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.

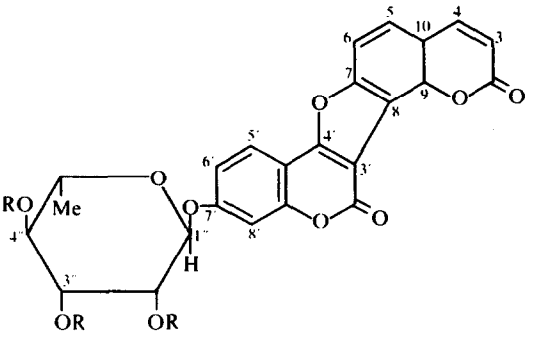
Abstract—A new furanobicoumarin rhamnoside has been characterized from the whole plant extract of *Lasiosiphon eriocephalus*.

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-

*CDRI communication No. 2801.



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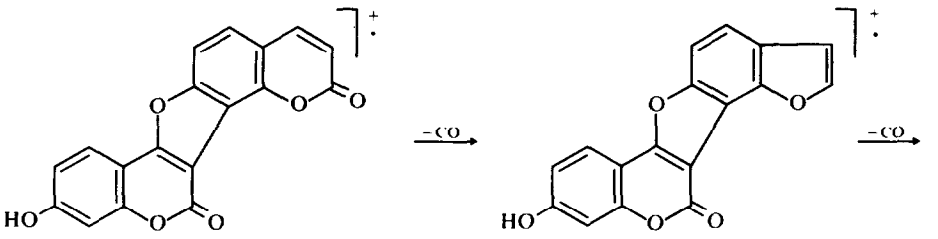

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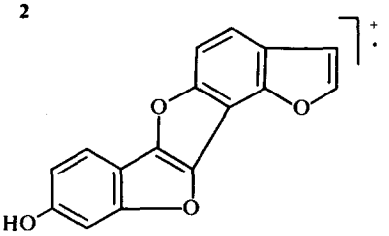

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Table 1. ^{13}C NMR spectral data of triacetate of **1** ($CDCl_3$, TMS as internal standard)

Carbon	Chemical shift	$^1J_{CH}$ (Hz)	Carbon	Chemical shift	$^1J_{CH}$ (Hz)
C-2	159.1 *s* (*br*)*	—	C-2′	159.1 *s* (*br*)	—
C-3	115.7 *d*	172.34	C-3′	103.3 *s*	—
C-4	143.3 *d*	163.57	C-4′	160.6 *s* (*br*)	—
C-5	123.1 *d*	166.02	C-5′	126.3 *d*	164.79
C-6	108.6 *d*	169.68	C-6′	114.2 *d*	166.02
C-7	156.9 *s* (*br*)	—	C-7′	159.4 *s* (*br*)*	—
C-8	115.7 *m*	—	C-8′	104.3 *d*	166.63
C-9	148.3 *s* (*br*)	—	C-9′	155.4 *s* (*br*)	—
C-10	115.7 *m*	–	C-10′	106.6 *s* (*br*)	—
			C-1″	95.8 *d*	174.56
			C-2″, 3″, 4″ and 5″	67.8, 68.6, 69.2 and 70.5	
			Me (rham.)	17.5	
			Me (acetyl)	20.8, 20.8, 21.0	
			MeCO (carbonyl)	169.7, 169.9, 169.9	

* These assignments could be reversed.

5″, a four-proton multiplet at 5.10–5.57 due to H-1″ to H-4″ along with signals due to five aromatic and two olefinic protons (H-3 and H-4 of a coumarin nucleus, which was also confirmed by D NMR), a two-proton singlet at δ 7.55 due to the equivalence of the H-5 and H-6 protons and a pair of two doublets (J = 9.5 Hz) at δ 6.48 and 7.92 (each 1 H) corresponding to H-3 and H-4 respectively. By analogy with the angular furanocoumarins [2], these results indicated that the substitution pattern of one of the coumarin units was C-7,8. Further, the additional aromatic proton signals which were obtained as a one-proton doublet (J = 8 Hz) at δ 7.81 and a two-proton multiplet centred at 7.18 were assigned to H-5′ and H-6′, H-8′ respectively of the second coumarin unit. On the basis of the above data, **1** was assigned the structure of a rhamnoside of a furanobicoumarin formed by condensation of C-7 to C-4′ through C–O–C and C-8 to C-3′ through C–C linkages to form a furan ring system.

The proposed structure for eriocephaloside (**1**) was fully supported by the ^{13}C NMR spectrum of its triacetate which exhibited 24 signals for 30 carbon atoms (Table 1). The most upfield signal at δ 17.5 was due to rhamnosyl methyl while signals at 20.8 and 21.0 were due to three acetoxy methyls. The chemical shifts of four methines of rhamnose were assigned to the signals at δ 67.8, 68.6, 69.2 and 70.5 and the acetoxy carbonyls to those at 169.7, 169.9 and 169.9. The anomeric carbon C-1″ appeared as a doublet at δ 95.8 ($^1J_{CH}$ = 174.56 Hz) which suggested that it had an α-anomeric configuration [3]. Inspection of the relative peak heights in proton noise-decoupled spectrum led to the recognition of non-hydrogen carrying carbon atoms. Such peaks were small because of reduced nuclear Overhauser enhancement of intensity and thus could readily be assigned to individual quaternary carbon atoms. The signal at δ 115.7 was composed of three superimposed resonances (for C-3, C-8 and C-10) and a partial separation of coupled signal was observed in off-resonance decoupled spectrum as $^1J_{C_3H_3}$ = 172 Hz [4], while C-8 and C-10 both resonated at δ 115.7 as a broad singlet which may be attributed to accidental coincidence. C-4 was assigned the chemical shift value of δ 143.3 ($^1J_{C_4H_4}$ = 163.57 Hz). Although in the ^{1}H NMR spectrum H-5 and H-6 appeared as a singlet, in the ^{13}C NMR spectrum the C-5 and C-6 resonances were 14.5 ppm apart and C-6, being *ortho* to a phenolic group, was assigned the higher field value (δ 108.6) than the C-5 signal (δ 123.1) [2]. As C-7 and C-9 are directly linked with oxygen, the two signals at lower field must correspond to C-7 and C-9 (δ 156.9 and 148.3). The signal at δ 103.3 was assigned to C-3′ (aryl-substituted carbon atom) which suffered shielding of *ca* 24 ppm on hydroxylation of C-4′ and deshielding of *ca* 10.6 ppm on substitution by an aryl group [5] while C-4′ resonated at δ 160.6. The signal at δ 126.3 was ascribed to C-5′ which appeared as a doublet ($^1J_{C_5H_5}$ = 164.79 Hz) in proton-coupled spectrum due to shielding by *ca* 4 ppm on account of oxygenation of C-4′ and deshielding by *ca* 1.45 ppm by hydroxylation at the C-7′ position. The C-6′ and C-8′ were assigned to δ 114.2 and 104.3 respectively, because being *ortho* to a phenolic group, both resonances showed an upfield shift of 10.7 and 13.4 ppm from the normal chemical shifts reported for these carbons in the case of coumarins [4]. The C-9′ which is directly linked with oxygen, was deshielded by 2.3 ppm as a result of hydroxylation at C-7′ and, thus, resonated at δ 155.4 as a broad singlet. The signal at δ 106.6 was assigned to C-10′ because of the shielding effects of C-7′ and C-4′ hydroxylation which are reported to be of the order of 7 and 2.4 ppm respectively. Both the carbonyl carbons C-2,2′ appeared at δ 159.1 as a broad singlet while C-7′ appeared at δ 159.4 as a broad singlet. Therefore, the structure of eriocephaloside was elucidated as **1**.

Bicoumarins are a rather rare group of coumarins and so far only eleven simple bicoumarins are known [6, 7]. In these, the two coumarin units are condensed through a C–C or an ether bond and one of these, lasiocephalin [8], has been obtained from this taxon. The present findings are significant in as much as this is the first report of a bicoumarin glycoside found in nature. Further, eriocephaloside may be considered as the second member of a new group of furanobicoumarins; the first member, lasioerin [9], was also isolated recently from this taxon.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded in $CDCl_3$, unless stated otherwise, with TMS as internal standard. R_f values are for Si gel plates: $CeSO_4$ as spray reagent.

The EtOAc-soluble fraction of the ethanolic extract of the plant [1] was chromatographed on Si gel (1.5 kg) and forty fractions were collected using $CHCl_3$–MeOH–H_2O (35:9:2). The residue from eluates 5–7 (0.410 g) crystallized from MeOH as colourless needles (eriocephaloside (**1**), 0.15 g), mp 350° dec., R_f 0.6 ($CHCl_3$–MeOH–H_2O, 35:9:2). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2950, 1750 (lactone carbonyl), 1640 (conjugated carbonyl), 1518, 1495 (Ar), 1438, 1420, 1338, 1280, 1260 (Ar-ether), 1238, 1182, 1124, 1022, 982, 844, 770; ^{1}H NMR (DMSO-d_6): δ 1.14 (3 H, d, J = 6 Hz, rham.–Me), 3.28–3.86 (5 H, m, rham.–H), 6.32 (1 H, d, J = 9.5 Hz, H-3), 7.00 (2 H, m, H-6′ and H-8′), 7.6 (2 H, s, H-5 and H-6), 7.74 (1 H, d, J = 8 Hz, H-5′), 7.95 (1 H, d, J = 9.5 Hz, H-4).

1 (Ac_2O/C_5H_5N overnight at room temp.) gave a peracetate as colourless needles, mp 240° (MeOH), R_f 0.7 ($CHCl_3$–MeOH, 99:1). ^{1}H NMR δ 1.25 (3 H, d, J = 6 Hz, rham.–Me), 2.08 (6 H, s, 2 × OCOMe), 2.24 (3 H, s, OCOMe), 3.96 (1 H, m, J = 6, 8 Hz, H-5″), 5.10–5.57 (4 H, m, H-1″, H-2″, H-3″ and H-4″), 6.48 (1 H, d, J = 9.5 Hz, H-3), 7.09–7.28 (2 H, m, H-6′ and H-8′), 7.55 (2 H, s, H-5 and H-6), 7.81 (1 H, d, J = 8 Hz, H-5′), 7.92 (1 H, d, J = 9.5 Hz, H-4); MS m/z (rel. int.): 542 (0.1), 403 (0.4), 362 (1.4), 349 (1.5), 322 (3.4), 320 (29.2), 292 (14.6), 273.0978 (53.5, $C_{12}H_{17}O_7$), 264.0464 (2.9, $C_{16}H_8O_4$), 236 (13.3), 213 (21.0), 208.0553 (1.1, $C_{14}H_8O_2$), 179 (1.5), 171.0669 (25.5, $C_8H_{11}O_4$), 153.0549 (100, $C_8H_9O_3$), 151 (1.7), 129 (9.6), 127 (8.1), 115 (2.8).

1 (60 mg) was refluxed in 2N aq. EtOH–HCl (4 ml) for 1 hr. The solution was concd *in vacuo*, diluted with H_2O, and the pptd aglycone filtered off. Co-PC of the aq. phase (BuOH–C_5H_5N–H_2O, 6:4:3/aniline phthalate) showed the presence of one spot which corresponded to rhamnose. The aglycone was obtained as a colourless powder, mp 350°. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1730 (lactone carbonyl), 1638, 1570 (Ar), 1418, 1320, 1238, 1180, 1124, 1058, 1000, 848, 764. On treatment with Ac_2O/C_5H_5N overnight at room temp., it yielded a monoacetate. IR ν_{max}^{KBr} cm^{-1}: 1775, 1740; MS m/z: 362 (M^+), 320, 292, 264, 236, 208, 152, 132.

Acknowledgements—We thank Prof. W. Herz, Tallahassee, U.S.A. and Dr. B.-G. Osterdahl, Uppsala, Sweden, for recording high resolution MS and ^{13}C NMR spectra; Messrs. E. Samson, Pati Ram and R. K. Singh for ^{1}H NMR, IR and MS spectra, respectively; and Mr. S. P. S. Bhandari for technical assistance.

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CRYSTAL STRUCTURE OF A LIGNAN FROM *JATROPHA GOSSYPIFOLIA*

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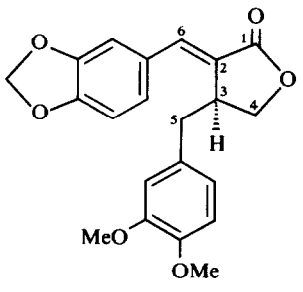
Key Word Index—*Jatropha gossypifolia*; Euphorbiaceae; 2-piperonylidene-3-verytryl-3*R*-γ-butyrolactone; X-ray analysis.

From the petrol extract of *Jatropha gossypifolia* (stem, roots and seeds) we have isolated a new lignan (**1**), $C_{21}H_{20}O_6$ (M^+ 368.126), mp 129° (C_6H_6), $[\alpha]_D^{25°}$ +87° ($CHCl_3$). The structure of this compound has been unambiguously settled from its X-ray crystallographic analysis.

The functionality of this lignan was revealed by its spectroscopic properties. The IR spectrum showed characteristic peaks for an α,β-unsaturated γ-lactone (1725 cm^{-1}), an olefinic double bond (1630 cm^{-1}), an aromatic nucleus (1595 and 1480 cm^{-1}) and a methylenedioxy group (910 cm^{-1}). The UV absorption of **1** (λ_{max}^{EtOH}: 333, 297, 288 and 223 nm; log ε 4.21, 3.98, 3.99 and 4.19) was closely similar to that of the lignan (−)-hibalactone (**2**), previously isolated from *Juniperus sabina* (Cupressaceae) [1], thereby indicating the presence of a dibenzylbutyrolactone skeleton with a double bond at the 2,6-position of the γ-butyrolactone ring. Several structural features of **1** could be ascertained from its 80 MHz ^1H NMR spectrum ($CDCl_3$). The spectrum revealed the presence of two OMe groups (δ 3.88, 3 H, *s* and 3.85, 3 H, *s*), one methylenedioxy group (6.04, 2 H, *s*), six aromatic protons (7.1–6.8, *m*) and one olefinic proton at C-6 (7.5, *s*). The other signals appeared at δ 4.27 (2 H at C-4, *d*, J = 4.1 Hz), 3.9–3.5 (1 H at C-3, *m*), 3.03 (1 H at C-5, *d*, J = 4 Hz) and 2.64 (1 H at C-5, *d*, J = 9.2 Hz). The compound was cleaved under electron impact and the fragmentation pattern revealed several details about the molecule. The characteristic ion peaks appeared at *m/z* 368, 217, 152, 151 (base peak), 135 and 28. The peaks at *m/z* 217 and 151 resulted from the benzylic cleavage at the 3–5 position. All the spectroscopic data suggested that the structure of the new lignan is **1**.

The structure of **1** was further corroborated from its



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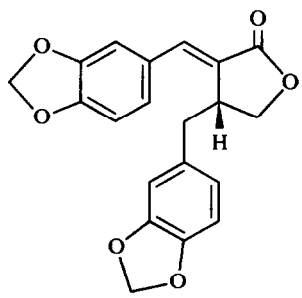

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