Phytochemistry, 1968, Vol. 7, pp 2065 to 2066 Pergamon Press. Printed in England

SHORT COMMUNICATION

CONSTITUENTS OF THE SEEDS OF *HERACLEUM SPHONDYLIUM*

W. LAWRIE, J. McLEAN and M. EL GARBY YOUNES

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1

(*Received* 10 *April* 1968)

Abstract—The volatile fraction of a petroleum extract of the seeds of *Heracleum sphondylium* contains *n*-octyl acetate and *n*-octyl caproate. The non-volatile fraction when saponified yields a mixture of hydrocarbons identified as *n*-pentacosane, *n*-heptacosane, *n*-octacosane *n*-nonacosane, *n*-triacontane and *n*-hentriacontane in addition to ceryl alcohol, β-sitosterol and the furanocoumarin, bergapten.

THE SEEDS of *Heracleum sphondylium* L. (Umbelliferae) were first investigated by Gutzeit[1] and shown to contain an undefined hydrocarbon of formula C_nH_{2n} and a substance of m.p. 185° which he called "heraclin" and which was later shown[2, 3] to be identical with the furanocoumarin, bergapten. Since then bergapten has been found[4] in many members of the Umbelliferae as has octyl alcohol, which occurs as the acetate ester.[4c, 5]

Our primary aim in reinvestigating the seeds of *H. sphondylium* was to elucidate the nature of Gutzeit's hydrocarbon fraction and simultaneously to examine the non-saponifiable portion of the extract for terpenoid constituents. Accordingly, a light-petroleum extract of the seeds was distilled in steam to afford a volatile and a non-volatile fraction. Examination of the volatile fraction by GLC showed the presence of nine components, seven of these being unidentified minor constituents, amounting together to about 10 per cent of the total volatile material, while the two major components were shown to be *n*-octyl acetate and *n*-octyl caproate by comparison (GLC, i.r., NMR and b.p.) with authentic samples.

The non-volatile fraction was hydrolysed with methanolic potassium hydroxide and the non-saponifiable portion chromatographed on alumina. Elution with light petroleum afforded a mixture of hydrocarbons which were saturated, according to tetranitromethane and to u.v. and i.r. spectroscopic examination. This fraction was shown by GLC to be a mixture of six components having the same retention times as authentic samples of *n*-pentacosane, *n*-heptacosane, *n*-octacosane, *n*-nonacosane, *n*-triacontane and *n*-hentriacontane, the C_{29} and C_{31} hydrocarbons being the major constituents.

Elution of the column with light petroleum–benzene (4:1) afforded ceryl alcohol (hexacosan-1-ol), identified by comparison (i.r. and m.p.) with authentic material and by conversion

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[1] M. GUTZEIT, *Chem. Zbl.* **50**, 727 (1879).

[2] C. POMERANZ, *Monatsh.* **12**, 379 (1891); **14**, 28 (1893).

[3] E. SPÄTH and S. RASCHKE, *Chem. Ber.* **67B**, 59 (1934).

[4] (*a*) K. BANERJEE and P. K. BOSE, *Ann. Biochem. Exptl Med.* (*Calcutta*) **19**, 181 (1959); (*b*) Y. NATH, B. N. NAZIER and K. L. HANDA, *Ind. J. Pharm.* **23**, 303 (1961); (*c*) L. HOERHAMMER, H. WAGNER and D. KRAEMER-HEYDWEILER, *Deut. Apotheker-Ztg.* **106**, 267 (1966).

[5] T. ZINCKE, *Ann.* **152**, 20 (1869).

to ceryl acetate, m.p. 59–60°. Elution with light petroleum–benzene (1:1) gave β-sitosterol as colourless plates, m.p. 133–134°, $[\alpha]_D - 37°$ (*c*, 1·07, chloroform), acetate, m.p. 127–129°, $[\alpha]_D - 38°$ (*c*, 0·95, chloroform), Comparison (i.r.) of the alcohol, and its acetate, with authentic samples confirmed their identity.

The saponifiable portion of the non-volatile fraction was acidified and extracted with ether to yield a viscous oil which on standing for a week, deposited bergapten, m.p. 187–188° (from ethyl acetate–methanol), λ_{max} 250, 260, 268, 312 nm (ϵ 24,100, 18,700, 17,300, 18,300). The identity was confirmed by conversion of the bergapten to 2,3-dimethoxycarbonylfuran, m.p. 34–35° (lit.[6] 36–37°) NMR peaks at τ 2·54, doublet, 1H (α-proton of furan ring); 3·28, doublet, 1H, (β-proton of furan ring); and by conversion to nitrobergapten, m.p. 258–259° (lit.[2] 256°).

Acknowledgements—The authors are indebted to Dr. Y. R. Naves for supplying a sample of bergapten, to Dr. P. Bladon for NMR spectra, and to the University of Assiut (U.A.R.) for a research grant (to M. E. G. Y.).

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[6] E. SPÄTH and A. J. F. SIMON, *Monatsh.* **67**, 344 (1936).