Tetrahedron Letters No.45, pp. 3367-3373, 1964. Pergamon Press Ltd.
Printed in Great Britain.

CONSTITUTION OF SELINIDIN: A NEW COUMARIN FROM SELINUM VAGINATUM CLARKE

T.R. Seshadri and M.S. Sood

Department of Chemistry,
University of Delhi, Delhi-6, India.

K.L. Handa and Vishwapaul
Regional Research Laboratory, Jammu, India.

(Received 25 September 1964)

Selinidin (I) a new coumarin having diuretic properties, has been isolated from Selinum vaginatum (Hindi, Bhoot-Keshi). It is a pleasant smelling solid and is conveniently obtained from the light petroleum (40-60°) extract of the powdered roots of this drug. It has the mol. formula $C_{19}H_{20}O_5$, m.p. 97-8°, $[\alpha]_D^{29}$, +20.3° (C=1.474, dioxan), mol.wt., 322, and has no methoxyl or free hydroxyl groups. The U.V. spectrum shows $\lambda_{max}^{methanol}$ 256 mμ (log ε 3.52) and 325 (4.17) and $\lambda_{min}^{methanol}$ 254 mμ (3.48) and 262 (3.14) and comparison of this data with those of known coumarins[1] provided at the outset strong evidence for the presence of a 7-oxygenated coumarin

chromophore, an assignment also supported by other evidences. The I.R. spectrum of selinidin includes the following chracteristic peaks: 1724 (conjugated 6-membered lactone), 1613 (aromatic and C = C of α-pyrone ring), 1242 (ester linkage), 1117 (Ar-O-R) and 846 cm^{-1} (1,2,3,4-aromatic substitution).

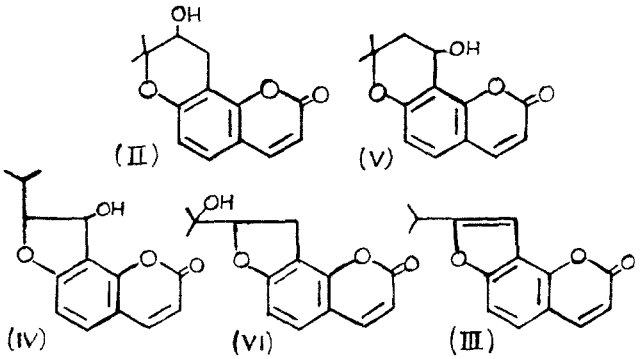
Catalytic hydrogenation of selinidin gave a tetrahydro-derivative, indicating the presence of one ethylenic bond other than the coumarin double bond. The I.R. spectrum of the tetrahydro-derivative shows two strong absorptions in the carbonyl region. The one at 1775 cm^{-1} has been assigned to the carbonyl of the dihydro-coumarin system[2] and the second absorption at 1725 cm^{-1} to the carbonyl of an aliphatic ester group; the latter was obviously merged with the coumarin carbonyl frequency in the I.R. spectrum of selinidin. On ozonolysis, selinidin gave acetaldehyde as a volatile fragment; its identity has been established through its D.N.P. by comparison with the authentic sample. These observations clearly indicate that selinidin contains an ethylidene group ($\overset{|}{\underset{|}{C}} = CH - CH_3$).

Since there were indications for the presence of ester group, selinidin was treated with aqueous

alkali (10%), when it gave a substance, which has been named selinetin (II) and tiglic acid in poor yield; most of the selinidin was recovered unchanged. However, it underwent complete hydrolysis with alcoholic alkali and gave good yields of selinetin and tiglic acid. The consumption of alkali indicated that these were formed in equimolecular quantities. Hence, selinidin could be a tiglyl ester of selinetin.

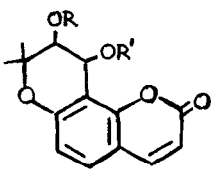
The constitution of selinetin was studied as follows. This coumarin, $C_{14}H_{14}O_4$, m.p. 183-4°, $[\alpha]_D^{29}$, +17.2 (C, 0.815; dioxan), has one free hydroxyl group, which is not phenolic in nature; it gave a mono-acetate, $C_{16}H_{16}O_5$, m.p. 136-37°. The U.V. spectrum of selinetin gives $\lambda_{max}^{methanol}$ 247 mμ (log ε 3.63), 257 (3.52) and 329 (4.19) and $\lambda_{min}^{methanol}$ 242 mμ (log ε 3.49), 252 (3.57) and 264 (3.24) and comparison with that of selinidin shows that hydrolysis has not brought about any change in the chromophore. The I.R. spectrum of selinetin includes the following characteristic bands: 3500 (OH), 1700 (α-pyrone C = O), 1281, 1075 (OH deformation and C-O streching) and 833 cm^{-1} (1,2,3,4 aromatic substitution).

Important evidence was obtained by the dehydration of selinetin with sulphuric acid-acetic acid or hydrogenbromide-acetic acid; the product was a coumarin which was identified as dihydro-oroselone (III) from its m.p.,U.V. and I.R. spectral data and this was confirmed by comparison with authentic sample kindly provided by Prof.Soine of Minnesota University. It could have arisen from the following possible structures of selinetin by dehydration and rearrangement; the detailed mechanism for the type of rearrangement involved has been discussed by Benеze *et al.*[3]



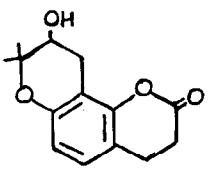
Structures (IV) and (V) could be ruled out, because selinetin does not undergo hydrogenolysis and does not therefore, have a benzylic alcohol group as found

in these formulae. Structure (VI), has been recently assigned to columabianetin.[4] Selinetin is different from columbianetin in m.p., U.V., I.R. and N.M.R. data and therefore structure (VI) can not be assigned to it leaving only structure (II) for consideration. This is confirmed by catalytic hydrogenation of selinetin to give dihydroselinetin (VII), which agreed in m.p. and U.V. spectrum with the product of known constitution obtained from samidin (VIII).[1] Another support is provided by its I.R. spectrum which agrees closely with that of the product obtained from pteryxin (IX) by a number of steps and given this constitution though racemic in nature.[5] While we were writing this note we received from Prof. Soine a reprint of his very recent publication on the constitution of lomatin[6] which has the same structure as we have given to selinetin; the agreement in all properties is quite close.



(VIII), R = $OC-CH=C(CH_3)_2$

R' = $OC-CH_3$



(VII)

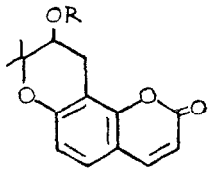
(IX), R = $OC-CH_3$

R' = $OC-C(=CH-CH_3)-CH_3$

The above structure of selinetin has been

further supported by N.M.R. studies in dimethyl sulphoxide solution. Two doublets at 2.09 and 3.78 τ (J = 9.4) correspond to the 3 and 4 protons of the coumarin ring. The other doublets at 2.52 and 3.26 τ (J = 8.6) can be assigned to 5 and 6 protons. The gemdimethyl protons are obtained as two singlets at 8.60 and 8.70 τ . The proton of the hydroxyl group gives a singlet at 6.48 τ which is appropriate for a secondary alcoholic group.

The constitution of the ester, selenidin was arrived at as follows. As previously mentioned, by alkaline hydrolysis it gives selinetin and tiglic acid. Since angelic acid is known to isomerize[7] to tiglic acid under these conditions it was necessary to determine whether sellinidin was an angelate or a tiglate. This has been achieved using the N.M.R. spectral evidence. The vinyl proton of angelate has been shown[8] to give a signal at 4.02 τ (centre of multiplet) and that of tiglate a multiplet centring at 3.43 τ . Since, in the spectrum of selinidin the signal is at 4.02 τ (centre of multiplet), selinidin (I) is an angelate of selinetin.



(I), R = $-OC-\overset{CH-CH_3}{\overset{\|}{C}}-CH_3$

REFERENCES

1. E. Smith, N. Hosansky, W.G. Bywater and E.E. Van Tamelen, J. Amer. Chem. Soc., 79, 3540 (1957).
2. J. Lecomte, Handbuch der Physik Vol. 26, p.556, Ed. S. Flugge, Berlin, Springer, (1958).
3. W. Bencze, J. Eisenbeiss and H. Schmid, Helv. Chim. Acta, 39, 923 (1956).
4. R.E. Willete and T.O. Soine, J. Pharm. Sci., 53, 275 (1964).
5. R.E. Willete and T.O. Soine, J. Pharm. Sci., 51, 149 (1962).
6. T.O. Soine and F.H. Jawad, J. Pharm. Sci., 53, 990 (1964).
7. R.E. Buckles, G.V. Mock and L. Locatell., Chem. Rev., 55, 659 (1955).
8. R.R. Fraser, Can. J. Chem., 38, 549 (1960).