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# THREE BENZOFURANS AND A 1,4-DIOXIN DERIVATIVE FROM *CALEA* SPECIES: THE MOLECULAR STRUCTURES OF CALEBERTIN AND CALETEUCRIN

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ABSTRACT.—Chemical analysis of *Calea prunifolia* afforded two new benzofurans, caleprunin A (**2**) and caleprunin B (**3**). From *Calea berteriana*, the benzofuran calebertin (**1**) and the known 1,4-dioxin derivative, caleteucrin (**4**), were obtained. Their structures were elucidated by $^1$H-nmr, $^{13}$C-nmr, and mass spectral methods. The molecular structures of calebertin and caleteucrin were determined by single crystal X-ray diffraction.

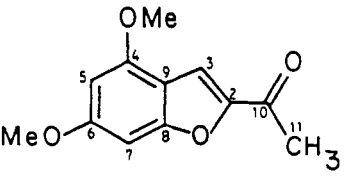
In our biochemical investigations of the genus *Calea* (1-3), we have chemically investigated *Calea prunifolia* Kunth (syn *Calea pittieri* B.L. Robinson and E.J. Greenman) from Costa Rica and *Calea berteriana* DC. from Venezuela. Analysis of the nonpolar fractions from *C. berteriana* yielded a new benzofuran derivative which we named calebertin (**1**). An additional constituent was the known, unusual 1,4-dioxin derivative, caleteucrin (**4**) (4). *C. prunifolia* afforded two new benzofuran derivatives, caleprunin A (**2**) and B (**3**).

Among the nearly twenty *Calea* species studied chemically, the presence of benzofurans has been reported only in *Calea teucrifolia* (4) and *Calea hymenolepis* (5) from Brazil, and in *Calea urticifolia* from Guatemala (6). We now report the structures of three benzofuran derivatives from *C. berteriana* and *C. prunifolia*. Because the structures of all the benzofuran derivatives isolated so far from *Calea* species were based on spectral arguments and biogenetic considerations, we also determined the molecular structure of calebertin (**1**) by single crystal X-ray diffraction.

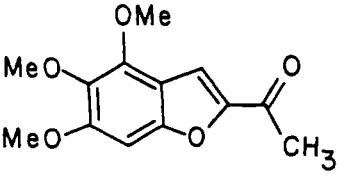
The molecular structure of the known 1,4-dioxin caleteucrin (**4**) (4) was established by single crystal X-ray diffraction. $^{13}$C-nmr and other spectral data not previously reported for compound **4** are also presented in this paper.

## RESULTS AND DISCUSSION

*Calebertin A* (**1**), $C_{12}H_{12}O_4$, is a crystalline compound that exhibited in the $^1$H-nmr spectrum a singlet at $\delta$ 7.49 (H-3) representing a deshielded vinylic proton and two one-proton doublets at 6.28 (H-5) and 6.60 (H-7) corresponding to aromatic protons. Two three-proton singlets at 3.88 and 3.83 indicated the presence of two methoxy groups on an aromatic ring, and a three-proton singlet at 2.51 (H-11) suggested an acetyl moiety. The eims analysis of **1** was in agreement with the molecular formula $C_{12}H_{12}O_4$, which was confirmed by cims, which gave a peak at *m/z* 221 $(M+1)^+$. The ir spectrum indicated the presence of a keto group with extended conjugation (1665 $cm^{-1}$), aromatic and double bond absorptions (1605, 1545, and 1500 $cm^{-1}$), and the typical bands for aliphatic C-H vibrations. These spectroscopic data suggested a benzofuran-type structure for compound **1**, with one olefinic proton and three substituents, two methoxy and one acetyl group. The assignments of the $^1$H-nmr signals of **1** are summarized in Table 1. The downfield vinylic signal at 7.49 indicated a deshielding effect of the acetyl carbonyl on the olefinic proton H-3 and suggested an $\alpha,\beta$-unsaturated ketone system, thus placing the acetyl group at C-2 in **1**. On the other hand, the coupling constant between H-5 and H-7 ($J_{5,7}$=2.0 Hz) clearly showed a *meta* relationship between these two protons. On the basis of the similar chemical shifts of the methoxy groups (3.88 and 3.83) and the lack of a measurable coupling between



1



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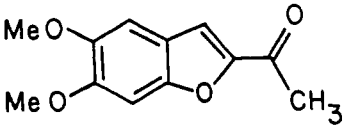

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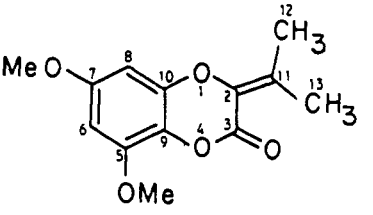

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TABLE 1. $^1$H-nmr Spectral Data[a] of Compounds **1-4**

| | Compound **1** | | Compound **2** | | Compound **3** | | Compound **4** |
|---|---|---|---|---|---|---|---|
| | $CDCl_3$ | $C_6D_6$ | $CDCl_3$ | $C_6D_6$ | $CDCl_3$ | $C_6D_6$ | $CDCl_3$ |
| H-3 . . . . . | 7.49 s | 7.42 s | 7.58 s | 7.38 s | 7.44 br s | 7.13 br s | — |
| H-4/H-5 . . . | — | — | — | — | 7.07 br s | 6.65 br s | 6.18 br |
| H-6 . . . . . | 6.28 d (2.0) | 6.22 d | — | — | — | — | |
| H-7/H-8 . . . | 6.60 d (2.0) | 6.40 d | 6.79 s | 6.47 s | 7.05 s | 6.59 s | |
| H-11 . . . . . | 2.51 s[b] | 2.11 s[b] | 2.55 s[b] | 2.18 s[b] | 2.57 s[b] | 2.24 s[b] | — |
| OMe . . . . . | 3.88 s | 3.27 s | 4.13 s | 3.76 s | 3.96 s | 3.40 s | 3.85 s |
| OMe′ . . . . | 3.83 s | 3.27 s | 3.92 s | 3.70 s | 3.94 | 3.26 s | 3.77 s |
| OMe″ . . . . | — | — | 3.85 s | 3.29 s | — | — | — |
| H-12 . . . . . | — | — | — | — | — | — | 2.01 s[b] |
| H-13 . . . . . | — | — | — | — | — | — | 2.25 s[b] |

[a]Spectra were run at 200 MHz with TMS as internal standard. Peak multiplicities are designated as usual. Chemical shifts are given in ppm relative to TMS. Figures in parentheses represent coupling constants ($J$ or line separations in Hz.

[b]Three-proton signal.

H-3 and the two aromatic protons, we postulated a 4,6-substitution pattern for the two methoxy groups on the aromatic ring.

$^{13}$C-nmr spectral data of **1** are given in Table 2, and the assignments of the multiplets are based on single-frequency off-resonance decoupling (SFORD) experiments. The singlet at δ 187.1 (C-10) corroborated the presence of a keto group in **1**. The chemical shifts of the aromatic doublets due to C-5 (87.8) and C-7 (95.1) were also consistent with a 4,6-substitution pattern. Definitive structural data for calebertin (**1**) were obtained by single crystal X-ray diffraction analysis, which will be discussed later in this paper.

*Caleprunin A* (**2**) is a yellow gum whose ir spectrum was similar to **1**, also indicating the presence of a keto carbonyl with extended conjugation (1670 $cm^{-1}$). The eims suggested molecular formula $C_{13}H_{13}O_5$, which was confirmed by cims, with a base peak at *m/z* 251. The mass spectral fragmentation pattern of compound **2** was similar to that of **1**, suggesting the same type of benzofuran skeleton for **2**. The $^1$H-nmr spectrum of **2** (Table 1), when compared with the parameters of **1**, showed the presence of only two downfield signals at δ 7.58 (H-3) and 6.79 (H-7) but three methoxy signals (4.13, 3.92, and 3.85), together with a methyl signal at 2.55 (H-11). The close spectral

TABLE 2. $^{13}$C-nmr Spectral Data[a] of Compounds **1**, **2**, and **4**

| | 1 | 2 | 4 |
|---|---|---|---|
| C-2 | 162.5 s | 155.8 s | 124.2 s |
| C-3 | 112.0 d | 112.1 d | 156.5 s |
| C-4 | 150.9 s | 147.0 s | —— |
| C-5 | 87.8 d | 137.4 s | 148.4 s |
| C-6 | 157.9 s | 151.3 s | 94.3 d |
| C-7 | 95.1 d | 90.0 d | 156.0 s |
| C-8 | 155.1 s | 153.0 s | 92.4 d |
| C-9 | 94.2 s | 100.0 s | 135.2 s |
| C-10 | 187.1 s | 187.4 s | 142.6 s |
| C-11 | 25.9 q | 25.9 q | 154.1 s |
| C-12 | —— | —— | 19.9 q |
| C-13 | —— | —— | 20.9 q |
| OMe | 55.7 q | 61.2 q | 55.7 q |
| OMe′ | 55.7 q | 60.5 q | 56.2 q |
| OMe″ | —— | 56.2 q | —— |

[a]Spectra were obtained in $CDCl_3$ at ambient temperature at 50.32 MHz. Chemical shifts are in ppm relative to TMS, as determined by proton noise decoupling. Peak multiplicity was obtained by off-resonance decoupling (3.5 ppm above TMS) and are designated as usual. Doublets were assigned by performing single-frequency off-resonance decoupling experiments (SFORD).

similarities between **1** and **2** clearly suggested a benzofuran structure for **2**, the difference being the presence of a third methoxy group in caleprunin A. Corroboration was obtained from the $^{13}$C-nmr spectrum of **2** (Table 2), which in comparison to **1**, indicated the presence of only two $sp^2$-carbon doublets at 112.1 (C-3) and 90.0 (C-7), and an extra methyl quartet in the region of a methoxy carbon. The appearance of a singlet at 137.4 ppm (C-5) was in agreement with the presence of a methoxy group at C-5 with each neighboring aromatic carbon also bearing a methoxy group. As in compound **1**, the presence of a singlet at 100.0 ppm (C-9) was in accord with the presence of a MeO group on C-4, thus indicating a 4,5,6-trisubstitution pattern in compound **2**.

Solvent shift $^1$H-nmr studies in $C_6D_6$ further corroborated the proposed substitution pattern (Table 1), since only one of the methoxy singlets experienced a large diamagnetic shift ($\Delta\delta$=0.56), indicating that only one of the three MeO-substituted aromatic carbons had an unsubstituted *ortho*-carbon (7,8).

*Caleprunin B* (**3**) is a gum with a mass spectrum in agreement with molecular formula $C_{12}H_{12}O_4$. The ir spectrum and the mass spectral fragmentation pattern of **3** were very similar to the ones of **1** and **2**, clearly suggesting a benzofuran skeleton. The $^1$H-nmr spectrum of **3** (Table 1) presented a downfield olefinic broadened singlet at $\delta$ 7.44 (H-3), two aromatic signals, one of them a broadened singlet at 7.07 (H-4) and the other a singlet at 7.05 (H-7). In addition, the spectrum exhibited two three-proton methoxy singlets at 3.96 and 3.94 and a three-proton singlet at 2.57 (H-11). Extensive decoupling experiments in $C_6D_6$ indicated the absence of any measurable coupling between the aromatic protons H-4 at 6.65 and H-7 (6.59), but a small coupling between H-3 (7.13) and H-4 (6.65) was observed. Saturation of the broadened singlet at $\delta$ 7.13 (H-4) sharpened the broadened singlet at 6.65 (H-4) with no effect on the singlet at 6.59 (H-7). In return, irradiation at H-4 (6.65) sharpened the broadened olefinic singlet at 7.13 (H-3) but did not affect the aromatic signal at 6.59 (H-7). Spin decoupling at 6.59 (H-7) had no effect on the other two downfield signals. The absence of a measurable coupling between the two aromatic protons H-4 and H-7 was an indication of their *para* relationship, and therefore we suggest a 5,6-substitution pattern of the

methoxy group in **3**. This was corroborated by $^1$H-nmr solvent shift studies in $C_6D_6$ (Table 1). Both methoxy signals experienced an appreciable diamagnetic shift ($\Delta\delta$=0.56 and 0.58, respectively) (7,8), in accord with the proposed structure for caleprunin B.

*Caleteucrin* (**4**) was a crystalline compound (mp 107.5-108°) with a mass spectrum indicating molecular formula $C_{13}H_{14}O_5$. The $^1$H-nmr spectrum of **4** (Table 1) suggested that the compound was identical with an oil previously isolated form *C. teucrifolia* (4). The observed mass spectral fragmentation pattern was also in accord with the published data. The structure of caleteucrin (**4**) had been previously determined by chemical and spectroscopic methods (4). Its molecular structure was confirmed by single crystal X-ray diffraction analysis as will be described later in this paper. $^{13}$C-nmr and uv spectral data not previously reported for compound **4** are also presented.

CRYSTAL STRUCTURE ANALYSES OF CALEBERTIN AND CALETEUCRIN.—*Calebertin* (**1**): The crystal structure for **1** is illustrated in Figure 1 and the coordinates are given

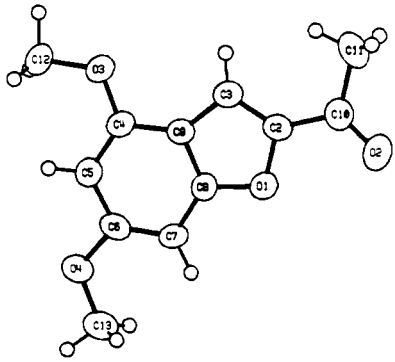


FIGURE 1. The Crystal Structure of Calebertin (**1**), Drawn by ORTEP (14).

in Table 3. The molecule lies on a mirror plane in the crystal, such that the entire molecule, except for two hydrogen atoms of each methyl group, is perfectly planar. The methyl keto substituent is oriented in the solid s-*trans* to the benzofuran double bond and hence is *syn* to the ring oxygen atom. The double bond C2=C3 has a length of 1.341(4)Å, C-C bonds of the benzo group average 1.386Å, and C($sp^2$)-O single bonds average 1.374Å. The angle at O1 is 105.8(2)°, and the angles at both methoxy carbon atoms are 117.5(2)°.

*Caleteucrin* (**4**): The structure of **4** contains two independent molecules (unrelated by symmetry), distinguished in Table 4 by atom names with and without primes. The two molecules, both of which are illustrated in Figure 2, have similar but nonidentical conformations. In both, the benzo ring is planar, while the dioxane ring deviates from

TABLE 3. Coordinates for 2-Acetyl-4,6-dimethoxybenzofuran (Calebertin, **1**)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| O1 | −0.1721(2) | 0.25 | 0.5300(1) | C6 | 0.0947(3) | 0.25 | 0.6758(2) |
| O2 | −0.3694(2) | 0.25 | 0.4179(2) | C7 | −0.0277(3) | 0.25 | 0.6574(2) |
| O3 | 0.2293(2) | 0.25 | 0.4453(2) | C8 | −0.0561(3) | 0.25 | 0.5647(2) |
| O4 | 0.1421(2) | 0.25 | 0.7630(2) | C9 | 0.0275(3) | 0.25 | 0.4949(2) |
| C2 | −0.1589(3) | 0.25 | 0.4355(2) | C10 | −0.2694(3) | 0.25 | 0.3824(3) |
| C3 | −0.0407(3) | 0.25 | 0.4129(2) | C11 | −0.2545(4) | 0.25 | 0.2797(3) |
| C4 | 0.1519(3) | 0.25 | 0.5173(2) | C12 | 0.3578(3) | 0.25 | 0.4648(3) |
| C5 | 0.1837(3) | 0.25 | 0.6079(2) | C13 | 0.0582(4) | 0.25 | 0.8374(2) |

TABLE 4. Coordinates for Caleteucrin (4)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| O1 | 0.1437(4) | 0.7712(3) | 0.7500(2) | O1′ | 0.3774(4) | 0.1043(3) | 0.1987(2) |
| C2 | 0.1961(6) | 0.7566(4) | 0.6567(3) | C2′ | 0.5267(6) | 0.1102(4) | 0.1353(3) |
| C3 | 0.2030(6) | 0.6352(4) | 0.6227(3) | C3′ | 0.5687(6) | 0.2331(4) | 0.0999(3) |
| O4 | 0.1289(4) | 0.5463(3) | 0.6781(2) | O4′ | 0.5100(4) | 0.3269(3) | 0.1538(2) |
| C5 | −0.0519(6) | 0.4867(4) | 0.8136(3) | C5′ | 0.3947(6) | 0.3908(4) | 0.3029(3) |
| C6 | −0.1401(6) | 0.5116(4) | 0.8992(3) | C6′ | 0.2994(6) | 0.3693(4) | 0.3880(3) |
| C7 | −0.1322(6) | 0.6249(4) | 0.9321(3) | C7′ | 0.2313(6) | 0.2580(4) | 0.4078(3) |
| C8 | −0.0388(6) | 0.7125(4) | 0.8829(3) | C8′ | 0.2564(6) | 0.1682(4) | 0.3455(3) |
| C9 | 0.0407(6) | 0.5752(4) | 0.7632(3) | C9′ | 0.4197(6) | 0.3013(4) | 0.2399(3) |
| C10 | 0.0460(6) | 0.6844(4) | 0.7981(3) | C10′ | 0.3524(5) | 0.1926(4) | 0.2618(3) |
| C11 | 0.2420(7) | 0.8556(4) | 0.6064(3) | C11′ | 0.6099(7) | 0.0072(4) | 0.1098(3) |
| C12 | 0.2299(8) | 0.9745(5) | 0.6491(4) | C12′ | 0.5557(8) | −0.1129(4) | 0.1517(4) |
| C13 | 0.3107(9) | 0.8573(5) | 0.5061(4) | C13′ | 0.7670(7) | −0.0010(5) | 0.0389(4) |
| O14 | 0.2685(5) | 0.6062(3) | 0.5475(2) | O14′ | 0.6516(4) | 0.2580(3) | 0.0277(2) |
| O15 | −0.0473(4) | 0.3788(3) | 0.7740(2) | O15′ | 0.4677(4) | 0.4959(3) | 0.2750(2) |
| C16 | −0.1229(8) | 0.2815(4) | 0.8275(4) | C16′ | 0.4416(7) | 0.5923(4) | 0.3362(3) |
| O17 | −0.2153(4) | 0.6591(3) | 1.0156(2) | O17′ | 0.1359(4) | 0.2276(3) | 0.4894(2) |
| C18 | −0.3146(6) | 0.5731(4) | 1.0703(3) | C18′ | 0.1107(8) | 0.3132(5) | 0.5587(3) |

planarity, such deviations being somewhat larger in the primed molecule. The conformation of this ring in both cases is similar to that of 1,3-cyclohexadiene (9,10), in which a twist away from planarity occurs about a pseudo-twofold axis, maintaining two near-zero torsion angles. In the present molecule, that axis bisects both the O1-C2 and O4-C9 bonds, maintaining the endocyclic torsion angles about C3-O4 and C9-O10 near zero. This twist is more severe for the primed molecule, with torsion angles about the bisected bonds being nearly twice as large as for the unprimed molecule. The exocyclic torsion angle C11-C2-C3-O14 is also much larger for the primed molecule (21.1 vs 8.5°), indicating a larger degree of overall nonpolarity. In both molecules, the methoxy groups are nearly coplanar with the benzo ring, with average C-C-O-C torsion angle magnitude 2.7°. Benzo C-C bond lengths average 1.381Å, dioxane C-O bond lengths average 1.384Å, the average C2=C11 double bond length is 1.323Å, and the average angle at dioxane oxygen is 117.8°.

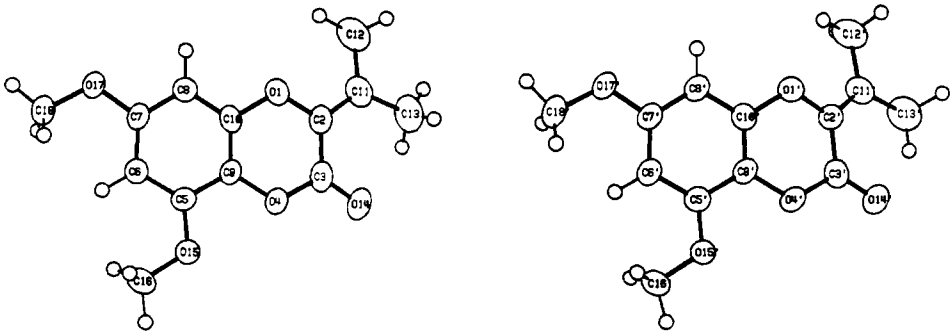


FIGURE 2. The Two Independent Molecules of Caleteucrin (4), Drawn by ORTEP (14).

## EXPERIMENTAL

PLANT MATERIAL.—*C. berteriana* was collected on December 10, 1979, in Santa Merida, Venezuela, along Rio Chama toward Chiguara (L. Urbatsch No. 3455). *C. prunifolia* was collected in Costa Rica on December 29, 1978, along Hwy 10 into Cartago, Costa Rica (J. Wussow and J. Pruski, No. 112). Vouchers are deposited at the Herbarium of Louisiana State University at Baton Rouge, Louisiana.

EXTRACTION.—Dried aerial parts of *C. berteriana* (968 g) were extracted according to a standard procedure (11) to yield 10.5 g of crude syrup. Column chromatography of the syrup on silica gel with petroleum ether-$Me_2CO$ mixtures of increasing polarity gave 50 fractions of 200 ml each. Fraction 3-5 (220 mg) gave 35 mg of **1** and 30 mg of **4** after purification by tlc (silica gel) with $CHCl_3$ and $CHCl_3$-$Me_2CO$ (97:3).

Dried plant material of *C. prunifolia* (746 g) provided 2.3 g of crude syrup (11), which was chromatographed on silica gel with petroleum ether-$Me_2CO$ mixtures of increasing polarity; 43 fractions of 125 ml each were collected. Rechromatography of fractions 8-9 (175 mg) on silica gel with $CHCl_3$-$Me_2CO$ (95:5) gave 44 mg of compound **2**. Purification of fraction 12-13 (49 mg) by the same procedure yielded 16 mg of **3**.

*Calebertin* (**1**), $C_{12}H_{12}O_4$, mp 118.5-119° ($CHCl_3$-petroleum ether); uv λ max (MeOH), 286 nm (ε $5.42\times10^4$), 330 nm (ε $4.91\times10^4$); ir ν max (film) 1665 (conj. carbonyl), 1610 (double bond, aromatic), 1550, 1500 (aromatic); eims *m/z* 220 (89.8, $M^+$), 205 (100.0, M-Me), 177 (7.7, M-MeCO); cims (isobutane) *m/z* 221 (100.0, M+1).

*Caleprunin* A (**2**), $C_{13}H_{14}O_5$, gum; uv λ max (MeOH) 288 nm (ε $3.14\times10^4$), 328 nm (ε $2.39\times10^4$); ir ν max (film) 1670 (conj. carbonyl), 1620 (double bond, aromatic), 1550 (aromatic); eims *m/z* 250 (99.5, $M^+$), 235 (100.0, M-Me), 220 (5.7, M-2Me), 207 (12.8, M-MeCO), 205 (7.1, M-3MeO), 192 (24.1, M-Me-MeCO), 177 (30.9, M-2Me-MeCO); cims (isobutane) *m/z* 251 (100.0; M+1).

*Caleprunin* B (**3**), $C_{12}H_{14}O_4$, gum; uv λ max (MeOH) 290 nm (ε $2.08\times10^4$), 340 nm (ε $1.25\times10^4$); ir ν max (film) 1670 (conj. carbonyl), 1620 (double bond, aromatic), 1548, 1495 (aromatic); eims *m/z* 220 (100.0, $M^+$), 205 (54.4; M-Me), 189 (1.9, M-MeO), 177 (12.5, M-MeCO), 149 (20.3), cims (isobutane) *m/z* 221 (100.0; M+1).

*Caleteucrin* (**4**), $C_{13}H_{14}O_5$, mp 107.5-108°; uv λ max (MeOH) 288 nm (ε $2.48\times10^4$); ir ν max (film) 1755 (lactone), 1630 (C=COR), 1515 (aromatic); eims *m/z* 250 (100.0, $M^+$), 235 (0.8, M-Me), 221 (28.0, M-CHO), 220 5.8, M-2Me), 207 (46.5, M-Me-CO), 193 (17.3, M-$C_3H_6$-Me); cims (isobutane) *m/z* 251 (100.0; M+1).

X-RAY DATA.[1]—*Calebertin* (**1**): A crystal of dimensions $0.16\times0.24\times0.52$ mm was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with MoKα radiation (λ=0.71073Å) and a graphite monochromator. Crystal data are: $C_{12}H_{12}O_4$, MW=220.2, orthorhombic space group Pnma, $a=10.992(2)$, $b=6.767(1)$, $c=14.643(4)$Å, Z=4, $d_c=1.343$ gcm$^{-3}$, μ(MoKα)=0.95 cm$^{-1}$. Data were collected by ω-2Θ scans of variable speed, designed to yield $I\approx50\sigma(I)$ for all significant reflections. One octant of data having $1°<\Theta<25°$ was measured, yielding 1045 unique reflections, of which 624 had $I>2\sigma(I)$, and were used in the refinement. Data reduction included corrections for background, Lorentz, and polarization effects; absorption was negligible. The structure was solved by direct methods (MULTAN) (12) and refined by full matrix, weighted least squares, using the Enraf-Nonius SDP (13). Nonhydrogen atoms were treated anisotropically. Hydrogen atoms were located from difference maps, and ring H atoms were isotropically refined with methyl H atoms were included as fixed contributions with B=7.0Å$^2$. Convergence was achieved with R=0.043, Rw=0.055, maximum residual electron density 0.16eÅ$^{-3}$, and extinction coefficient $2.9(9)\times10^{-7}$. Coordinates are given in Table 3.

*Caleteucrin* (**4**). Data collection and structure refinement paralleled those of calebertin. Particulars are: crystal size $0.16\times0.24\times0.48$ mm, $C_{13}H_{14}O_5$, MW=250.3, triclinic space group $P\bar{1}$, $a=7.786(2)$, $b=11.072(1)$, $c=14.623(1)$Å, α=85.79(1), β=83.49(1), γ=84.46(1)°, Z=4, $d_c=1.336$ gcm$^{-3}$, μ(MoKα)=0.96 cm$^{-1}$, one hemisphere of data with $1°<\Theta<23°$, 3456 unique data, 1848 used in refinement ($I>3\sigma(I)$), all H atoms fixed with B=6.0Å$^2$, R=0.051, $R_w=0.069$, residual density 0.21eÅ$^{-3}$, extinction $4(1)\times10^{-7}$. Coordinates are given in Table 4.

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[1]Atomic coordinates for the structures have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Rd., Cambridge, CB2 1EW, UK.

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