($C_{25}H_{32}O_{12}$), 492 (M − MeOH, 1), 480 (M − CO_2, 17), 464 (M − HOAc, 2), 438 (480 − MeOH, 9), 348 (M − RCO_2H, 1), 288 (348 − HOAc, 19), 57 (100).

$[\alpha]_{24}^{\lambda}$ =	589	578	546	436	365 nm
	+15.5	+16.5	+18.5	+41.5	+94.0

(c = 0.2, $CHCl_3$).

REFERENCES

1. Fischer, N. H., Olivier, E. J. and Fischer, H. D. (1979) *Progress in the Chemistry of Organic Natural Products*, Vol. 38, pp. 48–390.
2. Fischer, N. H., Wiley, R. A., Perry, D. L. and Haegele, K. D. (1976) *J. Org. Chem.* **41**, 3956.
3. Seaman, T. C. and Fischer, N. H. (1979) *Phytochemistry* **18**, 1065.

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SIX CADINENE DERIVATIVES FROM *AGERATINA ADENOPHORA**

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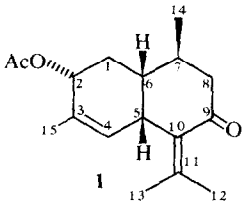
Key Word Index—*Ageratina adenophora*; Compositae; Eupatorieae, sesquiterpenes; cadinene derivatives.

The aerial parts of *A. adenophora* (Spreng.) K. et R. afforded β-farnesene, germacrene D, bisabolene, caryophyllene and six further sesquiterpenes, the cadinene derivatives **1**–**6**, of which only **1** had been isolated previously [1]. The structures of **2**–**6** followed from the ^{1}H NMR data (Table 1) and spin decoupling. The ^{1}H NMR signals of **2** could only be interpreted completely in C_6D_6. Spin decoupling clearly indicated the presence of a cadinene derivative. Irradiation of the signal at δ 1.53 collapsed the double doublets at δ 2.63 and 2.11 to doublets and changed the signals at δ 3.55 and 1.83 as well. The signal at δ 3.55 was further coupled with the signal of the olefinic proton at δ 5.83 and with that of the olefinic methyl (δ 1.74 *dd*) thus indicating the sequence H-1, H-6, H-5 and H-4 and the presence of a six-membered ring. The signal at δ 1.83 was further coupled with that of



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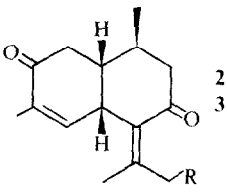
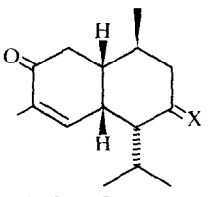
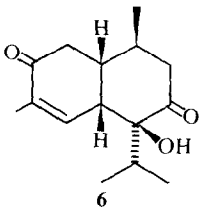


2 R = H
3 R = OH



4 X = O
5 X = β-OH, H



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*Part 333 in the series "Naturally Occurring Terpene Derivatives". For Part 332 see Bohlmann, F., Zdero, C., Pickardt, J., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1323.

Table 1. ^{1}H NMR data of compounds **2–6** (270 MHz, TMS as internal standard)

	2		**3**	**4**		**5**		**6**
	$CDCl_3$	C_6D_6	$CDCl_3$	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$
H-1	2.82	2.63 *dd*	2.80 *dd*	2.74	2.60 *dd*	2.79	2.78 *dd*	2.78 *dd*
H-1′	2.62	2.11 *dd*	2.56 *dd*	2.60	2.07 *dd*	2.46	2.15 *dd*	2.52 *dd*
H-4	6.22	5.83 *ddq*	6.33 *ddq*	6.41	6.22 *ddq*	6.63	6.70 *ddq*	6.35 *s* (*br*)
H-5	4.06	3.55 *ddq*	3.99 *ddq*	3.39	2.83 *dddq*	2.96	2.59 *dddq*	3.39 *dddq*
H-6	2.20 *m*	1.53 *ddddd*	2.20 *m*	2.20	1.38 *ddddd*	1.66 *m*	1.19 *ddddd*	2.56 *m*
H-7	2.11 *m*	1.83 *dddq*	2.0 *m*	2.02	2.32 *dddq*	2.11	2.01 *dddq*	2.05 *dddq*
H-8	2.42 *m*	2.31 *dd*		2.27	2.05 *dd*	1.84 *m*	1.42 *ddd*	2.28 *dd*
H-8′	2.20 *m*	1.67 *dd*		2.15	1.52 *dd*	1.20 *m*	1.32 *d*	2.87 *dd*
H-9	—	—		—	—	4.16	3.79 *ddd*	—
H-10	—	—		2.35	1.78 *dd*	1.85	1.35 *m*	—
H-11	—	—		2.30	1.78 *m*	2.0	1.77 *m*	—
H-12	2.03	2.07 *s*	4.78 *bd* (*br*) 4.15 *d* (*br*)	0.96	0.71 *d*	1.00	0.96 *d*	5.62 *s* (*br*) 5.52 *s* (*br*)
H-13	1.90	1.48 *s*	1.76 *s* (*br*)	0.92	0.58 *d*	0.92	0.76 *d*	1.87 *s* (*br*)
H-14	0.99	0.62 *d*	0.97 *d*	1.03	1.04 *d*	1.06	0.85 *d*	1.07 *d*
H-15	1.75	1.74 *dd*	1.77 *dd*	1.72	1.72 *dd*	1.77	1.93 *dd*	1.75 *dd*

J (Hz): 1, 1′ = 16; 1, 6 = 2.5; 1′, 6 = 4.5; 4, 5 = 4, 6 = 2; 4, 15 = 1.5; 5, 6 ~ 5; 5, 15 = 2; 6, 7 = 10; 7, 8 = 4; 7, 8′ = 12; 7, 14 = 6; 8, 8′ = 12 (**3**: 12, 12′ = 16.5; **4**: 5, 10 = 4; 10, 11 = 11; 11, 12 = 11, 13 = 6.5; **5**: 5, 10 = 4; 8, 9 = 8, 9′ = 9, 10 ~ 2.7; 10, 11 = 11; 11, 12 = 11, 13 = 6.5).

the secondary methyl (δ 0.62 *d*) and two double doublets at δ 2.31 and 1.61 for protons which were obviously both α to a second keto group, which also was conjugated causing a deshielding effect of one of the additional olefinic methyls (δ 2.07 *s* and 1.48 *s*). The stereochemistry at C-5 through C-7 followed from the observed couplings. The spectroscopic data of **3** and **6** showed that both had an additional hydroxyl group which was positioned in **3** at C-12, as was easily deduced from the absence of an olefinic methyl signal. The latter was replaced by two broadened doublets at δ 4.78 and 4.15, typical for an allylic CH_2OH group. In the spectrum of **6** one of the olefinic methyl signals was replaced by the signals of allylic protons. Inspection of all other signals showed that the hydroxyl could only be placed at C-10. The chemical shift of H-5 supported a β-orientation of the 10-hydroxyl group. The ^{1}H NMR data of **4** showed that the 10,11-double bond in **2** was hydrogenated. All the signals were assigned by spin decoupling and the stereochemistry was deduced from the observed couplings. Compound **5** was obviously derived from **4** by reduction of the 9-keto group. Inspection of a model showed that only a 9β-hydroxyl group would agree with the observed couplings. We have named compound **4**, without an oxygen function at C-9, ageraphorone.

Cadinene derivatives have so far been isolated mainly from *Chromolaena* species [2, 3], a genus not closely related to *Ageratina*.

EXPERIMENTAL

The air-dried aerial parts (320 g) of *A. adenophera*, collected north of Delhi, were extracted with Et_2O–petrol (1:2). The extract obtained was separated by column chromatography (Si gel) and further by repeated TLC (Si gel). The petrol fraction afforded 50 mg β-farnesene, 100 mg germacrene D, 15 mg bisabolene, 20 mg caryophyllene, 100 mg **1**, 5 mg **2**, 10 mg **3**, 20 mg **4**, 20 mg **5** and 5 mg **6**. Compounds **2–6** were separated by TLC (C_6H_6–CH_2Cl_2, 1:1; ×4).

9-Oxo-10,11-dehydro-ageraphorone (**2**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1685 (C=CCO); MS *m/z* (rel. int.): 232.146 (M^+, 100) ($C_{15}H_{20}O_2$), 217 (M − $^{\cdot}$Me, 12), 189 (M − $^{\cdot}C_3H_7$, 18), 161 (189 − CO, 88).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+297 \quad +306 \quad +356 \quad +630} \qquad (c = 0.1, CHCl_3).$$

9-Oxo-12-hydroxy-10,11-dehydro-ageraphorone (**3**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1690 (C=CCO); MS *m/z* (rel. int.): 248.141 (M^+, 5) ($C_{15}H_{20}O_3$), 205 (248 − C_3H_7, 11), 55 ($C_4H_7^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+40 \quad +44 \quad +50 \quad +56} \qquad (c = 0.8, CHCl_3).$$

9-Oxo-ageraphorone (**4**). Colourless oil, IR ν_{max}^{liq} cm^{-1}: 1720 (C=O), 1680 (C=CCO); MS *m/z* (rel. int.): 234.162 (M^+, 58) ($C_{15}H_{22}O_2$), 192 (M − C_3H_6, 33, McLafferty), 164 (192 − CO, 37), 136 (164 − CO, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+50 \quad +52 \quad +59 \quad +92} \qquad (c = 0.1, CHCl_3).$$

9β-Hydroxy-ageraphorone (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1675 (C=CCO); MS *m/z* (rel. int.): 236.178 (M^+, 5) ($C_{15}H_{24}O_2$) 218 (M − H_2O, 100), 203 (218 − $^{\cdot}$Me, 16), 175 (218 − $^{\cdot}C_3H_7$, 95).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+44 \quad +47 \quad +54 \quad +83} \qquad (c = 0.5, CHCl_3).$$

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REFERENCES

1. Bohlmann, F., Jakupovic, J. and Lonitz, M. (1977) *Chem. Ber.* **110**, 301.
2. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 487.
3. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1978) *Phytochemistry* **18**, 1177 and refs. cited therein.