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J. Nat. Prod., **1992**, 55 (10), 1477-1487• DOI: 10.1021/np50088a014 • Publication Date (Web): 01 July 2004

Journal of Natural Products
Vol. 55, No. 10, pp. 1477-1487, October 1992

DITERPENES OF *CALIBRACHOA PARVIFLORA*

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ABSTRACT.—Leaves of *Calibrachoa parviflora* gave the kauranoids corymbol 6-monoacetate [**4**] and corymbol 17-monoacetate [**5**], corymbol 17-(2-methylbutyrate) [**6**], and corymbol 6-acetate-17-(2-methylbutyrate) [**8**]. Other new kauranoids were *ent*-kaurane-7α,16β,17-triol [**9**], its 7-acetate [**10**], and its 7-acetate-17-(2-methylbutyrate) [**11**], the corresponding 7-ketodiol [**12**] and its 17-acetate [**13**]. New pimaranes were 15*R*,16-dihydroxy-*ent*-isopimar-8(14)-en-7-one [**14**] and the ring-closed analogues, 14α,16-oxido-*ent*-isopimar-7-en-15α-ol [**17**] and 14α,16-oxido-*ent*-isopimar-7-ene-6α,15α-diol [**20**]. The known diterpenes, *ent*-kaurane-16β,17-diol, its 17-acetate, *ent*-kaurane-6α,16β,17-triol (corymbol), and its 6,17-diacetate were also obtained. *C. parviflora* did not yield any of the ergostanoids that are characteristic of *Petunia* species, thus supporting its recent reassignment into a separate genus.

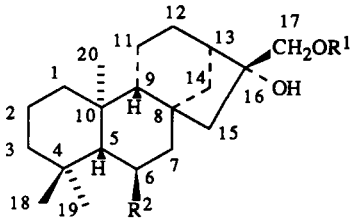
In a continuing investigation of plant resistance toward insect herbivores, we have shown that foliage of various *Petunia* (Solanaceae) species is toxic to certain insects, and that this effect can be related to the presence in the leaves of a large number of steroidal substances which we have termed petuniasterones and petuniolides (1,2). More recently (3), we reported the occurrence in *Petunia inflata* of a set of novel pyridine ring-containing analogues of these steroids (petunianines) which are also agents that inhibit insect growth and development. While evaluating plants that are closely related to *Petunia* it was of interest to examine the allied species *Calibrachoa parviflora* (=*Petunia parviflora*) Juss. (Solanaceae), which has the same range in South America as *Petunia* and is found in Mexico, Cuba, and the United States as far north as New Jersey. The plants of *C. parviflora* have 2n = 2x = 18 chromosomes, in contrast to all species of *Petunia* with 2n = 2x = 14 (4), and this genus has recently been distinguished from that of *Petunia* (5).

RESULTS AND DISCUSSION

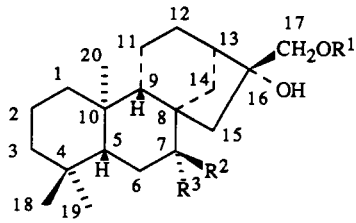
In the present study, larvae of the lepidopteran *Helicoverpa zea* (=*Heliothis zea* Boddie) survived well on fresh stems and leaves of *C. parviflora*, and it was, therefore, of interest to determine if any steroids similar to those responsible for toxicity in *Petunia* occurred in *Calibrachoa*, and if so, whether differing structure lessened toxicity. No steroidal substances of the *Petunia* type were isolated from *C. parviflora*; however, numerous diterpenes were present including several previously undescribed kauranoids and pimaranes. These findings support the conclusion that *C. parviflora* is correctly assigned in a genus distinct from *Petunia*.

KAURANES.—Compounds **1–13** belong to the *ent*-kaurane series. Diol **1** has been isolated previously from *Croton* and other genera, and its acetate **2** has been prepared (7,8). The ^{13}C-nmr spectra of **1** and **2** (Table 1) were in agreement with shifts reported for kauranoid systems (9,10) in general, and with values observed for the relevant carbons of abbeokutone acetate (11).

Compound **3** has the structure ascribed to corymbol isolated from *Turbina corymbosa* (12), but the observed mp, 217–220°, and optical rotation, [α]D −38° (pyridine, *c* = 0.5), were substantially different from the reported values of mp 282–283° and [α]D −3.8°. The optical rotation of its diacetate **7**, [α]D −60° ($CHCl_3$, *c* = 1.0), also differed from the reported value of −2.4° (12). X-ray analysis was obtained on **7**, and



1 $R^1=R^2=H$
2 R^1=Ac, $R^2=H$
3 $R^1=H$, R^2=OH
4 $R^1=H$, R^2=OAc
5 R^1=Ac, R^2=OH
6 R^1=2-methylbutanoyl, R^2=OH
7 R^1=Ac, R^2=OAc
8 R^1=2-methylbutanoyl, R^2=OAc



9 $R^1=R^3=H$, R^2=OH
10 $R^1=R^3=H$, R^2=OAc
11 R^1=2-methylbutanoyl, R^2=OAc, $R^3=H$
12 $R^1=H$, R^2,R^3=O
13 R^1=Ac, R^2,R^3=O

its molecular structure (not shown) was indeed confirmed as identical to corymbol diacetate. Also present were four new esters of corymbol: two monoacetates, **4** and **5**, and two esters of 2-methylbutyric acid at position 17, **6** and **8**. These could be related to **3** or **7** either by selective esterification (**4** and **5**) or by methanolysis (**6** and **8**). The ^{13}C-nmr spectra of corymbol [**3**] and its mono- and diacetates **4**, **5**, and **7** differed from those of **1** and **2**, showing the expected shift (δ_C ca. 67–71) for C-6 as well as downfield

TABLE 1. ^{13}C-nmr Spectral Data[a] for Compounds **1**, **2**, **3**, **4**, **5**, and **7**.

Carbon	Compound					
	1	**2**	**3**	**4**	**5**	**7**
C-1	43.2	40.2	obscured	40.2	40.3	40.1
C-2	19.3[b]	18.1[b]	17.9[b]	18.1[b]	18.1[b]	18.0[b]
C-3	43.2	42.0[c]	43.5	43.3	43.6	43.2
C-4	34.2	33.2	33.3	33.2	33.6	33.2
C-5	57.5[c]	56.6[d]	59.8	58.1	60.8	58.1
C-6	21.5	20.4	67.1	71.6	68.5	71.4
C-7	41.4	41.8[c]	52.7	47.3	52.3	47.1
C-8	45.7	44.8	44.1	44.2	44.8	44.3
C-9	58.3[c]	56.1[d]	55.9	56.1	56.0	56.0
C-10	40.5	39.3	obscured	40.9	40.9	40.9
C-11	19.6[b]	18.5[b]	18.1[b]	18.3[b]	18.4[b]	18.2[b]
C-12	27.3	26.3	25.9	25.9	26.1	25.9
C-13	46.3	46.0	44.8	45.2	46.0	45.8
C-14	38.2	37.1	37.5	37.4	37.6	37.2
C-15	53.9	53.1	53.2	53.3	53.2	53.2
C-16	82.8	79.9	80.2	81.8	79.6	79.6
C-17	66.8	68.5	65.3	66.2	68.5	69.0
C-18	34.1	33.5	36.7	36.1	36.7	36.0
C-19	22.0	21.5	22.1	22.2[c]	22.2	22.1[c]
C-20	18.4	17.7	19.0	18.9	19.1	18.9
6-Ac (Me)	—	—	—	22.0[c]	—	22.0[c]
6-Ac (CO)	—	—	—	170.9	—	170.2
17-Ac (Me)	—	20.9	—	—	20.9	20.9
17-Ac (CO)	—	171.3	—	—	171.3	171.3

[a]In ppm from internal TMS for $CDCl_3$ solutions for **2**, **4**, **5**, and **7**, CD_3OD for **1**, and DMSO-d_6 for **3**.
[b–d]Values in each column may be interchanged.

shifts for positions 5 and 7 and for Me-18 [a syn hydroxyl close to a methyl can cause significant deshielding of that group (13)]. In the ^{1}H-nmr spectra of compounds **3–8**, H-6 shows a triple doublet at ca. δ_H 3.9 for the free alcohols and ca. 5.1 for the 6-acetates consistent with α (equatorial) oxygenation at this position ($J_{ax\text{-}ax}$ = 10–11 Hz, $J_{ax\text{-}eq}$ = 4 Hz).

Compound **9** is a triol isomeric with corymbol, and its ^{13}C-nmr spectrum suggested hydroxylation at position 7, as deshielding of Me-18 was not observed (Table 2). Location of this hydroxyl in ring A or C appeared unlikely because significant alteration of chemical shifts for carbons 1 to 4, 11, and 12 of these rings did not occur. The ^{1}H-nmr spectrum of **9** exhibited a poorly resolved multiplet for H-7 although the acetate **10** showed a broad triplet consistent with α (axial) substitution of the oxygen function at this position ($J_{ax\text{-}eq} = J_{eq\text{-}eq}$ = ca. 3 Hz). Confirmation of the assigned structure was provided by X-ray analysis of **9** (Figure 1) which showed 5*R*,7*S*,8*R*,9*S*, 10*R*,13*R*, and 16*R* configuration. Also occurring in the plant was the corresponding 7-acetoxy-17-(2-methylbutyrate) **11**, which was related to **10** by selective methanolysis. The related ketone **12** (ir 1695 cm^{-1}) was accompanied by its monoacetate **13**. The location of the ketone could be inferred from information obtained by comparison of the ^{13}C-nmr spectra of two related kaurenoids, 7-keto-*ent*-kaur-16-en-19-oic acid and *ent*-

TABLE 2. ^{13}C-nmr Spectral Data[a] for Compounds **9**, **11**, **12**, and **13**.

Carbon	Compound			
	9	**11**	**12**	**13**
C-1	obscured	40.1	40.1	40.1
C-2	17.6[b]	17.5[b]	18.2[b]	18.1[b]
C-3	41.6	41.8	41.8	41.6
C-4	32.4	32.5	33.5	33.5
C-5	45.2	47.1	56.6[c]	56.6[c]
C-6	27.6	24.6	36.7	36.5
C-7	75.3	80.1	213.3	212.4
C-8	49.3	47.2	58.1	58.1
C-9	50.7	51.8	53.5[c]	53.7[c]
C-10	38.6	39.0	39.1	40.1
C-11	18.2[b]	18.4[b]	17.5[b]	17.4[b]
C-12	26.4	26.3	25.4	25.5
C-13	44.6	45.8	44.3	44.9
C-14	35.8	35.7	37.3	37.2
C-15	48.2	48.3	45.0	45.1
C-16	80.4	79.7	81.9	78.8
C-17	65.2	67.7	66.1	68.9
C-18	33.2	33.2	32.7	32.7
C-19	21.6	22.4	20.8	20.85
C-20	17.5	17.4	16.6	16.7
Ac (Me)	—	21.2	—	20.89
Ac (CO)	—	170.4	—	171.4
2-Methylbutanoyl signals				
C-1	—	176.5	—	—
C-2	—	41.1	—	—
C-3	—	26.7	—	—
C-4	—	11.6	—	—
C-α	—	16.7	—	—

[a]In ppm from internal TMS for $CDCl_3$ solutions for **11**, **12**, and **13**, and DMSO-d_6 for **9**.

[b,c]Values in each column may be interchanged.

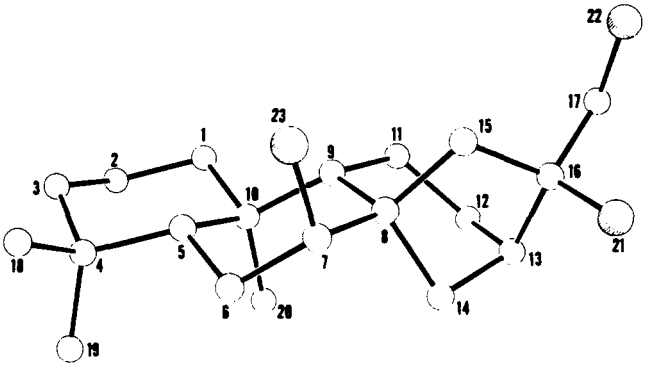


FIGURE 1. Perspective view of compound **9** with crystallographic numbering scheme. Open bonds represent double bonds, and shaded circles represent oxygen atoms.

kaur-16-en-19-oic acid (10), from which the substituent-induced chemical shift differences resulting from the presence of a carbonyl group at position 7 can be determined. Large shifts to lower field take place for carbons at positions 6 and 8 adjacent to the carbonyl (+17.0 and +13.6 ppm, respectively) with smaller increments to higher field for C-9 and C-13 (ca. −0.6 to −2.3 ppm), and with a much larger effect upon C-15 (−8.6 ppm). Application of these differences to the ^{13}C-nmr spectrum of **2** yields values close to those observed for **12**. Confirmation of the assignment of the carbonyl group to this position was provided by preparation of the 17-acetate from **9**, followed by oxidation of the secondary hydroxyl group at position 7 with Jones Reagent to yield the 17-acetoxy-7-ketone **13**. Ketone **12** was reduced to **1**, confirming the stereochemistry of compounds **9** to **13**.

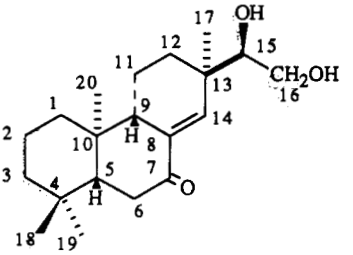
PIMARANES.—Several enantio-pimarane derivatives were isolated from *C. parviflora*. Compound **14** had strong uv absorption at 254 nm and showed ir bands at 1675 and 1605 cm^{-1} consistent with an α,β-unsaturated carbonyl group. The ^{13}C-nmr spectrum (Table 3) showed a carbonyl at δ 201.8 with olefinic signals at 136.4 and 143.4, and the ^{1}H-nmr showed an olefinic resonance at 6.81 ppm for the β proton. Also evident were four unsplit methyl signals and signals associated with a dihydroxyethyl moiety. Compound **14** has three rings, and examination of various diterpene types (16) indicated a pimarane system. The ^{13}C-nmr spectrum of **14** agreed with published values for pimaranes (17), and closely resembled that of 11β-hydroxy-7-ketosandaracopimar-8(14),15-diene (18) for the carbons of rings A and B. Complete structural information was given by X-ray crystallography (Figure 2), and further evidence that **14** is a member of the indicated ent series was provided by comparison of its cd data with that of the cis-enones, cholest-5-en-4-one, cholest-4-en-6-one, and 3β-acetoxy-5α-cholest-8(14)-en-7-one (19). The cd curve for **14** shows positive Cotton effects for the $n\rightarrow\pi^*$ band ($[\theta]_{332} = +2350$) and for band I ($[\theta]_{255} = +4880$), and is negative for band II ($[\theta]_{216} = -15020$). Of the three model cis-enones above, only cholest-5-en-4-one exhibited the same respective signs in the cd curve, showing that **14** was correlated to a compound bearing an enone chromophore of positive orbital helicity and therefore is of 5*R*,9*S*,10*R*,13*R*,15*R* configuration. This result is in agreement with the X-ray determination, which, however, was not statistically definitive (see Experimental section). Chemical correlation of **14** with **18** (vide infra) did provide conclusive evidence of the absolute configuration of **14**.

Tetracyclic compound **17**, having a 14,16-oxido linkage, showed nmr signals characteristic of a double bond (δ_C 130.5 and 133.7, δ_H 5.80), formed a monoacetate

TABLE 3. ^{13}C-nmr Spectral Data[a] for Compounds **14**, **15**, **17**, **19**, **20**, and **22**.

Carbon	Compound					
	14	**15**[b]	**17**	**19**	**20**	**22**
C-1	38.8	39.7	39.6	38.5	38.6	39.1
C-2	18.6[c]	18.9	18.7	18.7	19.7	18.1
C-3	41.9	42.2	42.1	42.1	45.1	42.8
C-4	33.1	32.8	32.7	32.8	34.1	32.1
C-5	49.8	49.5	49.6	49.3	56.8	62.9
C-6	37.3	23.8	23.7	23.8	69.6	192.5
C-7	201.8	130.5	130.5	132.3	136.2	132.7
C-8	136.4	133.7	133.7	132.2	134.9	150.6
C-9	51.1	48.3	48.6	48.3	49.1	49.1
C-10	35.9	35.1	35.0	35.0	40.9	40.8
C-11	18.5[c]	20.0	19.8	19.4	20.8	19.3
C-12	30.0	31.0	25.4	28.4	31.8	28.2
C-13	39.3	45.1	42.4	47.0	46.4	47.8
C-14	143.4	86.4	88.1	88.0	87.1	86.1
C-15	78.6	79.9	80.5	ca. 218	80.4	ca. 218
C-16	62.9	74.2	70.3	70.0	75.4	70.2
C-17	22.2	14.5	19.0	15.0	16.3	15.0
C-18	32.6	33.4	33.3	33.3	37.3	33.4
C-19	21.1	22.3	22.2	22.2	23.1	21.8
C-20	13.8	14.8	14.6	14.5	14.8	15.4

[a]In ppm from internal TMS for $CDCl_3$ solutions for **14**, **15**, **17**, **19**, and **22**, and CD_3OD for **20**.
[b]Data taken from Rao *et al.* (18).
[c]Values in each column may be interchanged.



14

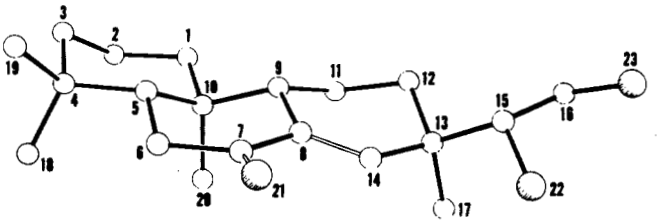
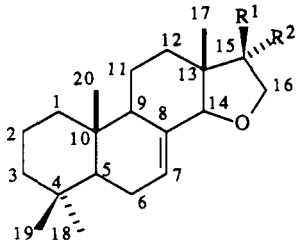
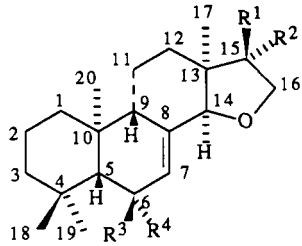


FIGURE 2. Perspective view of compound **14** with crystallographic numbering scheme. Open bonds represent double bonds, and shaded circles represent oxygen atoms.



15 R^1=OH, R^2=H
16 R^1,R^2=O



17 R^1=OH, R^2=R^3=R^4=H
18 R^1=OAc, R^2=R^3=R^4=H
19 R^1,R^2=O, R^3=R^4=H
20 R^1=R^3=OH, R^2=R^4=H
21 R^1=R^3=OAc, R^2=R^4=H
22 R^1,R^2=R^3,R^4=O

18, and could be oxidized to ketone **19** (ν max 1755 cm^{-1}). Spectral data for **17** and these derivatives were very similar to those reported (18) for premnenol [**15**], but detailed examination of the ^{13}C-nmr spectra of **15** and **17** showed that major differences occurred for signals associated with carbons near the hydroxyl group. Also, the considerations that had shown this hydroxyl to have the β configuration in **15** (18,20) indicate an α configuration in **17**. Thus, C-12 and C-17 of **17** give rise to signals at δ 25.4 and 19.0, respectively, and are in agreement with values for the corresponding carbons in 15α-tetrahydrofuranovirescenol B diacetate [δ 25.2 and 18.8, respectively, compared to 30.6 and 14.4 for the 15β-hydroxy epimer in that series (20)]. Ketone **19** had mp and ^{1}H-nmr data close to that reported (18) for premnenone [**16**], supporting the conclusion that **15** and **17** are identical except for the configuration at C-15; however, no optical data was reported for premnenone, so it was not clear whether **17** was a member of the *ent*-pimarane series as seemed likely on biogenetic grounds. Correlation of the structures of **14** and **17** was done by first cyclizing **14** to the corresponding 15α-hydroxytetrahydrofurano derivative followed by acetylation. Borohydride reduction gave an epimeric mixture of alcohols at position 7, and dehydration of the major product yielded acetate **18**, which had already been prepared from **17**, and which had the same sign and magnitudes for specific rotations of the latter material. Unequivocal evidence for the molecular structure and absolute configuration of **17** was provided by X-ray crystallographic analysis (Figure 3), showing 5*R*,9*S*,10*R*,13*S*,14*S*,15*R* configuration.

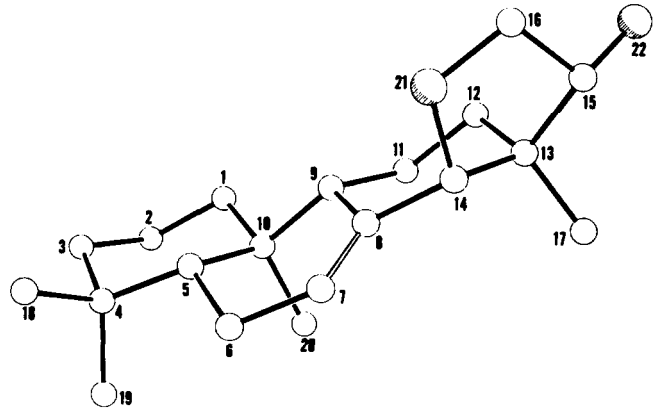


FIGURE 3. Perspective view of compound **17** with crystallographic numbering scheme. Open bonds represent double bonds, and shaded circles represent oxygen atoms.

This indicates that both **14** and **17** belong to the antipodal pimarane series in contrast to the configuration determined for premnenol (18).

The 6-hydroxy analogue **20** showed ^{1}H- and ^{13}C-nmr signals very similar to those of **17** with δ_C 69.6 for position 6 and a double broad triplet at δ_H 4.15 (J = 10, 2 Hz) for H-6 indicative of axial orientation of that proton. Diacetate **21** gave a multiplet at δ 5.42 in the ^{1}H nmr with coupling constants of 11, 3, and 2 Hz for H-6, with the largest value arising from diaxial coupling of H-6 to H-5, for an equatorial acetoxy group (α orientation). Oxidation of **20** gave a diketone **22** having ir absorption characteristic of both 5-membered ring and α,β-unsaturated ketones (ν max 1755, 1675 cm^{-1}) with uv absorption of 236 nm. The ^{1}H-nmr spectrum of **22** was similar to that of **19** but showed a singlet for H-5 at δ 2.30 and a doublet at 6.04 for H-7 in agreement with the assignment of an oxygen substituent at position 6.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra and specific rotations were determined on Perkin-Elmer 237 and 241 instruments, respectively, and uv spectra were taken using a Hewlett-Packard 8451 spectrophotometer. Cd data were obtained in MeOH at 27° using a Cary 60 spectropolarimeter equipped with a 6003 cd accessory which had been calibrated with (+)-10-camphorsulfonic acid. ^{1}H-nmr spectra were obtained on Varian EM-390 and Nicolet NT-200 spectrometers at 90 and 200 MHz, respectively, and ^{13}C-nmr spectra were taken at 50 MHz on the latter instrument. Nmr assignments were facilitated by proton-proton decoupling and by use of 2D correlation techniques. Mass spectral determinations were performed using a VG Micromass 70/70 HS instrument and are relative to a perfluoroalkane internal standard. Gc-ms analyses were obtained on a Finnigan 4500 GC/MS/DS using a DB-1 methyl silicone column with temperature programming from 50° to 250°. Spectral comparisons were with the NBS/NIH mass spectral library, augmented with added literature spectra and spectra obtained locally from authentic samples. Hplc grade solvents were pumped with Altex-Beckman Model 110A, Rainin Rabbit HPX, and Waters Associates Model 6000 A pumps. Detection was with Altex-Beckman Models 150 uv and 156 ri detectors, respectively. Low resolution chromatography was performed on Waters preparative C-18 packing. Preparative hplc was carried out using the following columns: Rainin Dynamax C-18 (size given below), Rainin Dynamax CN (10 × 250 mm), and Alltech RSil C-18 (10 × 250 mm).

PLANT MATERIAL.—Seeds of *C. parviflora* were obtained from The Royal Botanic Garden, and a voucher specimen is on deposit in the Beal-Darlington Herbarium at Michigan State University as MSC 256266. Plants were grown under greenhouse conditions in Albany, California, and portions were harvested at intervals and freeze-dried. Leaves were separated from stems by screening of the dry plant.

BIOASSAYS.—Neonate larvae of *H. zea* were placed on modified Berger diet (6) and allowed to grow for three days at 26°. The larvae were then transferred to plant material (ten larvae per sample) maintained in Petri dishes with moistened filter paper, and visual observations were made at hourly intervals for the first 10 h and once daily for the next 4 days. Larvae on *Petunia* leaves showed immediate distress after consuming very little, and high mortality occurred with the few survivors showing low growth. In contrast, larvae on *C. parviflora* freely accepted leaf material and grew at a rate close to that of subjects feeding on control artificial diet.

EXTRACTION AND FRACTIONATION.—Leaf material was ground with $CHCl_3$ (20 ml/g), using a Tekmar homogenizer on maximum speed, and filtered; this was repeated twice. After evaporation, the heavy oil was stirred with boiling MeCN (25 ml/g), and the mixture was then concentrated to ca. one fifth its volume. After storage at 5° for 16 h, the solid was filtered off, and remaining nonpolar substances were removed by passage of the MeCN-soluble material through a short column of preparative C-18 packing. Hplc was carried out on Dynamax C-18 (41.4 mm diameter) using 100% MeCN to give three broad zones having the following elution volumes: zone I 225–550 ml, zone II 550–950 ml, and zone III 950–1500 ml. Individual components were obtained by further hplc with the columns and conditions indicated below. Quantities are expressed in mg/kg (ppm) based on dry plant material.

*6α-Acetoxy-*ent*-kaurane-16β,17-diol* [**4**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 230–250 ml; RSil C-18, 30% H_2O in MeCN, elution volume 43–50 ml; and Dynamax CN, 40% H_2O in MeCN, elution volume 23–26 ml, yield 340 ppm. Mp 148–149° (EtOAc/isooctane); [α] (λ nm) −64° (589), −66° (578), −75° (546), −124° (436), −187° (365) ($CHCl_3$, c = 1.7); ir ν max ($CHCl_3$) cm^{-1} 3580, 3400 br, 1720; ^{1}H nmr δ ($CDCl_3$) 0.84 (s, H_3-19), 0.99 (s, H_3-18), 1.07 (s, H_3-20), 2.01 (s, -OAc), 3.62 (d, J = 11 Hz, 1/2 H_2-17), 3.74 (d, J = 11 Hz, 1/2 H_2-

17), 5.12 (td, J = 11, 4 Hz, H-6); ^{13}C nmr see Table 1; eims *m/z* $[M - CH_2OH]^+$ 333.2428 ($C_{21}H_{33}O_3$ requires 333.2421).

17-Acetoxy-ent-*kaurane*-6α,16β-*diol* [**5**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 200–215 ml, and RSil C-18, 30% H_2O in MeCN, elution volume 38–43 ml, yield 50 ppm. Mp 168–170° (EtOAc/isooctane); [α] (λ nm) −48° (589), −49° (578), −56° (546), −94° (436), −145° (365) ($CHCl_3$, c = 0.4); ir ν max ($CHCl_3$) cm^{-1} 3600, 3300 br, 1730; ^{1}H nmr δ ($CDCl_3$) 1.03 (s, H_3-18), 1.05 (s, H_3-19), 1.15 (H_3-20), 2.11 (s, OAc), 3.94 (m, H-6), 4.23 (s, H_2-17); ^{13}C nmr see Table 1; eims *m/z* $[M]^+$ 364.2602 ($C_{22}H_{36}O_4$ requires 364.2615).

17-(2-Methylbutanoyloxy)-ent-*kaurane*-6α,16β-*diol* [**6**].—From fraction II, followed by Dynamax C-18 (21.4 × 250 mm) 100% MeCN, elution volume 165–180 ml, and RSil C-18, 100% MeCN, elution volume 30–35 ml, yield 130 ppm. Mp 136–137° (MeOH); [α] (λ nm) −21° (589), −21° (578), −24° (546), −39° (436), −59° (365) ($CHCl_3$, c = 1.2); ir ν max ($CHCl_3$) cm^{-1} 3600, 3450 br, 1730; ^{1}H nmr δ ($CDCl_3$) 1.02 (s, H_3-18), 1.05 (s, H_3-19), 1.15 (s, H_3-20), 3.93 (td, 11, 4 Hz, H-6), 4.24 (m, H_2-17), 2-methylbutyrate signals: 0.92 (t, J = 7 Hz, terminal Me), 1.15 (d, J = 7 Hz, α-Me), 2.43 (sextet, J = 7 Hz, α-H); eims *m/z* $[M - H_2O]^+$ 388.2984 ($C_{25}H_{40}O_3$ requires 388.2979).

6α-*Acetoxy-17-(2-methylbutanoyloxy)*-ent-*kauran-16*β-*ol* [**8**].—From Fraction II, followed by Dynamax C-18 (21.4 × 250 mm) 100% MeCN, elution volume 180–210 ml, and RSil C-18, 15% H_2O in MeCN, elution volume 68–75 ml, yield 200 ppm. Mp 146–147° (EtOAc/heptane) [α] (λ nm) −57° (589), −59° (578), −67° (546), −111° (436), −168° (365) ($CHCl_3$, c = 2.5); ir ν max ($CHCl_3$) cm^{-1} 3600, 3400 br, 1720; ^{1}H nmr δ ($CHCl_3$) 0.87 (s, H_3-19), 1.02 (s, H_3-18), 1.09 (s, H_3-20), 2.03 (s, OAc), 4.24 (m, H_2-17), 5.16 (td, 11, 4 Hz, H-6); 2-methylbutyrate signals 0.95 (t, J = 7 Hz, terminal methyl), 1.16 (d, J = 7 Hz, α-methyl), 2.42 (sextet, J = 7 Hz, α-H); eims *m/z* $[M - H_2O]^+$ 430.3089 ($C_{27}H_{42}O_4$ requires 430.3085).

INTERCONVERSIONS OF COMPOUNDS **3**–**8**.—Partial acetylation of **3** was carried out with Ac_2O in pyridine by warming briefly to 70°. After 30 min at room temperature, evaporation and hplc gave monoacetate **5** and diacetate **7**. Monoacetate **4** gave diacetate **7** similarly. Methanolysis of **6** with 0.05 M NaOMe at room temperature for 1.5 h followed by removal of volatile material in vacuum with dry ice trapping gave **3** by hplc of the residue. Methyl 2-methylbutyrate was identified by gc-ms of the volatile fraction. Compound **8** treated similarly gave methyl 2-methyl butyrate and monoacetate **4**.

ent-*Kaurane*-7α,16β,17-*triol* [**9**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 125–140 ml, yield 750 ppm. Mp 220–221° (EtOAc); [α] (λ nm) +3° (589), +3° (578), +4° (546), +8° (436), +16° (365) (95% EtOH, c = 1.0); ^{1}H nmr δ (CD_3OD) 0.83 (s, H_3-19), 0.85 (s, H_3-18), 1.06 (s, H_3-20), 3.58 (d, J = 12 Hz, 1/2 H_2-17), ca. 3.60 (m, H-7), 3.70 (d, J = 12, 1/2 H_2-17); ^{13}C nmr see Table 2; eims *m/z* $[M]^+$ 322.2507 ($C_{20}H_{34}O_3$ requires 322.2509).

7α-*Acetoxy*-ent-*kaurane-16*β,17-*diol* [**10**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 250–280 ml, and RSil C-18, 15% H_2O in MeCN, elution volume 35–40 ml, yield 120 ppm. Mp 160–163° (EtOAc/heptane); [α] (λ nm) +16° (589), +16° (578), +18° (546), +34° (436), +52° (365), ($CHCl_3$, c = 0.5); ir ν max ($CHCl_3$) cm^{-1} 3550, 3450 br, 1725; ^{1}H nmr δ ($CDCl_3$) 0.76 and 0.78 (s's, H_3-18 and -19), 1.03 (s, H_3-20), 2.03 (s, OAc), 3.72 (m, H_2-17), 4.82 (br t, H-7); eims *m/z* $[M - CH_2OH]^+$ 333.2411 ($C_{21}H_{33}O_3$ requires 333.2431).

7α-*Acetoxy-17-(2-methylbutanoyloxy)*-ent-*kauran-16*β-*ol* [**11**].—From fraction II, followed by Dynamax C-18 (21.4 × 250 mm) 100% MeCN, elution volume 180–210 ml, and RSil C-18, 15% H_2O in MeCN, elution volume 75–85 ml, yield 100 ppm. Mp 163–165° (EtOAc/heptane); [α] (λ nm) +2° (589), +2° (578), +2° (546), +4° (436), +5° (365); ir ν max ($CHCl_3$) cm^{-1} 3600, 3450 br, 1725; ^{1}H nmr δ ($CDCl_3$) 0.76 and 0.78 (s's, H_3-18 and H_3-19), 1.03 (s, H_3-20), 2.03 (s, OAc), 4.22 (m, H_2-17), 4.82 (m, H-7), 2-methylbutyrate signals: 0.92 (t, J = 7 Hz, terminal Me), 1.16 (d, J = 7 Hz, α-Me), 2.44 (sextet, J = 7 Hz, α-H); eims *m/z* $[M - H_2O]^+$ 430.3121 ($C_{27}H_{42}O_4$ requires 430.3085).

7-*Keto*-ent-*kaurane-16*β,17-*diol* [**12**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 140–160 ml, yield 70 ppm. Mp 168–170° (heptane); [α] (λ nm) −12° (589), −12° (578), −10° (546), +24° (436), +198° (365); ir ν max ($CHCl_3$) cm^{-1} 3600, 3450 br, 1695; ^{1}H nmr δ ($CDCl_3$) 0.86 (s, H_3-18, -19), 1.19 (H_3-20), 3.73 (m, H_2-17); ^{13}C nmr see Table 2; eims *m/z* $[M]^+$ 320.2325 ($C_{20}H_{32}O_3$ requires 320.2353).

17-Acetoxy-7-keto-ent-*kauran-16*β-*ol* [**13**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 230–250 ml; RSil C-18, 30% H_2O in MeCN, elution volume 44–50 ml; and Dynamax CN, 40% H_2O in MeCN, elution volume 26–30 ml, yield 260 ppm. Mp 149–151° (EtOAc/heptane); [α] (λ nm) −23° (589), −24° (578), −24° (546), −15° (436),

+81° (365); ir ν max ($CHCl_3$) cm^{-1} 3600, 3450 br, 1730, 1695; ^1H nmr δ ($CDCl_3$) 0.85 (s, H_3-18, -19), 1.20 (H_3-20), 2.11 (s, OAc), 4.18 (d, J = 11 Hz, 1/2 H_2-17); 4.30 (d, J = 11 Hz, 1/2 H_2-17); ^{13}C nmr see Table 2; eims *m/z* $[M]^+$ 362.2428 ($C_{22}H_{34}O_4$ requires 362.2458).

INTERCONVERSIONS OF COMPOUNDS **9** TO **13**.—Compound **9** was treasted with Ac_2O in pyridine and chromatographed on RSil C-18, 15% aqueous MeCN to give the diacetate, elution volume 85–95 ml. ^1H nmr δ ($CDCl_3$) 2.00 and 2.07 (s's, OAc's), 4.20 (s, CH_2OAc), 4.84 (m, CHOAc). Selective deacetylation in 0.05 M NaOMe as above gave monoacetate **10**. Similarly, **11** gave monoacetate **10** and methyl 2-methylbutyrate. Acetylation of **12** gave **13**.

JONES OXIDATION OF 17-ACETOXY-*ent*-KAURANE-7α,16β-DIOL.—Compound **9** was treated with Ac_2O in pyridine at 20° for 3 h, evaporated, and chromatographed on RSil C-18, 30% H_2O in MeCN, to give the 17-monoacetate, elution volume 38–43 ml. ^1H nmr δ ($CDCl_3$) 2.07 (s, OAc), 3.70 (m, 7-CHOH), 4.22 (s, CH_2OAc). This was dissolved in 2 ml Me_2CO and .009 ml of Jones reagent (14) was added in one portion at room temperature. After 2 min, .01 ml MeOH was added, and the mixture was filtered through a 0.45 μ Nylon-66 syringe filter followed by evaporation and hplc to give **13**.

REDUCTION OF **12**—Ketone **12** 15 mg in 1.0 ml MeOH, was refluxed with 11 mg of toluenesulfonyl hydrazine (15) for 2 h, and allowed to stand at room temperature 16 h. An additional 1.0 ml of MeOH was added followed by $NaBH_4$ in three 25-mg portions over 1 h, and the mixture was refluxed 6 h. After addition to 25 ml Et_2O, the mixture was washed with 10 ml H_2O, 10 ml 1 N HCl, and 10 ml 1 N NaOH and dried over $MgSO_4$. Evaporation followed by hplc gave 3.2 mg of **1**, [α] (λ nm) −36° (589), −43° (578), −47° (546), −76° (436), −104° (365) ($CHCl_3$, c = 0.25). [lit. (8) [α] ^{16}D −36.2° ($CHCl_3$, c = 0.93)].

15R,16-Dihydroxy-ent-*isopimar-8(14)-en-7-one* [**14**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 30% H_2O in MeCN, elution volume 170–205 ml; RSil C-18, 30% H_2O in MeCN, elution volume 32–38 ml; and Dynamax CN, 20% iPrOH/hexane, elution volume 26–30 ml, yield 270 ppm. Mp 164–165° (EtOAc/heptane); [α] (λ nm) +16° (589), +18° (578), +23° (546), +81° (436), +478° (365) ($CHCl_3$, c = 1.0); cd (MeOH) $[\theta]_{216} = -15020$, $[\theta]_{255} = +4880$, $[\theta]_{332} = +2530$; ir ν max ($CHCl_3$) cm^{-1} 3450 br, 1675, 1605; uv λ max (MeOH) 254 nm (log ε max 3.91); ^1H nmr δ ($CDCl_3$) 0.82 (s, H_3-20), 0.86 and 0.89 (s's, H_3-18 and -19), 1.05 (s, H_3-17), 2.03 (m, H-8), 2.27 (dd, J = 19, 14 Hz, H-6ax), 2.55 (dd, J = 19, 5 Hz, H-6eq), 3.44 (dd, J = 4, 8 Hz, H-15), 3.63 (m, H_2-16), 6.81 (d, J = 2.5 Hz, H-14); ^{13}C nmr see Table 3; eims *m/z* $[M]^+$ 320.2351 ($C_{20}H_{32}O_3$ requires 320.2353).

14α,16-Oxido-ent-*isopimar-7-en-15α-ol* [**17**].—From fraction II, followed by Dynamax C-18 (21.4 × 250 mm) 100% MeCN, elution volume 165–180 ml, and RSil C-18, 100% MeCN, elution volume 35–38 ml, yield 155 ppm. Mp 147–150° (EtOAc/heptane); [α] (λ nm) +21° (589), +24° (578), +26° (546), +53° (436), +105° (365) ($CHCl_3$, c = 1.0); ir ν max ($CHCl_3$) cm^{-1} 3600, 3450 br; ^1H nmr δ ($CDCl_3$) 0.80 (s, H_3-20), 0.85 (s, H_3-18), 0.91 (s, H_3-19), 0.98 (s, H_3-17), 3.58 (dd, J = 7, 8 Hz, 1/2 H_2-16), 3.70 (br s, H-14), 4.02 (m, 1/2 H_2-16), 4.11 (m, H-15), 5.80 (m, H-7); ^{13}C nmr see Table 3; eims *m/z* $[M]^+$ 304.2403 ($C_{20}H_{32}O_2$ requires 304.2404).

15α-Acetoxy-14α,16-oxido-ent-*isopimar-7-ene* [**18**].—Compound **17** was treated with Ac_2O in pyridine and chromatographed on RSil C-18, 100% MeCN, to give **18**, elution volume 36–40 ml. [α] (λ nm) +27° (589), +29° (578), +33° (546), +64° (436), +116° (365) ($CHCl_3$, c = 0.7); ir ν max ($CHCl_3$) cm^{-1} 1725; ^1H nmr δ ($CDCl_3$) 0.79 (s, H_3-20), 0.85 (s, H_3-18), 0.90 (s, H_3-19), 1.01 (s, H_3-17), 2.07 (s, OAc), 3.62 (dd, J = 7, 9 Hz, 1/2 H_2-16), 3.72 (br s, H-14), 4.16 (dd, J = 8, 9 Hz, 1/2 H_2-16), 4.96 (dd, J = 7, 8 Hz, H-15), 5.84 (m, H-7).

14α,16-Oxido-ent-*isopimar-7-en-15-one* (ent-*premnenone*) [**19**].—Compound **17** was treated with Jones reagent as above and chromatographed on RSil C-18, 15% H_2O in MeCN, to give **19**, elution volume 68–72 ml. Mp 112–114° (MeOH/H_2O) [lit. (17) for premenone [**16**] 110–112°]; [α] (λ nm) −15° (589), −15° (578), −15° (546), −8° (436), +62° (365) ($CHCl_3$, c = 1.0); ir ν max ($CHCl_3$) cm^{-1} 1755; ^1H nmr δ ($CDCl_3$) 0.81 (s, H_3-20), 0.88 (s, H_3-18), 0.92 (s, H_3-19), 1.02 (s, H_3-17), 3.86 (d, J = 16 Hz, 1/2 H_2-16), 3.97 (br s, H-14), 4.29 (d, J = 16 Hz, 1/2 H_2-16), 5.98 (m, H-7); ^{13}C nmr see Table 3.

CORRELATION OF **14** WITH **18**.—A solution of **14** (50 mg) was prepared in 1.0 ml THF-d_8 in a standard nmr tube, and ca. 10 mg of LiH was added to give a suspension of material which was maintained at room temperature for 10 days. The reaction was followed by ^1H nmr at 90 MHz by observing the disappearance of olefinic signal (H-14) occurring at δ 6.77 in this solvent ($t_{1/2}$ ca. 50 h). The mixture was diluted with 2 ml of MeCN, filtered through a 0.45 μ Nylon-66 syringe filter, and chromatographed on RSil C-18, 15% H_2O in MeCN, to give 38 mg of cyclized product, elution volume 23–28 ml. This product was acetylated with Ac_2O in pyridine and chromatographed on RSil C-18, 15% H_2O in MeCN, elution volume 36–48 ml. ^1H nmr of the acetate δ ($CDCl_3$, 90 MHz) 0.80 (s, H_3-20), 0.85 (s, H_3-18), 0.98 and 1.00

(s's, H_3-17, -19), 2.03 (s, OAc), 2.3–2.6 (m, H_2-6 and H-8), 3.58 (dd, J = 7, 9 Hz, 1/2 H_2-16), 4.14 (br s, H-14), 4.24 (br t, J = 9 Hz, 1/2 H_2-16), 4.94 (br t, J = 9 Hz, H-15). This keto acetate was reduced with $NaBH_4$ in 3 ml MeOH for 1 h at room temperature and then chromatographed on RSil C-18, 15% H_2O in MeCN. Two hydroxy acetates were obtained, elution volumes 41–46 ml and 65–75 ml, 11 and 20 mg respectively, ir ν max ($CHCl_3$) cm^{-1} 3500 br and 1725, whose ^1H nmr spectra showed absence of signal at δ 2.40 and appearance of new signals at ca. 3.8–4 ppm. Treatment of the hydroxy acetate of greater elution volume with 0.025 ml $POCl_3$ in 0.5 ml, pyridine for 16 h at room temperature followed by chromatography on RSil C-18, 5% H_2O in MeCN, elution volume 50–57 ml, and Dynamax CN, 30% H_2O in MeCN, elution volume 28–32 ml, gave 15 mg of **18** spectroscopically identical to material previously obtained. The specific rotations for this product, [α] (λ nm) +21° (589), +23° (578), +26° (546), +51° (436), +107° (365) ($CHCl_3$, c = 0.7), were in close agreement with values obtained for **18**.

14α,16-Oxido-ent-*isopimar-7-ene-6α,15α-diol* [**20**].—From fraction I, followed by Dynamax C-18 (21.4 × 250 mm) 40% H_2O in MeCN, elution volume 200–240 ml, and RSil C-18, 40% H_2O in MeCN, elution volume 41–46 ml, yield 200 ppm. Mp 207–210° ($MeCN/H_2O$); [α] (λ nm) −16° (589), −17° (578), −19° (546), −29° (436), −38° (365) (95% EtOH, c = 1.0); ir ν max ($CHCl_3$) cm^{-1} 3580, 3350 br; ^1H nmr δ (CD_3OD) 0.88, 0.96, 1.08, 1.14 (s's, H_3-17, -18, -19, -20), 3.60 (dd, J = 2, 10 Hz, 1/2 H_2-16), 3.79 (dd, 5, 2 Hz, H-15), 3.85 (br s, H-14), 4.15 (d, br t, 10, ca. 2 Hz, H-6), 4.25 (dd, 10, 5 Hz, 1/2 H_2-16), 5.65 (br t, ca. 2 Hz, H-7); ^{13}C nmr see Table 3; eims m/z $[M]^+$ 320.2335 ($C_{20}H_{32}O_3$ requires 320.2353).

6α,15α,Diacetoxy-14α,16-oxido-ent-*isopimar-7-ene* [**21**].—Compound **20** was acetylated with Ac_2O in pyridine and chromatographed on RSil C-18, 100% MeCN, to give **21**, elution volume 24–27 ml. ^1H nmr δ ($CDCl_3$) 0.91, 0.97 (2), 1.00 (s's, H_3-17, -18, -19, -20), 2.05 and 2.08 (s's, OAc's), 3.63 (dd, J = 7, 10 Hz, 1/2 H_2-16), 3.71 (br s, H-14), 4.18 (dd, J = 8, 10 Hz, 1/2 H_2-16), 4.95 (dd, J = 7, 8 Hz, H-15), 5.42 (ddd, J = 11, 3, 2 Hz, H-6), 5.84 (br t, J = ca. 3 Hz, H-7).

14α,16-Oxido-ent-*isopimar-7-ene-6,15-dione* [**22**].—Compound **20** (27 mg) was treated with Jones reagent as above. Chromatography on RSil C-18, 15% H_2O in MeCN, gave **22**, elution volume 28–33 ml. Mp 145–146° (EtOAc/heptane); ir ν max ($CHCl_3$) cm^{-1} 1755, 1675; uv λ max (MeOH) 236 nm; ^1H nmr δ ($CDCl_3$) 0.93, 1.07, 1.11, 1.22 (s's, H_3-17, -18, -19, -20), 2.30 (s, H-5), 2.55 (m, H-9), 3.93 (d, J = 16 Hz, 1/2 H_2-16), 4.12 (br s, H-14), 4.32 (d, J = 16 Hz, 1/2 H_2-16), 6.04 (d, J = 3 Hz, H-7); ^{13}C nmr see Table 3.

X-RAY CRYSTALLOGRAPHY[1].—Intensity data were collected in the range of $3° \leq 2\theta \leq 114°$ on a Nicolet R3 diffractometer with graphite monochromatized Cu-K_α radiation (λ = 1.5418 Å) by the θ–2θ scan technique with variable scan speed (4–30° min^{-1}) at room temperature. The intensity data were corrected for background and Lorentz-polarization effects (21) but not for absorption. The crystal structures were solved by direct methods and refined by a blocked-cascade full-matrix least-squares procedure with the SHELXTL (22) program package. The function minimized was $[\Sigma\omega(|F_o| - |F_c|)^2]$, where $\omega = [\sigma^2|F_o| + 0.001|F_o|^2]^{-1}$. Unique reflections with the criteria of ($|F_o| \geq 3\sigma|F_o|$) were included in the structure refinement calculation. Scattering factors were from *International Tables for X-ray Crystallography* (23); those of oxygen were corrected for anomalous dispersion. Secondary extinction correction was included in the final cycles of refinement to minimize the discrepancy between observed and calcualted structure factors of the most intense reflections, which led to a small improvement in the R-index. Positions of all non-hydrogen atoms were refined anisotropically, and all hydrogen positions were estimated but verified in subsequent difference Fourier maps and included at invariant idealized values in the respective structure-factor calculation. Absolute configurations of structures **7**, **9**, and **17** were determined by Bijvoet's method (24) of comparing the observed intensities of 12 carefully selected Friedel-pairs, $I_{(hkl)}$ and $I_{(-h-k-l)}$, with their calculated values. However, this comparison for structure **14** was indefinitive in contrast to the other three structures, since 7 pairs favored one enantiomer and 5 the other.

ACKNOWLEDGMENTS

We thank Professor K.C. Sink of Michigan State University for supplying seeds of *C. parviflora* and for providing information about the plant. We also thank Dr. W.F. Haddon and Mr. Leslie Harden for ms determinations, Dr. R.A. Flath for gc-ms analyses, and Ms. S.C. Witt for obtaining nmr data.

[1]Atomic co-ordinates for these have been deposited at the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK. Note that the crystallographic numbering scheme of Figures 1–3 differs from that of structures **9**, **14**, and **17**.

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Received 17 April 1992