Phytochemistry, Vol. 28, No. 11, pp. 3227–3229, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00
Pergamon Press plc

SHORT REPORTS

TWO IRIDOID GLUCOSIDE ESTERS FROM *ANARRHINUM ORIENTALE*

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(*Received in revised form* 3 *April* 1989)

Key Word Index—*Anarrhinum orientale*, Scrophulariaceae; 6-*O*-nerol-8-oyl-antirrinoside; 6′-*O*-cinnamoyl-antirrinoside.

Abstract—Two new iridoid glucoside esters were isolated from *Anarrhinum orientale* and identified by spectral methods as 6-*O*-nerol-8-oyl-antirrinoside and 6′-*O*-cinnamoyl-antirrinoside.

INTRODUCTION

Iridoid glucosides are common in the Scrophulariaceae and related families, their presence being considered as a valuable systematic character [1]. Iridoid glucosides occupy an important position in the field of natural products chemistry and biology since they provide a structural link between terpenes and alkaloids [2] and display an interesting spectrum of biological activity [3].

Anarrhinum orientale Benth (Scrophulariaceae) is used in the traditional medicine in Al-Baha region (in KSA) as an antidiabetic. We wish to report the isolation and structure elucidation of two new iridoid glucoside esters from this plant.

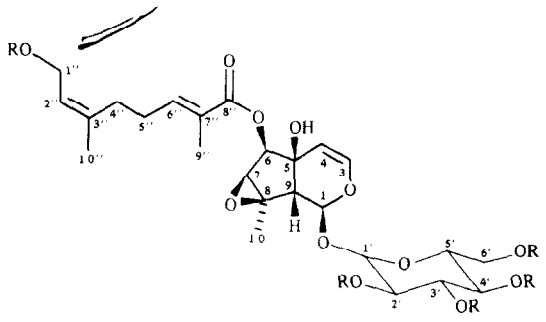
Table 1. ^{1}H NMR spectral data of compounds **1***, **1Ac**† and **2*** (400 MHz$_1$ δ values)

H		1	1Ac	2
Agly	1	5.42 (5.8) *d*	5.10 (8.2) *d*	5.22 (5) *d*
	3	6.37 (6.2) *d*	6.29 (6.2) *d*	6.26 (6.2) *d*
	4	4.90 (6.2) *br d*	4.95 (6.2) *d*	4.72 (6.2) *br d*
	6	4.83 (2.2) *d*	5.04 (1.5) *d*	3.70 (2.5) *d*
	7	3.50 (2.2) *d*	3.54 *br s*	3.30 (2.5) *br d*
	9	2.55 (5.8) *br d*	2.48 (8.2) *br d*	2.32(5) *br d*
	10	1.44 *s*	1.50 *s*	1.30 *s*
Glc	1′	4.62 (8) *d*	4.93 (8) *d*	4.53 (8) *d*
	2′	3.32 *m*	5.03 (8, 9.5) *dd*	3.34 *m*
	3′	3.48 *m*	5.24 (9.5, 9.5) *dd*	3.20 *m*
	4′	3.48 *m*	5.10 (9.5, 9.5) *dd*	3.34 *m*
	5′	3.32 *m*	3.72 (2.5, 4.5, 9.5) *ddd*	3.44 *m*
	6′	3.84 (12.5, 2.5) *dd*	4.26 (12.5, 4.5) *dd*	4.41 (12.5, 2.5) *dd*
		3.78 (12.5, 4) *dd*	4.19 (12.5, 2.5) *dd*	4.34 (12.5, 4.5) *dd*
OR	1″	4.06 (7) *br d*	4.55 (7) *br d*	7.58 (16) *d*
	2″	5.41 (7) *br t*	5.39 (7) *br t*	6.35 (16) *d*
	4″	2.20 (7) *br t*	2.30 (7) *br t*	7.41 *m*
	5″	2.32 (7, 7) *br dt*	2.20 *m*	7.27 *m*
	6″	6.84 (7, 1.5) *tq*	6.86 (7, 1.5) *tq*	
	9″	1.83 (1.5, 1) *dt*	1.86 *br s*	
	10″	1.71 (1, 1) *dt*	1.77 *br s*	
OH			2.20 *br s*	
OAc			2.08 *s*	
			2.04 *s*	
			2.03 *s*	
			2.02 *s*	
			2.00 *s*	

*In $CDCl_3$–CD_3OD mixture (400 MHz).
†In $CDCl_3$ (400 MHz).

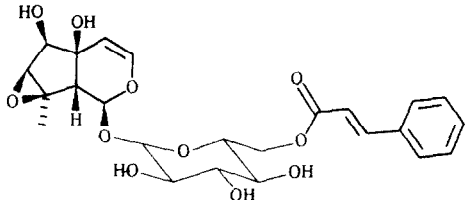
RESULTS AND DISCUSSION

Compound **1** is amorphous with $[\alpha]_D^{24} = -88.8^0$, molecular formula $C_{25}H_{36}O_{12}$, and UV absorption at 224 nm and IR absorption at 1660 (C=C) and 1720 cm^{-1} (C=O). The ^1H NMR data of **1** (Table 1) indicated also an iridoid structure and appeared almost identical with those reported for 6-angeloyl- (and senecioyl-) antirrinoside [4], differing only in signals for the ester residue. Also the spectrum of kickxioside [5] is very close to that of **1**. The difference in the nature of the ester group clearly followed from the signal of H-1″, H-2″ and H-10″. Starting with the signal for H-1 at δ4.06 *br d* (numbering as in nerol) the whole sequence of the ester group could be established leading to a monoterpene acid with the carboxylic group at C-8 or C-9. The acetylation of **1** with Ac_2O and pyridine gave the penta-acetate **1Ac** which produced a better resolved ^1H NMR spectrum. The results of the NOE experiments confirmed the stereochemistry at all chiral centres and the configuration of the double bonds of the ester group. NOE's were observed between H-10, H-9, H-7 and H-1, between H-9″ and H-5″ as well as between H-10″, H-2″ and H-5″. No effects were observed between H-1 and H-9. Thus, **1** is 6-*O*-nerol-8-oylantirrinoside. The ^{13}C NMR data of **1** and **1Ac** resembled those reported for antirrinoside mentioned before [4] and is in accordance with the structure.



1 **1Ac**

R H Ac



2

Table 2. ^{13}C NMR chemical shifts of compounds **1**, **1Ac** and **2** (100.6 MHz, $CDCl_3$, δ values)

C		1	1Ac	2
Agly	1	93.1	94.2	92.6
	3	142.2	142.6	142.5
	4	105.5	106.8	105.8
	5	73.4	73.2	73.7
	6	77.6	78.1	74.2
	7	63.1	62.8	65.0
	8	63.4	62.9	64.4
	9	51.3	52.0	51.0
	10	16.5	17.0	16.5
Glc	1′	98.2	96.1	98.2
	2′	72.8	70.7	72.7
	3′	76.2	72.1	75.9
	4′	69.8	68.1	69.7
	5′	75.9	72.2	75.5
	6′	63.1	60.8	63.1
OR	1″	58.2	61.4	167.2
	2″	125.3	120.1	117.3
	3″	137.1	141.3	145.5
	4″	30.0	30.7	134.0
	5″	26.5	27.4	128.8
	6″	142.9	141.2	128.0
	7″	127.1	127.6	117.3
	8″	167.6	167.4	128.0
	9″	12.0	12.4	128.8
	10″	22.7	23.3	

The structure of compound **2** was deduced from the ^1H and ^{13}C NMR data which were similar to those of **1**. The signals for the monoterpene were missing and the presence of cinnamate was indicated by the typical signals in the ^1H NMR spectrum (Table 1). As the signals for H-6 were now shifted upfield and those for H-6′ of the glucose part were downfield, the relative position of the cinnamate was established.

EXPERIMENTAL

The aerial parts of the flowering plant were collected from Al-Baha region, K.S.A., in April 1988 and identified by A. S. M. Al-Hajar (voucher 1272, deposited in the Herbarium of Biological Science, King, Abdul-Aziz University, Jeddah, Saudi Arabia). The air-dried material (600 g) was extracted with the solvent mixture Et_2O–petrol–MeOH, (1:1:1). The extract was defatted with cold MeOH. The resulting material (5.2 g) was then partially separated by CC (silica gel) eluted with petrol and increasing amounts of Et_2O and finally with Et_2O and increasing amounts of MeOH. Elution with Et_2O–MeOH (3:1) gave a glycoside material (1.2 g), one tenth of which is separated by HPLC technique (reversed phase column, methanol–H_2O, 1:1) to give two iridoid glucosides: **1** (37 mg) (R_t 10.4 min) and **2** (25 mg) (R_t 13 min).

6-O-Nerol-8-oyl-antirrinoside (**1**). Amorphous powder; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1720 (C=O), 1675, 1660 (enol ether); MS *m/z* (rel. int.): 182 [Agly, $C_9H_{10}O_4$]$^+$ (3.5), 166 [$C_9H_{10}O_3$]$^+$ (18), 148 [166–H_2O]$^+$ (12), 167 [ester, $C_{10}H_{15}O_2$]$^+$ (3.5), 121 [167 – H_2O – CO]$^+$ (87), 100 (97), 55 (100); $[\alpha]_D^{24}$ −88.8° (*c* 2.12;MeOH).

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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Phytochemistry, Vol. 28, No. 11, pp. 3229–3231, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00

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

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(*Received* 13 *February* 1989)

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