3-(β-D-*Glucopyranosyloxymethyl*)-2,4,4-*trimethyl*-2-*cyclohexen*-1-*one* (**2**). IR ν_{max}^{KBr} cm^{-1}: 3390 (OH), 2960, 2920, 2870, 1655 (C=O). ^{1}H NMR (300.13 MHz, CD_3OD): δ1.98 (3H, *s*, Me at C-2), 1.22/1.23 (2 × 3H, 2*s*, 2 × gem. Me at C-4), 1.84 (2H, *t*, $J_{5,6}$ = 6.8 Hz, H-5), 2.48 (2H, *t*, $J_{6,5}$ = 6.9 Hz, H-6), 4.25/4.67 (2H, 2*d*, J_{gem} = 10.9 Hz, CH_2 at C-3), 4.31 (1H, *d*, $J_{1',2'}$ = 7.8 Hz, H-1′), 3.18 (1H, *dd*, $J_{2',1'} = J_{2',3'}$ = 7.8 Hz, H-2′), 3.28–3.40 (3H, H-3′, H-4′, H-5′), 3.70 (1H, *dd*, $J_{6',5'}$ = 5.0 Hz, $J_{6'a,6'b}$ = 10.4 Hz, H_a-6′), 3.90 (1H, *d*, $J_{6b',6a'}$ = 10.4 Hz, H_b-6′). ^{13}C NMR: see Table 1.

Tetraacetate **2a**. $[\alpha]_D^{20}$ −21.4° ($CHCl_3$; *c* 0.499). EIMS (70 eV) *m/z*: $[M+H]^+$ 499 (0.4), 331 (18.5), 169 (56.8), 152 (34.6), 151 (10.1), 123 (11.8), 109 (33.0), 81 (12.6), 43 (100). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ1.80 (3H, *s*, Me at C-2), 1.15/1.16 (2 × 3H, 2*s*, 2 × gem. Me at C-4), 1.82 (2H, *t*, $J_{5,6}$ = 6.2 Hz, H-5), 2.49 (2H, *t*, $J_{6,5}$ = 6.9 Hz, H-6), 4.23/4.53 (2H, 2d, J_{gem} = 10.9 Hz, CH_2 at C-3), 4.54 (1H, *d*, $J_{1',2'}$ = 7.9 Hz, H-1′), 5.00 (1H, *dd*, $J_{2',1'} = J_{2',3'}$ = 8.0 Hz, H-2′), 5.21 (1H, *t*, $J_{3',2'} = J_{3',4'}$ = 9.4 Hz, H-3′), 5.09 (1H, *t*, $J_{4',3'} = J_{4',5'}$ = 9.4 Hz, H-4′), 3.70 (1H, *m*, H-5′), 4.22 (2H, *m*, H-6′), 1.99, 2.00, 2.03, 2.08, (12H, 4 × aliphatic OAc). ^{13}C NMR: see Table 1.

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GERMACRANOLIDES FROM *CHAENACTIS DOUGLASII*

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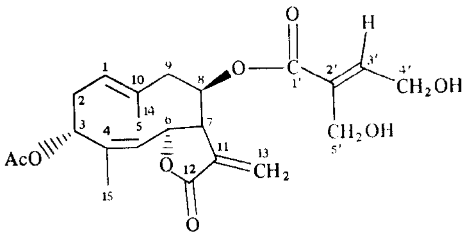
Key Word Index—*Chaenactis douglassi*; Compositae; new germacranolide; ^{13}C NMR investigation.

Abstract—The investigation of *Chaenactis douglasii* yielded one known germacranolide and a new oxidized germacranolide.

To date, *Chaenactis douglasii* has yielded only one reported germacranolide, eupatoriopicrin [1]. I wish to report the isolation of other germacranolides from *Chaenactis*. The ethyl acetate extract from the dried aerial parts of *Chaenactis douglasii* (Hook.) H. et A. has yielded two major germacranolides. These compounds were purified by column chromatography followed by HPLC.

The ^{1}H NMR and ^{13}C NMR spectra of the more polar component were identical with the known germacranolide eupaformosanin (**1**), which has been isolated from *Eupatorium formosanum* [2].

The less polar component (**2**) had a molecular formula of $C_{20}H_{24}O_7$ (HRMS). The IR spectrum of **2** indicated a large OH stretch and three C=O at 1760 (lactone), 1720 (ester) and 1680 cm^{-1} (unsaturated acid). The IR spectrum along with the ^{1}H NMR resonance at δ5.95 (*dd*) indicated the C-14 methyl had been oxidized to a carboxylic acid. The chemical shift of this proton indicated a *Z* alkene. This stereochemistry is in contrast to other oxidized germacranolides with the *E* configuration around this double bond [3]. The chemical shift of the protons with this configuration are at much lower field (δ7.0–7.2). Resonances at 1.87 (*br s*), and 6.85 (*br t*) and 1.80 (*d*) indicated that this germacranolide was esterified with a tiglic acid moiety [3]. The positions and relative stereochemistry of the hydroxyl and ester groups on the ring were established by analysis of the ^{1}H NMR spectrum of **2**, the acetate (**3**) (Table 1) and NOE experiments done on the acetate. The two broad singlets at δ4.48 (H-9) and 6.02 (H-8) in the parent compound appeared as a doublet at δ5.45 (H-9, J = 9.6 Hz) and a broad doublet at δ6.67 (H-8, J = 9.6 Hz) in the acetate. The H-8 proton



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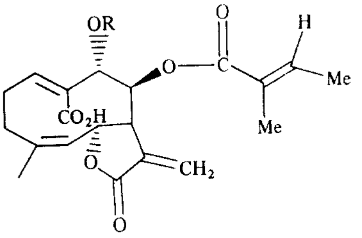

2 R = H
3 R = Ac

Table 1. ^{1}H NMR data for sesquiterpene lactones **1–3**

H	**1**	**2**	**3**
1	5.10 *t* (7.1)	5.95 *dd* (4.1, 13.6)	7.15 *dd* (4.1, 12.0)
2α	2.4 *m*	2.35 *m*	2.7 *m*
2β		3.41 *m*	
3α	—	2.3 *m*	2.5 *m*
3β	5.64 *dd* (13.6, 6.8)		
5	5.24 *d* (10)	4.88 *d* (9.4)	5.01 *d* (10.1)
6β	5.30 *m*	5.05 *t* (9.4)	5.15 *br t* (10.1)
7α	3.00 *m*	3.01 *m*	2.83 *m*
8α	5.27 *m*	6.02 *br s*	6.67 *br d* (9.6)
9α	2.73 *m*	—	—
9β		4.28 *br s*	5.45 *d* (9.6)
13	6.36 *d* (2)	6.30 *d* (2)	6.29 *d* (2.1)
13′	5.80 *d* (2)	5.75 *d* (2)	5.82 *d* (2.1)
14	1.79	—	—
15	1.90	1.78	1.78
3′	6.95 *t* (7)	6.85 *br q* (7)	6.81 *br t* (7)
4′	4.43 *d* (7)	1.80 *d* (7)	1.80 *d* (7)
5′	4.35 *br s*	1.87 *br s*	1.96 *br s*
OAc	2.10		2.01

Coupling constants (*J*, in Hz) are given in parentheses.

was then coupled to a broad doublet at δ2.83 (H-7). This coupling could be continued around to the C-15 methyl. Irradiation of H-9 gave an NOE enhancement (~ 10%) of H-6 indicating that they are on the same side of the ring. Irradiation of H-8 gave an NOE enhancement (15%) of H-13 only. Consideration of the coupling constants and these NOE experiments indicate the 8β,9α-configuration. It is interesting to note that the conformation of the ten membered ring changes quite a bit from the parent compound to the acetate, presumably due to H-bonding of the hydroxyl to the acid in the parent compound.

The ^{13}C NMR spectra of both of these compounds is shown in Table 2. These were assigned by consideration of the chemical shifts of the carbons and the multiplicites in the off resonance spectra. These spectra are consistent with the proposed structure.

Although this species of *Chaenactis* has been shown to contain eupatoriopicrin [1], no eupatoriopicrin could be detected by NMR or TLC in this collection.

EXPERIMENTAL

Chaenactis douglasii was collected on 10 July 1983 in Butte, MT. The sample was identified in Dr. Paul Sawyer, Montana Tech Biology Department.

IR: $CHCl_3$; ^{1}H NMR and ^{13}C NMR: in $CDCl_3$; MS VG 7070 EHF. The dried plant material was extracted with EtOAc and the extract separated first by CC (silica gel) and further by HPLC (Whatman, M9) using EtOAc–hexane mixtures as solvents. 500 g of aerial parts afforded 300 mg **1** and 500 mg **2**.

Eupaformosanin (**1**). Oil; IR ν_{max} cm^{-1}: 1760 (α-lactone), 1730 (OAc), 1715 ($C{=}CO_2R$). MS *m/z*: 420.1779 $[M]^+$ (0.5%) (Calc. for $C_{22}H_{28}O_8$ 420.1781), $[M-HOAc]^+$ 360 (1.6%), 288 (100%), 97 (70%), 43 (90%).

Douglasine (**2**). IR ν_{max} cm^{-1}: 3500 (OH), 1760 (α-lactone), 1720 ($C{=}C{-}CO_2R$), 1680 ($C{=}C{-}CO_2H$). MS *m/z*: 376.1515 $[M]^+$ (1.5%) (calc. for $C_{20}H_{24}O_7$ 376.1518), $[M-H_2O]^+$ 358 (19.1), 258 (19.3), 83 (100), 55 (86).

Douglasine acetate (**3**). Compound **2** (5 mg) was stirred with 0.5 ml of pyridine and 0.5 ml Ac_2O for 24 hr, the solvents removed *in vacuo* and the product separated by HPLC; IR ν_{max} cm^{-1}: 3500, 1760, 1720, 1680. MS *m/z*: 418, 358, 258, 55.

Table 2. ^{13}C NMR data for sesquiterpene lactones **1** and **2**

C	**1**	**2**
1	124.1 *d*	150.8 *d*
2	30.4 *t*	25.7 *t*
3	70.6* *d*	39.0 *t*
4	135.9 *s*	135.7 *s*
5	125.0 *d*	124.7 *d*
6	79.5 *d*	81.6 *d*
7	48.5 *d*	54.1 *d*
8	74.4* *d*	75.4* *d*
9	43.1 *t*	73.3* *d*
10	135.8 *s*	144.7 *s*
11	131.2 *s*	127.4 *s*
12	169.7 *s*	169.4 *s*
13	125.0 *t*	122.0 *t*
14	18.5 *q*	168.9 *s*
15	17.9 *q*	17.4 *q*
1′	165.8 *s*	167.5 *s*
2′	137.0 *s*	126.4 *s*
3′	145.1 *d*	139.9 *d*
4′	56.2 *t*	11.9 *q*
5′	58.9 *t*	14.5 *q*
Ac	178.3 *s*, 21.0 *q*	

*Indicates assignments may be reversed.

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HELIANGOLIDES FROM *ISOCARPHA OPPOSITIFOLIA* VAR. *ACHYRANTHES*

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Key Word Index—*Isocarpha oppositifolia* var. *achyranthes*; Compositae; sesquiterpene lactones; heliangolides.

Abstract—A new heliangolide and the known compounds hiyodorilactone F and eucannabinolide have been isolated form *Isocarpha oppositifolia* var. *achyranthes*.

INTRODUCTION

The taxonomic position of the tropical American genus *Isocarpha* (Compositae) which comprises ten species [1] is still a matter of discussion. Its position in the Eupatoriae tribe seems to be in good agreement with its morphological and chemical characteristics [2, 3]. The presence of 3 (2, H) furanone heliangolides in *I. atriplicifolia* [4] seemed to support its placement in the Heliantheae tribe [5], but these types of compounds, which are frequent in Heliantheae, has been found also in members of the Eupatoriae tribe [6–8].

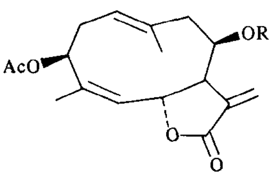
The chemical study of *Isocarpha oppositifolia* var. *achyranthes* collected in Northeastern, México, afforded germacranolides related to eucannabinolide, a type of compound common to both Eupatorieae and Heliantheae tribes.

RESULTS AND DISCUSSION

The aerial parts of *I. oppositifolia* (L.) Cass var. *achyranthes* (DC.) Keyland Stuessy afforded the known compounds hiyodorilactone F (**1a**) [9] and eucannabinolide (**1d**) [4]. The new heliangolide **1b** was found mixed with its isomer hiyodorilactone F (**1a**). The separation of the two compounds was very difficult.

The spectral data of lactone **1b** are almost superimposable on those of hiyodorilactone F (**1a**) (see Experimental) since the structure of both isomeric compounds only differ in the position of the acetate group of the ester side chain, the latter containing the acetate at C-5′ and **1b** at C-4′.

Compound **1c**, $C_{25}H_{32}O_8$, which preceded eucannabinolide in the chromatography was shown to be its acetonide, probably formed in the isolation process. The identification of **1c** was achieved by direct comparison with an authentic sample of eucannabinolide acetonide.



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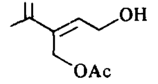

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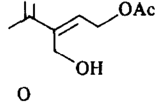

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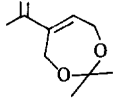

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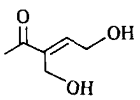

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