Phytochemistry, 1978, Vol 17, p 596 Pergamon Press Printed in England

TECTORIGENIN 7-GENTIOBIOSIDE FROM *DALBERGIA VOLUBILIS* STEM BARK

URMIL KHERA and SHYAM S. CHIBBER
Department of Chemistry, University of Delhi, Delhi-7, India

(*Received* 9 *September* 1977)

Key Word Index—*Dalbergia volubilis*; Leguminosae; isoflavonoids; tectorigenin-7-*O*-(β-D-glucopyranosyl 1→6)-β-D-glucopyranoside.

We wish to report the isolation from stem bark of *Dalbergia volubilis* of a new isoflavone glucoside, which we have identified as tectorigenin 7-gentiobioside.

EXPERIMENTAL

The air dried, powdered stem bark (1 kg) was extracted successively with petrol, C_6H_6 and EtOH. The EtOH extract was concd and chromatographed on a Si gel column using EtOAc as solvent. The eluate was subjected to repeated column chromatograpy followed by PLC($CHCl_3$–MeOH–H_2O, 8:2:0.5) to give the pure glycoside, mp 160–162°; $[\alpha]_D$ −37.21 (c = 0.65, MeOH) which analysed for $C_{28}H_{32}O_{16}$ and gave a green ferric reaction, a positive Molisch's test and a dark pink colour with Na amalgam followed by HCl suggesting an isoflavonoid structure. ν^{KBr} 3450 (—OH), 1639 (chelated carbonyl), 830 cm^{-1} (1,4-disubstituted benzene ring). λ_{max}^{MeOH}: 265, 335; +$AlCl_3$: 275, 330; +NaOAc: 265, 335 nm showed the presence of free 5-OH and that the 7-position was occupied. On hydrolysis with 5% H_2SO_4, it yielded tectorigenin [1], mp 225–226° (identified by direct comparison with an authentic sample) and glucose only. On acetylation with Ac_2O–Py it gave an acetate, mp 90–91°. PMR of the acetate (60 MHz, $CDCl_3$, TMS as int. stand.): δ 2.10 (7 × 3H, 7 × aliphatic—OAc), 2.35, 2.50 (2 × 3H, each s, 2 × phenolic —OAc), 3.80 (3H, s, —OMe), 4.13–5.53 (m, glucosyl protons), 7.20 (3H, d, $J_{3',5'}$ = 8.5 Hz, C-3′, C-5′, C-8 unresolved), 7.55 (2H, d, $J_{2',6'}$ = 8.5 Hz, C-2′, C-6′), 8.02 (1H, s, C-2). PMR of the acetate and quantitative aglycone estimation showed the compound to be a diglucoside. That both the glucose units were attached to the 7-hydroxyl was shown by complete methylation of the parent compound with Me_2SO_4–K_2CO_3–Me_2CO followed by acid hydrolysis when 7-hydroxy-5,6,4′-trimethoxyisoflavone [2], mp 216°. (Found: C, 65.6; H, 5.1. $C_{18}H_{16}O_6$ requires: C, 65.9, H, 4.9%) was isolated. The formation of tectoridin [3] and glucose in the controlled partial hydrolysis with Killiani's reagent [4] further confirmed that the parent glycoside was a 7-diglucoside. Permethylation of the parent glycoside by Hakomori's method [5] followed by acid hydrolysis of the permethylate yielded 2,3,4,6-tetra-*O*-methyl D-glucopyranose and 2,3,4-tri-*O*-methyl-D-glucopyranose. Thus both glucose units are in pyranose form with 1→6 inter-sugar linkage and attached to the 7-position of the aglycone by an anomeric OH. The β-configuration of glucosidic linkages was established by means of enzymatic hydrolysis with β-glucosidase and optical rotation considerations employing Klyne's rule [6, 7]. Since tectorigenin does not contribute to the molecular rotation of the glycoside, the entire $[M]_D$ value (−191.70°) was due to the sugar entities. Hence, the compound is tectorigenin-7-*O*-(β-D-glucopyranosyl 1→6)-β-D-glucopyranoside.

Acknowledgement—The authors thank Prof. T. J. Mabry, Austin, U.S.A., for kindly sending samples of tectorigenin and tectoridin.

REFERENCES

1. Donnelly, D. M. X., Thomson, J. C., Whalley, W. B. and Ahmed Saboor (1973) *J. Chem. Soc. Perkin I* 1737.
2. Krishnamurti, M. and Seshadri, T. R. (1954) *P. Sci. Ind. Res. (India)* **13B**, 1.
3. Markham, K. R., Mabry, T. J. and Swift, W. T. (1970) *Phytochemistry* **9**, 2359.
4. Killiani, H. (1930) *Ber. Dtsch. Chem. Ges.* **73**, 2836,
5. Hakomori, S. (1964) *J. Biochem.* **55**, 205.
6. Klyne, W. (1950) *J Biochem.* **XLI** 47.
7. Stanck, J. (1956) *Chem. Ind (Lond.)* 488.