1240 (OAc); MS m/z (rel. int.): 308 $[M]^+$ (17), 266 $[M - \text{ketene}]^+$ (15), 248 $[M - HOAc]^+$, (23), 230 $[248 - H_2O]^+$ (12), 55 (100); CD (MeCN) $\Delta_{\varepsilon 258} = -0.92$.

100 mg **1** in 5 ml Me_2CO was stirred for 1 hr with 0.1 ml Jones reagent at room temp. Usual work-up gave 92 mg of a crystalline solid, mp 195–197° (C_6H_6); IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1780 (γ-lactone), 1740 (C=O), 1660, 885 (C=C); MS m/z (rel. int.): 264 $[M]^+$ (14), 220 $[M - CO_2]^+$ (40), 55 (100).

On hydrogenation in the presence of palladium on carbon (100%), 100 mg **1** gave **3**, colourless crystals, mp 65–68°; IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3450 (OH), 1780 (γ-lactone).

Cyathocline lyrata (*collected near Dehradun, India*). The air-dried aerial parts (200 g) were extracted with Et_2O–petrol (1:1) and the extract obtained was separated by CC (silica gel, 50 ml). The fractions with Et_2O–petrol (1:10) gave by TLC (SiO_2, PF 254, detection of the zones by UV light, 255 nm) 5 mg thymohydroquinone dimethyl ether (R_f, 0.65) and 10 mg 10-isobutyryloxy-8,9-epoxythymol isobutyrate (R_f, 0.55). Fraction with Et_2O afforded on TLC (silica gel, Et_2O–petrol; 3:1) 20 mg parthenolide (R_f, 0.52) and 100 mg balchanin (R_f, 0.45). (All compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.)

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CADINA-4,11-DIENE FROM *VIGUIERA OBLONGIFOLIA*

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Key Word Index—*Viguiera oblongifolia*; *V. lanceolata*; Compositae; sesquiterpenes; cadinane derivative; furanoheliangolides.

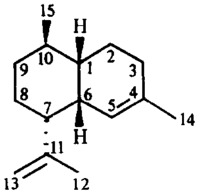
Abstract—*Viguiera oblongifolia* afforded two known furanoheliangolides and a new cadinane derivative whose structure was established by spectroscopic methods. From *V. lanceolata* 17,18-dihydrobudlein A was isolated.

Several species of the large genus *Viguiera* (tribe Heliantheae, subtribe Helianthinae) have been investigated chemically [1]. Most of them contain heliangolides, especially cytotoxic furanoheliangolides [1]. The aerial parts of *Viguiera oblongifolia* Gardn. afforded β-bisabolene, 7αH-silphiperfol-5-ene [2], dehydrofalcarinol, the furanoheliangolides atripliciolide angelate [3] and the corresponding 2-methyl butyrate [4] as well as a hydrocarbon, molecular formula $C_{15}H_{24}$ which appeared to be new. The ^{1}H NMR spectrum (Table 1) indicated the presence of two olefinic and one secondary methyl groups. Furthermore three olefinic protons must be assumed. The corresponding low field signals were coupled with the olefinic methyl groups and several allylic protons. The broadened singlet at $\delta = 2.55$ was due to one of the allylic protons. Spin decoupling made it possible to assign all signals and led to approximate coupling constants for those signals which overlapped. All data agreed with the presence of cadina-4,11-diene (**1**). The stereochemistry at

Table 1. ^{1}H NMR spectral data of compounds **1** in $CDCl_3$ (400 MHz, TMS as internal standard)

H-1	1.77 *m*	H-8β	1.24 *dddd*
H-2α	1.56 *dddd*	H-9α	0.96 *dddd*
H-2β	1.32 *dddd*	H-9β	1.67 *dddd*
H-3α	1.98 *br d*	H-10	1.40 *dddq*
H-3β	1.82 *br dd*	H-12	1.73 *dd*
H-5	5.50 *br s*	H-13	4.86 *ddq*
H-6	2.55 *br s*	H-13′	4.64 *br s*
H-7	1.95 *br d*	H-14	1.60 *br dd*
H-8α	1.50 *ddddd*	H-15	0.87 *d*

J (Hz): 1, 2α = 1, 2β = 2α, 3α = 2β, 3β = 6, 7 = 7, 8α = 8α, 9α = 8α, 9β = 8β, 9β ~ 3; 1, 10 = 2α, 2β = 2α, 3β = 3α, 3β = 7, 8β = 8α, 8β = 8β, 9α = 9α, 9β ~ 12; 3α, 5 = 3β, 5 = 3α, 6 = 3β, 6 = 3α, 14 = 5, 6 = 6, 8α = 7, 13 = 7, 13′ = 12, 13 = 13, 13′ ~ 1.5; 9α, 10 = 11; 10, 15 = 7.



1

C-1 and C-10 followed from the coupling $J_{1,10}$, while that at C-6 and C-7 only could be assigned indirectly as the corresponding signals for H-1 and H-7 were partly overlapped and that of H-6 was a broad unresolved singlet. The half width of the latter, however, excluded the presence of *trans*-diaxial couplings. Accordingly, H-1, H-6 and H-7 were at the same side. Inspection of a Dreiding model showed that the proposed stereochemistry agreed completely with the couplings observed. Especially a clear *W*-coupling of H-6 with H-8 required a *cis*-decalin derivative. The absolute configuration could not be determined. The aerial parts of *V. lanceolata* Britton afforded 17,18-dihydrobudlein A [1].

EXPERIMENTAL

The air dried plant material (voucher RMK 8585) was extracted with Et_2O–petrol, 1:2. The extracts were evaporated under vacuum. The CC fraction (silica gel) of the extract of the aerial parts (180 g) were as follows: 1 (petrol), 2 (Et_2O–petrol, 1:3) and 3 (Et_2O and Et_2O–MeOH, 10:1). TLC ($AgNO_3$ coated silica gel, petrol: detection by UV-light and $KMnO_4$ spray) of 1 gave 3 mg β-bisabolene (R_f 0.42), 4 mg **1** (R_f 0.38) and 1 mg 7αH-silphiperfol-5-ene (R_f 0.30). Fraction 2 on TLC (silica gel, Et_2O–petrol, 1:3) gave 25 mg dehydrofalcarinone (R_f 0.71) and fraction 3 afforded by TLC (silica gel, Et_2O) 6 mg atripliciolide angelate (R_f 0.47) and 2 mg atripliciolide [2-methyl butyrate (R_f 0.49)]. Known compounds were identified by comparing the ^1H NMR spectra and all spectral data with those of authentic material.

1β,6β,7β,10αH-Cadina-4,11-diene (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3065, 1640, 890 ($C{=}CH_2$); MS m/z (rel. int.): 204, 188 $[M]^+$ (58) ($C_{15}H_{24}$), 189 $[M-Me]^+$ (56), 162 (31), 161 (30), 121 (86), 119 (100), 105 (51), 93 (79), 91 (46).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{-8 \quad -9 \quad -11 \quad -38}\ CHCl_3;\ c\ 0.4$$

Isolation of 17,18-*dihydrobudlein A from* Viguiera lanceolata. The air dried aerial parts (250 g, voucher RMK 9023) was extracted with Et_2O–petrol, 1:2, and the polar CC fractions (silica gel) (Et_2O and Et_2O–MeOH, 10:1) were separated by TLC (silica gel, Et_2O–C_6H_6–CH_2Cl_2, 1:1:1) affording 30 mg 17,18-dihydrobudlein A (R_f 0.48) as followed from the ^1H NMR spectral data which agreed with those in the lit. [1] and were close to those of atripliciolide (2-methyl butyrate) [4] and similar furanoheliangolides.

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