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Leaf essential oil composition and terpenoid enantiomeric distribution of *Monarda bradburiana* Beck cultivated in South Alabama

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Abstract

In this work, the leaf essential oil of *Monarda bradburiana*, which was cultivated in south Alabama, was obtained by hydrodistillation and analyzed by gas chromatographic techniques. The leaf essential oil of *M. bradburiana* was dominated by thymol (60.1%), with lower concentrations of *p*-cymene (9.8%), carvacrol (5.7%), 1-octen-3-ol (4.9%), and γ -terpinene (4.7%). Chiral gas chromatography revealed the enantiomeric ratios of terpenoid components to be comparable to other *Monarda* species with the exception of camphene, 60.5% (–)-camphene, and linalool, which was 100% (–)-linalool.

Keywords: Beebalm, lamiaceae, terpenoids, enantiomers, chiral GC-MS

1. Introduction

There are 18 species of *Monarda* (Lamiaceae) native to North America^[1] and several of these have been used in the traditional herbal medicine of Native North Americans^[2]. *Monarda bradburiana*, the eastern beebalm (Figure 1), ranges naturally in southcentral North America (southern Illinois, Missouri, Arkansas, Kentucky, Tennessee, and as far south as northern Alabama)^[1]. In this report, we present the chemical composition and enantiomeric distribution of the leaf essential oil of *M. bradburiana* cultivated in southern Alabama.



Fig 1: *Monarda bradburiana* (Shutterstock image 1432093406, Jim Beers/Shutterstock.com).

2. Materials and Methods**2.1 Plant Material**

Monarda bradburiana seedlings (three) were purchased from Prairie Moon Nursery (Winona, Minnesota, USA), and were grown at Kirkland Gardens LLC (Newville, Alabama, USA; 31°26'27" N, 85°21'31" W). The seedlings were planted in May 2021, in a shady location in the garden with approximately 6 hours/day of direct sunlight. All three of *M. bradburiana* plants were harvested on 27 July 2021. The leaves were allowed to dry in doors in an air-conditioned area at approximately 23 °C for 10 days, then vacuum-sealed and shipped to the University of Alabama in Huntsville. The dry leaves (11.10 g) were hydro-distilled with a Likens-Nickerson apparatus with continuous extraction with dichloromethane for 4 h. The solvent was evaporated to give an orange-colored essential oil (390.3 mg). The essential oil was stored at –20 °C until further analysis.

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2.2 Gas Chromatography – Mass Spectrometry (GC-MS)

The leaf essential oil of *M. bradburiana* was subjected to gas chromatographic–mass spectral (GC–MS) analysis as previously reported [3]: Shimadzu GCMS-QP2010 Ultra, electron impact (EI) mode with electron energy = 70 eV, scan range = 40–400 atomic mass units, scan rate = 3.0 scans/s; ZB-5ms fused silica capillary GC column (60 m length, 0.25 mm inside diameter, 0.25 µm film thickness); He carrier gas, column head pressure = 208.3 k Pa, flow rate = 2.00 mL/min; injector temperature = 260 °C, ion source temperature = 260 °C; GC oven temperature program: initial temperature = 50 °C, temperature increased 2 °C/min to 260 °C. For each sample, a 5% w/v solution in CH₂Cl₂ was prepared, and 0.1 µL was injected using a split ratio of 24.5:1. Identification of the individual components of the essential oils was determined by comparison of their retention indices, determined using a series of *n*-alkanes, in addition to comparison of the mass spectral fragmentation patterns with those found in the MS databases [4-7], using the Lab Solutions GCMS solution software version 4.45, and with matching factors > 90%.

2.3 Gas Chromatography – Flame Ionization Detection (GC-FID)

The GC-FID analyses were carried out using a Shimadzu GC 2010 equipped with flame ionization detector, a split/splitless injector, and Shimadzu autosampler AOC-20i, with a ZB-5 capillary column (60m × 0.25mm inside diameter; film thickness 0.25 µm). The oven temperature was programmed as above for GC-MS. Injector and detector temperatures were maintained at 260 °C, respectively. The carrier gas was He and the flow rate was 1.0 mL/min. For each sample, a 5% w/v solution in CH₂Cl₂ was prepared, and 0.1 µL was injected using a split ratio of 31:1. The percent compositions of the essential oils were calculated from peak areas without

standardization.

2.4 Chiral GC-MS

Chiral GC–MS of the three leaf essential oils was carried out, as reported previously [3]: Shimadzu GCMS-QP2010S (Shimadzu Scientific Instruments, Columbia, MD, USA), electron impact (EI) mode, electron energy = 70 eV; scan range = 40–400 amu, scan rate = 3.0 scans/s; Restek B-Dex 325 chiral capillary GC column (30 m length × 0.25 mm inside diameter × 0.25 µm film thickness). Oven temperature program: starting temperature = 50 °C, temperature increased 1.5 °C/min to 120 °C, then 2 °C/min to 200 °C, and kept at 200 °C for an additional 5 min; carrier gas was helium, flow rate = 1.8 mL/min. For each essential oil sample, a 3% w/v solution in CH₂Cl₂ was prepared, and 0.1 µL was injected using a split ratio of 1:45. The enantiomers of the monoterpenoids were identified by comparison of retention times with authentic samples obtained from Sigma-Aldrich (Milwaukee, WI, USA). The enantiomer percentages were determined from peak areas.

3. Results and Discussion

3.1 Essential oil composition

Hydrodistillation of the dried leaves of *M. bradburiana* gave an orange-colored essential oil in 3.52% (w/w) yield. The essential oil composition is listed in Table 1. A total of 62 compounds were identified in the essential oils accounting for 100% of the composition. The major components in the essential oils were thymol (60.1%), *p*-cymene (9.8%), carvacrol (5.7%), 1-octen-3-ol (4.9%), and γ -terpinene (4.7%). The chemical composition is in agreement with a previous report on the essential oil of *M. bradburiana* cultivated in southern Mississippi, which showed thymol (57.7%), *p*-cymene (17.6%), carvacrol (4.6%), 1-octen-3-ol (6.7%), and γ -terpinene (0.5%) [8].

Table 1: Chemical composition of *Monarda bradburiana* leaf essential oil.

RI _{calc}	RI _{db}	Compound	% Composition	ED, (+) : (-)
925	925	α -Thujene	1.8	66.9:33.1
932	932	α -Pinene	0.4	88.8:11.2
942	943	Thujadiene	tr	
949	950	Camphene	0.1	39.5:60.5
972	972	Sabinene	0.1	100:0
973	973	1-Octen-3-one	tr	
977	978	1-Octen-3-ol	4.9	0:100
984	983	3-Octanone	0.1	
988	989	Myrcene	1.3	
996	996	3-Octanol	tr	
1004	1004	<i>p</i> -Mentha-1(7),8-diene	tr	
1007	1007	α -Phellandrene	0.3	96.1:3.9
1009	1009	δ -3-Carene	0.1	100:0
1017	1017	α -Terpinene	3.3	
1019	1022	<i>m</i> -Cymene	tr	
1026	1025	<i>p</i> -Cymene	9.8	
1027	1026	2-Acetyl-3-methylfuran	tr	
1029	1030	Limonene	0.6	61.8:38.2
1031	1031	β -Phellandrene	0.2	0:100
1032	1032	1,8-Cineole	tr	
1034	1034	(<i>Z</i>)- β -Ocimene	tr	
1042	1043	Phenylacetaldehyde	tr	
1045	1045	(<i>E</i>)- β -Ocimene	tr	
1058	1058	γ -Terpinene	4.7	
1069	1069	<i>cis</i> -Sabinene hydrate	0.7	98.5:1.5
1079	1079	1-Nonen-3-ol	tr	
1084	1086	Terpinolene	0.1	
1089	1091	<i>p</i> -Cymenene	tr	

1099	1101	Linalool	0.2	0:100
1101	1101	<i>trans</i> -Sabinene hydrate	0.1	
1103	1104	Nonanal	tr	
1106	1107	1-Octen-3-yl acetate	tr	
1180	1180	Terpinen-4-ol	0.4	68.2:31.8
1189	1189	<i>p</i> -Cymen-8-ol	tr	
1199	1198	α -Terpineol	0.1	81.3:18.7
1254	1252	Thymoquinone	0.4	
1291	1289	Thymol	60.1	
1300	1300	Carvacrol	5.7	
1344	1345	Thymyl acetate	tr	
1350	1356	Eugenol	0.2	
1375	1375	α -Copaene	tr	
1383	1382	β -Bourbonene	tr	
1389	1390	<i>trans</i> - β -Elemene	tr	
1393	1392	β -Cubebene	tr	
1419	1417	(<i>E</i>)- β -Caryophyllene	1.5	0:100
1429	1430	β -Copaene	tr	
1451	1452	(<i>E</i>)- β -Farnesene	0.1	
1455	1454	α -Humulene	0.1	
1474	1475	γ -Muuroolene	0.1	
1480	1480	Germacrene D	0.9	0:100
1483	1483	<i>trans</i> - β -Bergamotene	0.9	
1485	1485	γ -Thujaplicin	tr	
1488	1489	β -Selinene	tr	
1491	1490	γ -Amorphene	tr	
1495	1497	α -Selinene	tr	
1497	1497	α -Muuroolene	tr	
1512	1512	γ -Cadinene	tr	
1517	1518	δ -Cadinene	0.1	0:100
1549	1549	Thymohydroquinone	0.4	
1581	1587	Caryophyllene oxide	0.1	
1638	1639	<i>cis</i> -Guaia-3,9-dien-11-ol	0.1	
1654	1655	α -Cadinol	0.1	
		Monoterpene hydrocarbons	23.0	
		Oxygenated monoterpenoids	67.6	
		Sesquiterpene hydrocarbons	3.6	
		Oxygenated sesquiterpenoids	0.6	
		Benzenoid aromatics	0.2	
		Others	5.0	
		Total identified	100.0	

RI_{calc} = Retention indices calculated in reference to a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Retention indices obtained from the databases [4-7]. ED = Enantiomeric distribution (dextrorotatory enantiomer: levorotatory enantiomer). tr = "trace" (< 0.05%).

The enantiomeric distribution of the monoterpenoids in *M. bradburiana* essential oil is comparable to those observed in *M. citriodora*, *M. fistulosa*, and *M. punctata* [9]. That is, the dominant enantiomers for *Monarda* species were (+)- α -thujene, (+)- α -pinene, (+)-sabinene, (+)- α -phellandrene, (+)- δ -3-carene, (-)- β -phellandrene, (+)-*cis*-sabinene hydrate, (+)-terpinen-4-ol, and (+)- α -terpineol. Limonene seems to be variable in distribution, both between and within *Monarda* species [9]. (-)-Limonene dominated the essential oil of *M. fistulosa*, while (+)-limonene was the major enantiomer seen in *M. bradburiana*. Interestingly, there was a slight excess of (-)-camphene over (+)-camphene (60.5% and 39.5%, respectively) in *M. bradburiana* essential oil, but (+)-camphene dominated the essential oils of *M. fistulosa* and *M. punctata*. Likewise, linalool was nearly evenly distributed in *M. citriodora* and *M. fistulosa*, but (-)-linalool was the exclusive enantiomer detected in *M. bradburiana*. The non-terpenoid (-)-1-octen-3-ol was the exclusive enantiomer observed in this work, in agreement with that found by Tabanca and co-workers [8].

4. Conclusions

The leaf essential oil composition of *M. bradburiana* has been determined. This work complements the previous report on *M. bradburiana* essential oil by Tabanca and co-workers [8], not only by confirming the essential oil composition of the essential oil, but also by extending our knowledge of the phytochemistry by including the enantiomeric distribution of the chiral components. It also complements our own previous study on *M. citriodora*, *M. fistulosa*, and *M. punctata* leaf essential oils [9].

5. Acknowledgments

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6. Conflicts of Interest

The authors declare no conflicts of interest.

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