ESSENTIAL OILS FROM BRAZILIAN VERBENACEAE. GENUS *LIPPIA*

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ABSTRACT.—Essential oils from six species of the Verbenaceae family; *Lippia alba, L. alnifolia, L. affinis aristata, L. aristata, L. grata* and *L. aff. sidoides* were analyzed by gc-ms-computer library search programs. Several monoterpenes, sesquiterpenes, aromatic compounds, alcohols, and ketones were identified.

Thymol and α-phellandrene are the major constituents of the essential oil of *L. aff. sidoides*. The other five species contain mainly caryophyllene followed by carvacrol in *L. alnifolia* and *L. grata*, γ-cadinene in *L. aff. aristata*, sabinene in *L. aristata*, and geranial in *L. alba*.

As part of an intensive screening program of odoriferous flora of northeastern Brazil including botanical, pharmacological, and chemical aspects, we decided to investigate the chemical composition of the essential oils from six species of the Verbenaceae family, genus *Lippia*.

Previous work on essential oils of this genus has been on *Lippia alba, L. adoensis, L. micromeria, L. turbinata, L. carviodora, L. juneliana, L. dulcis, L. hastulata, L. helleri, L. polistachia, L. citriodora, L. lyciodes* and *L. asperifolia* (1–19).

The residual waters from the steam distillation of *L. aristata* and *L. aff. sidoides* have shown high molluscicidal activity (1: 100 dilutions) against *Biomphalaria glabrata*, the most important host of *Schistosoma mansoni* in Brazil (20).

This communication describes the results of an investigation of the essential oils constituents from *L. alba, L. alnifolia, L. aff. aristata, L. aristata, L. grata* and *L. aff. sidoides* widely grown in northeastern Brazil (table 1).

DISCUSSION

The results of the analysis of the chemical composition of the essential oils are presented in table 2. Individual identifications were made by computer library search programs which involved mass spectral (ms) data and gas chroma-

TABLE 1. Essential oils from *Lippia* species: Voucher registry no., collection sites, part studied and yields.

File[a]	Species	Voucher[b]	Collection sites (Brazil)	When collected	Part studied	yield[c]
F-193	*L. alba* Braun	3504	S. Bernardo-Ma.[d]	Oct. 77	leaves	0.1
F-140	*L. alnifolia* Schau.	3397	Jacobina-Ba.[e]	Jun. 77	leaves+stems	0.1
F-518	*L. aff. aristata* Schau.	6225	Alagoa Grande-Pb.[f]	Sept. 79	leaves	0.4
F-517	*L. aristata* Schau.	5695	Mossoró-RN[g]	Nov. 77	leaves	1.5
F-165	*L. grata* Schau.	3337	Junco-do-Seridó-Pb.[h]	Jul. 77	leaves	2.9
F-401	*L. aff. sidoides* Cham.	3646	Jucuri-RN.[i]	Aug. 77	leaves	4.0

[a]File no. in the Dept. de Química Orgânica e Inorgânica—Universidade Federal do Ceará—Brazil.
[b]Registry no. in the Herbarium of Dept. de Biologia—Universidade Federal do Ceará—Brazil.
[c]Yields calculated on dry plant material.
[d]Lat. 3°22′S Long. 42°24′W.
[e]Lat. 11°13′S Long. 40°30′W.
[f]Lat. 7°3′S Long. 35°35′W.
[g]Lat. 5°12′S Long. 37°12′W.
[h]Lat. 6°58′S Long. 36°42 W.
[i]Lat. 5°12′S Long. 37°45′W.

tographic (gc) retention indexes. These programs were written in BASIC language and implemented in our laboratory for automatic analysis of essential oils (21–22).

Confirmations of the identifications were carried out by visual comparison of the full ms with standards from a certified collection (23), by other spectrometric

TABLE 2. Chemical composition of essential oils of Verbenaceae species, genus *Lippia*.

Constituent	*L. alba*	*L. alnifolia*	*L. aff. aristata*	*L. aristata*	*L. grata*	*L. aff. sidoides*	Confirmation
camphene	—	1.0	—	—	—	—	a, b
car-3-ene	0.8	—	1.3	1.9	0.6	—	—
limonene	—	—	6.3	16.8	—	—	a, b, c
myrcene	2.5	—	—	—	7.0	6.5	a, b, c
α-phellandrene	—	—	1.0	—	—	22.4	—
α-pinene	—	—	1.2	1.4	1.0	0.6	a, b, c
γ-terpinene	1.2	2.8	1.2	—	14.4	4.3	a, b
sabinene	—	—	11.0	21.1	—	—	a, b
α-thujene	—	—	1.2	1.1	3.3	2.0	—
p-cymene	0.8	13.7	1.6	—	22.2	8.6	a, b
camphor	—	—	—	—	—	0.6	a
1:8,cineol	—	—	—	—	—	1.2	a, b
geranial	12.9	—	—	—	—	—	—
linalool	—	—	0.8	1.2	—	—	a, b
neral	9.6	—	—	—	—	—	—
terpinen-4-ol	—	—	—	—	0.6	—	—
carvacrol	—	27.3	—	—	20.0	4.3	a
carvacrol acetate	—	—	—	—	1.0	—	—
eugenol	—	—	—	—	—	0.8	a, b, c
O-methyl-thymol	—	4.4	—	—	1.8	—	—
thymol	—	3.1	—	—	18.8	43.5	a
thymol acetate	—	—	—	—	1.5	—	—
alloaromadendrene	—	1.5	—	—	0.5	—	—
γ-cadinene	0.7	—	15.8	8.4	—	—	—
δ-cadinene	2.4	—	—	—	—	—	—
β-caryophyllene	24.3	37.4	32.5	23.3	1.8	9.7	a, b, c
α-copaene	1.8	—	—	—	0.6	-	—
β-elemene	1.5	—	0.8	0.5	—	—	—
γ-elemene	—	—	12.4	12.7	—	—	a, b
α-muurolene	—	—	—	—	0.6	—	—
γ-muurolene	0.4	—	—	—	—	—	—
α-humulene	2.2	2.1	4.3	1.2	—	—	a, b
caryophyllene oxide?	—	—	4.5	—	—	—	—
2-undecanone	9.0	—	—	—	—	—	—
Total*	70.1	93.3	96.9	89.1	95.7	82.1	—

a. Kovat's indexes; b. nmr; c. ir.
*Summation of the % amount of each compound identified in the oil.

data and by comparison with authentic samples when they were available (see table 2).

Lippia aff. aristata (table 1) has some minor morphological differences as compared with the description of *L. aristata* in the literature (24). From table 2, it is seen that essential oils of both species have the same major constituents, *i.e.*, β-caryophyllene, γ-elemene, and limonene; α-phellandrene (1.0%) was found only in *Lippia aristata*, whereas p-cymene (1.6%) was identified only in *L. aff. aristata* (see table 2).

Data from table 2 show that the essential oil of *Lippia alba* from Brazil is largely composed of β-caryophyllene (24.3%) geranial (12.9%), neral (9.6%), and 2-undecanone (9%). These results do not agree with the chemical composition of the essential oil from the same species from Argentina which chiefly consist of dipentenes, d-limonene, and l-piperitone (19).

EXPERIMENTAL

The plant materials were collected at locations mentioned in table 1.

Botanical identifications were made by A. G. Fernandes and P. Bezerra. A voucher of each species, under the number specified in table 1, is kept in the herbarium of Departamento de Biologia da Universidade Federal do Ceará, Brazil.

Essential oil extraction (25) was carried out by steam distillation of finely ground material for approximately one hour. The yields are reported in table 1.

The fresh oils were analyzed in a Finnigan 3300 quadrupole mass spectrometer coupled to gas chromatography with an open tubular glass column (30m x 0.25mm). SP. 2100 (methylsilicone) was used as the stationary phase. The gc experiments were carried out under programmed temperature conditions (50°-250°) at a rate of 4°/min with helium as carrier gas. The ms fragmentations were carried out at 70 eV electron impact. Mass chromatographic retention data were calculated as Kovat's indexes (26) by co-injection of the essential oil with eight standard *n*-hydrocarbons (C_8, C_9, C_{10}, C_{11}, C_{12}, C_{14}, C_{16}, and C_{18}). The reconstruction of the individual chromatograms of essential oil and *n*-hydrocarbons were carried out with ions *m/z* 91 and *m/z* 85, respectively (22).

All data processing was performed on a 6115 Finnigan computer with 32K bites of core memory equipped with a 3 megabite disk and with magnetic tapes.

Other spectrometric data (nmr, ir) were obtained with the aid of Varian EM 360, Varian XL-100 nmr instruments and a Perkin Elmer 720 infrared spectrophotometer.

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