Tetrahedron Letters No.36, pp. 3191-3196, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ISOLATION OF LANCEOLARIN, A NEW GLYCOSIDE OF BIOCHANIN-A, FROM THE ROOT-BARK OF *DALBERGIA LANCEOLARIA*

by

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(Received 13 July 1965)

The trees belonging to the genus *Dalbergia* are important in many respects. Many of them provide excellent timber and one tree, *Dalbergia lanceolaria*, acts as a host to the economically important lac insect. The chemical study of these trees has revealed the existence of novel structures of organic compounds viz. 4-phenyl coumarins[1], dalbergenones[2-5] and isoflavones[6-10]. The presence of biochanin-A 7-glucoside (sissotrin) in the leaves of *Dalbergia sissoo* has been recorded earlier[11,12] and 7-methyltectorigenin 4'-glucoside has recently been found in the pods of the same tree[13]. We wish to report the occurrence of 7-apioglucoside of biochanin-A, named lanceolarin, in the root-bark of *Dalbergia lanceolaria*. This is another example of the occurrence of the rare sugar apiose in glycosidic combination, the only instances earlier known being apiin[14,15] and graveobioside-A and -B[16] and whereas the earlier compounds were flavones, the present example belongs to the isoflavone group.

The air-dried and coarsely powdered root-bark was successively extracted with hot petroleum ether, ether, acetone and alcohol. The acetone concentrate on keeping for a few days deposited the colourless crystalline lanceolarin which was purified by two recrystallisations from methanol; m.p. 165-170° sintering earlier and collecting at 190-193°. That the compound was homogeneous was checked by paper chromatography; circular R_f, 0.7 (5% acetic acid, 23°, alcoholic ferric chloride spray). It gave a purple-violet colour with alcoholic ferric chloride. Reduction test for flavonoids (magnesium and hydrochloric acid in alcoholic solution) was negative but a red colour developed on reduction with sodium amalgam in alcoholic solution followed by acidification (positive test for isoflavones). Durham test for isoflavanones was not answered. The compound rapidly reduced Tollens' reagent but reduction of Fehling's solution was slow. Molisch's test was indefinite. The substance dissolved in strong sulphuric acid to a pale yellow solution without any fluorescence. It has a bitter, astringent taste. U.V. absorption: λ_{max}^{EtOH} 262 mμ (log ε, 4.55) and 335 mμ (log ε, 4.06); $[\alpha]_D^{22}$ -96.9° (c, 1.032, 80% methanol).

Analytical data of the new glycoside agreed with the molecular formula $C_{27}H_{30}O_{14}$; it gave a heptaacetate, $C_{41}H_{44}O_{21}$, m.p. 181° and $[\alpha]_D^{30}$ -47.9° (c, 1.252, dimethylformamide). Complete hydrolysis of the glycoside by refluxing with 4% aqueous sulphuric acid gave biochanin-A, identified by m.p., m.m.p., colour reactions, chromatography on paper and silica gel (thin-layer), preparation of the acetate and the methyl ether. The sugars were found to be glucose and apiose by paper chromatography and TLC (silica gel) using authentic specimens prepared by acid hydrolysis of apiin[15] and graveobioside-A[16]. Apiose was further confirmed by the characteristic yellow spot on chromatograms showing an yellowish-white fluorescence in U.V. light when benzidine-trichloroacetic acid reagent was used for developing[17,18]. Quantitative acid hydrolysis of lanceolarin showed that it contained biochanin-A, glucose and apiose in equimolar proportions.

Complete methylation of the glycoside followed by acid hydrolysis of the sugar groups yielded 5,4'-dimethoxy-7-hydroxy isoflavone[19,20], identified by m.p., preparation of the acetate and the ethyl ether. The position of the hydroxyl group in this partial methyl ether was confirmed by a comparison of its U.V. spectrum with those in the presence of sodium acetate (bathochromic shift of 10 mμ) and of aluminium chloride (no change). This result showed that in lanceolarin glucose and apiose are attached to the 7-hydroxyl group of biochanin-A as a biose unit.

Partial hydrolysis of the glycoside could be effected by refluxing with 0.5% sulphuric acid for 30 min. when apiose was removed yielding biochanin-A 7-glucoside, m.p.220°,

$[\alpha]_D^{30}$ -35.3° (c, 1.644, dimethylformamide). It gave an acetate m.p. 204°, $[\alpha]_D^{30}$ -16.97° (c, 1.885, dimethylformamide). The biochanin-A 7-glucoside thus obtained agreed with sissotrin[11,12] in its properties and on further hydrolysis gave biochanin-A and glucose. Geissman *et al.*[21] have recently reported the occurrence of this glucoside in the seedlings of *Cicer arietinum*.

It, therefore, follows that in lanceolarin glucose is attached to the 7-hydroxyl group of biochanin-A and apiose is attached to one of the hydroxyls of the glucose unit. Work is in progress to determine the positions of linking between the apiose and the glucose residues.

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