H	H	H



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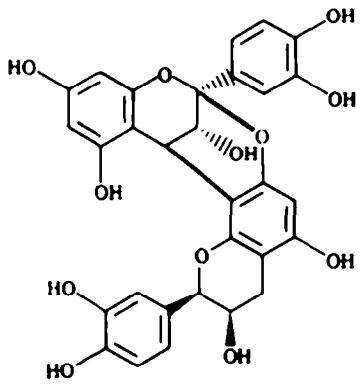

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Table 1. ^{13}C NMR data* of compounds 1†, 2, and 7 (50.32 MHz)

Carbon	1	2 ($CDCl_3$)	8 (MeOH-d_4)
C_1	141.7 *s*	141.6 *s*	142.5 *s*
C_2	128.5 *d*	128.4 *d*	129.4 *d*
C_3	128.5 *d*	128.4 *d*	129.4 *d*
C_4	126.0 *d*	125.9 *d*	127.0 *d*
C_5	128.5 *d*	128.4 *d*	129.4 *d*
C_6	128.5 *d*	128.4 *d*	129.4 *d*
C'_1	106.6 *s*	-	105.9 *s*‡
C'_2	159.2 *s*	158.2 *s*	191.0 *s*
C'_3	109.0 *s*	108.6 *s*	104.0 *s*‡
C'_4	159.2 *s*	162.7 *s*	174.5 *s*
C'_5	108.6 *s*	108.6 *s*	65.7 *s*
C'_6	161.5 *s*	158.2 *s*	198.0 *s*
C_α	44.7 *t*	46.1 *t*	41.9 *t*
C_β	31.0 *t*	30.6 *t*	32.4 *t*
CO	205.2 *s*	205.7 *s*	201.9 *s*
OMe	61.9 *q*	60.3 *q*	
C-3'-Me	7.5 *q*	8.2 *q*	7.0 *q*
C-5'-Me	8.6 *q*	8.8 *q*	28.8 *q*

*Peak multiplicities of compounds 2 and 8 were determined by heteronuclear multipulse programs (DEPT).

†Data obtained from ref. [5].

‡Assignments are interchangeable.

*We wish to thank Professor E. Haslam for a generous gift of the A-2 dimer.

δ100 in the ^{13}C NMR spectrum indicated an A-type dimer [13, 14]. Co-TLC and ^{1}H NMR comparisons with the authentic sample of the acetate prepared from an A-2 dimer* confirmed its structural identity.

Ceratiolin (8) was obtained from fresh plant material by soaking whole leaves in water at ambient temperature. Compound 8 was the major constituent present in the water washes extracted with EtOAc $CHCl_3$ (1:1). Elemental analysis and the observed molecular ion (M, 302) from the GC-MS of the acetylated derivative gave the molecular formula $C_{17}H_{18}O_5$. The mass spectral peaks at m/z 91, 105 and 133 were typical of a β-phenylpropionyl moiety. Formation of two 2,4-dinitrophenylhydrazones indicated the presence of at least two carbonyl groups. An IR band at 1668 cm^{-1} was consistent with a cross-conjugated carbonyl system and another band at 1640 cm^{-1} was in accordance with a further carbonyl group that is both conjugated and hydrogen-bonded [10]. The ^{1}H NMR spectrum of 8 was similar to those of 1 and 2 except for the chemical shifts of the two methyl groups. A three-proton singlet at δ1.50 ppm as well as a quartet at δ28.8 in the ^{13}C NMR spectrum was in accordance with a methyl group on a carbon bearing a hydroxyl group. Another three-proton singlet at δ1.85 ppm indicated the presence of a methyl group on a double bond. The appearance of a quartet at 7 ppm in the ^{13}C NMR spectrum strongly suggested a methyl group on a double bond which is part of an enol moiety [5, 15]. The CD data failed to detect an optically active centre which

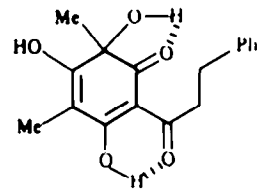
implied the presence of a nonenzymatically formed racemic mixture at C-5'. The ^{13}C NMR assignments were made by comparison of the spectrum to those of the dihydrochalcones **1** and **2**.

An *in situ* trichloroacetylisocyanate (TAI) derivatization [16] revealed the presence of two reactive hydroxyl groups. The tertiary hydroxyl group which gave a slower reaction caused an expected β shift of $\Delta\delta + 0.141$ for the methyl signal at $\delta 1.50$. The presence of a D_2O exchangeable ^1H NMR signal at $\delta 18.86$ along with a dark green positive $FeCl_3$ test suggested the presence of an enol group. The large downfield shift of this signal could be accommodated by a tricarbonylmethine system as in **8** or **9** [17]. In similar systems, the tautomer with extended conjugation is the more favoured form as the 2 : 1 ratio of the tautomers **10** and **11** indicates [18].

Despite the similarity of the A-ring in compounds **10** and **11** with ceratiolin (**8**), the latter compound surprisingly exists as a single tautomer (**8**) as detected by ^1H NMR in a temperature range between $-80°$ (in CD_2Cl_2) and $+100°$ (CD_3-NO_2). This exclusive preference for **8** may be due to two factors: in tautomer **9** the electron-rich tertiary alcohol function is adjacent to the enol group which is a less stable molecular arrangement [19]. Moreover, for tautomer **8** a second hydrogen bonding is possible between the hydroxyl at C-5' and the carbonyl oxygen at C-6' which further contributes to a higher stability of **8** over **9**. This second contribution also supports the biogenetically favoured positions of the hydroxyl group at C-4' and methyl at C-3' rather than the possible isomer with a reverse attachments of substituents. Biogenetically, ceratiolin appears to be an oxidative derivative of the dihydrochalcone (**12**). Epoxidation at C-5' of **12** followed by opening of the epoxide ring, as indicated by the arrows, would provide ceratiolin (**8**).

The successive losses of *m/z* 43 and *m/z* 18 in the mass spectrum of **8** can be formulated as a benzilic acid type rearrangement of the six-membered ring resulting in a five-membered ring. Rearrangements of this type have been observed [20] and variations of it reported for constituents of *Myrica gale* [4]. Biogenetic pathways involving similar rearrangements have also been proposed [21].

Ceratiolin (**8**) slowly decomposes either neat or in water solution at ambient temperature to yield hydrocinnamic acid along with other unidentified products, a process involving an acid cleavage of the tricarbonyl methine group. Ceratiolin itself exhibits only moderate inhibitory activity in germination and radicle growth bioassays, but



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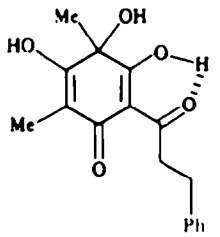

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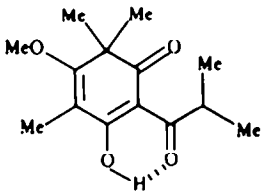

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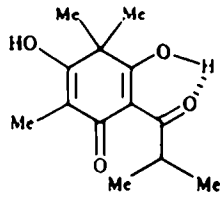

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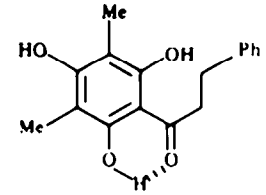

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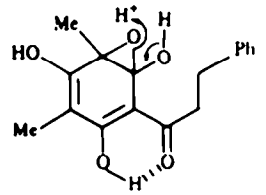

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[O] → **8**

hydrocinnamic acid shows considerable inhibitory activity on seed germination and radicle growth. The differences in activity may explain why field collections of decomposing litter of *C. ericoides* are much more active than the fresh leaves [1].

Crystal structure analysis of 6,8-*dimethylpinocembrin* (3)

The molecular structure of 6,8-dimethylpinocembrin (3) is illustrated in Fig. 1, and its conformation is described by the torsion angles in Table 2. The space group is centrosymmetric, and thus the compound is shown to be racemic. The phenyl group is disordered into two conformations, and the model chosen for its refinement led to some unrealistic bond distances and angles. The geometry in the remainder of the molecule appears much more chemically reasonable. The heterocyclic ring has a puckered conformation in which endocyclic torsion angles about C4–C10 and C9-C10 are both near zero, thus only C2 is significantly out of plane. This conformation has approximate local C_s symmetry, with C10 and C2 lying on the mirror. This conformation can be compared with that of (−)-6-bromocryptostrobin [22], which differs only by substitution of bromine for methyl at C6. The heterocyclic ring in that molecule is somewhat more puckered and more deviant from local mirror symmetry (Table 2).

The fused aromatic ring has its six atoms an average of 0.009(4) Å from their common plane, with maximum deviation 0.015(5) Å for C9. Full substitution of this ring causes several of its substituents to lie out of this plane, deviations for O3, C4, C11, and C12 being 0.037(4), 0.035(5), −0.061(6) and 0.061(5) Å, respectively. Except for those affected by disorder, bond distances are normal, with esds 0.003–0.004 Å. C–C distances in the aromatic ring average 1.394 Å, C–OH bonds average 1.362 Å and C–C (methyl) bonds average 1.505 Å. Bonds which appeared anomalously long in 6-bromocryptostrobin due to data collection difficulties, notably C7–C8 and C8–C12, are normal here: 1.392(3) and 1.511(3) Å, respectively.

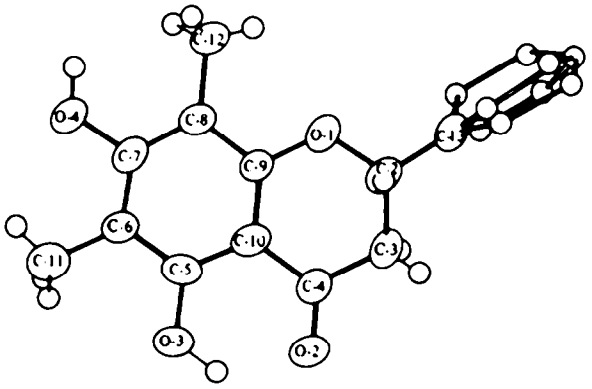

Fig. 1. The molecular structure of 6,8-dimethylpinocembrin. H atoms and disordered phenyl carbon atoms are represented by circles of arbitrarily small size.

Table 2. Selected torsion angles (deg.)

Atoms	6,8-Dimethyl-pinocembrin	6-Bromocrypto-strobin
O1–C2–C3–C4	−37.0	−53.8
C2–C3 C4–C10	19.0	32.1
C3–C4–C10–C9	−1.0	−4.8
C4–C10–C9–O1	−0.2	−1.3
C10 C9 O1 C2	−17.5	−21.9
C9–O1–C2–C3	36.7	49.3

The compound displays both intramolecular and intermolecular hydrogen bonding in the crystal. The intramolecular H bond O2 . . . O3 is short, with distance 2.568(3) Å and angle at H *ca* 128°. The carbonyl oxygen atom O2 also accepts a hydrogen bond from hydroxyl O4 of a neighbouring molecule, with O2 . . . O4 distance 2.725(2) Å, and angle *ca* 153° at H.

EXPERIMENTAL

Plant material. Aerial parts of *Ceratiola ericoides* Michx. (Empetraceae) were collected in Sun Ray, Florida, in June and September 1984 (Hansen and Richardson No. 6956 and 6163; vouchers deposited at the University of South Florida Herbarium).

Isolation of compounds **1**–**6**. Air dried ground leaves of *C. ericoides* (130 g) collected in September, 1986, were soaked in hexane to remove fatty material. The mark was then soaked in CH_2Cl_2. 14.2 g of crude extract thus obtained and dried *in vacuo* was chromatographed over Sephadex LH-20 using a mixture of $CHCl_3$–MeOH (1:1). Thirty-six fractions of 50 ml each were obtained. Fractions 10–17 (2.3 g), composed mainly of flavonoids, were combined. 150 mg of this material was chromatographed over silica gel with increasingly polar mixtures of CH_2Cl_2 with 12 fractions being taken. Fractions 2 and 3 contained **1** (5 mg) and **2** (8 mg). Fractions 4–6 yielded **3** (9 mg), **4** (12 mg) and fraction 9 gave **5** (1 mg) and **6** (13 mg).

Isolation of ceratiolin (**8**). Fresh leaves (500 g) were soaked in 2 l. H_2O for 6 hr and resoaked for 20 hr. The combined washes were extracted with 3 × 500 ml EtOAc–$CHCl_3$ (1:1). Concentration of the extract *in vacuo* yielded 400 mg of a crude mixture with **8** as the major constituent as determined by ^{1}H NMR. A solution of **8** in MeOH (5 ml) when kept at −15° for several days provided 140 mg of ceratiolin (**8**) which was recrystallized twice from MeOH, mp 148–149°.

Isolation of compound **7**. Air-dried, ground *C. ericoides* leaves (600 g) collected in June, 1984, were successively soaked in 2 × 2 l. hexane and 2 × 2 l. CH_2Cl_2 at ambient temperature to remove nonpolar compounds. The mark was then soaked in 2 × 2 l. MeOH for 30 hr to obtain 17.2 g of extract following evaporation *in vacuo*. The extract was partitioned between EtOAc H_2O (2 l. each). Upon evaporation of EtOAc, 4.1 g of crude extract were obtained. The extract was chromatographed over silica gel with increasingly polar mixtures of CH_2Cl_2 Me_2CO as solvent 18 100 ml fractions being obtained. Fractions 11–14 were acetylated with Ac_2O pyridine. Silica gel TLC (1 mm) with ether 5% EtOAc as solvent yielded 1 mg catechin pentaacetate, 24 mg epicatechin pentaacetate from 39 mg of Fr 11. 35 mg of a mixture of Fr 13–14 yielded 19 mg of the nonaacetate of epicatechin-(4β → 8; 2β → O → 7)-epicatechin (**7**) along with smaller quantities of other unidentified dimers and epicatechin acetate.

6,8-*Dimethylpinocembrin* (**3**). ^{1}H NMR (ppm): δ2.08 (6H, *s*) 2.84 (1H, *dd*, $J_{2,3a}$ = 3Hz, $J_{3a,3b}$ = 17.5 Hz), 3.05 (1H, *dd*, $J_{2,3b}$ = 13 Hz, $J_{3a,3b}$ = 17.5 Hz) 5.41 (1H, *dd*, $J_{2,3a}$ = 3 Hz, $J_{2,3b}$ = 13 Hz), 7.44 (4H, *m*); EIMS *m/z* (rel. int.): 284 [M]$^+$ (71), 266 [M − H_2O]$^+$ (3), 207 [M − C_6H_5]$^+$ (45), 180 [M − C_8H_8]$^+$ (75), 152 [M − C_8H_8 − CO]$^+$ (100).

8-*Methylpinocembrin* (4). ^{1}H NMR (ppm): δ2.06 (3H, *s*), 2.82 (1H, *dd*, $J_{2,3a}$ = 3 Hz, $J_{3a,3b}$ = 17.5 Hz), 3.09 (1H, *dd*, $J_{2,3b}$ = 13 Hz, $J_{3a,3b}$ = 17.5 Hz), 5.37 (1H, *dd*, $J_{2,3a}$ = 3 Hz, $J_{2,3b}$ = 13 Hz), 6.01 (1H, *s*), 7.44 (4H, *br s*), 12.31 (1H, *s*); EIMS *m/z* (rel. int.): 270 [M]$^+$ (96), 269 [M − H]$^+$ (49), 193 [M − C_6H_5]$^+$ (100), 166 [M − C_8H_8]$^+$ (48), 138 [M − C_8H_8 − CO]$^+$ (64). UV λ_{max}^{MeOH} (nm): 225 sh, 290 (317 with $AlCl_3$, MeOH), 335 sh (370 with $AlCl_3$, MeOH).

7-*Hydroxyflavanone* (5). ^{1}H NMR (ppm): δ2.84 (1H, *dd*, $J_{2,3a}$ = 3 Hz, $J_{3a,3b}$ = 17.5 Hz), 3.06 (1H, *dd*, $J_{2a,3b}$ = 13 Hz, $J_{3a,3b}$ = 17.5 Hz), 5.48 (1H, *dd*, $J_{2,3a}$ = 3 Hz, $J_{2,3b}$ = 13 Hz), 6.48 (1H, *d*, $J_{6,8}$ = 2 Hz), 6.56 (1H, *dd*, $J_{5,6}$ = 8.5 Hz, $J_{6,8}$ = 2 Hz), 7.44 (4H, *m*), 7.87 (1H, *d*, $J_{5,6}$ = 8.5 Hz); EIMS *m/z* (rel. int.): 240 [M]$^+$ (91), 239 [M − H]$^+$ (64), 163 [M − C_6H_5]$^+$ (73), 136 [M − C_8H_8]$^+$ (100), 108 [M − C_8H_8 − CO]$^+$ (51), 104 [C_8H_8]$^+$ (56).

2′,4′-*Dihydroxychalcone* (6). ^{1}H NMR (ppm): δ6.44 (1H, *d*, $J_{6,8}$ = 1.5 Hz), 6.45 (1H, *dd*, $J_{6,8}$ = 1.5 Hz, $J_{8,9}$ = 7.9 Hz) 7.74–7.03 (5H, m), 7.58 (1H, *d*, $J_{a,b}$ = 9.4 Hz), 7.85 (1H, *d*, $J_{a,9}$ = 7.9 Hz), 7.90 (1H, *d*, $J_{a,b}$ = 9.4 Hz); EIMS *m/z* (rel. int.): 240 [M]$^+$ (12), 239 [M − H]$^+$ (77), 163 [M − C_6H_5]$^+$ (100), 137 [M − C_8H_7]$^+$ (77), 77 [C_6H_5]$^+$ (47).

Nonaacetate of epicatechin-(4β → 8; 2β → O → 7)-*epicatechin* (7). ^{1}H NMR (ppm): δ1.50 2.30 (27H, CO CH_3), 2.80 (1H, *dd*, $J_{3,4b}$ = 4 Hz, $J_{4a,4b}$ = 17.5 Hz), 2.94 (1H, *dd*, $J_{3,4a}$ = 2 Hz, $J_{4a,4b}$ = 17.5 Hz), 4.61 (1H, *d*, $J_{3,4}$ = 4 Hz), 5.20 (1H, *d*, $J_{3,4}$ = 4 Hz), 5.30 (1H, *br s*), 5.23 (1H, *br s*), 6.50 (1H, *d*, $J_{6,8}$ = 2 Hz), 6.51 (1H, *s*), 6.83 (1H, *d*, $J_{6,8}$ = 2 Hz), 7.14 7.59 (6H, *m*).

Ceratiolin (8). $C_{17}H_{18}O_5$, yellow solid, mp 148 149°; IR ν_{max}^{KBr} cm^{-1}: 3450, 1668, 1639, 1578; λ_{max}^{MeOH} (nm) (log ε): 228 (4.12), 325 (3.99), 358 (3.97); ^{1}H NMR (ppm): δ1.50 (3H, *s*, CH_3), 1.85 (3H, *s*, CH_3), 2.99 and 3.25 (4H, *m*, H_α and H_β), 7.26 (5H, *s*-broadened, Ar-H), 18.86 (1H, *s*, OH, ex. D_2O); EIMS *m/z* (rel. int.): 302 [M]$^+$ (3.7), 284 [M − H_2O]$^+$ (2.2), 259 [M − C_2H_3O]$^+$ (40.5), 241 [M − C_2H_3O − H_2O]$^+$ (11.6), 180 [M − C_8H_9 + H]$^+$ (16.0), 133 [C_9H_9O]$^+$ (18.0), 105 [C_8H_9]$^+$ (57.3), 91 [C_7H_7]$^+$ (100). (Calc. for $C_{17}H_{18}O_5$: C, 67.54; H, 5.96%. Found: C, 67.25; H, 6.25.)

TAI derivatization. ^{1}H NMR ($\Delta\delta$) = δ1.50 ($\Delta\delta$ + 0.141), 1.85 ($\Delta\delta$ + 0.068), 2.99 ($\Delta\delta$ + 0.041), 3.25 ($\Delta\delta$ + 0.041).

X-Ray data of 6,8-*dimethylpinocembrin* (3). A crystal of dimensions 0.20 × 0.24 × 0.30 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with CuKα radiation (λ = 1.54184 Å) and a graphite monochromator. Crystal data are: $C_{17}H_{16}O_4$, M_r = 284.3, monoclinic space group $P2_1/c$, a = 4.829(1), b = 24.573(4), c = 12.678(2) Å, β = 100.38(1)°, V = 1479.8(8) Å^3, Z = 4, d_c = 1.276 g cm^{-3}, μ(CuKα) = 7.1 cm^{-1}, T = 24°C. Data were collected by ω-2θ scans of variable speed, 1.18–4.0 deg/min. One quadrant of data having 2° < θ < 60° was measured and yielded 2195 unique data of which 1387 had $I > 3\sigma(I)$ and were used in the refinement. Data reduction included corrections for background, Lorentz, polarization and absorption effects.

The structure was solved by direct methods, using MULTAN 78 [23], and refined by full-matrix least squares, using the Enraf-Nonius SDP programs [24]. Except for the half-populated carbon atoms of the disordered phenyl group, which were refined isotropically, all C and O atoms were refined anisotropically. Hydrogen atoms were located in difference maps and included as fixed contributions with B = 5.0 Å; disordered H atoms were ignored. Convergence was achieved with R = 0.085, Rw = 0.097 for 187 variables, and maximum residual electron density 0.41 eÅ3. Supplementary material has been deposited at the X-ray crystallographic data centre at Cambridge.

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