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ESSENTIAL OIL VARIATION IN *CALYPTRANTHES SPRUCEANA*

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Abstract—Two chemical races in *Calyptranthes spruceana* were examined. One of them contains limonene, geranial and perillaldehyde as the main constituents of its essential oil. The other is shown to contain α-pinene, β-pinene, neral and geranial as its major oil components.

Calyptranthes spruceana Berg is a small tree which grows wild in the 'Varzea' along the Solimões and Negro rivers in the Amazon, it is known as 'laranjinha' and 'cuminhirana' because of the characteristic odour in its leaves. An earlier analysis of the essential oil of the leaves of *C. spruceana* using a packed column GC showed the main constituents to be limonene and perillaldehyde [1].

As part of an ongoing study of Amazonian plants, we also analysed the volatiles of essential oils from the leaves of two collections of *C. spruceana* using capillary column GC/MS. One of them (variety A) was composed primarily of limonene and perillaldehyde and thus was similar to that described in the first report [1]. In the other oil (variety B), perillaldehyde was not detected and limonene occurs in small concentrations (3.6%). Furthermore, we have now established the presence of additional monoterpenes and δ-cadinene (Table 1).

In GC/MS analysis of variety B the major constituents were α- and β-pinene, neral and geranial. The concentrations of α- and β-pinene comprise 50% of the total oil and these are of considerable industrial importance [2, 3].

Since the two types of trees of *C. spruceana* differ in the composition of their essential oils, they are chemical races within the same species. The existence of infraspecific chemical variation has also been established in the genera *Eucalyptus* [4], *Mentha*, *Lippia*, *Satureja* [5], *Cinnamomum* [6] and *Ocotea* [7].

The chemical relationship between the mono- and bicyclic monoterpenes found in the essential oils of *C. spruceana* has been established by biosynthetic studies [2, 9, 10, 11]. The results indicate that only a small change in the biosynthetic pathway to these essential oils separates these otherwise indistinguishable morphological forms.

It should be borne in mind that the determination of the oil composition of plants may be subject to production of artifacts arising during or subsequent to the isolation of the oil. In the present case the essential oils of varieties A and B were obtained by diverse procedures. Since the extracted oils of each variety produce identical GC results, the presence of artifacts was unlikely. Relative concentrations of individual peaks of the two varieties of *C. spruceana* and their retention data are shown in Table 1.

Table 1. Constituents of the essential oils of *C. spruceana*

Peak No.	Compound	RR_t*	% of oil† Var. A	% of oil† Var. B
1	α-Thujene‡	0.401	—	0.52
2	α-Pinene‡	0.416	2.16	15.17
3	Camphene‡	0.439	0.18	0.25
4	β-Pinene‡	0.499	3.71	34.04
5	Myrcene‡	0.523	0.32	0.87
6	α-Phellandrene‡	0.546	—	0.26
7	α-Terpinene‡	0.570	—	0.19
8	*p*-Cymene‡	0.587	—	1.54
9	Limonene‡	0.596	34.35	3.60
10	γ-Terpinene‡	0.657	—	0.63
11	γ-Terpinolene‡	0.717	—	0.33
12	Linalol‡	0.742	0.28	0.39
13	Fenchol‡	0.768	—	0.10
14	*Trans*-Pinocarveol	0.820	0.38	0.48
15	4-Terpineol	0.902	0.98	1.45
16	α-Terpineol‡	0.930	1.85	0.79
17	Myrtenal‡	0.940	1.32	0.53
18	*Trans*-Carveol	0.986	0.20	0.11
19	Neral‡	1.039	4.83	12.49
20	Nerol‡	1.061	—	0.52
21	Geranial‡	1.100	13.55	19.29
22	Perillaldehyde‡	1.110	19.87	—
23	β-Caryophyllene‡	1.372	—	0.28
24	δ-Cadinene	1.555	—	0.10

*Retention time relative to methyl pelargonate (IS).
†Relative to quantitation report of the data system.
‡Identity confirmed by MS and GC comparisons with authentic standard.

EXPERIMENTAL

Plant material of *C. spruceana* was collected in the Janauari (lower Rio Negro) (variety A), and Ariau rivers (upper Rio Negro) (variety B) in the State of Amazonas. Voucher specimens (Nos 114, 214 and 80, 424) were deposited in the INPA herbarium in Manaus. Air-dried leaves were subjected to steam distillation according to old cohobation and current techniques [12]. The oils obtained were dried in the presence of anhydrous Na_2SO_4 and produced yields of 1 7 and 1 8 %, respectively

Physical constants of the volatile oils were Variety A, Sp gr ^{25} 0 8627, n_D^{20} 1 4802, $[\alpha]_D^{25}$ +60 5 ($CHCl_3$, *c* 5 290) Variety B, Sp gr^{25} 0 8626, n_D^{20} 1 4912, $[\alpha]_D^{25}$ −7 2 ($CHCl_3$, *c* 6 268) The volatile oils were analysed on a FID/GC using a 30 m × 0 25 mm fused silica capillary column (WCOT) containing a 0 25 μm film of SE-54 H_2 was used as the carrier gas, adjusted to a linear velocity of 33 cm/sec (measured at 150°), split flow was adjusted to give a 20 1 ratio, and septum sweep was a constant 10 cm^3/min Splitless injection of 2 μl on a 1 1000 *n*-hexane soln was followed by a delay of 30 sec before purging Injection was done with the oven at 50° After a 3 min initial wait, temperature was programmed at 6°/min to 230°

The essential oils were submitted to a quadrupole GC/MS with data system An identical 30 m SE-54 silica capillary column was installed in the GC, in a Grob-type injector and directly coupled to the ion source of the MS He was used as carrier gas and injection and oven-programming temperature were the same as above except a 4°/min gradient was used The mass spectrometer was in EI mode at 70 eV The quadrupole filter was scanned from 34 to 434 daltons once every second, and resulting spectra were stored on computer discs for later recall

Peaks whose identities were confirmed by comparison of their spectra and their GC retention data with those of authentic compounds are so indicated Other identifications were made by comparison of mass spectra with those in the data system library or from the literature and are considered tentative

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