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STRUCTURE AND PLANT GROWTH ACTIVITY RELATIONSHIP IN TERPENOID LACTONES

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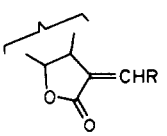
Key Word Index—Terpenoid lactones; root promoters; germacranolides; eudesmanolides; guaianolides; elemanolides.

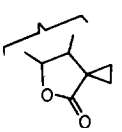
Abstract—In order to obtain structure–biological activity data the synthesis of 15 new terpenoid lactones from germacranolides, eudesmanolides, guaianolides and elemanolides was undertaken. These and 15 other compounds were then tested as plant growth regulators. These studies established that the biological activity associated with the α-methylene-γ-lactone moiety in a terpenoid lactone is further enhanced when a cyclopropane ring is placed in the α,β-position to the lactone carbonyl. No exception to this structure–activity data has been noted so far. Significantly, this activity is increased when a trisubstituted (*Z*)-double bond is in the position of conjugation and the only exception to this is (*Z*)-C_{13}-methyl dehydrosaussurea lactone which is only as active as water. Almost always a C-4 epoxy, or a C-4, C-10 ether group in the guaianolide systems further enhances the biological activity associated with the parent lactone. A similar effect of the epoxy group is not observed in the case of eudesmanolides.

INTRODUCTION

The plant growth activity of several α-methylene-γ-lactones is well documented [1]. It is established that this activity is due to the exomethylene group conjugated with the lactone carbonyl [2] and that this structural feature (**1**) is almost indispensable for the display of this action. Work from our laboratory has shown that γ-lactones, in which a trisubstituted double bond (**2**) or a cyclopropane ring (**3**) is conjugated with the lactone carbonyl, are even more active than the parent α-methylene-lactones [3].



1 R = H
2 R = Me



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It has been observed [Kalsi, P. S., unpublished work] that a large variation in biological activity is displayed by γ-lactones having similar active moieties in the α,β-position to the lactone carbonyl but with different underlying carbon skeleta. We have, therefore, evaluated the biological activity of the compounds prepared earlier [4] and also report the synthesis and biological activities of a number of new compounds. The major biological parameter studied was rooting in stem cuttings of *Phaseolus aureus*.

RESULTS AND DISCUSSION

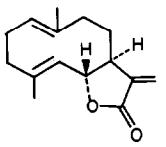
Germacranolides and their derivatives

Two germacranolides were tested (Table 1). Costunolide (**4**) is considerably more active than the control. This activity is enhanced almost four times at 20 mg/l. when the methylenic double bond of **4** is replaced by a cyclopropane ring in **5**.

Table 1. Effect of 5, 10, 15 and 20 mg/l. germacranolides on the number of roots per rooted segment produced on hypocotyl cuttings of *P. aureus* after 7 days

	Number of roots*			
Compound	5	10	15	20
4	4.9 ± 0.7	4.6 ± 0.7	6.0 ± 1.6	7.3 ± 1.0
5	5.1 ± 0.8	8.9 ± 0.8	11.9 ± 1.4	28.4 ± 3.0

*Control experiment, water = 4.8 ± 0.8.



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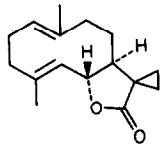

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Eudesmanolides and their derivatives

Twelve compounds were tested in this series. Inspection of Table 2 shows that the activity of each of the C_{16} derived isomers **7**, a cyclopropane derivative, and **8** is greater than that of the parent compound α-cyclocostunolide (**6**), as is that of **11** when compared with β-cyclocostunolide (**10**). Also, as compared with α- and β-cyclocostunolide the derived (*Z*)-C_{16} γ-lactones, **8** and **12**, are more active. In the β-cyclocostunolide series the activity up to 15 mg/l. is distinctly higher than in the α-

Table 2. Effect of 5, 10, 15 and 20 mg/l. eudesmanolides on the number of roots per rooted segment produced by hypocotyl cuttings of *P. aureus* after 7 days

Compound	Number of roots*			
	5	10	15	20
6	8.2 ± 1.3	6.9 ± 1.2	P	P
7	4.4 ± 0.5	6.2 ± 16	10.6 ± 1.2	18.4 ± 3.0
8	5.4 ± 1.6	7.0 ± 0.9	10.0 ± 1.8	20.0 ± 2.0
10	4.3 ± 0.6	8.2 ± 1.8	10.6 ± 1.4	7.0 ± 1.4
11	6.4 ± 0.7	8.6 ± 1.8	13.6 ± 1.6	12.2 ± 1.5
12	13.1 ± 1.7	16.7 ± 2.5	18.7 ± 3.0	17.2 ± 2.8
16	5.8 ± 1.2	10.3 ± 2.6	12.5 ± 2.6	Toxic
17	6.3 ± 1.1	11.5 ± 1.7	14.0 ± 2.0	14.6 ± 1.7

*Control experiment, water = 4.2 ± 0.4.
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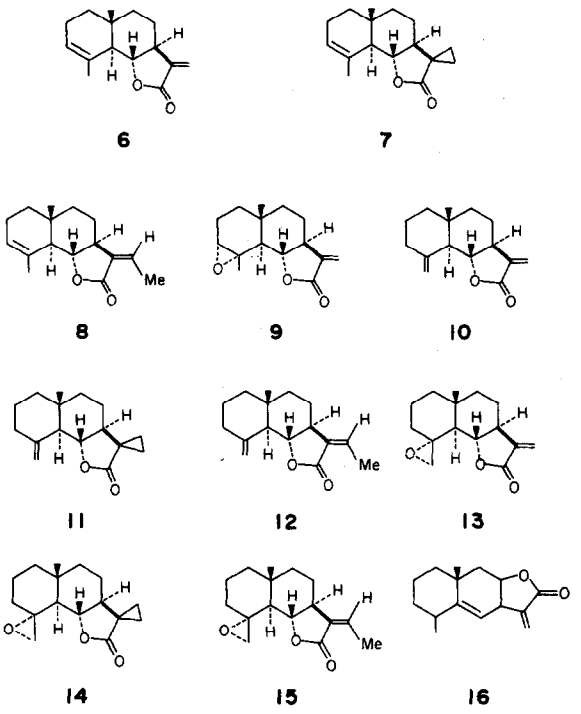


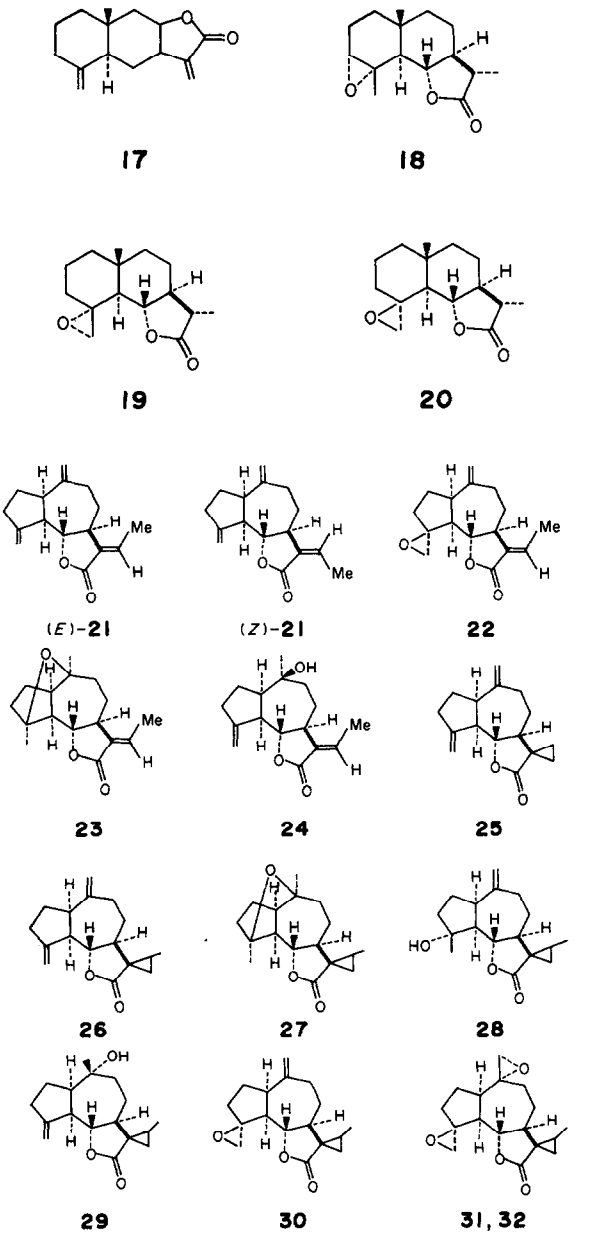
cyclocostunolide series. Thus, apart from the conjugated γ-lactone moiety, exocyclic location of the isolated double bond enhances the biological activity. This is also borne out by further comparing the activity of alantolactone (**16**) with that of isoalantolactone (**17**).

To study the effect of placing an epoxide group close to the lactone moiety on the biological activity of eudesmanolides, four new epoxides were prepared by reaction of **6** and **10–12** with perbenzoic acid to give **9** and **13–15**. That the epoxide of **9** is α, was established by controlled hydrogenation to the known **18** [6]. Epoxides **13–15** show mutual coupled doublets at δ 2.48 and 2.81 (*J* = 5 Hz) for H-15a and H-15b (Table 3). In the spectra of epoxide **19** the H-15 signals appear as a pair of doublets at δ 2.81 and 2.56 and in **20** they appear at δ 2.32 and 3.25 to reveal that in a β-epoxide the separation of signals is of the order of δ 0.93, while in an α-epoxide the separation is δ 0.29. Since the three new epoxides show a signal separation of δ 0.32, α-stereochemistry is assigned [7].*

No enhancement of biological activity is obtained in these eudesmanolides by placing an epoxide, at the 3,4 or 4,12 positions.

Guaianolides and their derivatives

In earlier reports [5, 8] from our laboratory placing a cyclopropane ring in the α,β-position of the lactone carbonyl of a guaianolide enhanced the biological activity associated with the parent α-methylene-γ-lactone. The activity is increased even more when a methyl group is



*Additionally, an α-epoxide is favoured, since the 10-methyl group is not deshielded in **13–15** when compared with the parent compounds, **10–12**.

Table 3. Spectral data for epoxyeudesmanolides

Compound	IR (cm^{-1})	^1H NMR					
		H-3	H-6	H-13	H-14	H-15	H-16
9	1760, 820	2.8 (1H, *br s*)	3.75 (1H, *t*) $J = 10$	5.3, 5.93 (1H each, *br s*)	0.9 (3H, *s*)	1.41 (3H, *s*)	
13	1760, 820	—	3.5 (1H, *t*) $J = 10.5$	5.22, 5.85 (1H each, *br s*)	0.97 (3H, *s*)	2.48, 2.81 (1H each, *d*) $J = 5$	—
14	1760, 825	—	3.68 (1H, *t*) $J = 10.5$	0.5–0.9 (4H, *m*)	0.97 (3H, *s*)	2.48, 2.81 (1H each, *d*) $J = 5$	0.5–0.9 (4H, *m*)
15	1750, 820	—	3.48 (1H, *t*) $J = 10.5$	5.8 (1H, *dq*) $J = 2, 8$	0.97 (3H, *s*)	2.48, 2.81 (1H each, *d*) $J = 5$	2.03 (3H, *dd*) $J = 3, 8$

Coupling constants (J) in Hz.

placed on the cyclopropane ring, as in **26**, particularly at concentrations of 20 mg/l.

Introduction of either an epoxy group at C-4 or an ether linkage at C-4 and C-10 of guaianolides greatly increases the root forming potential associated with the parent conjugated γ-lactones [5, 8]. No such effect is displayed by hydroxyl groups at these positions or by an epoxy group at a remote position [8].

In confirmation of these structural–biological activity relationships, the root promoting activity of (*E*)-**21** which is 50% [9] that of (*Z*)-**21** at concentrations of 20 mg/l. showed the expected increase in activity on conversion to either **22** or **23**.

The epoxidation of (*E*)-**21** with perbenzoic acid gave **22**, mp 113°. The ^1H NMR spectrum of this compound shows the protons on the oxirane ring as mutually coupled doublets at δ 3.32 and 2.82 (J = 5 Hz). The large difference in the chemical shifts of the oxirane protons is due to the influence of the lactone ring [5] and the very similar shifts of the methylene protons clearly rule out C-10 as the probable site of the oxirane ring. Oxymercuration–demercuration on (*E*)-**21** led to the formation of two crystalline compounds, mp 135° and 144°. The IR spectrum of the compound with mp 135° shows the absence of a hydroxyl group and the ^1H NMR spectral features (Table 4) are sufficient to assign structure **23** to this compound. Interestingly, H-6 in this ether appears as a doublet, as compared to a triplet seen in other compounds of this series, and is due to distortion of the dihedral angle between H-5 and H-6 to *ca* 100° which thus reduces the coupling constant to a small value.

The compound having mp 144° in its IR spectrum shows a band at 3450 cm^{-1} due to the presence of a hydroxyl group. The ^1H NMR spectrum displays signals due to the exocyclic methylene protons at δ 4.95 and 5.25 (1H each, *br s*). The separation of exocyclic methylene protons makes it possible [10] to place the hydroxyl group at C-10. H-6 is considerably deshielded from its normal value of *ca* δ 4.0 and this spectral feature [8] is in agreement with stereostructure **24** for this compound.

Oxymercuration–demercuration on **26** afforded compounds **27**–**29**. The hydroxyl derivatives (**28** and **29**) show activity up to concentrations of 10 mg/l. which is just like their parent compound, **26**. It is of further significance to note that unlike all the C-4 and C-10 ethers in the case of guaianolides, the ether **27** does not show enhancement in activity over its parent compound, **26**. Epoxidation of **26** with perbenzoic acid afforded three compounds, **30**–**32**, the structures of which are based on spectral data (Table 4). All three epoxides are more active than their parent compound, **26** (Table 5).

Elemanolides and their derivatives

Compound **33** on reaction with diazomethane afforded a mixture of two pyrazolines, mp 112° (major) and 102° (minor). The IR spectra of these two isomers clearly rules out the possibility of tautomerism as neither isomer has any band due to a –NH group. The alternative mode of addition of diazomethane to afford **34** is ruled out by the NMR data (Table 4). Thus, from these spectral features these compounds are stereoisomers at C-11.

In one of the isomers, mp 112°, H-6 is appreciably deshielded and appears at δ 4.30 whereas in the other it appears at δ 4.13. Based on the deshielding of the –N=N– grouping the compound with mp 112° is represented by **35** whereas the other pyrazoline must be represented by **36**.

Pyrolysis of either **35** or **36** furnished the same mixture from which only one compound mp 135°, could be isolated. The spectral features of this compound are in complete accord with structure **37**.

The pyrazoline of costunolide, when subjected to pyrolysis under controlled conditions, in addition to known compounds [4] afforded a compound, $C_{16}H_{22}O_2$, mp 82°. On the basis of its IR and NMR spectral features (Table 6), it is assigned structure **39**.

Table 7 shows that in this series dehydrosaussurea lactone [11] (**38**) is slightly more active than water, being an α-methylene-γ-lactone. Significantly, unlike the situation in the other series, **33** and **37** are only as active as water. As seen in all series of compounds, the cyclopropane derivative, **39**, shows maximum activity.

EXPERIMENTAL

The general procedure used for the work-up of the reaction mixtures consisted of addition of cold H_2O, extraction with

Table 4. Spectral data for guaianolides

Compound	IR (cm^{-1})	^1H NMR H-6	H-15	H-16	H-11	H-12	H-17
22	1750, 1660, 1640, 920	4.0 (1H, *dd*) J = 9.5, 10.5	6.77 (1H, *dq*) J = 3, 7.5	1.9 (3H, *dd*) J = 3, 7.5	4.88, 4.98, (1H each, *br s*)	2.82 (1H, *d*) J = 5 3.32 (1H, *d*) J = 5	—
23	1740, 1660	4.0 (1H, *d*) J = 10	6.75 (1H, *dq*) J = 2, 8	1.95 (3H, *dd*) J = 2, 8	1.3, 1.4	(3H each, *s*)	—
24	3700, 1740, 1660, 1220, 960	4.5 (1H, *t*) J = 9	6.85 (1H, *dq*) J = 2, 8	1.95 (3H, *dd*) J = 2, 8	1.4 (3H, *s*)	5.0, 5.25 (1H each, *br s*)	—
27	1770, 1650, 1125, 830	4.15 (1H, *d*) J = 11	0.65–0.85 (*m*)	0.65–0.85 (*m*)	1.2, 1.35	(3H each, *s*)	1.45 (3H, *d*) J = 6
28	3400, 1760, 1640, 920	4.25 (1H, *t*) J = 9.5	0.65–1.0 (*m*)	0.65–1.0 (*m*)	1.45 (3H, *s*)	4.8, 4.95 (1H each,	1.35 (3H, *d*) J = 6
29	3500, 1770 1660, 930	4.15 (1H, *dd*) J = 9, 11	0.65–1.0(*m*)	0.65–1.0 (*m*)	4.95 (2H, *s*)	1.40 (3H, *s*)	1.35 (3H, *d*) J = 6
30	1755, 1660, 890	4.20 (1H, *t*) J = 10	0.65–1.0 (*m*)	0.65–1.0 (*m*)	4.9 (2H, *s*)	3.25, 2.75 (1H each, *d*) J = 5	—
31	1750	4.20 (1H, *t*) J = 10	0.62–1.0 (*m*)	0.62–1.0 (*m*)	2.80 (2H, *s*)	3.30, 2.75, 2.75, (1H each, *d*) J = 5	1.40 (3H, *d*) J = 6
32	1740	4.15 (1H, *t*) J = 10	0.50–1.0 (*m*)	0.50–1.0 (*m*)	2.70 (2H, *s*)	3.35, 2.85 (1H each, *d*) J = 5	1.40 (3H, *d*) J = 6

Coupling constants (J) in Hz.

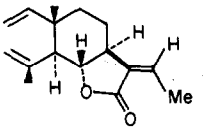
Table 5. Effect of 5, 10, 15 and 20 mg/l. guaianolides on the number of roots per rooted segment produced on hypocotyl cuttings of *P. aureus* after 7 days

Compound	Number of roots* 5	10	15	20
21	4.0 ± 0.3	6.0 ± 1.1	6.9 ± 0.7	9.5 ± 1.2
22	15.6 ± 1.8	18.5 ± 3.8	12.7 ± 3.3	—
23	6.3 ± 1.1	10.0 ± 1.7	14.6 ± 1.5	13.1 ± 0.6
24	4.4 ± 0.5	5.5 ± 0.6	6.5 ± 0.9	9.3 ± 1.6
25	6.8 ± 0.8	11.3 ± 2.2	13.3 ± 2.5	7.3 ± 1.7
26	7.1 ± 1.0	8.3 ± 1.4	13.8 ± 1.9	17.5 ± 0.9
30	8.8 ± 1.2	11.9 ± 1.0	15.0 ± 1.6	19.0 ± 2.5
31	8.5 ± 1.8	11.6 ± 2.4	14.5 ± 1.9	18.0 ± 2.8
32	10.2 ± 2.8	14.7 ± 1.7	16.0 ± 1.6	13.0 ± 2.2

*Control experiment, water 4.2 ± 0.7.

Et_2O, neutralization of the extracts and drying over Na_2SO_4. After removal of the solvent the reaction products were separated by CC on Si gel. IR spectra were taken in nujol suspensions. ^1H NMR spectra were recorded in $CDCl_3$ with TMS as the int. standard.

Epoxidation of α- and β-cyclocostunolide. Compound **6** (0.8 g) in $CHCl_3$ (20 ml) was reacted with an equal number of mmols of perbenzoic acid (18 ml 0.36 N perbenzoic acid in $CHCl_3$) for 20 hr at 0°. On work-up, elution of the column with petrol–Et_2O



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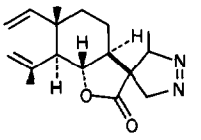

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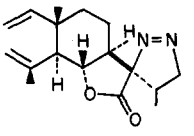

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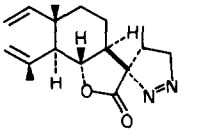

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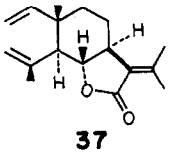

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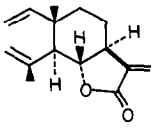

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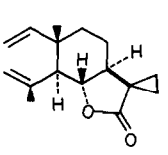

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Table 6. Spectral data for the elemanolides

Compound	IR (cm^{-1})	^1H NMR								
		H-1	H_a-2	H_b-2	H_a-3 and H_b-3	H-6	H-14	H-15	H-16	H-17
35	3080, 1780, 1640, 1560, 1000, 920, 900	5.85 (1H, *dd*) $J = 9, 11$	4.93 (1H, *br s*) $J = 9$	4.7 (1H, *d*) $J = 18$	5.1 (*br s*)	4.3 (1H, *t*) $J = 11$	1.1 (3H, *s*)	1.82 (3H, *br s*)	4.79 (*m*)	1.12 (3H, *d*) $J = 7$
36	3080, 1760, 1640, 1560, 990, 920, 900	5.88 (1H, *dd*) $J = 11, 18$	5.35 (1H, *br s*) $J = 11$	4.84–5.0 hidden	5.1 (*br s*)	4.13 (1H, *dd*) $J = 9, 10$	1.2 (3H, *s*)	1.85 (3H, *br s*)	4.84–5.0 (*m*)	1.25 (3H, *d*) $J = 7.5$
37	3070, 1750, 1660, 1640, 1000, 920, 890	5.8 (1H, *dd*) $J = 10, 16$	4.83 (1H, *d*) $J = 10$	4.88 (1H, *d*) $J = 16$	5.0 (*br s*)	4.02 (1H, *t*) $J = 10$	1.08 (3H, *s*)	1.78 (3H, *br s*)	1.95 (3H, *d*) $J = 1.5$	1.95 (3H, *d*) $J = 1.5$
39	3082, 1770, 1650, 1000, 920, 890	5.85 (1H, *dd*) $J = 10, 16$	4.85 (1H, *d*) $J = 10$	4.9 (1H, *d*) $J = 16$	5.0 (*br s*)	4.26 (1H, *t*) $J = 10$	1.1 (3H, *s*)	1.8 (3H, *br s*)	0.6–1.0 (4H, *m*)	0.6–1.0 (4H, *m*)

Coupling constants (J) in Hz.

Table 7. Effect of 5, 10, 15 and 20 mg/l. elemanolides on the number of roots per rooted segment produced on hypocotyl cuttings of *P. aureus* after 7 days

Compound	Number of roots*			
	5	10	15	20
33	4.2 ± 0.7	4.5 ± 0.8	4.5 ± 1.0	4.8 ± 0.6
37	4.9 ± 0.3	4.8 ± 0.4	4.2 ± 0.5	4.9 ± 0.8
38	4.7 ± 0.7	5.1 ± 0.9	6.0 ± 1.3	P
39	4.8 ± 0.6	7.6 ± 1.6	10.7 ± 1.7	11.6 ± 1.9

*Control experiment, water 4.4 ± 0.5.
P, Primordias.

(9:1) yielded unreacted lactone. Further elution with petrol–Et_2O (4:1) afforded pure **9**, mp 137°. (Found: C, 72.15; H, 8.01. $C_{15}H_{20}O_3$ requires: C, 72.55; H, 8.12%.) A similar epoxidation of β-cyclocostunolide (**10**) with perbenzoic acid afforded its corresponding epoxide (**13**), mp 115°. (Found: C, 72.18; H, 8.12. $C_{15}H_{20}O_3$ requires: C, 72.55; H, 8.12%.)

Hydrogenation of **9**. Compound **9** (0.2 g) was hydrogenated in MeOH using a Pt catalyst. The vol. of H_2 absorbed (30 min) corresponded to one double bond. The product on crystallization afforded the dihydro derivative **18**, mp 142°, mmp with an authentic sample (mp 140°) remained undepressed.

Epoxidation of **11**, **12**, (E)-**21** *and* **26**. Epoxidation of **11** and **12** with perbenzoic acid (conditions as described above) gave the corresponding isomeric epoxides **14** and **15**, mp 110° (Found: C, 73.72; H, 7.75. $C_{16}H_{22}O_3$ requires: C, 73.25; H, 8.45%.) and 132° (Found: C, 73, 14; H, 8.34. $C_{16}H_{22}O_3$ requires: C, 73.25; H, 8.45%.), respectively.

Epoxidation of (*E*)-21 (0.8 g) was carried out under the standard conditions. Elution of the column with petrol–Et_2O (9:1) yielded unreacted parent lactone. Further elution with petrol–Et_2O (4:1) afforded **22**, mp 113°. (Found: C, 73.40; H, 8.09. $C_{16}H_{20}O_3$ requires: C, 73.85; H, 7.74%.)

Epoxidation of **26** gave a mixture of three components. This was chromatographed to yield a liquid compound (**30**) (Found: C, 74.42; H, 8.08. $C_{17}H_{22}O_3$ requires: C, 74.46; H, 8.58%.) on elution with petrol–Et_2O (9:1) and two crystalline compounds **31**, mp 145° (Found: C, 70.11; H, 7.58. $C_{17}H_{22}O_4$ requires: C, 70.32; H, 7.60%.), and **32**, mp 138° (Found: C, 70.21; H, 7.68. $C_{17}H_{22}O_4$ requires: C, 70.32; H, 7.60%.) on elution with petrol–Et_2O (4:1).

Oxymercuration–demercuration of (E)-**21**. To a soln of (*E*)-**21** (1.3 g) in THF (20 ml) was added, drop-wise with stirring, an aq. soln of mercuric acetate (4.5 g). After disappearance of the initial yellow colour, stirring was continued for a further 10 min. To this was added (under cooling) satd aq. $NaHCO_3$ (28 ml) and a soln of $NaBH_4$ (0.5 g) in aq. $NaHCO_3$ (28 ml). After 30 min the reaction mixture was satd with aq. NaCl. The THF layer was separated and the material was chromatographed. Elution with petrol–EtOAc (9:1) afforded the unreacted compound. Further elution with the same solvent gave **23** (Found: C, 72.45; H, 8.65. $C_{16}H_{22}O_3$ requires: C, 72.25; H, 8.45%.), mp 135°. Elution of the column with petrol–EtOAc (4:1) afforded another crystalline compound, **24**, mp 144°. (Found: C, 73.10; H, 8.35. $C_{16}H_{22}O_3$ requires: C, 73.25; H, 8.45%.)

Oxymercuration–demercuration of **26**. Oxymercuration–demercuration of **26** was carried out as above to give a mixture of three components. The mixture on chromatography afforded unreacted **26** with petrol–Et_2O (9:1), **27**, mp 114° (Found: C, 73.78; H, 8.76. $C_{17}H_{24}O_3$ requires: C, 73.88, H, 8.75%.) with petrol–ether (9:1), **28**, mp 208° (Found: C, 73.31; H, 8.80. $C_{17}H_{24}O_3$ requires: C, 73.88; H, 8.75%.) with petrol–Et_2O (4:1) and, finally, **29**, mp 92° (Found: C, 78.51; H, 9.62. $C_{17}H_{24}O_2$ requires: C, 78.42; H, 9.29%.) was eluted with the same solvent in the tail fractions.

Reaction of **33** *with* CH_2N_2. A soln of **33** (5.0 g) in Et_2O (100 ml) was allowed to react with an ethereal soln of CH_2N_2 until the yellow colour persisted for 30 min at room temp. The two component mixture was chromatographed to yield the two isomeric compounds, **35** (Found: C, 70.50; H, 8.19. $C_{17}H_{24}O_2N_2$ requires: C, 70.80; H, 8.39%.) and **36** (Found: C, 70.49; H, 8.29. $C_{17}H_{24}O_2N_2$ requires: C, 70.80; H, 8.39%.), mps 112° and 102°, respectively, on elution with petrol–Et_2O (4:1).

Pyrolysis of **35**. The pyrazoline (**35**, 1.0 g) was heated at 130° for 30 min. The product mixture was chromatographed to furnish **37**, mp 135° (Found: C, 78.32; H, 9.15. $C_{17}H_{24}O_2$ requires: C, 78.24; H, 9.29%.) upon elution with petrol–Et_2O (9:1).

Biological testing. For the root initiation study, on hypocotyl cuttings of *Phaseolus aureus*, seedlings were grown under continuous illumination. When the hypoctyls were 5–6 cm long, cuttings were made by excision, 4 cm below the cotyledonary node leaving the cotyledonary leaves and apex intact. In all, four concentrations (5, 10, 15, 20 mg/l.) along with H_2O as control were tested. For all treatments 10 replicates were cultured in vials each containing 30 ml test soln. The final observations were recorded on day 8. The expt was repeated × 3 at 27 ± 2°.

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