Phytochemistry, 1966, Vol. 5, pp. 921 to 926. Pergamon Press Ltd. Printed in England

THE ESSENTIAL OILS OF SOME VENEZUELAN *CROTON* SPECIES

R. Bracho and K. J. Crowley

Department of Chemistry, Instituto Venezolano de Investigaciones Cientificas, Apartado 1827,
Caracas, Venezuela

(*Received* 28 *June* 1965)

Abstract—Essential oils have been obtained from eleven *Croton* species. α-Pinene, β-pinene, p-cymene and citronellol were present in all the oils examined, while camphene, myrcene, α-phellandrene, dipentene, 1,8-cineole, fenchone, *allo*aromadendrene, methyleugenol, and palmitic acid were detected in some.

INTRODUCTION

Essential oils have been isolated from fourteen *Croton* species[1,2] but the constituents were not generally examined. Eugenol, isoeugenol, elemicin (3,4,5-trimethoxy-1-allylbenzene) and *p*-cymene are the only volatile compounds to have been positively identified, while palmitic acid, stearic acid, and cascarillic acid (of unknown constitution) have been reported in cascarilla oil from *C. eluteria.*

The present work began as an examination[3] of the essential oil from *C. malambo*, the bark of which is sucked by the Guajira Indians of Venezuela and Colombia, as a remedy for the common cold. It was extended to other *Crotons* as part of a search for new natural products and also because of the possible chemotaxonomic interest, particularly since the genus presents some taxonomic problems.

RESULTS AND DISCUSSION

The steam-volatile oils were obtained in the usual way from the species listed in Table 1. The oil yield from each species is given in the same table, together with details of the material extracted and the collection sites. Except for that from *C. populifolius*, which was bright green, and that from *C. speciosus*, which was blue, all the oils were greenish yellow. The high-boiling fractions from *C. malambo* became blue during distillation, but no azulenic compounds were identified in either this oil or that from *C. speciosus.*

The oils available in sufficient quantity were fractionated through spinning band columns and, in some cases, further separated by chromatography over alumina. The monoterpenic constituents were identified by gas–liquid partition chromatography (GLC) using a capillary column of high resolving power; a packed column was used for the less volatile compounds. When possible (see Table 2) the identifications were confirmed by the i.r. spectra of the purified

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[1] E. Gildemeister and F. Hoffman, *Die Atherischen Ole*, Vol. V, pp. 697–9, Akademie Verlag, Berlin (1959).

[2] F. W. Freise, *Pharm. Zentralhalle* **76**, 469 (1935), (*Chem. Abstr.* **29**, 7017); W. M. Sessler and W. Spoon, *West Indische Gids* **33**, 49 (1952), (*Chem. Abstr.* **47**, 5631); G. A. Fester, J. A. Retamar, A. I. A. Ricciardi and L. R. Fonseca, *Rev. Fac. Ing. Quim.* **28**, 9 (1959), (*Chem. Abstr.* **55**, 10809); W. F. McCaughey and T. E. Buehrer, *J. Pharm. Sci.* **50**, 658 (1961), (*Chem. Abstr.* **55**, 25167).

[3] R. Bracho, Thesis presented in partial fulfilment of the requirements for degree of Licenciado en Química, Universidad Central de Venezuela, 1963.

constituents, this being done at least once for each of the less volatile compounds which could not be passed through the capillary column. Further confirmation of the identities of the latter were obtained by a mixed melting point determination (palmitic acid), a nuclear magnetic resonance spectrum (citronellol), and the preparation of derivatives from linalool, *allo*aromadendrene and methyleugenol.

TABLE 1. YIELD OF STEAM-VOLATILE OILS FROM *Croton* SPECIES

Species*	When collected (1963)	Site		Material extracted	Yield of oil (%)
		Long.	Lat.		
C. malambo Karst.	April	71° 58′	10° 16′	Heartwood	1·03
C. gossypifolius Vahl.	March	66° 53·5′	10 18·5′	Bark†	1·01
C. xanthochloros Croiz.	March	66° 58·5′	10° 23′	Bark†	0·68
C. turumiquirensis Stey.	August	67° 8′	10° 27·5′	Bark†	0·49
C. deserticolus Stey.	April	71° 47′	10 57′	Bark and wood	0·22
C. speciosus Muel.—Arg.	April	66 58·5′	10 23′	Bark and wood‡	0·44
C. populifolius Lam.	May	66° 56·7′	10° 35′	Bark and wood	0·36
C. argyrophyllus H. B. K.	April	71° 56′	10 22′	Bark and wood	0·14
C. bredemeyeri Muel.—Arg.§	May	66° 58′	10° 33′	Bark and wood	0·26
C. glandulosus Muel.—Arg.	April	68° 21·6′	10° 27′	Stem and leaves	~0·04
C. rhamnifolius H. B. K.	April	71° 47′	10° 57·5′	Stem and leaves	~0·03

* Local names and botanical details of most of these species have been described.[4]

† The heartwood contains little or no oil.

‡ The leaves gave an oil of similar composition in 0·14 per cent yield.

§ Probably synonymous with *C. scaber* Willd.

TABLE 2. STEAM-VOLATILE CONSTITUENTS OF *Croton* SPECIES

Species	Proportions of components identified*													
	α-Pinene	Camphene	β-Pinene	Myrcene	α-Phellandrene	Dipentene	1,8-Cineole	*p*-Cymene	Fenchone	Linalool	Citronellol	*allo*Aromadendrene	Methyleugenol	Palmitic acid
C. malambo	**2**		**2**					tr		**2**	**4**		**58**	**1**
C. gossypifolius	**11**	tr	tr	tr	tr	2	1	**2**	2		**12**			
C. xanthochloros	**19**	tr	**5**	tr	**6**	3		**13**			6			
C. turumiquirensis	**12**		**8**				**8**	tr		tr	3	**19**		
C. deserticolus	**14**	tr	**11**			**3**		**2**	1		**10**			
C. speciosus	**5**	tr	tr	tr		tr		**2**			46			
C. populifolius	12	tr	4		tr	**4**		tr			22			
C. bredemeyeri	5		tr		**1**			tr			29			
C. argyrophyllus	3		7					1			11			
C. glandulosus	tr		?					tr			40			

* Components are listed in order of elution by GLC; a bold face number indicates that the compound was isolated and its identification confirmed by methods other than GLC; tr — trace.

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[4] L. SCHNEE, *Rev. Fac. Agron. Univ. Central Venezuela*, Alc. No. 3 (1960).

The results listed in Table 2 suggest that the co-occurrence of α-pinene, β-pinene, *p*-cymene and citronellol is a characteristic of the genus. It is thus surprising that only one of these, *p*-cymene, has been previously found (in *C. echinocarpus* and *C. eluteria*) particularly as they are all widely distributed in Nature. Although methyleugenol has not been found in other *Crotons*, the related elemicin has been reported in *C. parvifolius*, isoeugenol in *C. echinocarpus*, and eugenol in *C. eluteria*. The essential oil of the latter has also yielded palmitic acid. The present identification of *allo*aromadendrene appears to afford the first instance of its occurrence in the *Euphorbiaceae* family.

EXPERIMENTAL

The GLC experiments were carried out with a Perkin–Elmer 154-D fractometer. For the GLC identification of citronellol, methyleugenol, and the constituents of the oils from *C. argyrophyllus* and *C. glandulosus*, a 2-meter packed column of polyethylene glycol adipate was used; all other GLC identifications were made using a capillary column (150 ft × 0·01 in.) operated under conditions giving separations of 25,000–50,000 theoretical plate equivalents. In every case the compound was not separated from the admixed authentic sample. The quantitative composition of the oils was determined by the triangulation method of measuring the area under the peaks. Samples (0·5–5·0 μl) were injected with Hamilton micro-syringes.

Infrared spectra were obtained with a Perkin–Elmer spectrometer, Model 237, liquids being examined as films without solvent. Melting points were determined on a Fisher–Johns apparatus.

Camphene, α-pinene, linalool and palmitic acid were obtained from Eastman Organic Chemicals Inc., β-pinene and myrcene from L. Light & Co., α-phellandrene, limonene, *p*-cymene and fenchone from British Drug Houses, and cineole and citronellol from Aldrich Chemical Co.

Eight main unidentified compounds (designated A–H in order of increasing retention time) were detected by GLC. Where these were isolated they did not correspond, in i.r. spectra, with any of the terpenes listed by Sorm *et al.*[5] Most could not be satisfactorily purified by fractional distillation, and other methods were tried where possible. Those isolated in fair purity were each found in only one oil, and are described in the appropriate sections. Of the others, compound B (b.p. 72–75°/1·75 mm) was detected in *C. deserticolus* and *C. xanthochloros*; D (b.p. 75–78°/3·9 mm) in *C. deserticolus* and *C. gossypifolius*; E (b.p. 66–68°/0·25 mm) in *C. xanthochloros*; and F (b.p. 113–115°/0·25 mm) in *C. gossypifolius, C. turumiquirensis, C. speciosus, C. populifolius*, and *C. bredemeyeri.*

Extraction of the Oils

The material from the first five plants listed in Table 1 was available in 10–40 kg quantities and was thus extracted in a large drum fitted with a condenser and a high-voltage fog precipitator. The other plant materials (0·5–2·0 kg) were extracted in a 10 l. flask. In every case the finely ground material, with excess water, was boiled for 1–3 days, and the aqueous condensate was returned through a Dean and Stark separator. The yields of oil so obtained are listed in Table 1.

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[5] J. Pliva, M. Horak, V. Herout and F. Sorm, *Die Terpene*, Akademie Verlag, Berlin. Teil I (1960), Teil II (1963).

Identification of the Constituents

C. malambo. The oil (420 g), fractionated through a 36 in. spinning band column, gave the following fractions.

Fr.	Final b.p.	Press. (mm)	Wt. (g)	Constituents identified
1	56	37	1·1	α-Pinene
2	53	23	1·1	α-Pinene, β-pinene
3	56	23	1·8	α-Pinene, β-pinene
4	98	23	11·1	β-Pinene, *p*-cymene, linalool, citronellol
5	134	23	133·5	Linalool, citronellol, methyleugenol
6	94	6	166·0	Methyleugenol
7	134	5·5	56·5	
Res.			49·0	Palmitic acid

α-Pinene comprised 92% of fraction 1. It was identified by GLC and its i.r. spectrum.
β-Pinene comprised 72% of fraction 3, and was identified similarly.
Linalool was obtained in 98% purity as a liquid, b.p. 96°/20 mm, n_D^{23} 1·4633, on redistillation of fraction 5. It was identified by GLC and its i.r. spectrum, and by the preparation of the napthylurethan, m.p. 53–54°, undepressed on admixture with an authentic specimen.
Citronellol and p-*cymene* (fr. 4) were identified only by GLC.
Methyleugenol was obtained in 99% purity from a previous distillation. It had b.p. 93·2–93·4°/6 mm, n_D^{23} 1·5339, λ_{max} 278 mμ (log ϵ 3·45), λ_{max} 228 mμ (log ϵ 3·89) (in iso-octane). (Found: C, 74·15; H, 7·86; OCH$_3$ 34·03. Calc. for $C_9H_8(OCH_3)_2$: C, 74·13; H, 7·91; OCH$_3$, 34·82%.) In agreement with the literature values for methyleugenol[6] this compound gave the tribromo-derivative, m.p. 77–78°, the picrate, m.p. 114–116°, the nitrate, m.p. 125°, and veratric acid, m.p. 180–181°. It also gave an i.r. spectrum identical with that of a sample prepared by the methylation of eugenol[7] and with the published spectrum.[8]
Palmitic acid was obtained from the residue of an earlier distillation by repeated recrystallization from acetone at −80°. It had m.p. 58·5°, undepressed on admixture with an authentic sample; its i.r. spectrum (KCl disc) showed it to be palmitic acid[9] containing a small amount of impurity which absorbs strongly at 12·4 μ. (Found: C, 74·81; H, 12·66; O, 12·30. Calc for $C_{16}H_{32}O_2$: C, 74·95; H, 12·58; O, 12·47%.) One of the constituents of fraction 7 was isolated in 78% purity, by low temperature crystallization from pentane of a fraction, b.p. 132–134°/5·5 mm, which had been obtained from a previous distillation. This liquid (compound H: 3% of the whole oil) had n_D^{24} 1·5528, λ_{max} 265 mμ (log ϵ 4·06), λ_{max} 220 mμ (log ϵ 4·44) (in iso-octane), ν_{max} 3·34 (epoxide ?), 3·53 (methyl ?), 6·35, 6·66, 6·85, 7·09, 7·28 (w), 7·49, 7·85 (w), 8·1, 8·68, 8·9 (s), 9·9, 10·4, 10·75 (w), 11·85, 12·8, and 14·45 μ. (Found: C, 70·14; H, 7·89; O, 21·78%; M. W. (Rast) 220. $C_{13}H_{18}O_3$ required: C, 70·26; H, 8·12; O, 21·62%; M. W. 222.) Treatment of this compound with perchloric acid gave a small amount of a product, m.p. 214–216°. The compound was not present in any of the other oils listed.

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[6] F. Guenther, *The Essential Oils*, Vol. II, p. 519, Van Nostrand, New York (1949).
[7] The method employed by W. H. Perkin, Jr. and C. Weizman, *J. Chem. Soc.* **89**, 1649 (1906), for the preparation of veratrol from catechol was used.
[8] E. Briner and S. Fliszár, *Helv. Chim. Acta* **42**, 2063 (1959).
[9] D. Swern, L. P. Witnauer, C. R. Eddy and W. E. Parker, *J. Am. Chem. Soc.* 77, 5537 (1955).

C. gossypifolius. The oil was fractionated as in the previous case.

α-Pinene, obtained in >90% purity from the first fraction, b.p. 54–58°/30 mm, was identified by GLC and its i.r. absorption.

p-*Cymene*, obtained in 67% purity from the fraction, b.p. 62–75°/30 mm, and was identified by GLC and its i.r. spectrum.

Citronellol was obtained in 80% purity by elution with methanol from an alumina column of part of the fraction, b.p. 72–75°/2·3 mm: it was identified by GLC, and by its i.r. and NMR spectra. Previous elution with petroleum ether, gave an unidentified sesquiterpene (86%) (compound A), which comprised 3% of the original oil: it had no u.v. absorption indicative of conjugation, and gave ν_{max} 3·24, 3·38, 3·5, 6·09, 6·82, 7·05, 7·21, 7·27, 7·32, 7·91, 8·1, 9·1, 9·5, 9·82, 9·95, 10·96, 11·15, 11·31, and 12·3 μ. (Found: C, 87·45; H, 11·84. $C_{15}H_{24}$ required: C, 88·16; H, 11·84%.)

Camphene, *β-pinene*, *α-phellandrene*, *dipentene*, 1,8-*cineole*, and *fenchone* were identified only by GLC.

The fraction, b.p. 102–104°/0·15 mm, consisted mainly of a single alcohol (72%) (compound G). It gave ν_{max} at 3·00 (s), 3·24, 3·37–3·5 (s), 6·1, 6·85, 7·25, 7·34, 7·7, 8·21, 8·85, 9·12, 9·27, 9·47, 9·6, 9·8, 10·09, 10·52, 11·3, 12·0, and 12·5 μ.

C. xanthochloros. The oil was distilled as usual.

α-Pinene comprised 98% of the fraction, b.p. 52–55°/22 mm, and was identified by GLC and i.r. spectroscopy.

β-Pinene (52%), admixed with α-pinene, was present in the fraction, b.p. 59–63°/22 mm, and was identified similarly.

α-Phellandrene (74% of the fraction, b.p. 71–73°/22 mm) and p-*cymene* (84% of the fraction, b.p. 74–77°/22 mm) were also identified by the same procedure.

Camphene, *dipentene*, *myrcene* and *citronellol* were identified by GLC under the same conditions indicated above.

C. turumiquirensis. The oil was distilled as usual, and several of the fractions were then re-distilled.

α-Pinene (90%), *β-pinene* (85%) and 1,8-*cineole* (70%) were identified by GLC and i.r. spectroscopy.

p-*Cymene*, *linalool* and *citronellol* were identified by GLC.

allo*Aromadendrene* (84%) had b.p. 77°/0·5 mm, n_D^{23} 1·4985, and gave an i.r. spectrum similar to that reported.[10] (Found: C, 87·95; H, 11·84%. Calc. for $C_{15}K_{24}$: C, 88·16; H, 11·84%.) In ethyl acetate over palladized charcoal the compound absorbed one equivalent of hydrogen and, when ozonized, reduced, and isomerized as described,[11] it gave the reported[10–12] ketone, m.p. 82°, which was characterized as the known oxime, m.p. 104–105° and semicarbazone, m.p. 200·5° (decomp.).

C. deserticolus. The usual fractionation of the oil gave *α-pinene* (90%), *β-pinene* (87%) and dipentene (62%) which were identified by GLC and i.r. spectroscopy.

Fenchone comprised 37% of the fraction, b.p. 62–82°/20 mm, and was identified by GLC.

Citronellol was obtained in 96% purity from the fraction, b.p. 67–69°/1·75 mm, by elution with methanol from a column of neutral alumina. It was identified by GLC and its i.r. spectrum.

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[10] L. Dolejs, O. Motl, M. Soucek, V. Herout and F. Sorm, *Coll. Czech. Chem. Commun.* **25**, 1483 (1960).

[11] A. J. Birch and F. N. Lahey, *Australian J. Chem.* **6**, 379 (1953); (*Chem. Abstr.* **48**, 12068).

[12] C. B. Radcliffe and W. F. Short, *J. Chem. Soc.* 1200 (1938); see also J. Simonsen and D. H. R. Barton, *The Terpenes*, Vol. III, p. 72, Cambridge University Press, London (1952).

C. speciosus. The monoterpenic constituents of this oil (14 ml) were separated by a flash distillation at 30 mm pressure. The i.r. spectrum of the distillate indicated the presence of *α-pinene* and p-*cymene*. GLC confirmed this, and also showed small amounts (>2%) of *camphene*, *β-pinene*, *myrcene* and *dipentene*.

Distillation of the residue through a spinning band column gave *citronellol* (65%), b.p. ~ 55°/0·35 mm, which was identified by GLC and its i.r. spectrum.

C. populifolius *and* C. bredemeyeri. The oils from these two species were treated as in the previous case; the distillates and residues were found, by GLC, to contain the compounds indicated in Table 2.

C. argyrophyllus *and* C. glandulosus. These oils, examined only on the packed column, were found to contain the compounds shown in Table 2.

Acknowledgement—The authors thank Mr. G. E. Agostini for assistance in the collection of the plant materials, for their identification, and for helpful discussions.