Phytochemistry, Vol. 31, No. 12, pp. 4159–4161, 1992
Printed in Great Britain.

0031–9422/92 \$5.00+0.00

ACETYLENES FROM THE ROOTS OF *SOLIDAGO* SPECIES

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(*Received* 8 *April* 1992)

Key Word Index—*Solidago* species; Astereae; Compositae; roots; acetylenes; spiroacetal enol ethers; oxidation; chemotaxonomy.

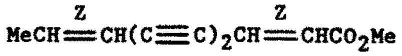
Abstract—Roots of six *Solidago* species were examined for their content of acetylenes. The *E* and *Z* isomer of dehydromatricaria ester, (*Z*,*Z*)-matricaria ester, (*Z*)-dehydromatricaria lactone and a C_{16}-acetylene were isolated and identified. The *Z* and *E* isomer of dehydromatricaria lactone were furthermore produced by oxidation of 2,4-hexadiynyliden-1,6-dioxaspiro-[4.4]nona-2,8-dien-4-ol with activated MnO_2.

INTRODUCTION

The large genus *Solidago* is placed in the tribe Astereae (Compositae) [1]. Acetylenes have only been found in a few species of *Solidago* [2–13], although several species of this genus have been investigated chemically. Acetylenes are widespread within Astereae [4, 5, 13] and their occurrence in *Solidago* could, therefore, be of chemotaxonomic importance. We have now investigated the roots of six *Solidago* species for their content of acetylenes.

RESULTS AND DISCUSSION

The roots of the six *Solidago* species investigated were extracted with petrol–diethyl ether (1:1). The extracts were subjected to flash chromatography and to repeated prep. TLC. The acetylenes **1**, **2a**, **2b**, **3b**, **4** and **5** were isolated and characterized (Table 1). In addition we isolated large amounts of the diterpene solidagenone from *Solidago elongata* (Experimental). Solidagenone has previously been isolated from the genus *Solidago* [8, 12, 14]. The *E* isomer of **3b** has been produced by Bohlmann *et al.* from the spiroacetal enol ether **8a** by direct periodate oxidation, under acidic conditions [15]. Direct oxidation of **8a** with activated MnO_2 proved to be unsuccessful [15]. However, we have now been able to produce the *E* and *Z* isomers of dehydromatricaria lactone (**3a**, **b**) from the spiroacetal enol ethers‡ **8a** and **b** by direct oxidation with activated MnO_2 (Experimental). Oxidation of **8a** with MnO_2 afforded **3a**, whereas oxidation of **8b** afforded **3a** and **b**. The spectral data (UV, IR, MS and NMR) of **3b** were in accordance with those reported in the literature for (*Z*)-dehydromatricaria lactone [7, 16]. The UV, IR and mass spectra of **3a** resembled those of **3b** and by comparing the ^{1}H NMR spectrum of **3a** with that of **3b** only significant differences in the chemical shifts of H-3 and H-5 could be observed (see Experimental). From the



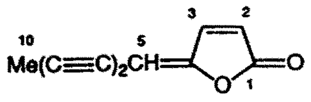
$\mathrm{MeCH\overset{Z}{=}CH(C{\equiv}C)_2CH\overset{Z}{=}CHCO_2Me}$

1

$\mathrm{Me(C{\equiv}C)_3CH{=}CHCO_2Me}$

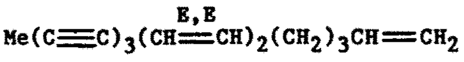
2a E isomer

2b Z isomer



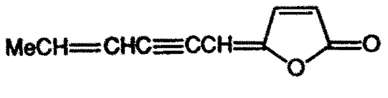
3a E isomer

3b Z isomer



$\mathrm{Me(C{\equiv}C)_3(CH\overset{E,E}{=}CH)_2(CH_2)_3CH{=}CH_2}$

4



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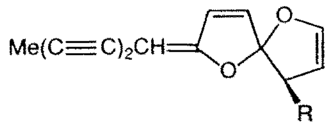
‡All the spiroacetal enol ethers used were obtained from *Santolina chamaecyparissus* L. and *Leucanthemum vulgare* Lam. (Anthemideae).



6a R = H, E isomer

6b R = H, Z isomer

7a R = OAc, E isomer

7b R = OAc, Z isomer

8a R = OH, E isomer

8b R = OH, Z isomer

above results **3a** was determined to be (*E*)-dehydromatricaria lactone. Direct oxidation of the four spiroacetal enol ethers **6a**–**7b** with activated MnO_2 gave no oxidized products (see Experimental).

Dehydromatricaria ester (**2a, b**) and dehydromatricaria lactone (**3a, b**) are only frequently detected in the tribe Anthemideae, especially in the genera *Artemisia*, *Anthemis* and *Matricaria* [17]. In the tribe Astereae these compounds do not seem to be widely distributed. (*Z*)-Dehydromatricaria lactone (**3b**) has previously been isolated from *Solidago altissima* [7] only, whereas dehydromatricaria ester (**2a, b**) has been isolated from *S. altissima* [7], *S. chinensis* [5, 13], *S. odora* [8], *S. flexicaulis* [2], *S. sempervirens* [13], *Calotis erinacea* [18] and from *Aster ptarmicoides* [19], within Astereae. The co-occurrence of dehydromatricaria ester (**2a, b**) and (*Z*)-dehydromatricaria lactone (**3b**) in *Solidago altissima*, *S. elongata*, *S. nemoralis* and *S. petiolaris* (Table 1) are, therefore, of chemotaxonomic importance, indicating a close relationship between the genus *Solidago* (Astereae) and certain genera of the tribe Anthemideae. Thus the genus *Solidago* could be a transitional link which connects the tribes Astereae and Anthemideae in a close relationship. The occurrence of matricaria ester (**1**), matricaria lactone (**5**) and C_{17}-acetylenes in Anthemideae [17] supports this hypothesis, as these compounds are also common in many genera of Astereae, including *Solidago* (see Table 1 and refs [2–5, 8–13]).

EXPERIMENTAL

Plant material. Roots of *Solidago altissima* L., *S. canadensis* L., *S. elongata* Nutt., *S. graminifolia* (L.) Salisb., *S. nemoralis* Ait. and *S. petiolaris* Ait. were obtained from the Botanical Garden of Aarhus (Denmark).

Extraction, isolation and identification. Fresh roots (washed and air-dried) of the six *Solidago* species investigated were ground and extracted with petrol–Et_2O (1:1). The combined extracts were subjected to flash CC (silica gel 60, 230–400 mesh; ART. No. 9385) using petrol and petrol containing increasing proportions of Et_2O as eluents. For further sepn repeated prep. TLC (silica gel 60; ART. No. 7748) was used. The acetylenes isolated (**1**–**2b**, **3b**, **4**, **5**) from the six *Solidago* species investigated are shown in Table 1. The roots of *Solidago elongata* also contained large amounts (2 g) of the diterpene solidagenone. The values given in Table 1 are based on the amount of fr. plant material in each single investigation. For complete identification of isolated compounds UV, IR, NMR, MS and TLC were used. Compounds isolated in small amounts (less than 1 mg) were identified by UV, MS and TLC. The spiroacetal enol ethers **6a**–**7a**, **8a** and **7b** were isolated from *Santolina chamaecyparissus* L. [20] and *Leucanthemum vulgare* Lam. (= *Chrysanthemum leucanthemum* L.) [15, 21], respectively. Compound **8b** was obtained by hydrolysis of **7b**.

Oxidation of compounds **8a** *and* **b** *with activated* MnO_2. Activated MnO_2 (100 mg) was added to a solution of **8a** (20 mg) in Et_2O (50 ml) and the mixt. stirred at room temp. for 4 hr. The reaction mixt. was filtered and the residue washed with Et_2O. The filtrate was concd under red. pres. and the residue purified by prep. TLC. (petrol–Et_2O, 3:1) to give **3a** (10 mg). Direct oxidation of **8b** (10 mg) with activated MnO_2, as described above, gave **3a** (2 mg) and **b** (3 mg). The four spiroacetal enol ethers **6a**–**7b** gave no oxidized products by direct oxidation with activated MnO_2.

(*E*)-*Dehydromatricaria lactone* (**3a**). UV $\lambda_{max}^{Et_2O}$ nm: 343, 362 (sh). IR $\nu_{max}^{CHCl_3}$ cm^{-1} (see also ref. [15]): 2240 (C≡C), 1790, 1750 (unsaturated lactone). EIMS 70 eV *m/z* (rel. int.): 158 $[M]^+$ (25), 130 $[M-CO]^+$ (10), 102 (45), 82 (17), 76 (95), 61 (12), 54 (50), 50 (100). HRMS *m/z*: 158.0365 ($C_{10}H_6O_2$ requires: 158.0368). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.02 (3H, *d*, $J = 1.3$ Hz, Me-10), 5.72 (1H, *m*, H-5), 6.30 (1H, *dd*, $J_{2,5} = 1.8$ Hz, and $J_{2,3} = 5.5$ Hz, H-2), 7.71 (1H, *d*, $J_{2,3} = 5.5$ Hz, H-3).

Table 1. Acetylenes isolated from the roots of *Solidago* species*

	Acetylenes isolated					
Species	**1**	**2a**	**2b**	**3b**	**4**	**5**
S. altissima L. (1064 g)	<1	—	2.5	13	—	tr
S. canadensis L. (274 g)	<1	—	—	—	—	—
S. elongata Nutt. (1000 g)	tr	—	3	7	—	—
S. graminifolia Salisb. (265 g)	<1	<1	2	—	2	—
S. nemoralis Ait. (1118 g)	—	—	4	22	—	—
S. petiolaris Ait. (500 g)	tr	<1	27	7	—	—

*Quantities (in mg) are based on the amount of fresh plant material given in parentheses.

tr, Present in trace amounts only.

—, Not detected.

(Z)-*Dehydromatricaria lactone* (**3b**). UV $\lambda_{\max}^{\mathrm{Et_2O}}$ nm: 333, 352 (sh). IR spectrum in accordance with lit. values [7, 16]. EIMS 70 eV *m/z* (rel. int.): 158 $[\mathrm{M}]^+$ (20), 130 $[\mathrm{M}-\mathrm{CO}]^+$ (10), 102 (40), 82 (15), 76 (90), 61 (15), 54 (50), 50 (100). HRMS *m/z*: 158.0364 ($C_{10}H_6O_2$ requires: 158.0368). ^{1}H NMR (200 MHz, $CDCl_3$) (see also refs [7, 16]): δ 2.02 (3H, *d*, $J = 1.3$ Hz, Me-10), 5.30 (1H, *m*, H-5), 6.26 (1H, *dd*, $J_{2,5} = 0.8$ Hz and $J_{2,3} = 5.5$ Hz, H-2), 7.35 (1H, *d*, $J_{2,3} = 5.5$ Hz, H-3).

Acknowledgements—The use of the MS and NMR instruments at the University of Aarhus, sponsored by the Danish Research Councils (SNF and STVF), the Carlsberg Foundation and Aarhus University Research Foundation, is acknowledged. The authors express their gratitude to the Danish Natural Science Research Council (SNF) for financial support.

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