at *m/e* 59 due to the ion $(CH_3)_2C{=}OH^+$. There was no peak at *m/e* 223 as has been observed in the MS of mollugogenol A.

The methylated aglycone on Jones oxidation yielded a product which gave positive Zimmerman's colour test for a 3-keto group [8] and showing that the saccharide side chain in the mollugocin A must be linked through the C-3 hydroxyl. Acid hydrolysis of the permethylated product gave 2,3,6-tri-*O*-methyl-D-glucose, 2,3,5-tri-*O*-methyl-L-arabinose and 2,3-di-*O*-methyl-L-arabinose respectively (PC and *p*-nitrobenzoates [9–12].

Identification of the methylated sugars not only suggested the pyranose ring form for D-glucose and furanose ring form for the end L-arabinose respectively, but also the straight chain nature of the saccharide unit. Enzymatic hydrolysis with β-glucosidase confirmed the β-linkage of D-glucose with the aglycone. The central can be either in the pyranose or furanose form but the ease of acid hydrolysis strongly suggests [13] the furanose ring form and α-L-glycosidic linkage between the two arabinose units and between arabinose and glucose units. It is a general observation that D-sugars occur with β-glycosidic and L-sugars with α-glycosidic linkage [14].

On the basis of the data discussed above, the structure of mollugocin A can be represented as (**1**).

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PRENYLATED FLAVANONES FROM *MILLETIA OVALIFOLIA* SEEDS

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Key Word Index—*Milletia ovalifolia*; Leguminosae; Lanceolatin-B; karanjin; kanjone; pongaglabrone; β-sitosterol and two new prenylated flavanones.

Plant. Milletia ovalifolia (Leguminosae). *Past work*—on leaves and bark [1], on related species [2,3]. Present work on seeds obtained from L.R. Brothers, Saharanpur, India. Air-dried seeds were powdered and Soxhlet extracted with light petrol (bp 60–80°). Solvent was removed and the residue extracted with EtOH. The extract was concentrated and partitioned between *n*-hexane and acetonitrile. The acetonitrile fraction was column chromatographed on silica gel using petrol with increasing amounts of benzene as the eluent. Besides the already known compounds lanceolatin-B [4], karanjin [5], kanjone [5], pongaglabrone [6] and sitosterol, two new prenylated flavanones (A and B) were isolated.

Flavanone *A* crystallised from EtOAc–petrol as white needles mp 135–136°, mol. formula $C_{25}H_{28}O_3$ (M^+ 376). It was soluble in aq. alkali and gave no colour with $FeCl_3$. λ_{max}^{MeOH} 280 nm. ν_{max}^{KBr} 3350, 1660, 1450, 1070, 765 cm^{-1}. NMR (δ values; solvent $CDCl_3$): showed one –OH group at 6.29 (*s*, 1H) (+ D_2O exchanged); two isolated aromatic proton peaks at 7.69 (*s*, 1H) (H-5) and 7.50 (*s*, 5H) (C_6H_5); three aliphatic protons at 5.45 (*m*, H-2 proton overlapping two =C<u>H</u>–CH_2–protons); Four protons at 3.40 (*m*, two $(Me)_2C{=}CH{-}C\underline{H}_2$–units) two protons at 2.97 (*m*, H-3 proton) and a sharp doublet at 1.8 (*Jδ*, = 2Hz, 12H) δ, two $(\underline{Me})_2C{=}CH$– units). δ, These data are in agreement with the structure of 7-hydroxy-6,8-di-*C*-prenylflavanone for *A*. This was confirmed by the fact that the IR spectrum of *A* (in $CHCl_3$) was identical with that of a synthetic sample prepared from 3,5-di-*C*-prenyl resacetophenone [7] by treatment with benzaldehyde under basic conditions. The mixture of chalkone [8] and the corresponding 7-hydroxy-6,8-di-*C*-prenylflavanone was separated by TLC on silica gel.

Flavanone *B*, mp 144–45°, mol. formula $C_{20}H_{20}O_3$ (M^+ 308). It was soluble in aq. alkali and gave no colour with $FeCl_3$. λ_{max}^{MeOH} 285 nm. ν_{max}^{KBr} 3125, 1650, 1570, 1430, 1040, 815 cm^{-1}. NMR (δ values; solvent $CDCl_3$): showed one –OH group at 7.15 (*s*, 1H) (+D_2O exchanged); two isolated aromatic protons at 7.75 (*d*, *J* = 10 Hz, 1H) (H-5) and 6.55 (*d*, *J* = 9 Hz, 1H) (H-6); sharp peak at 7.45 (*s*, 5H) (C_6H_5); aliphatic proton peak at 5.34 (*m*, 2H) (H-2 proton overlapping $(Me)_2C{=}C\underline{H}{-}CH_2$–proton); doublet at 3.18 (2H, *J* = 8 Hz) $(Me)_2C{=}CH{-}C\underline{H}_2$–protons); peak at 2.65 (2H, *m*) (two H-3 protons) and one sharp singlet at 1.35(6H) $(C\underline{H}_3)_2$ C=CH–CH_2–protons). It is concluded that *B* is 7-hydroxy-8-*C*-prenyl flavanone This was confirmed by comparing the IR spectrum of *B* (in $CHCl_3$) which was

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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