identical with that of a synthetic sample prepared from 3-*C*-prenyl resacetophenone [7] by treatment with benzaldehyde under basic conditions. The mixture of chalkone [8] and the corresponding 7-hydroxy-8-*C*-prenyl flavanone was separated by TLC on Si gel.

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A NEW FLAVONOL GLYCOSIDE FROM THE LEAVES OF *SYMPLOCOS SPICATA*

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Key Word Index—*Symplocos spicata*; Symplocaceae; rhamnetin 3-digalactoside.

Symplocos spicata is widely distributed throughout India and is reputed for its medicinal importance. Hörhammer and Rao [1] isolated two sapogenins, Tiwari and Vasudeva [2] isolated a leucopelargonidin glycoside from its stem bark.

A flavonol glycoside mp 195° (decomp.) was isolated from the ethanolic extract of *Symplocos spicata* leaves, the glycoside on acid hydrolysis giving an aglycone $C_{16}H_{12}O_7$ mp 294–296° and galactose (PC, TLC, and phenyl osazone). On the basis of standard colour reactions, UV, and IR, and chemical degradations, the aglycone was identified as 3,5,3'4'-tetrahydroxy-7-methoxyflavone, rhamnetin [3, 4]. Methylation of the glycoside with dimethyl sulphate followed by acid hydrolysis gave quercetin 7,5,3',4'-tetra methyl ether (mmp, UV, and cochromatography with authentic sample). This confirms the attachment of sugar in position 3 of the aglycone.

The glycoside was fully methylated and hydrolysed and the resulting partially methylated sugars were identified as 2,3,6-tri-*O*-methylgalactose and 2,3,4,6-tetra-*O*-methylgalactose which established that two galactose units are present in the form of bioside linked at position 3 of the aglycone. The glycoside was completely hydrolysed by emulsin, thereby showing the presence of β-linkages. The nature of the disaccharide was also confirmed by periodate oxidation one mole of glycoside consumed three moles of periodate with the liberation of one mole of formic acid. On the basis of these results the glycoside was identified as rhamnetin 3-*O*-β-D-galactosyl-4-*O*-β-D-galactopyranoside.

EXPERIMENTAL

Isolation of the glycoside. The dry and defatted leaves were extracted with boiling EtOH. The extract was concentrated and poured into H_2O. It was filtered, and the concentrated filtrate was extracted with petrol, Et_2O, and EtOAc. The EtOAc fraction on concentration gave a light yellow compound mp 195° (decomp.) (C, 52.34; H, 5.05; Calc. for $C_{28}H_{32}O_{17}$; found C, 52.5; H, 5.00).

Isolation of aglycone. The glycoside was hydrolysed with 7% aq. H_2SO_4 and the aglycone extracted with EtOAc. After the solvent was recovered, the residue was crystallized from EtOAc–petrol mp 294–296° (C, 60.52; H, 3.7; Calc. for $C_{16}H_{12}O_7$; found C, 60.7; H, 3.8); UV (EtOH); λ_{max} 257 and 370 nm. IR: identical with the authentic sample. Acetate: mp 191–193° (Found COMe, 34.972; Calc. for $C_{16}H_8O_7$ $(COMe)_4$ 35.55%. The methyl ether (Me_2SO_4–K_2CO_3) mp 171–173°. (Found: OMe, 40.05. Calc. for $C_{16}H_5O_2$ $(OMe)_5$, 41.66%). On KOH fusion, monomethyl ether of phloroglucinol mp 78° and protocatechuic acid mp 198° were isolated.

Methylation of the glycoside and hydrolysis of the methylated product. The glycoside was methylated with Me_2SO_4–NaOH and the methyl ether was hydrolysed with 4N H_2SO_4 and the aglycone and the partially methylated sugars were identified by PC.

Hydrolysis with emulsin. The glycoside dissolved in aq. EtOH (1:1) was heated with aq. solution of emulsin from sweet almonds [5]. The mixture was kept at 37–40° for 4 days. The aglycone was extracted with EtOAc and purified. The remaining solution on paper chromatographic examination revealed the presence of galactose.

Periodate oxidation. The glycoside was treated with $NaIO_4$ in aq EtOH at room temperature for 48 hr. The amount of IO_4 used and formic acid produced estimated by standard procedures [6].

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