Tetrahedron Letters No.9, pp. 853-855, 1967. Pergamon Press Ltd. Printed in Great Britain.

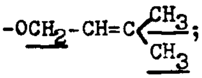
CONSTITUTION OF SELINONE,
A NEW FLAVANONE FROM *SELINUM VAGINATUM CLARKE*

T. R. Seshadri and M. S. Sood
Department of Chemistry, University of Delhi, Delhi.7, India

(Received 23 December 1966)

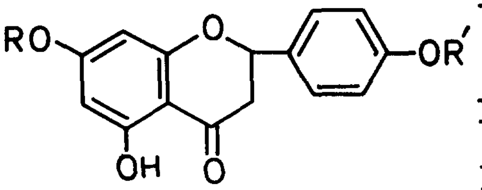
In earlier papers the distinction between the roots of *Selinum vaginatum* and *Nardostachys jatamansi* was clearly brought out[1] and a detailed study made of the coumarins present in petroleum ether extract of the roots of *S. vaginatum*.[2] Further extraction of the residue with benzene yielded a large amount of extract which could be separated into alkali soluble and insoluble portions. The former when subjected to column chromatography yielded angelicin and a new flavanone derivative which has been named '*Selinone*'. The neutral fraction yielded the same coumarins as earlier found in the petroleum ether extract.

Selinone is a colourless crystalline solid, m.p.151-52; $[\alpha]_D^{29} = -50^{\circ}$(C, 0.610 in methanol) and its elemental analysis agrees with the molecular formula $C_{20}H_{20}O_5$. Its colour reactions and solubility properties are characteristic of flavanones having free hydroxyl in the 5 and 7 positions. Its UV spectrum shows maxima at 290 and 328 mμ with bathochromic shifts with Na-acetate and $AlCl_3$ as expected for a 5,7-dihydroxyflavanone derivative. On refluxing with dimethyl sulphate and potassium carbonate in acetone medium (1 hr) it gives a mono methyl ether m.p. 89-90°, molecular formula $C_{21}H_{22}O_5$; UV maxima at 288 and 335 $m\mu$. The positive ferric reaction and bathochromic shift with $AlCl_3$ indicate the presence of free hydroxyl group at 5 position, while the absence of shift with NaOAc shows that 7-hydroxyl has undergone methylation.

The NMR spectrum of 7-methyl selinone contains the following signals; a singlet at τ 3.85 (2H) due to protons in positions at 6 and 8 as expected for a 5,7-dihydroxyflavanone derivative[3,4] a pair of doublets at τ 2.55 and τ 3.0 (J = 9 cps; 2H each) assigned to A_2B_2 system of the 4'-substituted B ring of the flavanone, a triplet at τ 7.05 (2H) characteristic of methylene protons at the 3 position, a singlet at τ 6.05 (3H) attributable to the methoxyl group; the signals at τ 8.2 (doublet; J = 2 cps; 6H), τ 5.45 (doublet; J = 7 cps; 2H) can be assigned to two methyls and a methylene of the system  $-\underline{OCH_2}-CH=C<\begin{matrix}CH_3\\ \underline{CH_3}\end{matrix}$; a multiplet centred at τ 4.55 (2H) due to a olefinic proton of dimethyl allyl residue and a benzylic proton at the 2 position of the flavanone.

The colour reactions, analytical and spectral data indicate that selinone is 4'-γ,γ-dimethylallylnaringenin (I). The following reactions provide confirmation:

(i) Selinone and its 7-methylether, when refluxed (1 hr) with EtOH + Conc. HCl (1:1) lost the C_5 unit and yielded naringenin (II) and sakuranetin (III) respectively, identified by m.p. (m.m.p., undepressed), UV and TLC comparisons with authentic samples. (ii) When sakuranetin was refluxed with γ,γ-dimethylallylbromide (1 hr) in acetone-potassium carbonate, it yielded 4'-γ,γ-dimethylallyl sakuranetin which was found to be identical with selinone-7-methyl ether in m.p. (m.m.p. undepressed), UV and TLC behaviour. The co-occurrence of coumarins and flavanone in this plant is of biogenetic interest; the same C_9 unit seems to be involved in both the types.



I. $R = H$; $R' = CH_2\text{-}CH{=}C(CH_3)_2$.

II. $R = R' = H$.

III. $R = CH_3$; $R' = H$.

REFERENCES

1. T.R. Seshadri and M.S. Sood, Phytochemistry (in press).
2. T.R. Seshadri, M.S. Sood, K.L. Handa and Vishwapaul, Tetrahedron Letters 3367 (1964); ibid., Tetrahedron (in press).
3. T.J. Batterham and R.J. Highet, Aust. J. Chem. **17**, 428 (1964).
4. L.M. Jackman, Progress in the Chemistry of Organic Natural Products Vol. XXIII, p. 349. Springer Verlag (1965).