6-O-*Nerol-8-oyl-antirrinoside penta-acetate* (**1Ac**). Amorphous powder; MS *m/z* (rel. int.): 720 $[M-H_2O]^+$ (0.04), 660 [720 $-AcOH]^+$ (0.05), 420 [720–5 $AcOH]^+$ (0.6), 331 [glc tetraacetate]$^+$ (39), 271 $[420-C_{10}H_{13}O]^+$ (3.5), 169 (100), 109 (43).

6'-O-*Cinnamoyl-antirrinoside* (**2**). Amorphous powder; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1720 (C=O), 1670, 1640 (enol ether); MS *m/z* (rel. int.): 331 $[M-CH_2$cinnamate$]^+$ (0.1), 293 [M $-Agly]^+$ (3.9), 275 $[293-H_2O]^+$ (1.3), 183 [agly, $C_9H_{11}O_4]^+$ (1.5), 131 [cinnamoyl, $C_9H_7O]^+$ (100), 103 $[131-CO]^+$ (57), 77 $[103-C_2H_2]^+$ (55); $[\alpha]_D^{24°}-67.3°$ (MeOH; *c* 0.4).

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WRIGHTOL, A SESQUITERPENE OF THE EREMOPHILANE TYPE FROM *SOLIDAGO WRIGHTII*

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Key Word Index—*Solidago wrightii*; Asteraceae; Astereae; Solidagininae; α-spinasterol; sesquiterpenoids; 6β-cinnamoyloxy-1β-hydroxyeudesm-4 (15)-ene; wrightol.

Abstract—The dichloromethane extract of the aerial parts of *Solidago wrightii* furnished a new eremophilane sesquiterpene, wrightol (6β-cinnamoyloxy-1β-hydroxy-7α (H)-11,12-dihydroeremophil-9-ene), in addition to a known isomeric eudesmane sesquiterpene (6β-cinnamoyloxy-1β-hydroxyeudesm-4(15)-ene) and α-spinasterol.

INTRODUCTION

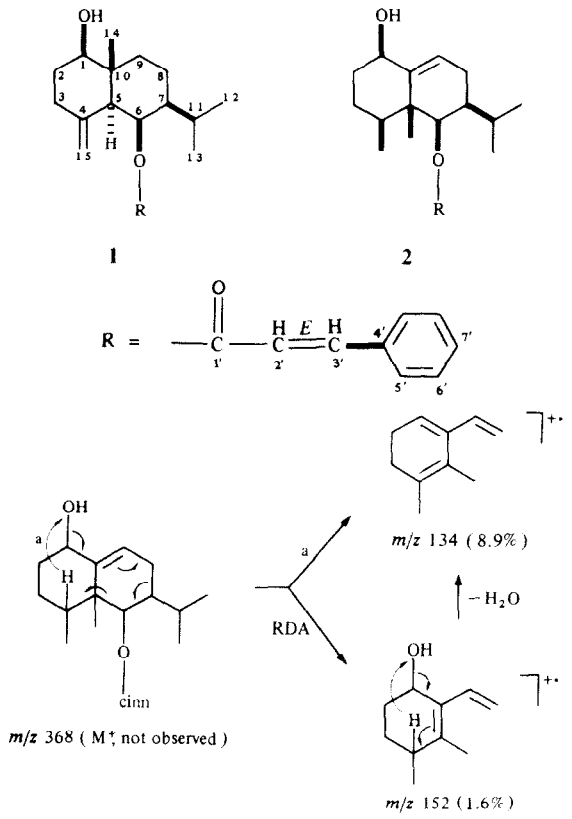
As part of our continuing investigation of the chemistry of arid-adapted Asteraceae, we have examined the dichloromethane extract of the aerial parts of *Solidago wrightii* Gray var. *adenophora* Blake. This species is distinguished by the presence of stipitate glands on the involucre, pedicels, stems and leaves and grows in the mountains of Graham, Pinal, Cochise and Pima counties of Arizona.

RESULTS AND DISCUSSION

The petrol-soluble portion of the dichloromethane extract of the aerial parts of *S. wrightii*, after washing with 20% aqueous methanol followed by silica gel CC, gave several fractions from which α-spinasterol and two isomeric sesquiterpene cinnamates were isolated by PLC. One of the sesquiterpenes was a previously reported eudesmane derivative, 6β-cinnamoyloxy-β-hydroxyeudesm-4(15)-ene (**1**) [1], and the other, named wrightol, was a new eremophilane derivative characterized as 6β-cinnamoyloxy-1β-hydroxy-7α(H)-11,12-dihydroeremophil-9-ene (**2**).

Structure of wrightol (**2**)

The structure of **2**, isomeric with **1**, followed from the IR, $^1H/^{13}C$ NMR (Table 1) and mass spectral data and comparison with the spectral data of **1**. The IR ($CHCl_3$) spectrum of **2**, which was very similar to that of **1**, showed absorptions for OH (3620 cm^{-1}), α,β-unsaturated ester (1705 cm^{-1}), unsaturation [3060, 1640 (strong), 860 cm^{-1}], phenyl (1580, 1497 cm^{-1}) and *gem*-dimethyl (1370/1355 cm^{-1}, doublet) groups but, unlike **1**, lacked exocyclic double bond absorption. The EIMS of **2**, unlike **1**, did not show an $[M]^+$ peak (*m/z* 368) but, except for differences in the relative intensity of peaks, was almost identical with that of **1**, exhibiting *m/z* 131 as the base peak, two complementary halves of the molecule as obtained by α-cleavage {*m/z* 237[sesquiterpene $-O]^+$ (5.5%) and 131$[C_6H_5$–CH=CH–C=$O]^+$ (base)} and {*m/z* 219 [sesquiterpene $(-H_2O)-O]^+$ (2.8%) and 131} before and after dehydration, respectively, and fragments of cinnamate at *m/z* 147 (5.2%, $C_9H_7O_2$), 131 (base), C_9H_7O), 103 (14.8%, C_8H_7) and 77 (6.3%, C_6H_5); elemental compositions were verified by HRMS. Other diagnostic peaks of appreciable intensity, all associated



Scheme 1.

Table 1. ^1H and ^{13}C shifts (δ, $CDCl_3$) and coupling constants (in Hz, in parentheses) for **1** and **2**

Atom No.	1 C	2 C	2 H
1	71.1	74.4[a]	4.36 *br s*
2	30.7[a]	25.2[b]	
3	34.5[a]	26.7[b]	
4	144.9	39.6[c]	~1.39 *m*
5	51.6	43.4	
6	80.0	75.6[a]	5.61 *br s*
7	50.2	41.5[c]	
8	20.4	35.2	2.04 *m*, 2.08 *m*
9	37.3[a]	123.3	5.75 *t* (4.2)
10	40.3	143.7	
11	28.0	28.4	~1.65 *m*
12	20.3	20.6	0.99 *d* (6.0)
13	21.9	21.1	1.01 *d* (6.0)
14	13.2	15.9[d]	1.13 *s*
15	108.8	16.2[d]	0.89 *d* (6.0)
1′	166.8	167.2	
2′	118.5	118.3	6.46 *d* (16.0)
3′	144.8	144.7	7.67 *d* (16.0)
4′	134.3	134.1	
5′	128.8	128.8	7.53 *m*
6′	128.1	128.0	7.38 *m*
7′	130.2	130.1	

[a–d] May be interchanged with same letter within column.

with the sesquiterpene moiety and its functional groups, occur at *m/z* 220 $[M-C_6H_5CH{=}CHCOOH]^+$ (15.1%, $C_{15}H_{24}O$), 205 $[220-Me]^+$ (3.6%, $C_{14}H_{21}O$), 202 $[220-H_2O]^+$ (32.3%, $C_{15}H_{22}$) 187 $[202-Me]^+$ (10.1%, $C_{14}H_{19}$), 177 $[220-isopropyl]^+$ (17.0%, $C_{12}H_{17}O$), 160 $[M-(H_2O+C_6H_5CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O+isopropyl)]^+$ (7.8%, $C_{12}H_{16}$), 159 $[202-isopropyl]^+$ (51.4%, $C_{12}H_{15}$) and 145 $[160-Me]^+$ (12.8%, $C_{11}H_{13}$). That the double bond in **2** is at 9,10 was deduced from a significant peak at *m/z* 134 [8.9%, $C_{10}H_{14}$ (HRMS), insignificant in **1**] which could be formed either directly from $[M]^+$ or *via* *m/z* 152 [1.6%, $C_{10}H_{16}O$ (HRMS), not observed in **1**] by a RDA process followed by dehydration (Scheme 1) only if the double bond was located in the 9,10-position. This also defined the site of the OH group being in ring A and in an allylic position to the ethylenic bond in agreement with the $[M]^+$ not being observed in **2** due to facile dehydration.

The ^1H and ^{13}C NMR spectra strongly support the constitution and, with biogenetic considerations, the stereochemistry depicted for **2**. The equatorial nature of the proton on C-1 is clear from its lack of a large coupling constant. The failure of the proton on C-6 to couple appreciably with other protons parallels its behaviour in **1** and is consistent with **1** and **2** having similar stereochemistry. The *E*-cinnamate must be present from the 16 Hz coupling constant between its vinyl protons. The usual eudesmane absolute configuration is very likely on biogenetic grounds; indeed, it appears as if **1** and **2** result from different fates of the same carbocation precursor.

EXPERIMENTAL

Plant material was collected at an elevation of 2250 m in the Huachuca Mountains, Cochise County, Arizona, on September 11, 1987. A voucher specimen (SPM 4291) has been deposited in the Herbarium at the University of Arizona, Tucson. All plant material was air-dried, ground to 3 mm particle size and stored at 5° prior to extraction.

Extraction and isolation. Percolation of ground *S. wrightii* (1750 g) with CH_2Cl_2 (24 hr) gave an extract (70 g) after freeing from solvent. The extract was taken up in petrol (1500 ml), left overnight, stirred (6 hr) at room temp. left in the refrigerator overnight and filtered. The petrol-soluble filtrate was extracted with 20% aq. MeOH (500 ml × 3). The non-polar petrol phase, after separation and evapn of the solvent, gave a residue (33.3 g) which was submitted to silica gel CC (1500 g, packed in *n*-hexane). Elution with *n*-hexane containing increasing concn of EtOAc (0–50%) followed by CH_2Cl_2–MeOH (1:1) gave 25 frs from which α-spinasterol and compounds **1** and **2** were isolated qualitatively as described below.

α-Spinasterol. Isolated from fr. 9 (0.66 g). The residue was dissolved in isopropyl ether and left in the refrigerator. Colourless crystals that separated were filtered, washed with cold isopropyl ether several times and dried. Identified as α-spinasterol (IR, ^1H NMR and TLC comparison).

6β-Cinnamoyloxy-1β-hydroxyeudesm-4(15)-ene (**1**). Isolated from CC fr. 15 (0.46 g). The residue when submitted to PLC [*n*-hexane–EtOAc (2:1), one development)] gave 3 frs (A–C). Fr. C (242 mg) which on TLC showed one major spot, when resubmitted to 2 × PLC [*n*-hexane–EtOAc (8:3), 3 developments; 3:1, 2 developments)] gave **1** as a colourless foam, identified as 6β-cinnamoyloxy-1β-hydroxyeudesm-4(15)-ene by IR, ^1H and

^{13}C NMR (Table 1) and MS {*m/z* 368 $[M]^+$(1.2%), the remaining spectrum was almost identical with that of **2**} spectra and comparisons with lit. data [1].

6β-Cinnamoyloxy-1β-hydroxy-7α(H)-11,12-dihydroeremophil-9-ene (**2**). Isolated from CC fr. 10 (2.17 g). The residue was resubmitted to silica gel CC (50 g, packed dry). Elution with *n*-hexane containing 0–30% EtOAc under vacuum gave 15 frs. Fr. 11 (240 mg), which showed one major spot on TLC, when submitted to PLC [*n*-hexane–EtOAc (4:1), 2 developments] gave **2** as a colourless foam, characterized as 6β-cinnamoyloxy-1β-hydroxy-7α(H)-11,12-dihydroeremophil-9-ene based on the spectral data described in the text.

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FUROEREMOPHILANES FROM *HERTIA PALLENS*

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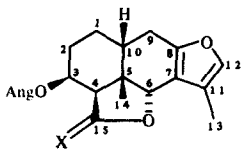
Key Word Index—*Hertia pallens*; Compositae; sesquiterpenes; furoeremophilane; eremophilanolides.

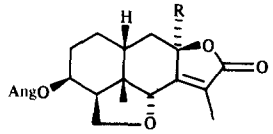
Abstract—The aerial parts of *Hertia pallens* afforded a new furoeremophilane and two eremophilanolides. The structures were elucidated by high field NMR spectroscopy. The proposed relationship of *Hertia* to *Othonna* is strongly supported by the chemistry.

INTRODUCTION

The twelve species of the genus *Hertia* (Compositae, tribe Senecioneae) are distributed over South and North Africa and South West Asia. The sterile disc styles indicate a close relationship to *Othonna* [1]. So far nothing is known on the chemistry of these plants. Therefore we have studied the constituents of *Hertia pallens* Kuntze. The results are discussed in this paper.



1 X = H_2
1a X = O

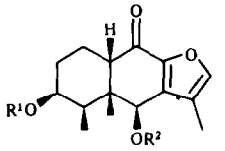


2 R = H
3 R = OH

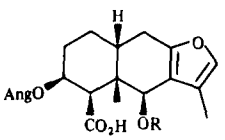
RESULTS AND DISCUSSION

The extract of the aerial parts afforded germacrene D, tremetone, oleanolic acid and the corresponding ketone, the furoeremophilanes **1** [2], **4** [3], **5** [4], **6** [4], **7** [5], **8**, **9** [3], **10** [4] and **11** [3] as well as the lactones **1a** [3] **2** and **3**.

The structure of **2** followed from its ^1H NMR spectrum (Table 1) where all signals could be assigned by spin decoupling. The couplings of H-10 indicated the presence of a *cis*-decalin derivative. Inspection of a model showed that H-6 must be β-orientated. The same is true for compound **1** where the configuration at C-6 has to be revised compound **31** in ref. 2.



	4	**5**	**6**	**7**	**8**
R^1	Ang	Ang	Sen	Ang	MeBu
R^2	Ang	Sen	Ang	*i*Bu	Ang



9 R = Sen
10 R = Ang
11 R = *i*Bu