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REFERENCES

1. Thappa, R. K., Dhar, K. L. and Atal, C. K. (1979) *Phytochemistry* **18**, 671.
2. Chetty, G. L., Zalkow, V. B. and Zalkow, L. H. (1968) *Tetrahedron Letters* 3223.
3. Huffman, J. W. and Zalkow, L. H. (1973) *Tetrahedron Letters* 751.
4. Kaiser, R. and Naegeli, P. (1972) *Tetrahedron Letters* 2009.
5. Corbett, R. E. and Smith, R. A. J. (1967) *Tetrahedron Letters* 1009.
6. Brecknell, D. J. and Carman, R. M. (1978) *Tetrahedron Letters* 73.
7. Andersen, N. H. (1970) *Tetrahedron Letters* 4651.
8. Andersen, N. H. (1970) *Phytochemistry* **9**, 145.

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A CARYOPHYLLENE DERIVATIVE FROM *LEUCANTHEMUM MAXIMUM*[*]

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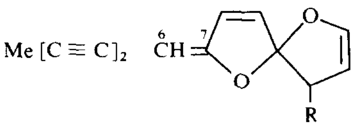
Key Word Index—*Leucanthemum maximum*; Compositae; new caryophyllene derivative.

Investigation of the aerial parts of *Leucanthemum maximum* (Ramond) DC afforded, in addition to the known acetylenes **1**–**7** [1], the lupeol isomer **8** [2], germacrene D and the alcohol **9** [3]. A secondary alcohol was also present. Inspection of the ^{1}H NMR spectral data (Table 1) led to the structure **10**, a 10β-hydroxycaryophyllene. Comparison of the chemical shifts and coupling constants with those of caryophyllene and the observed Eu(fod)$_3$-induced shift showed that we were dealing with a derivative of caryophyllene.

The position of the OH group followed from the change of the 9-H signal, which in caryophyllene derivatives is a typical three-fold doublet and was replaced in the spectrum of **10** by a doublet of doublets. Also the observed Eu(fod)$_3$-induced shifts clearly showed that the *O*-function can only be placed at C-10 (shift of 9-H, 12-H and 15-H). Double resonance experiments supported the assignments. Irradiation of the signal at δ 2.54 (in C_6D_6) collapsed the multiplet at 2.20 to a broadened doublet and the signal at 3.74 to a singlet clearly indicating the assignments of 1-, 9- and 10-H. Irradiation of the methyl singlet at 1.58 collapsed the broadened doublet at 5.33 to a clear double doublet, while saturation of the signal at 1.94 changed the multiplets at 2.35, 1.47 and 1.31. Consequently, we were dealing with the signals of 2-, 2′, 3- and 3′-H. In the ^{1}H NMR spectrum most signals were accompanied by small additional bands, most probably due to a second conformer. Similar observations were made in the case of other caryophyllene derivatives [4].

EXPERIMENTAL

Fresh aerial parts (700 g) (grown from seeds, Botanical Garden Dijon, voucher 79/1397) were extracted with Et_2O–petrol (1:2).



1 R = H (6, 7*E*)
2 R = H (6, 7*Z*)
3 R = OAc (6, 7*E*)
4 R = OH (6, 7*E*)

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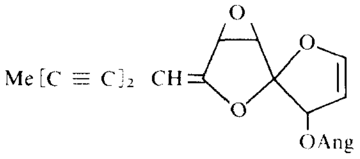
[*] Part 273 in the series "Naturally Occurring Terpene Derivatives". For Part 272 see Bohlmann, F. and Lonitz, M. (1980) *Chem. Ber.* **113**, (in press).

Table 1. The ^{1}H NMR spectral data of compound **10** (270 MHz, TMS as internal standard)

	$CDCl_3$	C_6D_6*	Δ
1-H	2.13 *m*	2.2 *m*	
	1.55 *m*	1.47 *m*	
2-H			
	1.35 *m*	1.31 *m*	
	1.95 *ddd*	1.94 *ddd*	0.31
3-H			
	2.28 *m*	2.35 *m*	
5-H	5.30 *m*	5.33 *dd*(*br*)	0.27
6-H	2.13 *m*	2.1 *m*	
7-H	2.28 *m*	2.3 *m*	
9-H	2.65 *dd*	2.54 *dd*	0.40 (0.40)
10-H	3.86 *d*	3.74 *d* (3.77)	0.97 (1.3)
12-H	1.00 *s*	2.08 *s* (1.14)	0.51 (0.78)
13-H	0.98 *s*	0.94 *s* (0.97)	0.20 (0.28)
14-H	1.59 *s*(*br*)	1.58 *s*(*br*) (1.94)	0.16 (0.20)
15-H	5.02 *d*	4.92 *d* (4.84)	0.32 (0.56)
15′-H	4.89 *d*	4.86 *d* (4.98)	0.56 (1.08)

* Signals of the second conformer in parentheses.

J (Hz): 1,9 = 10; 1,10 = 7; 1,15 = 1; 3,15 = 2; 3,3′ = 2,3 = 12; 2′,3 = 5; 1,9 = 10; 1,10 = 7; 1,15 = 1; 2,3 = 3,3′ = 12; 2′,3 = 5; 7.15 = 2.



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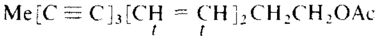
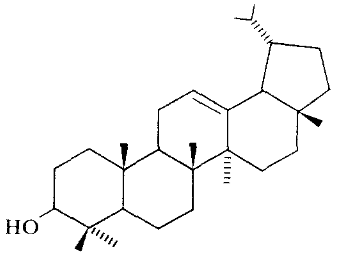


$Me[C\equiv C]_3[\underset{t}{CH}=\underset{t}{C}H]_2CH_2CH_2OAc$ **6**

$Me[C\equiv C]_3CH_2CH=CH(CH_2)_3OAc$ **7**



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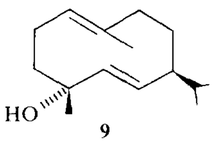

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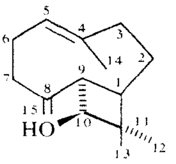

10

The resulting extract was treated with MeOH to remove long chain saturated hydrocarbons and then separated by CC (Si gel, act. grade II). TLC (Si gel, GF 254) afforded 25 mg germacrene D, 40 mg **1**, 5 mg **2**, 10 mg **3**, 120 mg **4**, 10 mg **5**, 5 mg **6**, 5 mg **7**, 50 mg **8**, 10 mg **9** and 5 mg **10** (Et_2O–petrol, 1:3).

10β-Hydroxycaryophyllene (**10**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH 3620; C=CH, 1635, 850; MS *m/e* (rel. int.): 220.183 (M^+, 4) ($C_{15}H_{24}O$), 202 ($M - H_2O$, 4), 148 ($M - HOCH{=}CMe_2$, 81), 187 (202 − Me, 21), 133 (148 − Me, 100).

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REFERENCES

1. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
2. Bohlmann, F. and Knoll, K.-H. (1978) *Phytochemistry* **17**, 599.
3. Bohlmann, F., Knoll, K.-H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., LeVan, N., Abraham, W.-R. and Natu, A. A. (1977) *Phytochemistry* **16**, 965.
4. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2381.