Isolation of the components A and B 3 kg of the powdered leaves were extracted with ether and the solvent evaporated *in vacuo* at 40° The residue was then refluxed 5 times (each of 800 ml) with petroleum (b p 40–60°), filtered and the filtrate discarded The petroleum-insoluble residue was dissolved in boiling ethanol (1500 ml), filtered while hot, concentrated *in vacuo* to about 200 ml and left to stand at room temp for 48 hr The pale greenish crystalline deposit was filtered, washed with cold ethanol, dissolved in about 300 ml $CHCl_3$ and passed through a column of SiO_2 gel (70 cm × 1 cm) Elution was first carried out with $CHCl_3$ then with methanol

Component A (daphnoretin) Component A (obtained from the $CHCl_3$ eluate) gave on crystallisation ($CHCl_3$–petroleum) pale yellowish white needles m p 252° ($C_{19}H_{12}O_7$ (352) required C, 64 83, H, 3 44, found C, 64 64, H, 3 78%) The monoacetate (Ac_2O-pyridine at 100° for 3 hr) melted at 242° and the methyl ether (Me_2SO_4 and K_2CO_3 in dry acetone at 60° for 5 hr) at 238° (m m p)

Component B (β-sitosterol-β-D-glucoside) Component B (methanol eluate), after crystallization from large volume of methanol melted at 296–298° ($C_{35}H_{60}O_6$ required C, 72 87, H, 10 48, found C, 72 20, H, 10 05%) The tetraacetate (Ac_2O-pyridine at 100° for 1 hr) melted at 167–169° Hydrolysis of 20 mg (in 20 ml ethanol containing 1 ml conc HCl under reflux for 8 hr) afforded glucose and β-sitosterol

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Key Word Index—Thymela hirsuta, Thymelaceae, coumarin, daphnoretin, β-sitosterol glucoside

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UMBELLIFERAE

EXTRACTIVES OF *ANGELICA GLAUCA*

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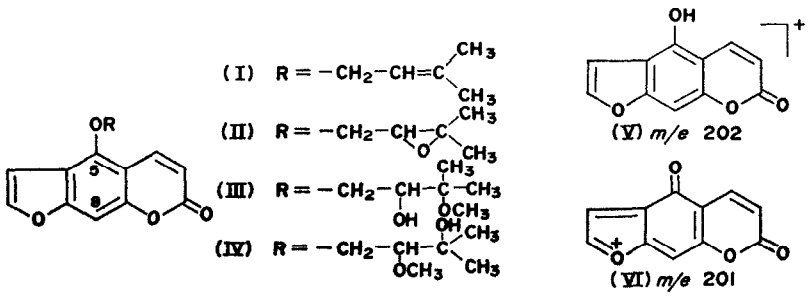
Plant Angelica glauca Edgw. *Occurrence.* Higher regions of Kashmir.[1] *Uses* Medicinal.[2] *Previous work.* Investigation of fruits[3] and roots [4]

Present work Extraction with hexane followed by separation on alumina afforded three crystalline products, isoimperatorin (I) m p 109–110, prangolarin (II) m.p. 103–104 and a new coumarin m p. 119–120 C_{17} $H_{18}O_6$ to which structure (III) has been assigned on the basis of spectral data. λ_{max}^{EtOH} 220, 250, 266 and 300 nm, ν_{max}^{KBr} 3500, 1725, 1375, 1380 and 1265 cm^{-1}. In the NMR spectrum (60 Mc $CDCl_3$) the furocoumarin nucleus is defined by the doublets at 2·41; 2·94 and 1 78, 3·78τ having $J = 2$ and 9 cps respectively There is evidence of only one free position in the benzene ring and that this must be at C-8 is shown by the singlet at 3·01τ, the resonance of the C-5 proton occurring usually at 2·6 to 2·75τ This leaves position C-5 for attachment of the C-6 side chain. The side chain methoxyl is

[1] R N CHOPRA, S L NAYAR and I C CHOPRA, *Glossary of Indian Medicinal Plants*, p 19 (1956)
[2] *The Wealth of India, Raw Material*, C S R I R , New Delhi, **1**, 79 (1948)
[3] S S CHAUDHARY, YOGINDER NATH and K L HANDA, *Proc , Nat Acad Sci. India* **29**, 283 (1960)
[4] R N CHOPRA, I C CHOPRA, K L HANDA and L. D KAPUR, *Chopra's Indigenous Drugs of India*, p 640 (1958)

indicated by the singlet at 6·71 and the gemdimethyl by the 6 proton singlet at 8·75τ. D_2O exchange removes the broad signal of the hydroxylic proton at 7·03τ, presence of which is indicated by the absorption at 3500 cm^{-1} in the IR. Apart from this the NMR spectrum shows a complex 3 proton multiplet at 5·2–6 15τ which can be attributed to the methylene and methene protons of the side chain as shown in (III) This multiplet can be analysed in terms of an ABX system which results due to the asymmetry of the methene carbon, the proton on which is responsible for the typical X quartet centered at 6 01τ of the ABX system.



There are only two possible structures which accommodate these features of which (IV) can be eliminated by analysis of the mass spectrum which shows the base peak at *m/e* 73 corresponding to the elimination of the $H_3CO{=}C\ (CH_3)_2^+$ from the parent ion $(M)^+$ at *m/e* 318 Elimination of the side chain with rearrangement gives a strong peak at *m/e* 202 corresponding to the ion (V) Successive eliminations of CO from this lead to fragments of *m/e* 174, 173, 146, 145, 117 and 89 The interesting point in the spectrum of this coumarin is, however, that in each case these peaks are accompanied by peaks one mass unit less which arise from the ion (VI) This type of elimination is not present in compounds having unsaturation[5] at the usual position in the side chain which apparently favours migration of H from the allylic position to such an extent that only the *m/e* 202 ion is formed

The evidence presented left some doubt regarding the position of the side chain but while this work was in progress Seshadri *et al*[6] reported isolation of a coumarin having an identical side chain at the C-8 position. The m p of their compound differs substantially from that of the coumarin from *Angelica glauca* which can be designated as tert-*O*-methyloxypeucedanin hydrate

Acknowledgement—The authors are grateful to the Ministry of Health, Government of India for financia assistance

[5] H. BUDZIKIEWICZ, C. DJERASSI and D H WILLIAMS, *Structure Elucidation of Natural Products by Mass Spectrometry*, p 259, Holden-Day, San Francisco (1964)
[6] M BANDOPADHYAY and T R SESHADRI, *Indian J Chem* **8**, 855 (1970)

Key Word Index—Angelica glauca, Umbelliferae, coumarins, isoimperatorin, prangolarin, tert-*O*-methyloxypeucedanin hydrate