American Journal of Essential Oils and Natural Products

Available online at www.essencejournal.com

AkiNik

AJEONP American Journal of Essential Oils and Natural Products

ISSN: 2321-9114
AJEONP 2019; 7(3): 31-35

Received: 24-05-2019
Accepted: 26-06-2019

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Leaf essential oil compositions of bear's foot, *Smallanthus uvedalia* and *Polymnia canadensis*

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Abstract
The leaves of *Smallanthus uvedalia* and *Polymnia canadensis*, two members of the Asteraceae important in Native American traditional herbal medicine, were collected in north Alabama. The essential oils were obtained by hydrodistillation and analyzed by gas chromatography – mass spectrometry. Caryophyllane sesquiterpenoids dominated the leaf essential oil of *S. uvedalia*, including (*E*)-caryophyllene (16.5-24.5%), caryophyllene oxide (14.2-19.8%), 14-hydroxy-9-*epi*-(*E*)-caryophyllene (6.2-8.9%), 14-hydroxy-9-*epi*-(*Z*)-caryophyllene (4.3-8.2%), caryophylla-4(12),8(13)-dien-5β-ol (2.3-5.5%), and caryophylla-4(12),8(13)-dien-5α-ol (0.9-2.0%). *P. canadensis* leaf oil, on the other hand, was rich in germacrene D (44.5-63.7%). The high concentrations of caryophyllane and germacrane sesquiterpenoids likely account for the traditional uses of these plants to reduce inflammation and swelling.

Keywords: Yellow flower leafcup, white flower leafcup, Asteraceae, traditional herbal medicine

1. Introduction

Smallanthus uvedalia (L.) Mack. (syn. *Polymnia uvedalia* (L.) L., bear's foot, yellow flower leafcup) and *Polymnia canadensis* L. (bear's foot, white flower leafcup) are both perennial members of the Asteraceae. These closely related species can be differentiated by leaf shape (palmately lobed in *S. uvedalia*, pinnately lobed in *P. canadensis*) and ray flower color (yellow in *S. uvedalia*, white in *P. canadensis*) [1]. Both species were used by Native Americans as poultices to treat swellings and inflammations [2].

Previous investigations of *S. uvedalia* and *P. canadensis* have found germacranolide sesquiterpene lactones, *ent*-kaurene diterpenoids, and cadinene sesquiterpenoids [3–5]. To our knowledge, however, the essential oils of *S. uvedalia* and *P. canadensis* have not been previously examined, and in this work we present the essential oil compositions of the leaves of *S. uvedalia* and *P. canadensis*.

2. Materials and Methods

2.1 Plant Material

Fresh leaves of *S. uvedalia* were collected from plants from two different locations in north Alabama, Monte Sano (6 February 2016, 34°44′28.22″ N, 86°33′10.12″ W, 269 m elevation) and Blue Spring (9 February 2016, 34°45′32.86″ N, 86°11′29.01″ W, 194 m elevation). Fresh leaves of *P. canadensis* were also collected from two different locations Tollgate Road (26 September 2015, 34°44′14.24″ N, 86°33′34.87″ W, 256 m elevation) and Buck's pocket (11 December 2016, 34°28′20.95″ N, 86°03′08.91″ W, 272 m elevation). The fresh leaves were chopped and hydrodistilled using a Likens-Nickerson apparatus with continuous extraction with dichloromethane (see Table 1).

Table 1: Essential oil hydrodistillation yields for *Smallanthus uvedalia* and *Polymnia canadensis*.

Plant	Mass Leaves (g)	Yield Essential Oil (mg)
S. uvedalia (Monte Sano)	35.0	14.0
S. uvedalia (Blue Spring)	35.4	10.0
P. canadensis (Tollgate Road)	22.6	30.0
P. canadensis (Buck's Pocket)	16.8	18.0

previously [6]: Agilent 6890 GC, Agilent 5973 MSD, EI (70 eV); range of 40-400 amu, scan rate of 3.99 scans/sec, HP-5ms column, He carrier gas, head pressure of 92.4 kPa, flow rate of 1.5 mL/min, GC oven temperature program of 60 °C initial temperature, held for 5 min, then increased at 3 °C/min up to 280 °C, 1% solutions of essential oils in CH_2Cl_2, splitless injection. Identification of components was based on retention indices and by comparison with MS fragmentation with those in the literature [7] and stored in our in-house library.

3. Results and Discussion

3.1 *Smallanthus uvedalia*

The essential oil compositions of two different leaf essential oil samples of *S. uvedalia* are presented in Table 2. *S. uvedalia* leaf essential oils were dominated by caryophyllane sesquiterpenoids (69.1% and 44.4%, respectively), including (*E*)-caryophyllene (24.5% and 16.5%), caryophyllene oxide (19.8% and 14.2%), 14-hydroxy-9-*epi*-(*E*)-caryophyllene (8.9% and 6.2%), 14-hydroxy-9-*epi*-(*Z*)-caryophyllene (8.2% and 4.3%), caryophylla-4(12),8(13)-dien-5β-ol (5.5% and 2.3%), and caryophylla-4(12),8(13)-dien-5α-ol (2.0% and 0.9%).

Although the two essential oil samples are qualitatively similar, there are some notable differences. The number of components in sample #1 from Monte Sano was much greater (71 components) than those in sample #2 from Blue Spring (51 components), the concentration of monoterpenoids was higher in sample #1 compared to sample #2 (9.6% vs. 1.3%), and the concentration of caryophyllanes was higher in sample #1 than in sample #2.

The leaf essential oil of *S. maculatus* from Costa Rica had α-pinene (32.9%), germacrene D (13.7%), and (*E*)-caryophyllene (10.7%) as major components [8]. One sample of *S. quichensis* leaf oil from Costa Rica, had α-pinene (35.5%), *p*-cymene (11.5%), and β-phellandrene (9.2%) while a second sample was rich in α-pinene (64.5%) [9]. The leaf essential oil composition of *S. sonchifolius*, grown in China, showed β-phellandrene (26.3%), β-cubebene (17.6%), (*E*)-caryophyllene (14.0%), and α-cubebene (10.2%) [10].

Table 2: Leaf essential oil compositions of two samples of *Smallanthus uvedalia*.

RI(calc)	Compound	Percent Composition	
		Sample 1	Sample 2
		Monte Sano	Blue Spring
831	Isovaleric acid	---	0.5
861	(3*Z*)-Hexen-1-ol	0.2	---
870	1-Hexanol	0.1	---
878	2-Butylfuran	---	0.3
935	α-Pinene	1.3	---
959	Thuja-2,4(10)-diene	0.4	0.4
980	β-Pinene	0.1	---
996	Myrcene	0.2	---
1025	*p*-Cymene	0.4	---
1028	Limonene	4.7	---
1042	Benzene acetaldehyde	tr	0.1
1124	α-Campholenal	0.3	---
1135	*trans*-Pinocarveol	0.3	---
1142	*cis*-Verbenol	0.1	0.3
1158	Isoborneol	tr	---
1160	Pinocarvone	0.1	---
1176	Terpinen-4-ol	0.1	---
1183	*p*-Methylacetophenone	0.1	---
1185	*p*-Cymen-8-ol	0.2	---
1195	Myrtenol	0.1	---
1195	Myrtenal	0.1	---
1198	Methyl chavicol (= Estragole)	0.1	---
1207	Verbenone	0.2	0.3
1216	*cis*-Sabinene hydrate acetate	0.6	---
1219	*trans*-Carveol	0.2	---
1245	Carvone	0.1	---
1367	Cyclosativene	0.2	0.3
1373	α-Ylangene	0.1	0.5
1376	α-Copaene	0.2	1.1
1385	β-Bourbonene	0.5	2.9
1394	β-Elemene	0.2	0.6
1407	(*Z*)-Caryophyllene	0.1	---
1418	(*E*)-Caryophyllene	24.5	16.5
1420	α-Santalene	0.5	1.1
1437	α-*trans*-Bergamotene	0.4	0.9
1443	6,9-Guaiadiene	0.1	0.4
1448	*epi*-β-Santalene	0.2	0.2
1453	α-Humulene	2.0	2.3
1460	(*E*)-β-Farnesene	0.1	0.1
1465	*cis*-Cadina-1(6),4-diene	---	0.2
1476	γ-Muurolene	0.8	2.9
1481	α-Amorphene	---	0.2

1484	β-Selinene	0.2	0.6
1485	Neryl isobutyrate	0.3	0.3
1487	(*E*)-β-Ionone	tr	0.3
1494	Valencene	0.1	0.4
1494	γ-Amorphene	0.1	0.4
1501	α-Muurolene	0.1	0.7
1511	β-Bisabolene	0.2	0.4
1514	γ-Cadinene	0.8	2.7
1514	Nootkatene	0.8	---
1522	*trans*-Calamenene	0.5	---
1524	δ-Cadinene	0.4	3.7
1537	α-Cadinene	0.4	0.7
1542	α-Calacorene	0.3	1.2
1549	Elemol	0.8	---
1565	1,5-Epoxysalvial-4(14)-ene	---	0.4
1567	(*E*)-Nerolidol	0.5	1.1
1579	Spathulenol	0.7	7.5
1583	Caryophyllene oxide	19.8	14.2
1591	Salvial-4(14)-en-1-one	0.1	0.9
1602	Copaborneol	---	2.1
1609	Humulene epoxide II	0.7	2.1
1611	Unidentified	0.5	2.1
1614	Unidentified	0.1	0.5
1630	Caryophylla-4(12),8(13)-dien-5α-ol	2.0	0.9
1634	Caryophylla-4(12),8(13)-dien-5β-ol	5.5	2.3
1639	Unidentified	0.7	---
1640	τ-Cadinol	---	2.3
1646	Unidentified	---	0.9
1647	β-Eudesmol	1.6	---
1651	α-Eudesmol	1.7	1.5
1653	α-Cadinol	---	2.0
1656	14-Hydroxy-9-*epi*-(*Z*)-caryophyllene	8.2	4.3
1663	Unidentified	0.7	---
1670	14-Hydroxy-9-*epi*-(*E*)-caryophyllene	8.9	6.2
1684	Germacra-4(15),5,10(14)-trien-1α-ol	0.6	2.6
1694	Unidentified	0.6	---
1832	Unidentified	---	1.9
1872	Unidentified	0.7	---
	Total Identified	95.2	91.7
	Monoterpene hydrocarbons	7.0	0.4
	Oxygenated monoterpenoids	2.6	0.9
	Sesquiterpene hydrocarbons	34.0	40.9
	Oxygenated sesquiterpenoids	54.2	53.9
	Others	1.1	3.0
	Caryophyllane sesquiterpenoids	69.1	44.4

3.2 *Polymnia canadensis*

The chemical compositions of the two different *P. canadensis* leaf essential oils are listed in Table 3. Both samples were rich in sesquiterpenoids, particularly germacrene D (63.7% and 44.5% for the Tollgate Road and Buck's Pocket samples, respectively). Other major components found in *P. canadensis* leaf oils were (*E*)-caryophyllene (15.9 and 14.8%, respectively), α-humulene (5.1 and 3.9%, respectively), and bicyclogermacrene (5.4 and 2.7%, respectively). There was much more chemical diversity in the sample from Buck's pocket, collected in 2016, with 16 different monoterpenoids, 32 different sesquiterpenoids, and three diterpenoids identified.

Table 3: Leaf essential oil compositions of two samples of *Polymnia canadensis*.

RI(calc)	Compound	Percent Composition	
		Sample 1	Sample 2
		Tollgate Road	Buck's pocket
853	(2*E*)-Hexenal		0.7
922	Tricyclene	2.0	tr
928	α-Thujene		tr
934	α-Pinene		4.9
950	Camphene		0.4
977	Sabinene		0.4
980	β-Pinene		0.4
996	Myrcene		0.2
1007	α-Phellandrene		2.9
1024	*p*-Cymene		0.3

1027	Limonene		0.2
1034	(*Z*)-β-Ocimene		0.1
1050	(*E*)-β-Ocimene		0.1
1060	γ-Terpinene		0.1
1106	Linalool		0.1
1170	Borneol		0.1
1182	Terpinen-4-ol		0.1
1238	Thymol methyl ether		0.8
1338	δ-Elemene	0.6	
1342	7-*epi*-Silphiperfol-5-ene		1.0
1356	Silphiperfol-4,7(14)-diene		0.1
1360	Eugenol		0.1
1366	Cyclosativene	0.2	0.1
1376	α-Copaene	0.6	0.3
1379	Modheph-2-ene		0.5
1385	β-Bourbonene		0.1
1386	α-Isocomene		0.1
1392	β-Cubebene	0.3	0.1
1394	β-Elemene	0.2	0.2
1404	β-Isocomene		0.2
1420	(*E*)-Caryophyllene	15.9	14.8
1430	β-Copaene	1.8	0.1
1445	Aromadendrene	0.4	
1454	α-Humulene	5.1	3.9
1463	cis-Cadina-1(6),4-diene	0.7	
1475	γ-Muurolene		0.2
1482	Germacrene D	63.6	44.5
1484	β-Selinene		0.4
1486	Valencene		0.3
1490	*trans*-Muurola-4(14),5-diene	tr	0.1
1499	Bicyclogermacrene	5.4	2.7
1500	Epizonarene	0.8	
1500	α-Muurolene		0.3
1513	γ-Cadinene	tr	0.5
1518	Bornyl isovalerate		0.6
1524	δ-Cadinene	2.3	1.2
1525	Kessane		0.7
1527	Liguloxide		1.1
1537	α-Cadinene		0.1
1567	(*E*)-Nerolidol		3.1
1582	Neryl isovalerate		1.2
1621	Junenol		0.2
1647	τ-Cadinol		1.1
1654	α-Cadinol		0.9
1684	α-Bisabolol		0.2
1687	Ylangenol		0.2
1802	6-Methoxythymyl 2-methylbutanoate		0.2
2192	Rosa-5,15-diene		1.0
2196	Kauran-16β-ol		5.4
2210	Phyllocladanol (=Kauran-16α-ol)		0.3
	Monoterpene hydrocarbons	2.0	9.8
	Oxygenated monoterpenoids	0.0	3.0
	Sesquiterpene hydrocarbons	98.0	71.8
	Oxygenated sesquiterpenoids	0.0	7.5
	Diterpenoids	0.0	6.7
	Others	0.0	0.8
	Total identified	100.0	99.6

The high concentrations of sesquiterpenoids found in both *S. uvedalia* and *P. canadensis* likely account for the traditional uses of these plants to reduce inflammation and swelling. (*E*)-Caryophyllene, α-humulene, and caryophyllene oxide have shown anti-inflammatory effects [11–13]. Additionally, essential oils rich in germacrene D, *Ageratum fastigiatum* [14] and *Aspilia africana* [15,16] have shown anti-inflammatory activities. (*E*)-Caryophyllene [17–19] and germacrene D [20–23] are known to dominate the bioactive leaf essential oils of several species of Asteraceae.

4. Conclusions
The chemical compositions within the same species showed variation depending on collection location and time of year. Both species are rich in biologically active sesquiterpenoids, *P. canadensis* in germacranes and *S. uvedalia* in caryophyllanes.

5. Acknowledgments
This work was carried out as part of the activities of the Aromatic Plant Research Center (APRC,

https://aromaticplant.org/). No funding was received for this project. The authors declare no conflicts of interest.

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