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EPICUTICULAR WAX OF *CORTADERIA SELLOANA* SEEDS

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Key Word Index—*Cortaderia selloana*; Gramineae; Paja brava; seeds; epicuticular wax, hydrocarbons; esters; sterols

INTRODUCTION

The epicuticular waxes present on leaves of agriculturally important Gramineae have received considerable attention [1–4], and are considered of importance in the behaviour towards external agents (pesticides, herbicides and other solutions), and in the internal water dynamics of the plants [5, 6]. The epicuticular waxes of Gramineae seeds have been less studied [7, 8], although they should be valuable for the seed's storage properties and viability, and for their eventual nutritional value [8].

Cortaderia selloana belongs to the Tribe Arundineae [9]. In Uruguay the plant is a perennial with a summer growth cycle, bearing seed in early Autumn (March–April). It is native to the region, and grows favourably in humid areas [9]. In this paper we report the composition of the epicuticular wax isolated from the seeds.

RESULTS AND DISCUSSION

The total wax extracted represented 0.65 % of the dry seed wt. This is roughly equivalent to the amount of wax present on the leaves [2]. Column chromatography and prep-TLC were used to separate the different fractions (hydrocarbons, 26 %; esters, 27 %; sterols, 39 %; minor unidentified components, 8 %).

The composition of the hydrocarbon and ester fractions was determined by GLC, and the results are presented in Table 1. The principal hydrocarbons were C_{27}, C_{29} and C_{31} and the esters C_{42}, C_{44} and C_{46}. Hydrolysis of the ester fraction and analysis of the acids and alkanols obtained showed that the ester homologues were derived mainly from C_{20} and C_{22} acids and C_{22}, C_{24} and C_{26} alkanols. The main component of the sterol fraction was identical to sitosterol (MS, TLC, mp, mmp) [10]. The unidentified minor components did not include free acids or free *n*-alkanols in noticeable quantities.

The epicuticular wax of *C. selloana* leaves has already been analysed by Martin-Smith *et al.* [2] and represented 0.4 % of the wt of the fresh leaves. The seed-wax is much richer in hydrocarbons than the leaf-wax, but the composition itself is similar. The ester fraction shows a different range for the acids and *n*-alkanols, both being of longer chains in the seed-wax. These differences should result in a less permeable and more inert coating, and seem to represent the adaptation of the wax coating to the function of protecting the seeds during extended dormancy periods. The seed-wax also presents an important percentage of sitosterol, which is not reported for the leaf-wax [2].

Table 1 Composition % of hydrocarbon and ester fractions of *C. selloana* seed-wax

			Hydrolysis products of esters	
Homologues	Hydrocarbons	Esters	Acids	*n*-Alkanols
16	—	—	4	—
18	—	—	6	—
20	—	—	29	2
22	—	—	45	19
23	1	—	—	—
24	—	—	9	42
25	9	—	—	—
26	1	—	3	20
27	22	—	—	—
28	2	—	1	2
29	33	—	—	—
30	3	—	—	2
31	29	—	—	—
40	—	2	—	—
42	—	12	—	—
44	—	32	—	—
46	—	28	—	—
48	—	9	—	—
50	—	2	—	—
52	—	2	—	—
54	—	3	—	—
56	—	3	—	—
58	—	1	—	—
Unidentified*	—	6(4)	3(1)	13(5)

* Number of components in parentheses

EXPERIMENTAL

Collection of wax. Mature seeds of *C. selloana* (Schult.) Aschs. et Graebn. were collected from field grown plants. Herbarium voucher samples were kept at the Herbario José Arechavaleta (Facultad de Química, Montevideo) as MVFQ No. 1223. The wax was extracted by immersion (15 sec) of the seeds in petrol (60–80°) to avoid extraction of internal lipids.

Adsorption chromatography. Column chromatography was carried out as described in ref. [11] (Kieselgel Woelm. 0.063–0.2 mm). TLC's were run on Si gel G, using petrol–Et_2O–HOAc (45:5:1) as solvent. GLC was carried out using the usual procedures [12–14]. Parafilm was used as standard for the hydrocarbon identifications [14]. The fatty acid Me esters and the *n*-alkanols were obtained from the ester fraction by methanolysis with BF_3-MeOH [16]

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REFERENCES

1. Eglinton, G., Hamilton, R. J. and Martin-Smith, M. (1962) *Phytochemistry* **1**, 137.
2. Martin-Smith, M., Subramanian, G. and Connor, H. E. (1967) *Phytochemistry* **6**, 559.
3. Martin-Smith, M., Ahmed, S. and Connor, H. E. (1971) *Phytochemistry* **10**, 2167.
4. Tulloch, A. P. and Weenink, R. O. (1969) *Can. J. Chem.* **47**, 3119.
5. Troughton, J. H. and Hall, D. M. (1967) *Australian J. Biol. Sci.* **20**, 509.
6. Holloway, P. J. (1970) *Pestic. Sci.* **1**, 156.
7. Iwana, F. and Maruta, S. (1969) *Kogyo Kagaku Zasshi* **72**, 2605.
8. Tulloch, A. P. personal communication.
9. Rosengurtt, B., Arrillaga de Maffei, B. and Izaguirre de Artuccio, P. (1970) *Gramíneas Uruguayas.* p. 219. Universidad de la República, Depto. de Publicaciones, Montevideo.
10. Chaudhuri, R. K. and Ghosal, S. (1970) *Phytochemistry* **9**, 1895.
11. Tulloch, A. P. and Hoffman, L. L. (1971) *Phytochemistry* **10**, 871.
12. Tulloch, A. P. and Hoffman, L. L. (1973) *Lipids* **8**, 617.
13. Streibl, M., Konecny, K. and Stránský, K. (1970) *Fette, Seifen Anstrichmittel* **72**, 777.
14. Streibl, M. and Stránský, K. (1970) *Fette, Seifen Anstrichmittel* **72**, 856.
15. Gaskin, P., MacMillan, J., Firn, R. D. and Pryce, R. J. (1971) *Phytochemistry* **10**, 1155.
16. Sands, D. M., Hehl, J. and Schlenk, H. (1971) *Biochemistry* **10**, 2536.

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NEW ACETYLENIC COMPOUNDS FROM *EMILIA* SPECIES*

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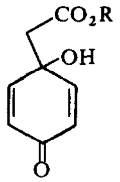
Key Word Index—*Emilia coccinea*; *E. sagittata*; Senecioneae; Compositae; new acetylenes.

Little is known of the chemical constituents of the genus *Emilia* (tribe Senecioneae); only from *E. flammea* has the pyrrolizidine alkaloid emiline been isolated [1]. Present examination of the roots of *E. coccinea* (Sims.) G. Don and of *E. sagittata* (Vahl.) DC. failed to show any characteristic compounds to be present. However, the aerial parts of both species yielded nearly the same constituents; besides the ketoesters **1** and **2** isolated previously from *Senecio* species [2], two types of acetylenes are present. The less polar ones are a mixture of a senecio acid and methylsenecio acid esters with an enediynene chromophore, in which the 10, 11-double bond exists in both *cis*- and *trans*-configurations. The ^{1}H-NMR-data (Table 1) are in agreement with the structures **3**–**6**. These structures were confirmed by manganese dioxide oxidation to the corresponding 3-ketones. The more polar compound isolated from both species turned out to be a triol with an enediyne chromophore. The ^{1}H-NMR data (see Table 1) are in good agreement with structure **11**.



1 : R = Me
2 . R = Et

The isolation of these unusual C_{12}-acetylenes may be of chemotaxonomic importance, since C_{12}-compounds have not been isolated previously from the Compositae. C_{11}-Acetylenes, which are probably bio-

Table 1. ^{1}H-NMR-data of **3**–**11** (δ-values, 270 MHz, $CDCl_3$, TMS as internal standard)

	3/4	**5/6**	**7/8**	**9/10**	**11**
1-H	*m* 4.34		*t* 4.41		*m* 3·88
2-H	*m* 1.8		*t*(*br*) 2.90		*m* 1.79
3-H	*m* 4.40			—	*m* 4.49
4-H	*dd* 6.30		*d* 6.62	*d* 6.60	*dd* 6.34
5-H	*d*(*br*) 5.85		*d*(*br*) 6.75	*d*(*br*) 6.73	*dd* 5.84
10-H	*d*(*br*) 5.55	*d*(*br*) 5.56	*d*(*br*) 5.60	*d*(*br*) 5.60	*t* 4.42
11-H	*dq* 6.16	*dq* 6.29	*dq* 6.25	*dq* 6.41	*dq* 1.75
12-H	*dd* 1·92	*dd* 1.82	*dd* 1.94	*dd* 1.85	*t* 1.01

J(Hz): 3,4 = 5; 3,5 = 1; 4,5 = 16; 5,10 = 1; 11,12 = 7; **3/10**. 10,11 = 15; 10,12 = 1.5; **11**. 10, 11 = 6.5; O Sen: *qq* 5.68, *d* 2.17, *d* 1.90; Mesen: *tq* 5.66, *d* 2.17, *q* 2.18, *t* 1.07.

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* Part 245 in the series: 'Polyacetylenic Compounds'; for part 244 see: Bohlmann, F. and Hühn, C. (1977) *Chem. Ber.* **110**, 1183.