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THE VOLATILE CONSTITUENTS OF CAMPHORWEED, *HETEROTHECA SUBAXILLARIS*

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Key Word Index—*Heterotheca subaxillaris*; Asteraceae; essential oil; monoterpene; sesquiterpene.

Abstract—Forty-one mono- and sesquiterpenoids are identified from the leaf volatiles of *Heterotheca subaxillaris*. Affinities to related genera are briefly discussed.

INTRODUCTION

The objectives of the present study were to determine the identities and proportions of the principle volatile compounds accumulated in the leaves of *Heterotheca subaxillaris*. Although the leaf chemistry of many Asteraceae have been investigated, members of the tribe Astereae have received only limited attention [1]. These taxa appear to be characterized by a lack of sesquiterpene lactones or alkaloids, but commonly accumulate mono-, sesqui- and diterpenoids. The leaf chemistry of *H. subaxillaris* has been partially studied and several sesquiterpenoids have been previously identified [2–7].

RESULTS

The observed identity and proportion (% of total volatiles in sample 1, % of total volatiles in sample 2) of the volatile constituents were: 2-ethylfuran (0.02, 0.01), α-pinene (8.60, 0.15), camphene (2.44, 0.08), β-pinene (1.37, 0.16), sabinene (0.11, 0.04), myrcene (9.82, 0.37), α-terpinene (0.14, 0.13), limonene (5.57, 0.34), *trans*-2-hexenal + unknown (0.71, 0.07), *cis*-ocimene (0.16, 0.02), γ-terpinene (0.11, 0.48), *trans*-ocimene (2.91, 0.60), *p*-cymene (0.71, 0.22), terpinolene (0.08, 0.14), *cis,cis*-allo-ocimene (0.07, 0.09), *cis*-3-hexenol (0.12, 0.01), *trans*-2-hexenol (0.03, 0.01), 1-octen-3-ol (0.38, 0.19), *trans*-sabinene hydrate (0.07, 1.44), α-cubebene (0.15, 0.09), camphor (1.25, 1.53), *cis*-sabinene hydrate (0.05, 1.69), bornyl acetate (5.20, 4.62), *trans*-α-bergamotene (5.46, 2.48), β-elemene (0.12, 0.65), terpinen-4-ol (0.98, 3.60), caryophyllene (11.07, 1.70), α-himachalene (tentative) (0.23, 0.12), unidentified sesquiterpene hydrocarbon (0.56, 0.77), α-humulene (0.61, 0.38), borneol (8.07, 9.84), germacrene D (5.68, 7.30), bicyclogermacrene (tentative) (1.08, 0.02), carvone (1.12, 1.23), γ-elemene (0.31, 0.87), δ-cadinene (1.59, 1.71), α-curcumene (0.55, 0.42), calamenene (0.31, 0.37), geranyl acetone (0.09, 0.21), nerolidol (0.09, 0.21), epicubenol (1.95, 6.87), α-cadinol (0.13, 0.91), unidentified sesquiterpene alcohol (1.98, 6.22), unidentified sesquiterpene alcohol (1.44, 8.12).

DISCUSSION

The subtribal boundaries in the Astereae are not well defined [8] and, although there is still not sufficient

chemical evidence to define groupings within the tribe, the present analysis provides some linkages of *Heterotheca subaxillaris sensu stricto* to other genera in the tribe [9]: some of the identified terpenoids also occur in *Happlopappus, Erigeron* and *Solidago* [10–12]. Although several of the terpenoids have not been previously described from the Asterinae, this is probably due to the paucity of information on the occurence of mono- and sesquiterpenes in members of the subtribe.

Heterotheca subaxillaris is a widespread weed, spanning the coastal plain of the southern and eastern United States, and is morphologically polymorphic. The quantitative differences between the two samples in the present analysis (see above) suggest that the species may also be chemically polymorphic.

EXPERIMENTAL

Leaves of all ages were collected at two sites from rosette stage plants of *H. subaxillaris* (Lam.) Britton and Rusby: Sample 1 on March 17, 1981 at the Savannah River Plant, Aiken, SC, and Sample 2 of November 16, 1982 near Columbia, SC. A documentary specimen from the latter site (Aulbach-Smith #2447) has been deposited (USCH). The sampling sites were *ca* 80 km apart but both are geographically near the collection site for the type specimen of the species [13]. Sample one was dried at 40° for 7 days, while sample two was distilled as fresh herbage. The leaves were steam distilled in a Likens-nickerson-type apparatus with the volatiles trapped in pentane. The majority of the pentane was removed with a stream of N_2.

Mass spectra were obtained on a Finnegan Model 4021C with ionizing voltages of 20 eV and 70 eV. A fused-silica capillary column coated with SE-54 and a glass capillary column coated with SP-1000 were both used for GC/MS analysis and for determination of the proportions of the constituents. The identities of constituents were determined by comparison of observed spectra with those from commercially obtained samples and from previously identified compounds [14]. Percentage composition was determined using a splitless inlet and an FID detector with a digital integrator.

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