FIXED AND VOLATILE CONSTITUENTS OF *CROTON AFF. NEPETIFOLIUS*[1]

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Croton aff. nepetifolius Bail is a small tree of the Euphorbiaceae family widespread in the Brazilian northeast. The plant reaches a height of 4–6 m. It is commonly known as Marmeleiro Sabiá and is used in folk medicine for gastric disease treatment. The present chemical study was conducted as part of a general screening program of Brazilian essential oil producing plants having pharmacological activity.

DISCUSSION

The specimen was collected in Sobral, State of Ceará, on March 1977. Essential oils from stems, leaves, bark, and wood were obtained by steam distillation. Volatile constituents in each sample are described in table 1. Monoterpenoids constitute the major part of the essential oil from lesser lignified tissues (leaves and bark), whereas sesquiterpenoids and propenylbenzene derivatives are the major products in the oil of lignified tissues (stems and wood).

Chromatography of the benzene extract of the wood yielded isolation of five pure known substances, namely, 2-hydroxy-3,4,6-trimethoxyacetophenone (1), 2-hydroxy-4,6-dimethoxyacetophenone (xanthoxylin) (2), 1, 2-dimethoxy-5-(2-propenyl)-benzene (methyl eugenol) (3), 1,2,3-trimethoxy-5-(2-propenyl)-benzene(elemicin) and n-octacosanol (4). Only elemicin and methyl eugenol (3, 5) have been reported so far from extractives of the genus *Croton;* whereas, α-bergamoptene, α-cubebene, δ-elemene, α-santalene, and *n*-propyl catechol are being reported for the first time as volatile constituents in this genus.

EXPERIMENTAL

Taxonomic identification was made by G. L. Webster, University of California, Davis, and A. G. Fernandes, Universidade Federal do Ceará, Brazil. A voucher specimen is deposited in the herbarium of the Departamento de Biologia, Universidade Federal do Ceará, under number 3185.

The plant was separated into leaves, stems, bark, and wood and then finely ground before extraction.

Isolation of constituents.—*a*) A benzene extract of the wood submitted to chromatographic filtration on silica yielded fractions which were eluted with hexane, benzene and acetone. Silica chromatography of the benzene eluate with chloroform-methanol mixtures as eluent produced three solids and two oily substances. The solids were purified by crystallization from cyclohexane and the oils by preparative tlc. *b*) Essential oil extractions were carried out by steam distillation of each part in an apparatus developed in our laboratory (6). Yields are reported in table 1. Each essential oil, after separation, was dried with anhydrous sodium sulfate, filtered, and sealed in glass vials under nitrogen atmosphere. The oils were submitted to gc/ms separation on a Finnigan 3300 quadrupole mass spectrometer coupled to a gc equipped with capillary glass column (0.25 mm x 30 m) coated with SP 2100 (methyl silicone) with helium as the carrier gas and ms spectra recorded at 70 ev.

Substances isolated from the benzene extract were identified by spectrometric analysis (ir, nmr and ms) and derivative preparation. Xanthoxylin identification was confirmed by comparison of the mixture mp with that of an authentic sample.

Constituents of essential oils were identified chiefly by two ms library search programs, BUSC 6 and modified Finnigan PF (7), and by a library search program for automatic determination of Kovats retention indexes.

Results of the above computer programs were confirmed by ms visual analysis and/or comparison with authentic samples (table 1).

[1]Extracted in part from the MSc Thesis of T. N. C. Dantas presented at Universidade Federal do Ceará, 1979.

TABLE 1. Chemical composition of the essential oil of *Croton aff. nepetifolius* Bail.

Constituent	Part of plant and yields of individual components (%)				Identification process[b]
	Leaves	Stems	Bark	Wood	
MONOTERPENOIDS					
camphene	—	—	1.0	—	ms, ri
camphor	—	—	0.5	—	ms, as
1,8-cineole	37.5	—	—	—	ms, ri
α-pinene	1.5	—	1.5	—	ms, ri, as
β-pinene	1.5	—	1.5	—	ms, ri, as
sabinene	3.0	—	—	—	ms, ri, as
α-terpineol	4.0	—	—	—	ms, ri
TOTAL	47.5	—	4.5	—	—
SESQUITERPENOIDS					
α-bergamoptene[c]	—	4.0	6.5	3.0	ms
δ-cadinene[c]	—	—	3.0	13.0	ms
β-caryophyllene	23.0	—	—	—	ms, ri, as
α-copaene	—	45.0	37.5	32.5	ms, ri
α-cubebene	—	1.0	2.0	1.0	ms, ri
β-elemene[c]	1.0	—	—	—	ms
γ-elemene	12.0	—	—	—	ms, ri
δ-elemene	4.5	—	—	—	ms, as
humulene	2.0	—	—	—	ms
α-santalene	—	6.5	2.0	3.0	ms
others sesquiterpenes	—	39.5	29.0	25.0	—
TOTAL	42.5	96.0	80.0	77.5	—
PHENYLPROPANOIDS					
elemicin	4.0	1.0	15.0	14.0	ms, as
methyl eugenol	0.5	—	—	—	ms, as
propyl catechol	1.0	—	—	—	ms
TOTAL	5.0	1.0	15.0	14.0	—

[a]Percent yields of oil relative to dry part of the plant were: leaves (0.9%), stems (0.4%), bark (1.3%), wood (0.1%).
[b]ms = Mass Spectrum; ri = Kovats Retention Index; as = authentic sample.
[c]Comparison with reference spectrum. No authentic samples available.

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