4 Minato, H and Horibe, I (1968) *J Chem Soc* 2131
5 Bohlmann, F, Mahanta, P K, Jakupovic, J, Rastogi, R C and Natu, A A (1978) *Phytochemistry* **17**, 1165
6 Ciccio, J F, Castro, V H and Calzada, J G (1979) *Rev Latinoam Quim* **10**, 134
7 Herz, W and Kumar, N (1981) *Phytochemistry* **20**, 93
8 Ortega, A and Romo de Vivar, A (1970) *Rev Latinoam Quim* **1**, 81
9 Holub, M and Samek, Z (1977) *Collect Czech Chem Commun* 1053
10 Bohlmann, F and Dutta, L N (1979) *Phytochemistry* **18**, 676
11 Ohno, N and Mabry, T J (1980) *Phytochemistry* **19**, 609
12 Herz, W and Kumar, N (1981) *Phytochemistry* **20**, 99
13 Herz, W. and Kumar, N (1981) *Phytochemistry* **20**, 1339
14 Spring, A, Albert, K and Gradman, W (1981) *Phytochemistry* **20**, 1883
15 Ohno, N., Gershenzon, J, Neumann, P and Mabry, T J (1981) *Phytochemistry* **20**, 2393
16 Pal, R, Kulshreshta, D K and Rastogi, R P (1977) *Indian J Chem Sect B* **15**, 208
17 Baruah, N C, Sharma, A. P, Madhusudanan, K P, Thyagarajan, K P, Herz, W and Masari, R (1979) *J Org Chem* **44**, 1831
18 Bohlmann, F, Ziesche, J, Robinson, H and King, R M (1981) *Phytochemistry* **20**, 267
19 Romo de Vivar, A, Guerrero, C, Diaz, E, Bratoeff, E A and Jiminez, L (1976) *Phytochemistry* **15**, 525
20 Guerrero, C, Santana, M and Romo, J (1976) *Rev Latinoam Quim* **7**, 41
21 Ortega, A, Lara, R, Martinez, R and Diaz, E (1980) *Phytochemistry* **19**, 1545
22 Romo de Vivar, A, Bratoeff, E A, Ontiveros, E, Lankim, D and Bhacca, N S (1980) *Phytochemistry* **19**, 1795
23 Baruah, N C, Sharma, R P, Madhusudanan, K P, Thyagarajan, G, Herz, W and Murari, R (1979) *J Org Chem* **44**, 5007
24 Bohlmann, F, Burkhardt, T and Zdero, C (1973) *Naturally Occurring Acetylenes* Academic Press, New York
25 Bohlmann, F and Jakupovic, J (1978) *Phytochemistry* **17**, 1677
26 Gonzalez, A G, Bermejo, J, Massanet, G M, Amaro, J M and Dominguez, B (1976) *Phytochemistry* **15**, 991
27 Ohno, N, Mabry, T J, Zabel, V and Watson, W H (1979) *Phytochemistry* **18**, 1687
28 Pyrek, J St (1970) *Tetrahedron* **26**, 5029
29 Stipanovic, R D, O'Brien, D H, Rogers, C E and Thomson, T E (1979) *J Agric Food Chem* **27**, 458
30 Bohlmann, F and Zdero, C (1977) *Phytochemistry* **16**, 776
31 Bohlmann, F, Zdero, C and Mahanta, P K (1977) *Phytochemistry* **16**, 1073

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TWO EUDESMANOLIDES FROM *SONCHUS MACROCARPUS**

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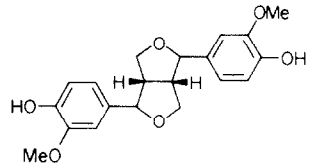
Key Word Index—*Sonchus macrocarpus*, Compositae, sesquiterpene lactones, eudesmanolides

Abstract—The aerial parts of *Sonchus macrocarpus* afforded, in addition to known triterpenes, two new eudesmanolides

Sonchus macrocarpus Boulos et Jeffrey so far has not been investigated chemically. The aerial parts afforded lupeyl acetate and its Δ^{12} isomer, β-amyrin and its acetate, lupeol, sitosterol and its glucoside, pinoresinol (**1**) and two sesquiterpene lactones, molecular formulae $C_{15}H_{20}O_4$ and $C_{15}H_{22}O_4$, which could not be separated. The ^{1}H NMR spectral data (Table 1), especially in deuteriobenzene, showed that the eudesmanolides **2** and **3** were present. The main compound, **2**, was obviously a methylene lactone because of the typical lowfield doublets at δ 5.97 and 4.83. Spin decoupling, starting with these two signals, allowed the assignment of all other signals. The presence of an aldehyde group at C-4 could be deduced from the doublet at 9.51 which was slightly shifted in the spectrum of **3**. The stereochemistry followed from the couplings observed. Though the signals of the minor



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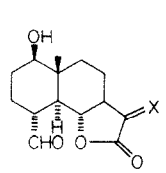

2 X = CH_2
3 X = α-Me,H

*Part 480 in the series "Naturally Occurring Terpene Derivatives" For Part 479 see Bohlmann, F, Ates (Goren), N, King, R M and Robinson, H (1983) *Phytochemistry* **22** (in press).

Table 1 ^{1}H NMR spectral data of compounds **2** and **3** (400 MHz, TMS as internal standard)

	2 (C_6D_6)	$CDCl_3$	**3** (C_6D_6)
H-1	2 71 *ddd*	3.48 *dd*	2 71 *ddd*
H-2	1 13 *dddd*	—	—
H-2′	1.30 *m*	—	—
H-3		—	—
H-3′	1.10 *m*	—	—
H-4	2.04 *dddd*	2 51 *m*	2.08 *ddd*
H-5	1.09 *dd*	1 83 *dd*	1.10 *dd*
H-6	3.06 *dd*	3.87 *dd*	3.05 *dd*
H-7	1.69 *m*	2.51 *m*	—
H-8	1.30 *m*	—	—
H-8′	0.87 *dddd*	1 54 *dddd*	—
H-9	1.69 *m*	—	—
H-9′	0.62 *ddd*	1.31 *ddd*	—
H-11	—	—	1 57 *dq*
H-13	5.97 *d*	6.08 *d*	0 99 *d*
H-13′	4.83 *d*	5.42 *d*	—
H-14	0.42 *s*	0.96 *s*	0.51 *s*
H-15	0.51 *d*	9 65 *d*	9.47 *d*
OH	0.69 *d*	—	—

J (Hz): 1, 2 = 4.5; 1, 2′ = 11, 2, 2′ = 14; 2, 3 = 3.5; 2, 2′ = 2, 3′ = 14, 3, 4 = 4; 3′, 4 = 12; 4, 15 = 3 5; 5, 6 = 6, 7 = 11; 7, 8 = 13, 7, 13 = 3.5; 7, 13′ = 3; 8, 8′ = 14; 8′, 9 = 3 5, 8′, 9′ = 13, 9, 9′ = 14; compound **3** 7, 11 = 12, 11, 13 = 7.

lactone **3** could be assigned only in part, the most important ones were visible and they allowed the assignment of the structure and the stereochemistry. As $J_{7,11}$ was 12 Hz the Me-11 group was α-orientated. Compound **2** we have named sonchucarpolide.

The chemistry of the genus *Sonchus*, which is placed in the tribe Lactuceae in the subtribe Crepidinae [1] or in a separate *Sonchus* group [2], still does not give any clear indications concerning relationships to other groups. Eudesmanolides are reported from two *Sonchus* species [3, 4], but the guaianolide jacquinelin was also isolated [5]. Several triterpenes and sterols of different types have been reported too [6, 7] as well as flavones [8] and some coumarins [8]. However, many more investigations are necessary to get a more distinct picture of the chemotaxonomy of this group and the whole tribe.

EXPERIMENTAL

The air-dried aerial parts (3 5 kg), collected near Alexandria, Egypt, were extracted with Et_2O–petrol (2 . 1) and the resulting extract was separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing with authentic material of mp, IR and ^{1}H NMR spectra. Finally, 1 2 g lupeol, 1 g of its acetate, 0.2 g of its Δ^{12}-isomer, 0.4 g β-amyrin, 0.1 g of its acetate, 0 2 g sitosterol, 0.1 g of its glucoside, 10 mg **1**, *ca* 8 mg **2** and 2 mg **3** (not separated) were obtained

Sonchucarpolide (**2**) *and* 11β,13-*dihydrosonchucarpolide* (**3**) Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 2740, 1730 (CHO), MS *m/z* (rel int.): 266.151 and 264 136 $[M]^+$ (2) ($C_{15}H_{22}O_4$ and $C_{15}H_{20}O_4$), 149 (59), 69 (88), 55 (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \text{ nm}}{-3 \quad -3 \quad -4 \quad -15} \text{ (CHCl}_3\text{; c 0 3).}$$

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REFERENCES

1. Stebbins, G L , Jr. (1953) *Madrono* **12**, 65.
2 Jeffrey, C. (1977) *Kew Bull.* **18**, 427
3 Bermejo, J., Breton, J L., Gonzales, A G and Villar del Fresno, A. (1968) *Analyt. Quim.* **64**, 893
4. Bermejo, J., Breton, J L., Fajaro, M and Gonzales, A. G (1968) *Analyt Quim.* **64**, 183.
5. Bermejo, J , Breton, J L and Gonzales, A G (1966) *J. Chem Soc* 1298
6. Gonzales, A G and Rodriguez de Leon, A (1963) *Analyt Quim.* **61**, 615.
7 Vedanthan, T., Subramaniam, S. S and Bhattacharya, T. (1978) *Indian J. Pharm Sci.* **40**, 209.
8 Bramwell, D and Dakshini, K M. M. (1971) *Phytochemistry* **10**, 2245