Tetrahedron Letters No.10, pp. 1277-1279, 1968. Pergamon Press. Printed in Great Britain.

NEW SYNTHETIC BIFLAVONYLS

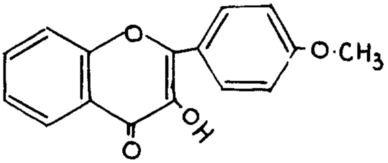
Divakar D.Berge and M.M.Bokadia

School of Studies in Chemistry, Vikram 'Varsity, Ujjain (India)

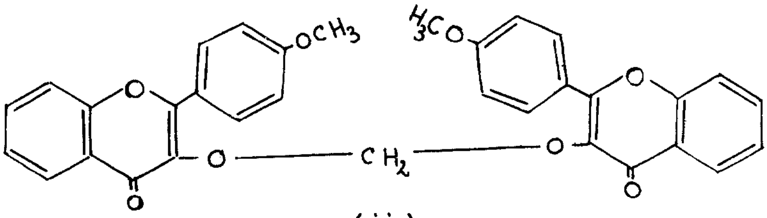
(Received in UK 30 October 1967)

Methylenation, regarded as a natural process has also been reported in the plant polyphenolics[1-5]. In the laboratory methylenation of a catechol unit in 6,7 positions was successful in 5,6,7,4' tetrahydroxy isoflavone[6] and vogoletin[7]. Methylenation of 7-hydroxy-flavonoids and carbonyl derivatives of resorcinol has been reported to yield bimolecular compounds linked by a methylenedioxy group in the reactive 7 and 4 positions respectively[8]. Phenolic-hydroxyl groups are found to take part in these methylenations.

We have succeeded in synthesising, the so far unreported Bi-(3-flavonyloxy)methanes involving the enolic hydroxy group in the position 3 of flavonols. During our studies with the condensation of flavonols it has been possible for us to get the biflavonoyloxy methane (ii) by the methylenation of the flavonol (i). The structure (ii) has been suggested on the basis of microanalytical data, absence of phenolic test with ferric chloride and molecular weight determination. The U.V., I.R. and NMR spectral data are also in close agreement with the proposed structure.



(i)



(ii)

Bi-(4'-methoxy 3-flavonyloxy)methane : 4'-methoxyflavonol (1.25g.) was refluxed with methyleneiodide (0.8ml) and anhydrous K_2CO_3 (6 g.) in dry acetone (25 ml.) till the alcoholic ferric chloride test (violet color) was negative (10 hrs.). The reaction mixture was cooled and filtered. The potassium carbonate was washed 3-4 times with acetone. The filterate and the washings on recovery of the solvent provided a dark red viscous liquid which quickly solidified on cooling. Repeated crystallisations with benzene provided a pale yellow crystalline solid (0.45 g.) m.p. 188-89°; λ_{max}^{EtOH} 238 mμ (logϵ 4.012) and 320 mμ (logϵ 4.036). It's IR in KBr phase has absorbtion bands at 1640, 1470, 1408, 1370, 1250, 1176, 1031, 980, 952, 900, 833 and 752 cm^{-1}. The NMR spectra shows proton signals at 1.95 (methylene protons), 2.2-3.7 (aromatic protons), 6.5 (methoxy protons) and this is collaborated by the integration curve; (Found C, 71.4; H, 4.2; mol.wt. by Rast method 514; $C_{33}H_{24}O_8$ requires C, 72.2; H, 4.3%; mol.wt. 548).

Further work is in progress in our laboratories.

Acknowledgements : Authors are thankful to Prof. W.V. Bhagwat, for providing laboratory facilities and to the CSIR New Delhi for a fellowship to one of us (DDB). The authors thanks are also due to Prof. Sir E.R.H. Jones, F.R.S., Dyson Perrins Laboratory, Oxford, for taking the IR and NMR spectra of the compound.

References :

1. K.W. Gopinath, A.R. Kidwai and L. Prakash, *Tetrahedron*, **16**,201 (1961)

2. W. Cocker, T. Dahl, C. Dempsey and T.B.H. McMurry, *Chem. & Ind.*, 216(1962)
3. B.L. Van Duuren, *J.Org.Chem.*, **26**, 5013 (1961).
4. A.J. Birch, B. Moore, S.K. Mukerjee, *Tetrahedron Letters*,No.**15**,673 (1962)
5. R.N. Khanna, T.R. Seshadri, *Tetrahedron*, **19**, 219 (1963).
6. S.K. Arora, A.C. Jain and T.R. Seshadri, *Tetrahedron*, **18**, 559 (1962).
7. S. Rangaswami and H. Rao, *Proc.Indian Acad.Sci.*, **A 49**, 241 (1959).
8. S.K. Grover, A.C. Jain and T.R. Seshadri, *Tetrahedron*, **20**, 555 (1964).

oOo