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SHORT COMMUNICATION

β-CARYOPHYLLENE IN NATIVE CLOVE BUD OIL

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Abstract—β-Caryophyllene was found to be a constituent of the oil in clove buds It was formerly reported to be an artifact of distillation of clove buds

INTRODUCTION

β-CARYOPHYLLENE is a sesquiterpene hydrocarbon found in many essential oils that are obtained by steam distillation [1–3] Naves[4] reported that it was not present in a benzene extract from clove buds (*Eugenia caryophyllata* Thunb, syn *Caryophyllus aromaticus* L), and was, moreover, an artifact of the distillation The principal sesquiterpene in the benzene extract was epoxydihydrocaryophyllene. Subsequently, the gamma isomer, also, has been considered to be an artifact [5]

The experiments reported here reveal the presence of β-caryophyllene as a major component in the organic solvent extracts from clove buds.

RESULTS AND DISCUSSION

Clove buds were extracted with benzene–ethanol in a Soxhlet, and with anhydrous ether at room temp. The benzene–ethanol extract was evaporated under nitrogen, distilled and analysed by GLC and by coupled GLC–MS (Table 1)

TABLE 1 COMPONENTS OF THE DISTILLATE FROM THE BENZENE–ETHANOL EXTRACT OF CLOVE BUDS

Compounds	Retention times (R_t) (min)	Percentages*
γ-Caryophyllene†	20 4	0 2
β-Caryophyllene	24 0	7 7
α-Caryophyllene	26 2	1 0
Eugenol	40 6	75 8
Eugenyl acetate	43 1	14 1

* Percentages were based on computer calculated area normalization

† Identification was based on mass spectroscopic data only

[1] R G BUTTERY, W H MCFADDEN, R E LUNDIN and M P KEALY, *J Inst Brewing* LXX, 396 (1964)
[2] J A ATTAWAY, A P PIERINGER and L J BARABAS, *Phytochem* 5, 141 (1966)
[3] L MARTIN, D M SMITH and C G FARMILO, *Nature, Lond* 191, 774 (1961)
[4] Y NAVES, *Helv Chim Acta* 31, 378 (1948)
[5] P DEMAYO, *Mono- and Sesquiterpenoids*, p 286, Interscience, New York (1959)

The ether extract was similarly evaporated, and the residue chromatographed over silica gel to separate the hydrocarbon fraction which was further separated by GLC The crude hydrocarbon fraction was analysed by IR spectroscopy, and, but for two weak absorption bands that were afterwards removed by purification, gave an IR spectrum consistent with a reference spectrum of β-caryophyllene The compound with R_t 24 0 min was trapped and studied through its IR and mass spectra These were identical with the corresponding reference spectrum for authentic β-caryophyllene

Naves' extraction with benzene could not be duplicated, because of insufficient information on procedure, but neither the benzene–ethanol extract nor the ether extract described in this paper contained epoxydihydrocaryophyllene

The pyrolysis of clove buds after exhaustive benzene–ethanol extraction resulted in low mol wt. hydrocarbons and furans The pyrolysis chromatogram of unextracted clore buds was quantitatively similar to the chromatogram of the extracted oil on which was superimposed the pyrolysis products from extracted clove buds These experiments suggest that β-caryophyllene is present in the intact buds, instead of originating from a labile precursor during steam distillation

EXPERIMENTAL

Instrumentation GLC analyses were performed on an F & M Model 5750 flame ionization gas chromatograph, using a stainless steel 8 ft × 1/8 in o d column of Carbowax 20M, 20% on 60/80 chromosorb W The identifications in Table 1 were made on a similar instrument coupled to a Hitachi Model RMU-6E mass spectrometer The IR and mass spectra of β-caryophyllene were obtained on a Beckman Model IR4 spectrophotometer and an AEI Model 902 mass spectrometer, respectively

Soxhlet extraction of clove buds 20 g of air-dried clove buds were crushed (with mortar and pestle) and extracted with 250 ml of benzene–EtOH (68 32) for 24 hr in a Soxhlet The solvent was evaporated under N_2 at 30°, and the residue (*ca* 12% (w/w) of clove buds) was distilled at 150° (vapor temp) and 5 cm, and analysed by computerized GLC and GLC–MS (Table 1)

Ether extraction of clove buds 20 g of crushed clove buds were magnetically stirred with 200 ml of anhydrous ether for 4 hr at room temp in a 250-ml screw-capped glass jar The solvent was evaporated under N_2 at 30°, and 2 ml of the residue was chromatographed over a 19 × 2 cm column of silica gel (Brinkmann, 0 05–0 20 mm), using heptane The first 30 ml of eluent was evaporated under N_2, leaving the hydrocarbon fraction which was shown by IR spectroscopy to consist mostly of β-caryophyllene

The hydrocarbon fraction was further separated by GLC and the compound with R_t 24 0 min was trapped and identified as β-caryophyllene by its IR and MS

Pyrolysis experiments A sample of crushed clove buds after benzene–EtOH extraction was wrapped in filter paper in the form of a 7-cm cylinder and affixed to the outlet of a 5-ml gas syringe with Tygon and glass tubing The cylinder was ignited, and 5 ml of vapor was withdrawn and directly injected into the GLC–MS apparatus The resulting chromatogram showed a high concentration of low mol wt hydrocarbon and furan compounds, and an absence of the oil components in Table 1 Unextracted clove buds were similarly ignited, and the chromatographic pattern resembled that obtained from the sum of the low mol wt pyrolysis products and the extracted oil

Key Word Index—Eugenia caryophyllata, Myrtaceae, β-Caryophyllene