Phytochemistry, 1968. Vol. 7, pp. 147 to 149. Pergamon Press. Printed in England

SHORT COMMUNICATION

CHEMICAL INVESTIGATION OF *SESELI SIBIRICUM*

S. K. KAPOOR, Y. N. SHARMA and A. R. KIDWAI

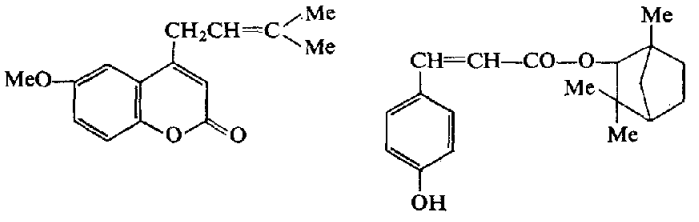
Department of Research in Unani Medicine, Tibbiya College,
and Department of Chemistry, Aligarh Muslim University,
Aligarh, India

(*Received* 5 *July* 1967)

Abstract—Osthol and Fenchyl *p*-hydroxycinnamate were isolated from *Seseli sibiricum* roots.

Seseli sibiricum Benth. (Umbelliferae) is a shrub growing extensively at high altitudes in the mountainous regions of Jammu and Kashmir. The plant is rich in essential oils which have been investigated by Handa *et al.*,[1] who isolated a number of monoterpenes including fenchone and fenchyl alcohol. The present work was limited to the investigation of two solid constituents obtained from the light petroleum extract of the roots.

The light petroleum extract, on concentration and chromatography on acetic acid deactivated alumina, afforded products (I) m.p. 84–85° and (II) m.p. 215–16°



(II)

The lower melting product analysed for $C_{15}H_{16}O_3$, and chromic acid oxidation gave an acid $C_{12}H_{10}O_5$, m.p. 253–54°, identical with ostholic acid. Decarboxylation of the acid gave 7-methoxy-8-methylcoumarin showing (I) to be osthol, which was confirmed by comparison with authentic material.

The u.v. spectrum of the compound (II) had maxima at 230 nm (log ϵ 4·19) and 320 nm (log ϵ 4·45) and was thus similar to that of *p*-hydroxycinnamic acid.[2] It formed a crystalline monoacetate indicating the presence of a free hydroxyl group. Hydrolysis under mild acidic or basic conditions gave *p*-coumaric acid and an alcohol, identified as fenchyl alcohol through its *p*-nitrobenzoate. Compound (II) was methylated with diazomethane but the monomethyl ether could not be crystallized. Hydrolysis of the monomethyl ether yielded fenchyl alcohol and *p*-methoxycinnamic acid which further excluded the presence of an ether linkage in compound (II) and confirmed its identity as fenchyl *p*-hydroxycinnamate.

[1] K. L. HANDA, D. M. SMITH and L. LEVI, *Perfumery Essent. Oil Record* 33 (1962).
[2] L. JURD, *Arch. Biochem. Biophys.* **63**. 376 (1956).

The occurrence of *p*-coumaric acid in plants has been reported both in the free state and in combination with alcohols[3] and sugars[4] but, to the best of our knowledge, it has never been obtained in combination with a monoterpene alcohol. The family Umbelliferae is rich in coumarins and geranyl and farnesyl derivatives[5–7] of coumarins are known. As we have not been able to isolate any free *p*-coumaric acid from *Seseli sibiricum* and the above ester was obtained in a uniform yield on several extractions there is no chance of its being an artifact. Fenchyl *p*-hydroxycinnamate (II) was synthesized by the condensation of *p*-acetoxycinnamyl chloride and fenchyl alcohol.

EXPERIMENTAL

All u.v. spectra were measured in a Beckman Model DU instrument in 95 per cent alcohol; i.r. spectra were measured in a Perkin–Elmer Infracord either in $CHCl_3$ or in nujol mulls.

Air-dried roots of *Seseli sibiricum* (5 kg) were extracted five times with boiling light petroleum in a soxhlet. The extract was concentrated under vacuum and the oily residue (400 g) was chromatographed on de-activated alumina (prepared by shaking 2 kg of alumina with 100 ml of 10 per cent aq. acetic acid for 2 hr).

Isolation of Osthol

Elution of the column with light petroleum (40–60°) yielded an oil which deposited a solid on keeping in an ice chest for 72 hr. Recrystallization of this from petrol afforded colourless needles melting at 84–85°. (Found: C, 73·99; H, 6·74. Calc. for $C_{15}H_{16}O_3$: C, 73·75; H, 6·60%). It gave no depression in mixed melting point determination with an authentic sample of osthol and the i.r. spectra were superimposable.

Isolation of Fenchyl p-*Hydroxycinnamate*

Further elution of the column with benzene and removal of the solvent gave a solid (5 g) which on recrystallization from methanol melted at 215–16°. (Found: C, 75·80; H, 8·36. $C_{19}H_{24}O_3$ requires: C, 75·97; H, 8·05%). The acetate crystallized from methanol as colourless needless, m.p. 95° (Found: C, 73·35; H, 7·51. $C_{21}H_{26}O_4$ requires: C, 73·66; H, 7·66%).

Hydrolysis of Fenchyl p-*hydroxycinnamate.* Fenchyl *p*-hydroxycinnamate (1 g) and 10% methanolic KOH (50 ml) were refluxed for 4 hr. The solvent was removed under reduced pressure and the residue was taken up in 10 ml of water and extracted thrice with 50 ml portions of ether. The ether extract was washed with water, dried and the solvent removed. The residue distilled at 70°/16 mm, and the distillate solidified on keeping in an ice chest to a colourless mass of crystals m.p. 39–40° (melting point reported[8] 38–39°). The aqueous layer from the above hydrolysis was acidified with HCl and extracted with ether. The ether extract was washed with water, dried and the solvent removed. The colourless residue was crystallized from light petroleum (40–60°) to give needles m.p. 208–212°. This was further purified by sublimation in vacuum. The m.p. of the sublimate 212–214° agrees well with that reported for *p*-coumaric acid.[9] (Found: C, 65·92; H, 5·24. Calc. for $C_9H_8O_3$: C, 65·85; H, 4·91%). The acetate of *p*-coumaric acid was obtained as colourless needles from MeOH, m.p. 208–210°.

Hydrolysis of Fenchyl p-*Hydroxycinnamate Monomethyl Ether*

Fenchyl *p*-hydroxycinnamate (1 g) was treated in methanolic solution with diazomethane in ether and left overnight. The solvent was removed and the residue hyrolysed directly with 10% methanolic KOH (25 ml). The hydrolysate was extracted with ether to remove fenchyl alcohol, acidified and again extracted with ether to give *p*-methoxycinnamic acid, m.p. 175°.

p-*Nitrobenzoate of Fenchyl Alcohol*

Fenchyl alcohol (100 mg) and *p*-nitrobenzoyl chloride (100 mg) were heated on a water bath for 45 min. The mixture was cooled and the product decomposed with 10% Na_2CO_3. The solid was filtered off, washed with 10% $NaHCO_3$ and then with water. Crystallization from methanol yielded slightly brown coloured rods, m.p. 107–109° (m.p. reported 108–109°). (Found: C, 67·27; H, 6·68. Calc. for $C_{17}H_{21}O_4N$: C, 67·31; H, 6·98%).

[3] H. J. KLOSTERMAN, F. SMITH and C. O. CLAGETT, *J. Am. Chem. Soc.* **77**, 420 (1955).
[4] A. KAMESWARAMMA and T. R. SESHADRI, *Chem. Abstr.* **41**, 4132 (1947).
[5] A. G. CALDWELL and E. R. H. JONES, *J. Chem. Soc.* 540 (1945).
[6] F. A. L. ANET, F. R. BLANKS and G. K. HUGHES, *Austral. J. Sci. Ser.* **A2**, 608 (1949).
[7] E. SPATH and F. VIERHAPPER, *Ber. Dtsch, Chem. Gest.* **71**, 1667 (1938).
[8] E. H. HUNTRESS and S. P. MULLIKEN, In *Identification of Pure Organic Compounds*, Vol. 1, p. 413. Wiley, New York (1953).
[9] F. B. POWER and C. W. MOORE, *J. Chem. Soc.* 243 (1909).

Synthesis of Fenchyl p-*Hydroxycinnamate*

p-Acetoxycinnamyl chloride (0·5 g) and fenchyl alcohol (1 ml) were heated on a water bath for 45 min. The reaction mixture was cooled and triturated with 5% $NaHCO_3$ and then washed with water till free from alkali. The gummy mass left behind was crystallized from methanol, m.p. 216–217°. No depression was observed in a mixed m.p. determination with the natural sample of fenchyl *p*-hydroxycinnamate.

Acknowledgement—The authors thank the Council of Scientific and Industrial Research, New Delhi, for a fellowship (to S.K.K.) and the Ministry of Health, Government of India, for financial assistance.