EXPERIMENTAL

Plant material was collected in southwestern British Columbia during the summer of 1969, *C. brevistylum* Cronq. and *C. arvense* (L.) Scop. were collected on the campus of the University of British Columbia, *C. vulgare* (Savi) Airy-Shaw was collected in Seymour Provincial Park, Vancouver, B.C., *C. edule* Nutt. was collected in Manning Provincial Park, B.C., and *C. undulatum* (Nutt.) Spreng. was collected on the Lillooet-Lytton Road, B.C.

Plant material was extracted thoroughly with 80% ethanol. Extracts were pooled, evaporated to dryness, and the residue extracted with boiling water with the aid of Celite. Filtration yielded the water soluble fraction which was extracted first with Et_2O and then exhaustively with EtOAc. Chromatography of the EtOAc fraction in *t*-BuOH–HOAc–H_2O (3:1:1) followed by 15% HOAc disclosed at least 10 compounds most of which appeared not to be flavonoids. The new glycoside, the major constituent, (R_fs in Table 1) was obtained by banding in these solvents and purification by re-running in *iso* PrOH–H_2O (4:1). It was eluted with 80% ethanol, the solvent removed and the residue crystallized from EtOAc. Two recrystallizations yielded cream-white microneedles with m.p. 278–281° (Kofler hotstage).

Acknowledgements—We should like to thank the National Research Council of Canada for support of this work. We express our appreciation to Dr. Tom Mabry, University of Texas at Austin, for the NMR spectrum, and to Dr. K. I. Beamish, University of British Columbia, for collecting *C. undulatum*.

Phytochemistry, 1971, Vol. 10, pp. 454 to 455. Pergamon Press. Printed in England.

A THIOPHEN FROM *LIATRIS PYCNOSTACHYA*[*]

R. E. ATKINSON and R. F. CURTIS

Department of Chemistry, University College of Swansea, Singleton Park, Swansea

(*Received* 17 *June* 1970)

Abstract—2-Acetyl-3-hydroxy-5(prop-1-ynyl)thiophen (II) was isolated from the roots of *Liatris pycnostachya*.

LARGE numbers of polyacetylenes and thiophens have now been isolated from the Compositae[1] but most of the isolation studies have been confined to a very few tribes in the family. There is, apparently, only one example of the isolation of a polyacetylene from a member of the tribe Eupatorieae, viz. the tridecapentaynene (I) which has been reported to be present as a trace component of *Piqueria trinervia* (Jacq.) Cav.;[2] we now report the first isolation of a thiophen from the Eupatorieae.

Liatris Schreb (sub tribe, Adenostylinae) "Blazing Star" or "Button Snake-Root" is represented by about thirty species native to temperate North America[3] and several are common in Europe. The species is reported as having been used for treatment of snakebite, the roots for various medicinal purposes and the leaves as a substitute for vanilla. There has been little chemical examination but the flavonoids[4] and the seed oils[5] have been investigated.

---

[*] Paper VI in the series "Naturally occurring Thiophens"; for Part V see *J. Chem. Soc.* (c) 1813 (1969).

[1] F. BOHLMANN, *Fortschr. Chem. Forsch.* **6**, 65 (1966).

[2] F. BOHLMANN and C. ZDERO, *Tetrahedron Letters* 1533 (1968).

[3] H. A. GLEASON, *Illustrated Flora of the Northeastern United States and adjacent Canada*, p. 495, Lancaster Press, Pennsylvania (1958).

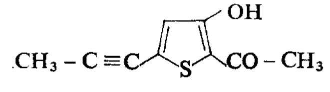
[4] J. KAGAN, *Phytochem.* **7**, 1205 (1969).

[5] F. R. EARLE, I. A. WOLFF and Q. JONES, *J. Am. Oil Chemists' Soc.* **37**, 254 (1960); F. R. EARLE, C. A. GLASS, G. C. GEISINGER, I. A. WOLFF and Q. JONES, *J. Am. Oil Chemists' Soc.* **37**, 440 (1960).

Roots of *Liatris pycnostachya* Mich. were extracted with a 1:1 mixture of petroleum–ether and the extract was concentrated and purified by chromatography over alumina with elution by pentane–ether (5:1) to give a major component, m.p. 92°, $C_9H_8O_2S$. Varusio spectra (see Experimental) were all consistent with the compound being 2-acetyl-3-hydroxy-5(prop-1-ynyl) thiophen (II), previously isolated[6] from *Artemisia arborescens* L., (sub-tribe Anthemideae).

$CH_3{-}(C{\equiv}C)_5{-}CH{=}CH_2$

I



II

Qualitative examination by TLC of extracts obtained in the same way from *L. spicata* (L). Willd. and *L. scariosa* (L). Willd. indicated that the same compound was also present in these species.

EXPERIMENTAL

The NMR spectrum was obtained with a Varian HA 100 spectrometer (Imperial Chemical Industries Limited, Dyestuffs Division). The mass spectrum was determined on an A.E.I. MS9 mass spectrometer at 70 e.V., source temp. 220°.

Extraction of Plant Material

Air dried roots of *Liatris pycnostachya* Michx. (600 g) were quickly chopped by hand and allowed to stand in ether at room temp. for 2 weeks. The extract was evaporated under reduced pressure to give a brown oil (3·4 g) which was purified by chromatography over deactivated alumina (300 g). Elution with pentane–ether (5:1) gave 2-acetyl-3-hydroxy-5(prop-1-ynyl)thiophen (II), (87 mg) as colourless needles from pentane, m.p. 92–94° (uncorr.) (lit.[6] 100·5°). (Found: C, 59·8; H, 4·9; S, 17·5. Calc: $C_9H_8O_2S$: C, 60·0; H, 4·5; S, 17·8%); λ_{max} (ether) 301, 327 nm (log ϵ, 4·24, 4·11); ν_{max} (KBr) 2225 ($R{-}C{\equiv}C{-}R$), 1626 (conjugated OH-bonded >CO) and 838 cm^{-1} (2,5-disubstituted thiophen);[7] $\tau(CS_2)$, 7·96 (3, singlet, $CH_3{-}CO{-}$) 7·75 (3, singlet, $CH_3{-}C{\equiv}C{-}$), 3·53 (1, singlet, H in 4-position of thiophen ring), —1·24 (1, broad singlet, H-bonded—OH); *m/e* 180·0237 ± 0·0004, calc. $C_9H_8O_2S$, 180·0245.

Qualitative examination of the other *Liatris* sp. was carried out using TLC on silica-gel G (Merck) developed with benzene–$CHCl_3$ (1:1) (by D. M. Jones).

Acknowledgements—We are grateful to British Petroleum Limited, for a studentship (R.E.A.) and Professor C. H. Hassall for laboratory facilities.

---

[6] F. BOHLMANN, K-M. KLEINE and H. BORNOWSKI, *Chem. Ber.* **95**, 2934 (1962).

[7] R. F. CURTIS and G. T. PHILLIPS, *Tetrahedron* 4419 (1967).

Phytochemistry, 1971, Vol. 10, pp. 455 to 457. Pergamon Press. Printed in England.

CRUCIFERAE

Dedicated to Prof. K. Mothes on the occasion of his seventieth birthday

GLUCOSINOLATES IN *LEPIDIUM* SPECIES FROM QUEENSLAND

ANDERS KJÆR and ANGELICA SCHUSTER
Department of Organic Chemistry, Technical University of Denmark, 2800 Lyngby, Denmark
and
ROBERT J. PARK
Division of Food Preservation, Meat Research Laboratory, CSIRO, Brisbane, Australia

(*Received* 7 *August* 1970)

Abstract—The sole glucosinolate in the seed-bearing portion of *Lepidium bonariense* L., collected in Queensland, is shown to be *p*-methoxybenzylglucosinolate (IV). Seed material of *L. hyssopifolium* Desv., collected in Queensland, contains solely 3,4,5-trimethoxybenzylglucosinolate (V). A previous report on the presence of benzylglucosinolate in *L. hyssopifolium* is discussed.