ISOLATION OF 3,5-NONADIYNE.—The fresh roots (2 kg) were shredded and steam distilled. The aqueous distillate was extracted with petroleum ether (60-80°). The extract worked up in the usual way gave 2.4 g (0.12%) of pale yellow oil. 3,5-Nonadiyne was separated from the oil by preparative gc.

Another 1.25 kg of root material was extracted with cold (−20°) petroleum ether (40-60°). Work-up of the extract gave 2.2 g (0.17%) of orange-red oil. The gc analysis of this oil showed it to contain >84% of 3,5-nonadiyne.

SYNTHESIS OF 3,5-NONADIYNE.—A slurry of $NaNH_2$ in liquid NH_3 was prepared from 0.25 g (0.011 mole) sodium. To the slurry were added dropwise, 0.92 g of 1,3-heptadiyne (4) in 2 ml DMSO and then 1.872 g (0.012 mole) C_2H_5I in 2 ml DMSO. The reaction mixture was stirred for another 30 min and the NH_3 allowed to evaporate. Et_2O (50 ml) was added to the residue, followed by 20 ml of H_2O (dropwise). The aqueous layer was extracted with two 25-ml portions of Et_2O; these were combined with the original Et_2O layer and dried over anhydrous $MgSO_4$. After filtration, evaporation of the Et_2O under reduced pressure left an oil that upon short-path distillation gave 1.05 g (88%) of 3,5-nonadiyne, bp 75-78°/15 mm. A portion of the distillate purified further by preparative gc exhibited spectra (Table 1) identical to those of the 3,5-nonadiyne isolated from the oil.

3,5-Nonadiyne-1,2-^{13}C was prepared analogously from 1,3-heptadiyne and ethyl iodide-1,2-^{13}C (90% ^{13}C at CH_2 and 63% ^{13}C at CH_3).

ACKNOWLEDGMENTS

The authors wish to thank Dr. T.W. Whaley of Los Alamos Scientific Laboratory for a gift of ^{13}C-enriched C_2H_5I; Dr. David Forkey of California State University, Sacramento for gc/ms; and Dr. Y.S. Pangtey of Kumaun University, Nainital for plant identification. One of us (THS) wishes to thank NIH for a predoctoral traineeship (GM07616-02).

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Received 17 October 1983

CONSTITUENTS OF THE ESSENTIAL OIL OF *BLEPHAROCALYX TWEEDIEI*

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In continuation of our research (1) on essential oils from Argentine indigenous plants, we now report the composition of an essential oil from *Blepharocalyx tweediei* Berg (Myrtaceae) with an anomalously high content of verbenone and carvone, as far as we know only surpassed by *Eugenia pseudomato* essential oil (2). The pleasing odor of this essential oil and high content of myrtenal and verbenone make it a potential new natural source of those chemicals, possibly useful in perfumery.

This tree is a medicinal plant commonly used against pulmonary and throat disease (3-4) with antispasmodic, antiseptic, and balsamic properties. Two different samples were investigated, one of green leaves and the other, a commercially dried and milled plant material. The latter provided less yield of essential oil than did fresh material, with the absence of α-thujene, α-terpinol, and citronellol.

As far as we know, this is the first full report on an essential oil from the genus *Blepharocalyx* (5).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Instruments used were: Finnigan 4000 (gc/ms), Varian EM 360 A (pmr), Hewlett Packard 5840 (gc), Perkin-Elmer 21 (ir).

PLANT MATERIAL.—Green leaves of *B. tweediei* were collected in early autumn near Parana City (Entre Rios Province, Argentina). The commercial sample was acquired at an herb shop in Rosario City (Santa Fe Province, Argentina). Plant materials were identified by J. Jozami (voucher specimens, IPNAYS, Nos. 88/89).

ESSENTIAL OIL.—It was obtained by hydrodistillation (with cohobation) with a modified Clevenger apparatus. Green leaves' essential oil: yield 0,27% $d^{20}{}_4$=0.9072; $\eta^{20}D$=1.4811; $[\alpha]^{20}D$=+5.49; acidity number 7.47; ester number 19.8. Dried material's essential oil: yield 0.09%; $d^{20}{}_4$=0.9153; $\eta^{20}D$=1.4859; $[\alpha]^{20}D$=+2.43; acidity number 6.57; ester number 12.87.

ISOLATION AND IDENTIFICATION.—Acidic and phenolic compounds were extracted with 7% KOH. Acids: green leaves 5.8%, dried material 4.7%, mainly formic, acetic and isovaleric acids. Phenols: green leaves 5.4, dried material 4.5%, mainly eugenol, o-cresol, carvacrol and probably guayacol. Neutral oil from green leaves was separated on silicic acid (Kirchner and Miller method) into hydrocarbons (29.4%) and oxygenated compounds (70.6%). Both fractions were separated by preparative glc yielding α-pinene, β-pinene, limonene, 1,8-cineole, linalool, anethole, myrtenal, verbenone, and carvone identified by pmr and ir. Limonene and α-pinene were the *dextro* isomers. Nineteen other minor compounds were identified by gc/ms and rt data.

Quantitative glc indicated for green leaves' neutral essential oil the following compounds in amounts expressed as percent: α-thujene 0.6; α-pinene 3.5; camphene 0.7; β-pinene 3.1; sabinene 0.8; myrcene 0.7; limonene 10.8; 1.8-cineole 15.3; γ-terpinene 1.4; p-cymene 1.2; terpinolene 1.0; linalool 3.6; unknown 0.1; citronellal 1.3; linalyl acetate 0.9; anethole 2.5; α-terpineol 1.8; citronellol 0.9; myrtenal 11.7; verbenone 13.5; carvone 6.3; caryophyllene 3.0; isocaryophyllene 1.1; nerol 1.3; humulene 1.4; geraniol 1.8; geranyl acetate; 1.0; unknown 0.2; nerolidol 1.4; sesquiterpenic alcohol mw 220 2.7; elemicine 4.5. Quantitative glc indicated for dried material's neutral essential oil: α-pinene 2.6; camphene 0.3; β-pinene 2.0; sabinene 0.5; myrcene 0.4; limonene 8.6; 1,8-cineole 9.9; γ-terpinene 1.1; p-cymene 0.9; terpinolene 0.7; linalool 2.2; unknown 0.1; citronellal 1.2; linalyl acetate 0.9; anethole 2.4; myrtenal 10.3; verbenone 16.2; carvone 18.0; caryophyllene 2.1; isocaryophyllene 1.2; nerol 1.2; humulene 2.0; geraniol 1.8; geranyl acetate 0.9; unknown 0.2; nerolidol 2.2; sesquiterpenic alcohol mw 220 4.5; elemicine 5.4.

The ir spectra of the essential oil was concordant with the indicated composition; the main bands were attributable to 1,8-cineole, verbenone, myrtenal, limonene, and carvone.

ACKNOWLEDGMENTS

We thank J. Jozami for plant identification, J. Fuse for gc/ms, and A. Retamar for pmr. We are also indebted to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET-Argentina) for financial support.

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Received 5 December 1983