SHORT COMMUNICATION

LEAF FURANOCOUMARINS OF HERACLEUM LANATUM

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Abstract—Sphondin is the principal furanocoumarin of *Heracleum lanatum* leaves; pimpinellin, isopimpinellin, bergapten, xanthotoxin, isobergapten, psoralen and angelicin were also identified. At least eleven other furanocoumarins were present.

THE GENUS Heracleum (Umbelliferae) is a well-known source of furanocoumarins, the roots and fruits of many species having been studied in recent years (e.g. Refs. 1-3). Therefore, it seemed curious that leaves of H. lanatum Michx. should have been reported^{4,5} to contain no furanocoumarins. Preliminary examination of leaves of local plants uncovered substantial quantities of sphondin (VII), and more thorough study showed the presence of at least eighteen other coumarins.

Fresh leaves were processed⁶ to give a coumarin-rich fraction, and this was chromatographed on silicic acid $(2 \times 35 \text{ cm column})$ eluting with ether: petrol. ether, b.p. 60-80° (1:1); fractions of 15 ml each were collected and allowed to evaporate to small volume.

$$R_1$$

- (I) Psoralen, $R_1 = R_2 = H$
- (II) Bergapten, $R_1 = OCH_3$, $R_2 = H$
- (III) Xanthotoxin, $R_1 = H$, $R_2 = OCH_3$
- (IV) Isopimpinellin, $\hat{R}_1 = R_2 = OCH_3$

- R₂
- (V) Angelicin, $R_1 = R_2 = H$
- (VI) Isobergapten, $R_1 = OCH_3$, $R_2 = H$
- (VII) Sphondin, $R_1 = H$, $R_2 = OCH_3$
- (VIII) Pimpinellin, $R_1 = R_2 = OCH_3$

Fractions 7-11 (combined) contained three major and five minor components, separated by GLC.⁷ The major components were isobergapten (VI), pimpinellin (VIII) and angelicin (V), identified by co-chromatography with authentic samples, by u.v. spectroscopy and by NMR analysis of material collected from the gas chromatograph.⁷ Isobergapten alone crystallized

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out from the concentrate from the liquid-adsorption column; m.p. 218-222° (literature 223-224°. Angelicin melted sharply at 137-138.5° (literature 138-139.5°8) upon collection from the GLC instrument. The five minor components were all furanocoumarins, according to their u.v. spectra, and appeared to comprise one derivative each of angelicin, xanthotoxin and sphondin, along with two of isobergapten.

Fractions 12–16 (combined) contained psoralen (I) and bergapten (II), identified again by co-chromatography, by u.v. and by NMR. Bergapten crystallized out, m.p. 187–189° (literature 188–190°3). Three minor GLC peaks once again had furanocoumarin spectra. One was clearly a bergapten derivative, another a xanthotoxin derivative, and the third uncertain. Fractions 18–23 (combined) contained only xanthotoxin (III) and isopimpinellin (IV); these were separated by GLC and identified by co-chromatography, u.v. and NMR. Recrystallization of material collected from the gas chromatograph gave crystalline xanthotoxin, m.p. 144–145° (literature 144–146°3) and isopimpinellin, m.p. 146–149° (literature 148–151°3). Fractions 26–34 (combined) deposited sphondin, m.p. 189–191° (literature 189–191°3), whose identity was confirmed by GLC, u.v. and NMR. Three xanthotoxol derivatives were also present, in traces, in these fractions.

Leaves from various localities gave essentially the same coumarins, the total furanocoumarin content being about 0·1-0·2 per cent. Umbelliferone and skimmin were also present. Analysis of the roots gave data agreeing with earlier work;^{2,5} isopimpinellin, not sphondin, was the principal coumarin of these organs.

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⁸ E. Späth and O. Pesta, Ber. 67, 853 (1934).