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TWO NEW EUDESMANE CINNAMATES FROM *VERBESINA SORDESCENS**

FERDINAND BOHLMANN, CHRISTA ZDERO, HAROLD ROBINSON† and ROBERT M. KING†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, W. Germany; †Smithsonian Institution, Department of Botany, Stop No. 166, Washington, DC 20560, U.S.A.

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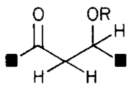
Key Word Index—*Verbesina sordescens*; Compositae; sesquiterpenes; eudesmane cinnamates.

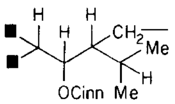
Abstract—From *Verbesina sordescens* two new eudesmane cinnamates were isolated.

In addition to acetylenic compounds, mainly terpene and sesquiterpene cinnamates have been isolated from the large genus *Verbesina* (tribe Heliantheae) [1–6]. Two species also afforded derivatives of elemanolides [7–9]. Other compounds isolated were less characteristic [10–12]. We now report on the constituents of *Verbesina sordescens* DC. The roots afforded germacrene D, caryophyllene, γ-humulene, bicyclogermacrene, α-selinene, tridecapentaynene, the eudesmane derivatives **1** [4], **2** [5], **5** [4] and **6** [5] as well as a further diol, the cinnamate **3**, which on acetylation afforded the mono acetate **4**. The ^{1}H NMR spectrum of **3** (Table 1) indicated the presence of an isomer of **2**. The signal of the proton under the hydroxyl group was at higher field but showed the same couplings. Therefore, this group could only be placed at C-3 or C-9. The former position was ruled out because **4** was not split by periodate. Also no acetonide could be obtained. Spin decoupling with **4** supported a 9β-acetoxy group. Irradiation of the H-11 signal allowed the assignment of the H-7 signal. Irradiation of the latter caused a sharpening of the H-6 signal and changed the multiplet which was also coupled with the proton under the acetoxy group, thus leading to the assignment of H-7, H-8 and H-9. The proposed stereochemistry at C-4 was supported by the chemical shifts of H-14 and H-15, which were typically shifted downfield, and which if compared with the shifts of epimeric compounds were obviously due to the effect of the 4-hydroxyl group [5].

The aerial parts afforded germacrene D, bicyclogermacrene, **1**, **2**, **5**, **6** and a further cinnamate, the ketone **7**, also present in the roots. Acetylation afforded the mono-acetate **8**. The ^{1}H NMR spectra of **7** and **8** (Table 1) clearly showed that the sequences **A** and **B** were present, which led to the proposed structures.

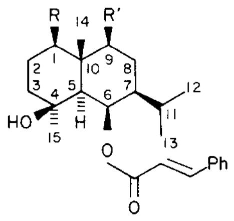


A

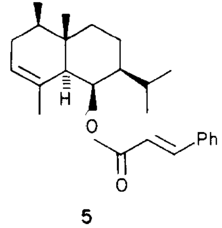


B

Heating of **7** with *p*-toluene sulfonic acid in benzene led to **9**, which further supported the proposed structure. Obviously *V. sordescens* belongs to the group of species characterized by the occurrence of eudesmane cinnamates.



1 R=R′= H
2 R=OH, R′=H
3 R=H, R′=OH
4 R=H, R′=OAc



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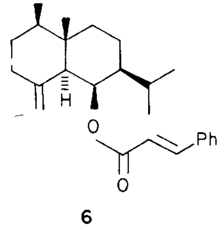

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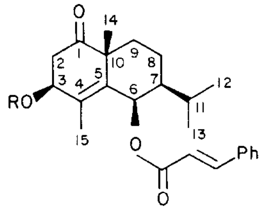
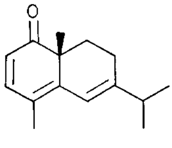


7 R=H
8 R=Ac



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*Part 409 in the series "Naturally Occurring Terpene Derivatives". For Part 408 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* 21, 1434.

Table 1. ^1H NMR spectral data of compounds **3**, **4** and **7–9** (400 MHz, $CDCl_3$, TMS as int. standard)

	3	**4**	**7**	**7**(C_6D_6)	**8**	**9**
H-2	—	—	2.63 *dd*	2.50 *dd*	2.70 *dd*	6.24 *d*
H-2′	—	—	2.58 *dd*	2.37 *dd*	2.59 *dd*	
H-3	—	—	4.11 *dd*	3.35 *dd*	5.01 *dd*	6.72 *d*
H-6	5.85 *s*(*br*)	5.84 *s*(*br*)	6.31 *d*	6.53 *s*(*br*)	6.31 *d*	6.41 *d*
H-7	—	1.67 *m*	—	—	—	—
H-8	—	1.58 *m* 1.96 *m*	—	—	—	—
H-9	3.22 *dd*	4.49 *dd*	—	—	—	—
H-11	1.50 *m*	1.48 *m*	—	1.67 *m*	—	2.44 *qq d*
H-12	0.97 *d*	0.95 *d*	0.99 *d*	1.04 *d*	0.99 *d*	1.13 *d*
H-13	0.90 *d*	0.89 *d*	0.98 *d*	0.92 *d*	0.97 *d*	1.12 *d*
H-14	1.36 *s*	1.42 *s*	1.30 *s*	1.27 *s*	1.35 *s*	1.15 *s*
H-15	1.43 *s*	1.43 *s*	2.03 *s*	2.43 *s*	2.04 *s*	1.95 *s*
OCOR	6.44 *d*	6.43 *d*	6.40 *d*	6.49 *d*	6.40 *d*	—
	7.70 *d*	7.70 *d*	7.67 *d*	7.87 *d*	7.67 *d*	—
	7.54 *m*	7.53 *m*	7.52 *m*	7.14 *m*	7.53 *m*	—
	7.39 *m*	7.39 *m*	7.39 *m*	7.02 *m*	7.39 *m*	—
OAc	—	2.07 *s*	—	—	2.09 *s*	—

J(Hz): Compounds **3** and **4**: $5,6 = 6,7 \sim 2$; $7,8\alpha \sim 1$; $8\alpha,9\alpha = 3.5$; $8\beta,9\alpha = 11.5$; $11,12 = 11,13 = 7$; compounds **7** and **8**: $2,2' = 15$; $2,3 = 5$; $2',3 = 13$; $6,7 = 2.5$; $11,12 = 11,13 = 7$; compound **9**: $2,3 = 10$; $6,11 = 2$; $11,12 = 11,13 = 7$.

EXPERIMENTAL

The air-dried plant material, collected in N.E. Brazil (voucher RMK 8748, deposited in the U.S. National Herbarium, Washington), was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing their ^1H NMR spectra with those of authentic material. The roots (210 g) afforded 5 mg caryophyllene, 5 mg γ-humulene, 5 mg germacrene D, 5 mg bicyclogermacrene, 10 mg α-selinene, 1 mg tridecapentaynene, 40 mg **1**, 3 mg **2**, 3 mg **3** (Et_2O–petrol, 3:1), 40 mg **5**, 30 mg **6** and 2 mg **7**, while the aerial parts (460 g) gave 20 mg germacrene D, 5 mg bicyclogermacrene, 100 mg **1**, 5 mg **2**, 150 mg **5**, 100 mg **6** and 2 mg **7** (Et_2O–petrol, 3:1).

4β,9β-Dihydroxy-6β-cinnamoyloxy-eudesmane (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3380 (OH), 1710, 1640 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 371.222 $[M-Me]^+$ (1) ($C_{23}H_{31}O_4$), 131 $[PhCH{=}CHCO]^+$ (100), 103 $[131-CO]^+$ (82). 3 mg **3** were heated for 1 hr with 0.1 ml Ac_2O. TLC (Et_2O–petrol, 1:1) afforded 2 mg **4**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735 (OAc), 1710, 1640 ($C{=}CCO_2R$), MS *m/z* (rel. int.): 413.233 $[M-Me]^+$ (0.3) ($C_{25}H_{33}O_5$), 220 $[M-HOAc, HO_2CR]^+$ (63), 131 $[PhCH{=}CHCO]^+$ (100).

3β-Hydroxy-6β-cinnamoyloxy-eudesm-4-en-1-one (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710, 1635 ($C{=}CCO_2R$, C=O); MS *m/z* (rel. int.): 382.214 $[M]^+$ (3) ($C_{24}H_{30}O_4$), 364 $[M-H_2O]^+$ (1), 234 $[M-PhCH{=}CHCO_2H]^+$ (11), 131 $[PhCH{=}CHCO]^+$ (100), 103 $[131-CO]^+$ (21).

1 mg **7** was acetylated as above affording 1 mg **8**, colourless gum (for ^1H NMR, see Table 1). 1 mg **7** in 1 ml C_6H_6 were heated for 30 min with 5 mg *p*-toluene sulfonic acid, TLC (Et_2O–petrol, 1:1) afforded 0.3 mg **9**, colourless gum (for ^1H NMR, see Table 1).

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