D_2O addition), 4.38 (1H *ddd*, *J* 11.5, 10 and 3 Hz, C-8), 5.98 (1H, *d*, *J* 3 Hz, C-13), 6.10 (1H, *d*, *J* 3.5 Hz, C-13); NMR ($CDCl_3$) (with 1/4 mol $Eu(dpm)_3$): δ 1.31 (3H, *d*, *J* 6 Hz, C-10 Me), 1.76 (3H, *s*, C-5 Me); ^{13}C-NMR ($CDCl_3$): δ 18.99 (Me), 20.02 (Me), 24.57 (CH_2), 30.21 (CH), 37.79 (CH_2), 44.28 (CH_2), 45.32 (CH) 52.35 (CH), 57.63 (C), 75.35 (CH—O), 76.14 (CH—O), 121.28 (=CH_2), 13936 (=C), 169.51 (O—C=O), 223.20 (C=O). Assignments were verified by an off-resonance experiment. The acetate crystallized from EtOH as colourless needless (19 mg), mp 184.5–185°; Found: C, 66.39; H, 7.42. Calc. for $C_{17}H_{22}O_5$: C, 66.65: H, 7.24%: ν_{max}^{KBr} cm^{-1}: 1768, 1743, 1670: NMR ($CDCl_3$): δ 1.98 (3H, *s*, OAc), 5.50 (1H, *d*, *J* 8 Hz, C-6).

Carabrone The fraction B (1.35 g) from the same Si gel column chromatography as above was rechromatographed with Si gel in C_6H_6–AcOEt (5:1) to give a crystalline fraction (0.55 g), which was recrystallized from Et_2O–*n*-hexane to give carabrone (0.22 g) as colourless prisms, mp 88–90°, $[\alpha]_D^{18}$ + 104.1° (c = 1.0, $CHCl_3$), NMR ($CDCl_3$): δ 0.5 (2H, *m*), 1.08 (3H, *s*), 2.13 (3H, *s*), 3.1 (1H, *m*), 4.77 (1H, *ddd*, *J* 11, 9 and 6 Hz), 5.53 (1H, *d*, *J* 2.5 Hz), 6.18 (1H, *d* *J* 3 Hz). 2,4-Dinitrophenylhydrazone, mp 185.5–187.5°.

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EIN NEUES EUPARIN-DERIVAT AUS *LIATRIS SQUARROSA*

FERDINAND BOHLMANN und ANTOINETTE SUWITA
Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Germany

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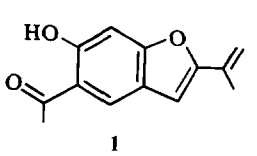
Key Word Index—*Liatris squarrosa*; Compositae; new euparine derivative.

Aus der Gattung *Liatris* sind schon mehrere Vertreter eingehend untersucht. Man findet hier vor allem Germacrolide [1] und andere Sesquiterpene [2] sowie Flavone [3]. Neben dem weitverbreiteten Pentainen [4] kommt in zwei Arten auch eine Thiophenacetylenverbindung vor [5]. *Liatris squarrosa* (L.) Michx. ist bisher noch nicht untersucht worden. Weder aus den Wurzeln noch aus den oberirdischen Teilen konnten Sesquiterpenlactone isoliert werden. Die Wurzeln enthalten neben Euparin (**1**) einen Ester des Dihydroeuparins, dem aufgrund der spektroskopischen Daten die Konstitution (**2**) zukommen muß. Ähnliche Verbindungen sind schon aus anderen Compositen, insbesondere aus Vertretern der Tribus Eupatorieae isoliert worden [6]. Euparin kommt auch in *L. pycnostachya* vor [7]. Die oberirdischen Teile ergeben ebenfalls **1** und **2** sowie Germacren D (**3**) und als Hauptinhaltsstoff Lupeol (**4**).



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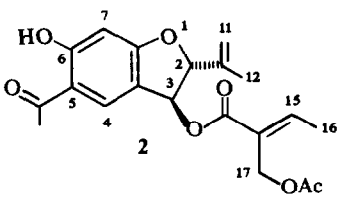

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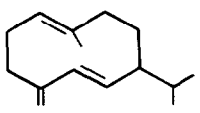

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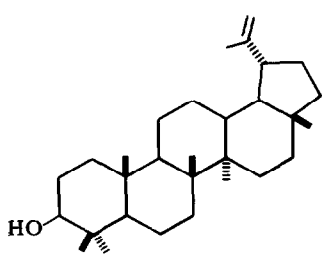

4

EXPERIMENTELLES

IR, Beckman IR 9, CCl_4; *NMR*. Varian HA 100, CCl_4; *MS*. Varian MAT 711. Die lufttrockenen Pflanzenteile (Dr. R. King, Washington, Herbar-N. 4939) extrahierte man mit Et_2O–petrol (1:2) und trennte die erhaltenen Extrakte zunächst grob durch

Tabelle 1. NMR-Signale von **2** ($CDCl_3$, δ-Werte bezogen auf TMS als innerem Standard)

2-H	*d(br)* 5·97	15-H	*q* 7.18
3-H	*d* 6.11	16-H	*d* 1.95
4-H	*s* 7.90	17-H	*s* 4.90
7-H	*s* 6.46	OAc	*s* 2.01
11-H	*s(br)* 4.97	COMe	*s* 2.55
11-H	*s(br)* 5.08	OH	*s* 13.02
12-H	*s(br)* 1.76		

J(Hz): 2,3 = 2.5; 15,16 = 7.

SC (Si gel, Akt. St. II) und anschließend weiter durch DC (Si gel, GF 254) als Laufmittel dienten Et_2O–petrol (=E–P)-Gemische. 150 g Wurzeln ergaben 3.5 g **1** und 3.8 g **2** (E–P 1:1). 300 g oberirdische Teile lieferten 15 mg **3**, 18 mg **1**, 10 mg **2** und 0.5 g **4**.

3β-[*2-Acetoxymethyl*-trans-*crotonyloxy*-)-*dihydro-euparin* (**2**). Farbloses Öl, *IR*. OH 3500–2600: OAc 1750: C=CCO_2R 1720, 1640; >C=O 1650 cm^{-1} *MS*. M^+ *m/e* 374.137 (3%) (ber. für $C_{20}H_{22}O_7$ 374.137); $-{}^{\cdot}CH_3$ 359(5); $-MeCH{=}C(CH_2OAc)CO_2H$ 216 (100); 216 $-{}^{\cdot}CH_3$ 201 (91); $MeCO^+$ 43 (95).

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TERPENOID LACTONES AS PLANT GROWTH REGULATORS

P. S. KALSI, V. K. VIJ, O. S. SINGH* and M. S. WADIA†
Department of Chemistry, Punjab Agricultural University, Ludhian, India

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Key Word Index—*Saussurea lappa*; *Phaseolus aureus*; costus root oil; terpenoid lactones; plant growth regulators.

Abstract—Plant growth regulating activity of dehydrocostus lactone possessing an α-methylene-γ-lactone moiety has been compared with its two derived C-16 lactones, in which a trisubstituted double bond and a cyclopropane ring are conjugated with the lactone carbonyl. The results show that the two latter compounds are slightly more active than dehydrocostus lactone.

INTRODUCTION

Compounds having a terpenoid skeleton and a lactone moiety as their structural specificity, are emerging as a group of plant growth regulators [1]. It has been shown that this activity of these terpenoid lactones is due to the exomethylene group conjugated to the lactone carbonyl and this structural feature is almost indispensable for this action [2]. The present investigations were made to learn if conjugated lactones other than the α-methylene containing group were equally effective in regulating growth activities such as rooting of mung bean cuttings. No reports on this type of work have appeared in the literature and it was hoped that this investigation would help to clarify the structural specificity required for growth activity of the terpenoid lactones.

RESULTS AND DISCUSSION

The present work confirms the dependence of plant growth regulating activity of the terpenoid lactones upon the presence of a α-methylene group in conjugation with the lactone carbonyl. This was seen (Fig. 1) in the case of the root forming potential of dehydrocostus lactone (**1**) which fell off as the exocyclic double bound in conjugation with the lactone carbonyl was removed either by forming a pyrazoline derivative (**2**) or by its reduction to give dihydrodehydrocostus lactone (**5**) which had identical activity compared with **2**. It is interesting to note that the C-16 lactones (**3** and **4**) in which the

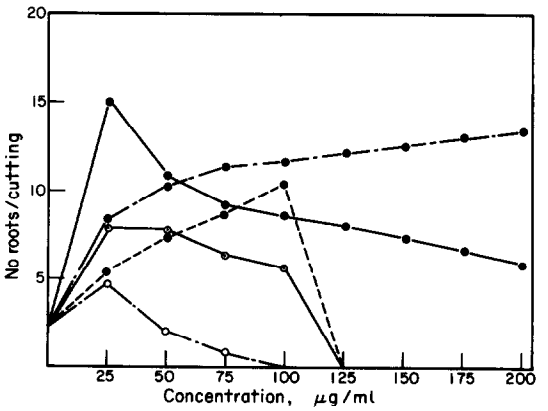

Fig. 1. Effect of terpenoid lactones on rooting in hypocotyl cuttings of *Phaseolus aureus* Roxb ●—● compound **3**, ●-·-● compounds **4**, ●--● costus root oil, ⊙—⊙ dehydro costus lactone, ○-·-○ adduct of dehydro costus lactone with diazomethane.

* Department of Botany, Punjab Agricultural University, Ludhiana, India.
† Department of Chemistry, University of Poona, India.