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3,3′-DI-*O*-METHYLELLAGIC ACID 4-*O*-RHAMNOSIDE FROM THE ROOTS OF *PROSOPIS JULIFLORA*

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Key Word Index—*Prosopis juliflora*; Leguminosae; 3,3′-di-*O*-methylellagic acid 4-*O*-α-L-rhamnopyranoside; procyanidin.

Abstract—From the roots of *Prosopis juliflora* a new glycoside, 3,3′-di-*O*-methylellagic acid 4-*O*-α-L-rhamnopyranoside, and procyanidin have been characterized.

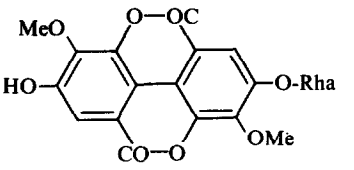
In a previous communication [1] we reported ellagic acid 4-*O*-α-L-rhamnosylgentiobioside from the pods of *Prosopis juliflora* DC. We now report the isolation and characterization of a new glycoside, 3,3′-di-*O*-methylellagic acid 4-*O*-α-L-rhamnopyranoside (**1**). Procyanidin was also isolated and identified by standard procedures [2].

1 was shown to be a non-reducing glycoside by a positive Molisch test and a negative aniline hydrogen phthalate test. A yellow colour with alkali and other diagnostic reactions [3], together with ν_{max}^{KBr} cm^{-1} at 1730 for α,β-unsaturated lactone suggested it was an ellagic acid derivative. IR peaks at 3440 (–OH) and 1170 (–OMe)cm^{-1} indicated that it could be a partial methyl ether of ellagic acid. This was further substantiated by its UV, λ_{max}^{EtOH} at 271 nm; 3,3′-di-*O*-methyl ellagic acid has λ_{max} 275 nm [4].

On acid hydrolysis the glycoside gave an aglycone and rhamnose, identified by paper co-chromatography and preparation of its osazone. The aglycone, $C_{16}H_{10}O_8$, mp 273°, λ_{max}^{EtOH} 275 nm, analysed for two methoxyl groups. A bathochromic shift of 33 nm with sodium ethylate suggested the presence of at least one free phenolic hydroxyl either at the 3,3′- or the 4,4′-positions of the ellagic acid molecule. The absence of a bathochromic shift with sodium acetate indicated that positions 3,3′ are substituted with two methoxyl groups [5]. The aglycone was therefore identified as 3,3′-di-*O*-methylellagic acid.

The glycoside **1** was methylated with diazomethane and the methyl ether on acid hydrolysis yielded an aglycone identified as 3,3′-4-tri-*O*-methylellagic acid by its mp 289° (lit. 288–289°) and its monoacetate mp 262° (lit. 264°) [6, 7]. Therefore, the remaining hydroxyl at position 4 must be linked to the sugar.

Quantitative sugar estimation suggested the glycoside to be a monosaccharide. Consumption of 2 mol of periodate by the glycoside methyl ether and consequent liberation of 1 mol of formic acid confirmed the pyranose form of the sugar. The hydrolysis of the glycosides with takadiastase confirmed the α-nature of the glycosidic linkage. This led to the formulation of the compound as 3,3′-di-*O*-methylellagic acid 4-*O*-α-L-rhamnopyranoside (**1**). This is the first report of **1** in nature, although its 4-*O*-glucoside has been reported earlier [4].



1

EXPERIMENTAL

Plant material. Plant material was collected locally and identified by the Allahabad branch of the Botanical Survey of India.

Chromatography. R_f values are for ascending PC except for the sugar, the solvents being (a) *n*-BuOH–HOAc–H_2O (4:1:5); (b) 2% HOAc and (c) 10% HOAc using Whatman No. 1 chromatostrips.

Extraction. Air-dried and powdered roots (3 kg) were exhaustively extracted by reflux with Me_2CO (5 × 4 l.) The combined concd Me_2CO extracts (150 ml) were successively extracted with hexane, C_6H_6 and EtOAc and the remaining mother liquor macerated with Me_2CO. The first two fractions were rich in steroids and fatty constituents and were rejected. The EtOAc-soluble fraction was charged on a column of Si gel to give pure procyanidin. The Me_2CO-soluble fraction was purified to yield chromatographically homogeneous **1**.

3,3′-Di-O-methylellagic acid 4-O-α-L-*rhamnopyranoside* (**1**). Mp 186° (d), R_f 0.19 and 0.45 in solvents (a) and (c) (spray: $FeCl_3$). Found: C, 54.99; H, 4.1; –OMe, 13.00; calc. for $C_{22}H_{20}O_{12}$: C, 55.47; H, 4.20, –OMe, 13.02%. UV λ_{max}^{EtOH} nm: 271, +NaOEt: 304 IR; ν_{max}^{KBr} cm^{-1}: 3440 (–OH), 1730 (α,β-unsaturated lactone), 1180 (–OMe), 1625, 1560, 1535, 1470, 1450, 1360, 1340, 1200, 1020 and 940.

Acid hydrolysis. **1** (0.02 g) was refluxed with aq. H_2SO_4 (7%, 3 ml) for 2.5 hr, the soln cooled and extracted with Et_2O. The Et_2O extract was evapd and the residue crystallized from dry Me_2CO–Et_2O as pale yellow crystals, mp 272° (lit. 274°). Found: C, 57.98; H, 3.3; –OMe, 18.11; calc. for $C_{16}H_{10}O_8$: C, 58.18, H, 3.33; –OMe, 18.78%. UV λ_{max}^{EtOH} nm: 275. The remaining H_2O layer was neutralized with $BaCO_3$, concd and chromatographed (PC), R_f 0.37 (solvent (a); spray: aniline hydrogen phthalate); phenylosazone, mp 190° (lit. 190°).

Quantitative acid hydrolysis. **1** (0.1 g) was refluxed with aq. H_2SO_4 (7%, 3 ml) for 2.5 hr. The soln was extracted with Et_2O containing traces of C_5H_5N, dried, concd and the solid isolated and weighed. The neutralized H_2O layer ($BaCO_3$) was made up to 25 ml and the sugar estimated by the colorimetric method of Folin and Wu. Found: dimethyl ether of ellagic acid, 68.10; reducing sugar, 33.91; calc. for $C_{22}H_{20}O_{12}$, dimethyl ellagic acid, 68.2 and reducing sugar, 37.8%.

Methylation and hydrolysis. **1** (0.1 g) was methylated with CH_2N_2 by standard procedures and the methylated glycoside (0.05 g) refluxed with aq. H_2SO_4 (7%, 3 ml) to give a yellow ppt. which crystallized from Me_2CO–Et_2O as yellow prisms. Found: –OMe, 26.8; calc. for $C_{17}H_{12}O_8$: –OMe, 27.1%.

Methyl ether acetate. To the methylated aglycone obtained above, Ac_2O (2 ml) and C_5H_5N (0.3 ml) were added and kept at 20° for 48 hr. The methyl ether acetate was obtained as pale yellow crystals from dioxan–petrol.

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A NOVEL TYPE OF BICOUMARIN RHAMNOSIDE FROM *LASIOSIPHON ERIOCEPHALUS**

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Key Word Index—*Lasiosiphon eriocephalus*; Thymelaeaceae; furanobicoumarin rhamnoside; eriocephaloside; ^{13}C NMR.

Abstract—A new furanobicoumarin rhamnoside has been characterized from the whole plant extract of *Lasiosiphon eriocephalus*.

In a previous paper [1] the characterization of erioside, a new 6,8-dihydroxy-7-glucosyloxy-coumarin from the ethyl acetate-soluble fraction of an ethanolic extract of *Lasiosiphon eriocephalus* was described. Examination of another eluate from the chromatography of this fraction resulted in the isolation of a new bicoumarin glycoside, which we have named eriocephaloside (**1**).

Eriocephaloside (**1**), $C_{24}H_{18}O_{10}$, developed an intense yellow colour with alkali, fluoresced white in UV radiation and gave a positive Fiegel test which indicated it was a coumarin glycoside (IR: 3400 and 1750 cm^{-1}). On acid hydrolysis, it yielded rhamnose and an aglycone which was insoluble in common organic solvents. The aglycone yielded a monoacetate, $C_{20}H_{10}O_7$, the IR spectrum of which contained a strong absorption band at 1775 cm^{-1} (Ar–OAc), which indicated that the site for *O*-glycosidation was the phenolic hydroxyl group. Its MS had M^+ at *m/z* 362 and this readily lost $-COCH_2$ from the phenolic acetoxy function to generate a fragment ion *m/z* 320 (**2**) which lost CO (twice) to give ions **3** and **4**. The fragmentation pattern was consistent with the presence of two coumarin units in the molecule.

1 was converted into a triacetate, $C_{30}H_{24}O_{13}$. In its high resolution MS printout most of the very weak peaks at *m/z* above 320 either did not register or did not compute in a way that made much sense but the lower peaks (see below) corroborated the deductions made in the preceding paragraph. The ^1H NMR spectrum of the acetate contained signals for three alcoholic acetoxy methyls at δ 2.08 (6 H) and 2.24 (3 H) and hence indicated the absence of a free phenolic OH group in the molecule. It also contained a three-proton doublet (J = 6 Hz) at δ 1.25 due to a rhamnosyl methyl, a multiplet at 3.96 due to H-

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