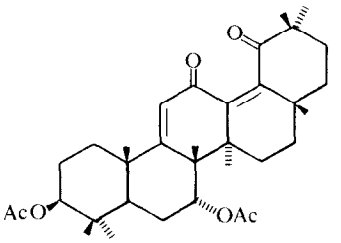
ene protons and compatible only with the (α) axial proton; the hydroxyl would therefore be β. On the basis of these data, the structure of castanopsin was elucidated as olean-9,12-diene-3β,7α-diol (**1a**). This is one of the rare pentacyclic triterpenoids found in nature having a homoannular diene system. So far only three such triterpenes with a homoannular diene system, saikogenin B [2], echinatic acid [7, 8], isomacedonic acid [9], are known in nature.



2

EXPERIMENTAL

Mps are uncorr. NMR spectra were measured in $CDCl_3$ with TMS as int. stand. In all cases, TLC spots on Si gel plates were developed with 1% $CeSO_4$ in 2 N H_2SO_4

Castanopsin. Mp 224–28°, $[\alpha]_D$ + 289 (*c*, 2.06 $CHCl_3$) λ UV λ_{max}^{MeOH}: 286 nm (log ε 3.9; IR ν_{max}^{KBr} cm^{-1}: 3575, 3290, 1630, 1375, 1365, 1065, 1050, 1035, 987, 835. NMR δ 0.83 (3H, *s*, Me) 0.09 (6H, *s*, 2 × Me), 1.03, 1.06, 1.10, 1.20, 1.26 (3H, each *s*, 5 × Me), 3.78 (1H, *q*, J = 6.5, 10 Hz) CHOH), 4.14 (1H, $W_{\frac{1}{2}}$ = 7 Hz, CHOH), 5.53, 5.71 (2H, *d*, J = 6 Hz —C=CH—CH=C—). MS (*m/e*): 440 (M^+), 422, 404, 286, 268, 255, 235, 205, 189, 183. (Found .C, 81.75, H 10.97 $C_{30}H_{48}O_2$ requires C, 81.81; H 10.99%).

Castanopsin monoacetate. Castanopsin (45 mg) was reacted for 18 hr with Ac_2O (0.4 ml) and dry C_5H_5N (0.4 ml) at 0° and worked up as usual. The derivative (46 mg) was crystallised from MeOH, mp 184–5° IR ν_{max}^{KBr} cm^{-1}: 3320, 1020 (OH), 1730, 1240. NMR: δ 0.83–1.2 (24H, 8 × Me), 2.00 (3H, *s*, OCOMe), 4.14 (1H, *t*, CHOH), 5.02 (1H, *q*, CHOAc), 5.5, 5.68 (2H, *dd*, J = 6 Hz, olefinic H).

Castanopsin diacetate. Castanopsin (48 mg) was mixed with AC_2O (0.5 ml) and dry C_5H_5N (0.5 ml) and heated on a water bath for 3 hr. After working up, the residue (50 mg) gave a colourless powder from dilute EtOH, mp 130–2°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1250 (OCOMe), 840, 820. NMR: δ 0.9 (9H, *s*, 3 × Me), 0.98, 1.03, 1.1 (9H, each *s*, 3 × Me), 1.2 (6H, *s*, 2 × Me), 2.00, 2.03 (6H, each *s*, 2 × OCOMe), 4.93 (1H, *t*, J = 8 Hz, CHOAc), 5.36 (1H, *t*, J = 3 Hz, CHOAc), 5.48 (2H, olefinic H). When castanopsin was reacted for 18 hr with Ac_2O and C_5H_5N at room temp., mono- and diacetates were formed in almost equal ratio.

SeO_2 oxidation of castonopsin diacetate. The diacetate (30 mg) was refluxed with freshly sublimed SeO_2 (30 mg) in HOAc (3 ml) for 3 hr. After work up, the residue gave a colourless powder (17 mg) from dilute EtOH, mp 190–2°. UV λ_{max}^{MeOH}: 282 nm (log ε 4.00). IR ν_{max}^{KBr} cm^{-1} 2940, 2860, 1730, 1245 (OCOMe), 1685, 1648, 1603 (dienedione), 1450, 1370, 1360.

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CROSS CONJUGATED TERPENOID KETONES: A NEW GROUP OF PLANT GROWTH REGULATORS

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Key Word Index—Plant growth regulators, terpenoid ketones; zerumbone.

The current trend in the researches on plant growth regulators is to clarify the structural specificity required for hormonal activity [1, 2]. The biological potentialities of terpenoids in general and of terpenoid lactones in particular as plant growth regulators are being explored intensively [3].

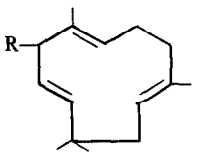
It had been established that the physiological activity of the terpenoid lactones is due to the conjugated exo-methylene moiety which is most probably essential [4]. Previous work from our laboratory showed that some terpenoid γ-lactones in which conjugation is of a different type [5] are physiologically more active than α-methylene-γ-lactones.

We have carried out extensive screening of terpenoids as plant growth regulators is an attempt to relate structure with growth activity. In this communication we

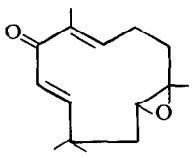
Table 1. Effect of terpenoids on the root formation of *Phaseolus mungo*

Concentration (ppm)	5	10	15	20	25	30
			Number of roots			
Zerumbone (**1**)	14.0 ± 1.4	18.5 ± 1.2	22.7 ± 1.7	25.7 ± 1.3	34.3 ± 1.8	29.6 ± 1.3
Zerumbone oxide (**2**)	20.0 ± 1.2	20.8 ± 1.6	24.9 ± 1.4	24.2 ± 1.2	23.0 ± 1.7	22.3 ± 1.4
Zerumbol (**3**)	6.0 ± 1.2	5.2 ± 1.3	5.0 ± 1.2	5.1 ± 1.7	6.2 ± 1.4	6.1 ± 1.1
Zerumbone oxide (**4**)	5.2 ± 1.3	5.9 ± 1.5	5.6 ± 1.2	—	5.9 ± 1.3	7.3 ± 1.2
Diepoxyzerumbone (**5**)	6.2 ± 1.3	6.8 ± 1.4	7.8 ± 1.7	6.5 ± 1.3	7.1 ± 1.2	6.2 ± 1.1
Santonin (**6**)	7.0 ± 1.8	12.5 ± 1.2	14.1 ± 1.6	15.2 ± 1.1	18.5 ± 1.4	23.2 ± 1.2

Mung bean rooting tests were performed in the laboratory using the basic methodology of Hess [10]. Control experiments: H_2O, 5.1 ± 1.2; IAA (10 ppm) 12.4 ± 1.4.



1 R = O
3 R = OH



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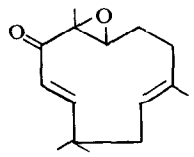

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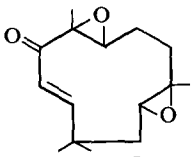

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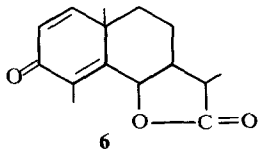

6

wish to report that a cross conjugated ketone moiety as present in zerumbone (**1**), causes adventitious rooting in the hypocotyl of mung beam cuttings.

It is well established that adventitious root formation is promoted by auxins as well as other groups of compounds such as phenolics [6]. It is interesting to report (Table 1) that activity of zerumbone is greater when compared with indole acetic acid (IAA). At lower concentrations the epoxidised form (**2**) of Zerumbone becomes even more active as compared with IAA. This observation is in agreement with an earlier report on α-methylene-γ-lactones in which the activity was en-enhanced if an epoxy group was present in the vicinity of this chromophore [6]. In the case of zerumbone oxide (**2**) the epoxy ring could be thought to be in the vicinity of a cross conjugated ketone moiety because of trans-annular effects.

To confirm that a cross conjugated ketone grouping is indeed responsible for adventitious root formation it was found that root promoting activity fell off quickly when this chromophore was modified as in the case of zerumbol (**3**) [7] or in various other epoxy derivatives (**4, 5**) [8, 9].

As expected santonin (**6**) was again found to be more active than IAA in causing root formation at a concentration higher than 10 ppm where IAA becomes toxic.

This observation confirms that growth activity of these terpenoids is a result of a cross conjugated ketone chromophore and is independent of other structural features in the terpenoids.

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