5,7,3',4'-Tetramethoxy Quercetin-3-O- β -D-Galactopyranosyl-(1 \rightarrow 4)-O- α -D-Xylopyranoside from Syn Sesbania aculeata

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Systematic phytochemical examination of the seeds of Sesbenia aculeata has yielded. 5.7.3'-4'-tetramethoxy quercetin-3-O- β -D-galactopyranosyl- $(1\rightarrow 4)$ -O- α -D-xylopyranoside.

INTRODUCTION

The legume genus Sesbania aculeata is native to Australia and Ceylon and is distributed throughout all over India. It is locally known as Dhaincha and is used for revegetation. The plant increases the nitrogen fixation and is used as a rich nitrogenous manure. It exchanges calcium and available phosphorus and decreases alkalinity of soil. Sesbania aculeata has many folklore uses in traditional medicine. The plant is supposed to have considerable medicinal value for curing wounds. The seeds when mixed with flowers are applied for the cure of ringworm and skin diseases.

A triterpenoid, saponin has been reported in its seeds. On hydrolysis the saponin yields an oleonolic acid and one other unidentified sapogenin. It is also reported to possess antifungal activity.

Plant seeds of Sesbania species other than aculeata genus contain important constituents and possess biological activities similar to Sesbania aculeata.

RESULTS AND DISCUSSION

The air dried powdered and defatted seeds of Sesbania aculeata were extracted with rectified spirit and the rectified spirit extract was concentrated to a brown viscous mass. The brown viscous mass was then concentrated and subsequently extracted with ethyl acetate. The ethyl acetate extracted when worked up by column chromatography yielded a glycoside identified as 5.7.3'-4'-tetramethoxy quercetin- $3-O-\beta$ -D-galacto-pyranosyl- $(1 \rightarrow 4)-O-\alpha$ -D-xylopyranoside from its roots.

The air dried and powdered seeds were defatted in petroleum ether and when worked up yielded yellow amorphous mass, m.p. 212°C, which was found to be homogeneous on TLC examination. It crystallised to yellow coloured needles, from methyl acetate 1:1, molecular formula $C_{30}H_{36}O_{16}$, molecular weight 652 (found C = 55.20, H = 5.62%, required C = 55.20, H = 5.50%); IR v_{max}^{KBr} 3334,

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2910, 2835, 1660, 1625, 1540, 1270, 1050 and 800 cm $^{-1}$; UV λ_{max}^{MeOH} 350, 247 nm; $\lambda_{max}^{\text{MeOH/AlCl}_3}$ 450, 318, 245 nm; $\lambda_{max}^{\text{MeOH/AlCl}_3}$ —HCl 420, 360, 300 nm.

It responded to positive test for flavone glycoside^{7,8} and when subjected to acetylation^{9, 10} yielded a hexa-acetyl derivative, m.p. 206°C, molecular formula $C_{42}H_{48}O_{22}$, M⁺ 904 (found C = 55.70, H = 5.25%; calculated for $C_{42}H_{48}O_{22}$, C = 55.75, H = 5.30%). Estimation of the methoxy group (Ziesel method) indicated the presence of four methoxy group.

On hydrolysis with acid the glycoside yielded an aglycone, m.p. 198-9°C, $C_{19}H_{18}O_7$, M⁺ 358 (found C = 63.66, H = 5.06%; calculated C = 63.66, H = 5.02%); IR v_{max}^{KBr} 3325, 2910, 2840, 1660, 1640, 1540, 1270, 1050, 785 cm⁻¹; UV $\lambda_{max}^{MeOH-AlCl_3/HCl}$ 415, 358, 300, 260 nm; $\lambda_{max}^{MeOH-AlCl_3/HCl}$ 415, 358, 300, 260 nm, $\lambda_{max}^{MeOH-NaOAC/H_3BO_3}$ 388, 260 nm; $\lambda_{max}^{MeOH-NaOAC/H_3BO_3}$

The appearence of peak in the IR at 3325 cm⁻¹ showed the presence of —OH group(s). Acetylation of the aglycone at room temperature with pyridine/Ac₂O yielded a monoacetyl derivative, m.p. 160-161°C, molecular formula C₂₁H₂₀O₈, $M^+ = 400$ (found C = 62.70, H = 4.86%, calculated C = 63.00, H = 5.00%); yet another peak in the IR at 2840 cm⁻¹ indicated the presence of methoxyl group(s). The number of methoxyl groups were estimated by Ziesel's method¹¹ and methyl percentage indicated the presence of four methoxy groups.

The aglycone yielded o-hydroxy-2,4-dimethoxy benzene (by m.m.p., Co-PC and TLC) and verceteric acid (by m.m.p., Co-PC and Co-TLC) on alkaline fusion and established the presence of methoxy groups at 5,7,3'-4' in it. The aglycone displayed characteristic colour reactions with oxychloride in citric acid and with boric acid sodium acetate thereby showing the presence of hydroxy group^{12, 13} at 5,7,3', and 4' positions.

The fact that the aglycone respons to positive colour reactions with zirconium oxychloride in citric acid and also with boric acid and sodium acetate which is characteristic for C-3 (OH) group, whereas the glycoside does not respond to this reaction, leads to the conclusion that the sugar-moiety was attached to the aglycone at C-3 position. The characteristic bathochromic shift of wavelength (58 nm, band I) with MeOH-NaOMe indicated that the OH group at the position C-3 was engaged in the glycoside formation formation but is free in the aglycone¹⁴.

The glycosidic hydrolysate when subjected to paper chromatographic examination indicated the presence of D-galactose and D-xylose. Periodic oxidation of the glycoside concluded that one molecule of the glycoside was made up of one molecule of the aglycone and one molecule each of D-glucose and D-xylose. Partial hydrolysis of the glycoside indicated the appearance of galactose first followed by xylose thereby confirming that galactose was the terminal sugar and xylose was be involved in glycoside formation. Permethylation of the glycoside followed by hydrolysis yielded 2,3,4,6-tetra-O-methyl-D-galactose and 2,3,di-O-methyl-D-xylose and confirmed the C₄ of D-xylose to be involved in linkage and further confirmed that both sugars were present in the pyranose form.

This glycoside was assigned the structure as 5,7,3'-4'-tetramethoxy quercetin-3-O- β -D-galactopyranosyl-(1-4)-O- α -D-xylopyranoside.

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