

MEARNSITRIN : A NEW FLAVONOL GLYCOSIDE FROM THE LEAVES OF ACACIA MEARNSII

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The large number of flavonoid compounds identified in extracts obtained from black wattle, Acacia mearnsii, have, with the exception of the flavonol-3-rhamnosides myricitrin and quercitrin, contained no other substituents than free hydroxyl groups (1,2,3). This communication reports the isolation from the leaves of the tree and the identification of a partially methoxylated flavonol rhamnoside, for which the name mearnsitrin is proposed.

During biosynthetic studies in these laboratories, a compound not identifiable with any known wattle constituent was found in the leaves of a small proportion of trees grown from commercial seed (4). Preparative paper chromatography of the tannin-free eluent obtained from a polyamide column resulted in the isolation of a compound which, although not obtained in crystalline form, gave a single spot, pale yellow in visible and dark brown under u.v. light, even when fumed with ammonia, on two-dimensional paper chromatograms.  $R_f$  values and reaction with various spray reagents pointed to the compound being a flavonol glycoside with a phloroglucinol A ring and no free ortho-dihydroxy groups.

Hydrolysis in dilute acid solution yielded a non-crystalline flavonol,  $C_{16}H_{12}O_8$ , which by analogy would be named mearnsitrin, and a sugar identified by the gas chromatographic technique of Kagan and Mabry (5) as rhamnose. Comparison of the ultra-violet absorption spectra in ethanolic aluminium chloride solution (6) of the glycoside and its aglycone established that the sugar residue was attached to the 3-position. Analysis of the trimethylsilyl derivative of the glycoside by n.m.r. spectroscopy, while not giving incontestable evidence regarding the structure of the aglycone because of a considerable degree of line broadening, did indicate a 1 : 1 mole ratio of sugar to aglycone.

Mearnsitrin forms a crystalline acetyl derivative which, on examination by n.m.r., was found to contain five O-acetyl groups, one O-methyl group, one pair of meta-coupled, and another pair of equivalent aromatic protons. This evidence indicates a symmetrical substitution pattern in the B phenyl ring, i.e. most probably 3', 5'-dihydroxy-4'-methoxy.

Demethylation with pyridinium chloride after Harborne (7) yielded myricetin (identified paper chromatographically). Final confirmation of the structure as 4'-methoxymyricetin (3,3',5,5',7-pentahydroxy-4'-methoxy-flavone) was obtained with the identification of 4-methoxygallic acid as a major product from KOH fusion according to conditions described by Roux (3).

To the best of the author's knowledge this compound has not previously been identified from any source, while to date no other methoxylated flavonoids have been found in wattle species. The genetic factors controlling the occurrence of mearnsitrin in black wattle have been discussed elsewhere (4).

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#### REFERENCES

1. H.H. KEPPLER, J.Chem.Soc., 2721 (1957).
2. S.E. DREWES and D.G. ROUX, Biochem.J., 87, 167 (1963) and references cited therein.
3. D.G. ROUX and E. PAULUS, Biochem.J., 82, 320 (1962).
4. F.C.J. ZEIJLEMAKER and A.M. MACKENZIE, Rep.Wattle Res.Inst. for 1965-1966, 57 (1966).
5. J. KAGAN and T.J. MABRY, Anal.Chem., 37, 288 (1965).
6. L. JURD, The Chemistry of Flavonoid Compounds, p.120. Ed.T.A. Geissman. Pergamon Press, Oxford (1962).
7. J.B. HARBORNE, personal communication.
8. D.G. ROUX, J.Amer.Leather Chem.Ass., 53, 384 (1958).