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COUMARIN CONSTITUENTS OF *SELINUM TENUIFOLIUM**

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Abstract—Three furocoumarins, bergapten, heraclenin and heraclenol have been isolated from the roots of *Selinum tenuifolium* (Umbelliferae) Another coumarin, m p 85–86°, isolated from the same source and provisionally designated as ST-1, has been proved to be mixture of imperatorin, and 8-geranyloxypsolaren by analyses of various reaction products and separation by preparative TLC on silica gel G impregnated with silver nitrate

INTRODUCTION

PHYTOCHEMICAL investigation of two species of *Selinum*, viz *S vaginatum* and *S monnieri* (Umbelliferae, Amminae) has revealed the presence of both angular furocoumarins and dihydrofurocoumarins [1,2] Moreover, angular dihydropyranocoumarin derivatives[2] also occur in *S vaginatum*, but neither of these 2 species is known to elaborate any linear furocoumarin These results prompted us to examine the constituents of *S tenuifolium*, growing in the Darjeeling area, West Bengal

RESULTS AND DISCUSSION

Extraction of the roots of *Selinum tenuifolium* with light petrol and benzene resulted in the isolation of the furocoumarins, bergapten (**10**), heraclenin (**7**), heraclenol (**11**), and a coumarin, m p 85–86°, provisionally designated as ST-1 The spectral and chemical properties of the latter resembled those of imperatorin (**2**) However, extensive chemical investigation revealed that it was not a single entity[3] but consisted of an inseparable mixture of two structurally similar compounds

The "coumarin", ST-1, m p 85–86°, displayed a single spot on TLC with a number of solvent systems indicating it to be homogeneous The furocoumarin nature of the "compound" was indicated by its UV and IR spectral data and its NMR and MS resembled those of imperatorin[4] (**2**) However, the analytical data and melting point of ST-1 showed wide variation from those of imperatorin and as the MS also lacked any M^+ peak, the molecular formula as well as the structural features of the "compound" had to be settled on the basis of spectral analyses of its various reaction products

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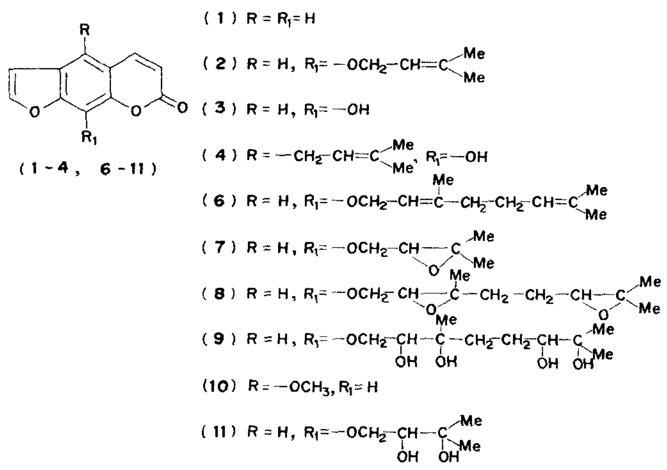
* This work was presented by N Ac in the IUPAC *Symposium on the Chemistry of Natural Products*, New Delhi, India, *Abs*, p 85 (1972)

[1] NIELSEN, B E (1971) in *The Biology and Chemistry of the Umbelliferae* (HEYWOOD, V H, ed), p 325, Academic Press, London

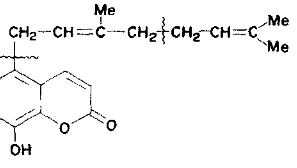
[2] SESHADRI, T R and VISWAPAUL (1971) *Indian J Chem* **9**, 418 and references cited therein

[3] ADITYACHAUDHURY, N and GHOSH, D (1971) *J Indian Chem Soc* **48**, 1067

[4] BUDZIKIEWICZ, H, DJERASSI, C and WILLIAMS, D H, (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol 2, p 259, Holden-Day, San Francisco



(1-4, 6-11)



(5)

Thus, ST-1 consumed 1 mol of hydrogen in 10–15 min on hydrogenation with 10% Pd–C to afford a compound, m p 245–248°, whose physical and spectral data were in accord with those reported for xanthotoxol (**3**) The latter was also identified as the sole reaction product when ST-1 was subjected to hydrolytic cleavage with AcOH–conc H_2SO_4 showing that ST-1 contained a 8-prenyloxypsoralen derivative The structural pattern of the prenyl moiety was settled by pyrolysis of ST-1 at 180–200 /0 05 mm to give alloimperatorin[5] (**4**, M^+ 270), m p 212°, as the main product and a minor product which proved to be a mixture of at least two compounds (TLC) The MS of the latter mixture showed peaks at *m/e* 338, 270, 255, 202 and 69 The peak at *m/e* 270 corresponded to the M^+ peak of alloimperatorin (**4**) while the ion species at *m/e* 338 suggested the presence of an isomeric compound (**5**, M^+ 338) formed by Claisen migration of a C-10 ether side chain to the C-8 position of the psoralen skeleton (**1**) In addition to the common ion species at *m/e* 202 and at *m/e* 69, an intense peak appeared at *m/e* 255 It should be noted that the MS of authentic alloimperatorin (**4**) [*m/e* 270 (M^+), 202, 69] does not give any peak at *m/e* 255 The intense peak at *m/e* 255 along with the two common ion species at *m/e* 202 and *m/e* 69 in the minor pyrolytic mixture might arise by cleavage of C_6H_{11}- and C_5H_9-fragments from a C-10 (geranyl) side chain at C_5 in the postulated isomeric compound (**5**) as shown by broken and dotted lines This experiment demonstrated the complexity of ST-1 and indicated further that it consisted of imperatorin (**2**) and most probably 8-geranyloxypsoralen (**6**)

To ascertain that ST-1 was a mixture of imperatorin (**2**) and 8-geranyloxypsoralen (**6**), it was subjected to perbenzoic acid oxidation giving oxyimperatorin (**7**) and a mixture, analysed by MS of oxyimperatorin (**7**, M^+ 286), a probable diepoxide (**8** M^+ 370) corresponding to a compound (**6**), and a probable tetrol derivative (**9** M^+ 406) formed by opening of the diepoxide (**8**) These data showed the non-homogeneity of ST-1 and suggested again that it was a mixture of imperatorin (**2**) and 8-geranyloxypsoralen (**6**) Confirmation that ST-1 was a mixture of (**2**) and (**6**) was obtained by comparing the integrated NMR spectra of ST-1 and a 1 1 mixture of authentic (**2**) and (**6**) The integrated protons due to $-C{=}C{-}\underline{CH_2}{-}\underline{CH_2}{-}C{=}C-$ system which appeared at δ 2 0 were

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[5] SPATH E and HOLZEN H (1933) *Chem Ber* **66**, 1137

compared[6] and the proportion of (**2**) (**6**) was found to be 3 1 in ST-1 A mixture of authentic (**2**) and (**6**) (3 1) when crystallized from light petrol–benzene mixture showed identical m p and TLC behaviour as a pure sample of ST-1

Attempts to separate ST-1 into its individual components by careful graded column chromatography over silica gel or preparative TLC over silica gel G using a number of solvent systems were met with failure However, it is possible to separate ST-1 into (**2**) and (**6**) by preparative TLC over silica gel G impregnated with silver nitrate solution using $CHCl_3$–MeOH (99 1) as the solvent system

Unlike the other two *Selinum* species,[1,2] *S tenuifolium* is thus found to be a rich source of linear furocoumarin derivatives

EXPERIMENTAL

M ps were determined either on a Kofler block or H_2SO_4 bath in open capillary and are uncorrect UV were recorded in aldehyde-free EtOH IR were determined in Nujol and only the major bands are quoted For column chromatography silica gel (Gouri Chemical Works, Calcutta, Batch 8, 60–100 mesh) was used Light petrol used had b p 60–80° TLC was carried out with silica gel G (Gouri Chemicals Works, Calcutta, Batch 8) as adsorbent, the developing system being C_6H_6–EtOAc (2 1)

Extraction of Selinum tenuifolium The air dried and milled roots of *S tenuifolium*[7] (1 kg) were successively continuously extracted with light petrol and C_6H_6 for 20 hr A crystalline solid mixed with a brown oil separated out from the petrol extract and as filtered (ST-1, yield 8 kg) The conc light petrol and C_6H_6 extracts were separately worked up The light petrol concentrate (12 g) dissolved in C_6H_6 (50 ml) was chromatographed over silica gel (250 g), the column being eluted with solvents of increasing polarity using light petrol, C_6H_6 and $CHCl_3$ in different proportions Light petrol–C_6H_6 (8 2) eluates furnished a pale yellow solid (compound A, yield, 0 2 g) Light petrol–C_6H_6 (1 1) fractions yielded another crop of ST-1 (yield, 0 2 g) C_6H_6 eluates provided yet another crystalline compound (compound B, yield, 0 3 g) Chromatography of the C_6H_6 extract (4 g) over silica gel (100 g) and elution of the chromatogram in a similar way as that followed for light petrol extract afforded the compound ST-1 in light petrol–C_6H_6 (1 1) fractions (yield, 0 5 g) Benzene eluates provided further quantity of compound B while C_6H_6–$CHCl_3$ fractions gave yet another crystalline component (compound C, yield, 1 g) The characterization of the compounds A, B and C was done in the following way

Bergapten (**10**) Compound A on recrystallization from acetone–light petrol afforded shining needles, m p 185–187°, $[\alpha]_D \pm 0°$ ($CHCl_3$), UV λ_{max} 249 (log ϵ 4 23), 268 (log ϵ 4 24) and 305 nm (log ϵ 4 23) IR ν_{max} 1735 (coumarin lactone), 1640 (aromatic ring), 1090 cm^{-1} (benzofuran) MS m/e 216 (M^+), other significant peaks at *m/e* 201, 173, 145, 117, 89 (Found C, 85 60, H, 4 71 Calc for $C_{12}H_8O_4$ C, 85 69, H, 4 79%) The identity of compound A with bergapten (**10**) was established by m m p, IR, and co-TLC with an authentic sample

Heraclenin[8] (**7**) Compound B on recrystallization from $CHCl_3$–light petrol gave colourless needles, m p 107–108°, $[\alpha]_D + 23°$ (pyridine) UV λ_{max} 249 (log ϵ 4 30) and 300 nm (log ϵ 4 00) IR ν_{max} 1735 (coumarin lactone), 1600 (aromatic right), 1100 cm^{-1} (benzofuran) NMR ($CDCl_3$) δ 6 4 (*d*, 1H, C-3), 7 8 (*d*, 1H, C-4), 7 7 (*d*, α-H of furan), 6 83 (*d*, β-H of furan), 7 4 (*s*, 1H, aromatic), 4 6 (*d*, 2H,$-O-\underline{CH}_2-CH-$), 3 3 (*d*, 1H, $-O-CH_2-\underline{CH}-$), 1 2, 1 4 (2*S*, 6H, *ter* $C\underline{H}_3$), MS *m/e* 286 (M^+), significant peaks at *m/e* 202, 85 59 (Found C, 67 00, H, 4 92 Calc for $C_{16}H_{14}O_5$ C, 67 12, H, 4 93%) The properties of compound B were found to be identical with those reported for heraclenin (**7**)

Heraclenol[9] (**11**) Recrystallization of compound C from $CHCl_3$–light petrol furnished colourless needles, m p 114–115°, $[\alpha]_D + 16°$ (pyridine) UV λ_{max} 249 (log ϵ 4 17) and 305 nm (log ϵ 4 45) IR ν_{max} 3350 (OH), 1700 (coumarin lactone), 1590 (aromatic), 1085 cm^{-1} (benzofuran) NMR ($CDCl_3$) δ 6 3 (*d*, 1H, C-3), 7 8 (*d*, 1H, C-4), 7 64 (*d*, α-H of furan), 6 83 (*d*, β-H of furan), 7 4 (*s*, 1H, aromatic), 4 5 (*m*, 2H, $-O-C\underline{H}_2-C{<}^{H}_{OH}-$), 3 9 (m, 1H, $-CH_2-C\underline{H}{=}OH-$), 1 26 (*s*, 6H, *ter* CH_3) MS *m/e* 304 (M^+), prominent peaks at *m/e* 202, 174, 59 The spectral data coupled with the physical properties agreed well with those reported for heraclenol (**11**)

Characterization of ST-1 The compound ST-1 was purified by repeated crystallization from C_6H_6–light petrol as glistening needles, m p 85–86°, $[\alpha]_D \pm 0°$ ($CHCl_3$), R_f 0 91, 0 82 and 0 56 in the solvent systems C_6H_6–EtOAc (2 1), C_6H_6–EtOAc (4 1), and light petrol–EtOAc (2 1) respectively (Found C, 71 68, H, 5 86%)

Hydrogenation of ST-1 *to xanthotoxol* (**3**) ST-1 (0 1 g) dissolved in 95% aldehyde-free EtOH (25 ml) was

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[6] Sharma, Y N, Zaman, A, Kidwai, A R, Bates, R B, and Thalacker, V P (1966) *Tetrahedron* **22,** 322

[7] The plant material used in this investigation was obtained from Mr R Sarker, United Chemical & Allied Products, 10, Clive Row, Calcutta 1, where a voucher specimen has been preserved

[8] Sharma, Y N, Zaman, A and Kidwai, A R (1964) *Tetrahedron* **20,** 87

[9] Sharma, Y N, Sharma, R C, Zaman, A and Kidwai, A R (1964) *Naturwissenschaften* **51,** 537

hydrogenated (15 min) with 10% Pd-C (10 mg) After working up in the usual way, a gummy residue was obtained which crystallized from acetone–light petrol as needles, m.p 248° (70 mg) The latter was identified as xanthotoxol (**3**) by m m p IR and co-TLC with an authentic sample

Acid catalysed cleavage of ST-1 to xanthotoxol (**3**) ST-1 (0 25 g) was refluxed with AcOH (5 ml) and conc H_2SO_4 (8 drops) for 1 hr at 120–130° The solution was poured onto ice and the yellow ppt crystallized from acetone–light petrol, m p 248° The latter did not depress the m p of authentic xanthotoxol (**3**)

Pyrolysis of ST-1 ST-1 (0 5 g) was heated in sublimation tube at 180–200°/0 05 mm A yellow sublimate (0 25 g) was obtained showing 3 distinct spots on TLC The latter was chromatographed over silica gel (5 g) and eluted with solvents of increasing polarity Eluates were collected in fractions of 5 ml each A crystalline compound (solid A), m p 175–180° was obtained from the C_6H_6 eluates showing two spots on TLC The mixture could not be separated by crystallization MS revealed two M^+ peaks at *m/e* 270 and 338 C_6H_6-$CHCl_3$ (1 1) eluates afforded a crystalline residue (Solid B), m p 200–205° which on recrystallization from $CHCl_3$–light petrol, furnished colourless needles (20 mg), m p 210-212 , identified as alloimperatorin (**4** m p , m m p IR, co-TLC, MS)

Epoxidation of ST-1 ST-1 (0 5 g) in min quantity of dry $CHCl_3$ was treated with perbenzoic acid soln (50 ml, 0 6 g) in $CHCl_3$ and kept at room temp for 72 hr The mixture was diluted with Et_2O and washed with aq satd $NaHCO_3$ The solvent was removed and the red gum dissolved in C_6H_6 and chromatographed over silica gel (10 g), the column being eluted successively with solvents of increasing polarity C_6H_6 eluates furnished a crystalline compound which on recrystallization afforded needles m p 112 114 characterized as oxyimperatorin (**7** m p m m p IR) C_6H_6 $CHCl_3$ eluates gave a crystalline mixture in poor yield m p 85-90°, which was found to be a mixture (TLC) MS prominent peaks at *m/e* 406 370 286, 202, 59

Separation of ST-1 into (**2**) *and* (**6**) Silica gel G (Merck, 6 g) in aq $AgNO_3$ (12 5% 14 ml) soln[10] was used dried at 110° for 1 hr with $CHCl_3$-MeOH (99 1) R_f imperatorin (0 68) geranyloxypsoralen (0 92)

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[10] BARUA, A K , DUTTA, S P and PAL S K (1967) *J Chromatog* **31**, 569