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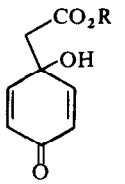
Key Word Index—*Emilia coccinea*; *E. sagittata*; Senecioneae; Compositae; new acetylenes.

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



1: R = Me
2. R = Et

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**.

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-

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

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.

$$Me\,CH{=}CH[C{\equiv}C]_2CH{=}CHCH(OH)CH_2CH_2OR$$

	trans	
cis	**3**: R = Sen*	**4**: R = *t*-Mesen*
trans	**5** R = Sen	**6**. R = *t*-Mesen

$$Me\,CH{=}CH[C{\equiv}C]_2CH{=}CHCOCH_2CH_2OR$$

	trans	
cis	**7**. R = Sen	**8**: R = *t*-Mesen
trans	**9**. R = Sen	**10**: R = *t*-Mesen

* Sen = Senecioyl, *t*-Mesen = 3-methylpent-2*E*-enoyl.

$$Me\,CH_2CH(OH)[C{\equiv}C]_2CH{=}CHCH(OH)CH_2CH_2OH \quad (trans)$$

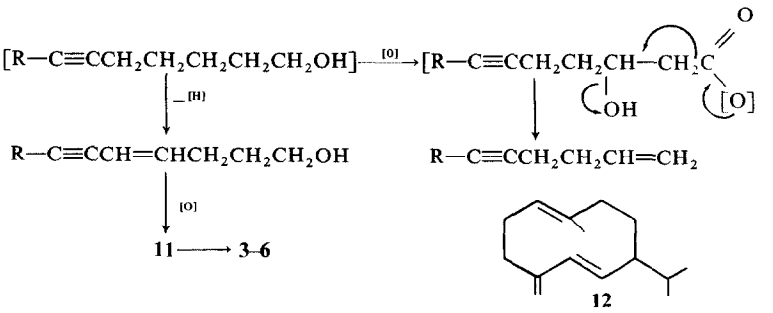
11

Emilia sagittata (*Vahl.*) *DC* (*voucher 77/958*). 50 g roots gave no characteristic compounds, while 150 g aerial parts afforded 10 mg **12**, 20 mg **1**, 7 mg **3–6** and 11 mg **11**.

1,3-Dihydroxy-dodeca-4t,10c or t-diene-7,9-diyne-1-senecioate- or- 1- (*2-methyl pent-2*(E)*-eoate*) (**3–6**). Colourless, inseparable oil, IR (CCl_4). OH 3605; C≡C 2210; C=C CO_2R 1710, 1650; *trans* CH=CH 1610, 950 cm^{-1}. UV (Et_2O). λ_{max} 312, 292, 276, 253 nm; MS M^+ *m/e*. $-RCO_2H$ 172.089 (27%) (calc. for $C_{12}H_{12}O$ 172.089); $C_5H_9CO^+$ 97 (50); $C_4H_7CO^+$ 83 (100).

$$[\alpha]_{24}^{\lambda\,\circ} = \frac{\begin{matrix}589 & 578 & 546 & 436\ nm\\ +25.8 & +27.2 & +31.6 & +65.6^\circ\end{matrix}}{}\ (c = 0.5)$$

10 mg **3–6** was oxidized in ether with MnO_2 (1 hr). After TLC (Et_2O–petrol, 1:3) **7–9** were isolated (65% yield), colourless oil, IR: C≡C 2238, 2200; C=CCO$_2$R 1721, 1653, C=CC=O 1698, 1590 cm^{-1}. UV. λ_{max}: (339), 320, (294) nm. MS. M^+ *m/e* $-RCO_2H$ 170 (100); $C_5H_9CO^+$ 97 (72);



genetically related to the C_{12}-compounds (see Scheme), have however been isolated in two instances: from *Psilothonna tagetes* (= *Steirodiscus*) [3] and from *Cineraria* spp. [4].

EXPERIMENTAL

IR: Beckman IR 9; ^{1}H-NMR: Brucker WH 270; MS. Varian MAT 711, 70 eV; optical rotation: Perkin–Elmer polarimeter, $CHCl_3$. Fr. plant material was extracted with Et_2O–petrol and the extracts first separated by column chromatography and further by TLC (Si gel GF 254) using Et_2O–petrol.

Emilia occinea (*Sims.*) *G. Don* (*voucher 77/957*). 50 g roots gave no characteristic compounds, while 150 g aerial parts afforded 3 mg **1**, 1 mg **2**, 10 mg **3–6** (Et_2O–petrol, 1:1) (not separated) and 2 mg **11** (Et_2O).

20 for 5 days with EtOH (95%) to prepare 5 l. extract. This

$C_4H_7CO^+$ 83 (58).

1,3,10-Trihydroxy dodeca-4t-en-7,9-diyne (**11**). Colourless oil, IR ($CHCl_3$). OH 3610; *trans* CH=CH 1605, 960 cm^{-1}. MS. M^+ *m/e*. $-H_2O$ 190.099 (15%) (calc. for $C_{12}H_{14}O_2$ 190.099), $-CH_3$ 175(20), $C_9H_5^+$ 117 (8); $C_9H_7^+$ 115 (11); $HOCH_2CO^+$ 73, (100). UV). (ether): λ_{max} 284, 269, 253, 242 nm.

$$[\alpha]_{24}^{\lambda\,\circ} = \frac{\begin{matrix}589 & 578 & 546 & 436\ nm\\ -26.2 & -27.0 & -31.0 & -56.0^\circ\end{matrix}}{}\ (c = 0.5)$$

LITERATURE

1. Kohlmünzer, S., Tomczyk, H. and Saint-Firmin, A. (1971) *Diss. Pharm. Pharmacol.* **23**, 419.
2. Bohlmann, F. and Suwita, A. (1976) *Chem. Ber.* **109**, 2014.
3. Bohlmann, F. and Zdero, C. (1971) *Chem. Ber* **104**, 954.
4. Bohlmann, F and Abraham, W R unpublished