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A NEW TRITERPENOID GLYCOSIDE FROM THE SEEDS OF *GLINUS LOTOIDES*

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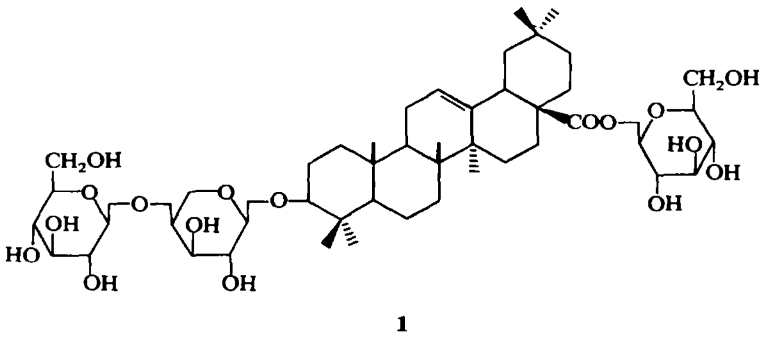
Key Word Index—*Glinus lotoides*; Aizoaceae; triterpene glycoside; oleanolic acid; anthelmintic.

It was reported recently that the anthelmintic property of the seeds of *Glinus lotoides* is due to saponins [1, 2]. The isolation of several sapogenins and a saponin from *Mollugo hirta* (which is synonymous with *G. lotoides*) has also been reported [3]. In this communication we report on the structure of a new triterpene glycoside isolated from the seeds.

The powdered seeds (100 g) were defatted and extracted with 80% aqueous ethanol. Addition of diethylether gave a precipitate (6 g) which was acetylated with acetic anhydride and pyridine. The crude acetylated product (5 g) was chromatographed using 300 g Si gel 60 and eluted with chloroform containing increasing amounts of ethyl acetate (300 ml fractions). Fractions 32–46 (eluted with 30% ethyl acetate) gave 2.0 g of a compound which was homogeneous on TLC. Repeated recrystallization from methanol gave a crystalline substance $C_{67}H_{96}O_{27}$, mp. 186–189°, $[\alpha]_D^{21}$ + 37° (MeOH; *c* 1.5). Deacetylation with methanolic ammonia [4] gave a biologically active saponin (**1**) which could be reacetylated to the same compound obtained from the column.

Deacetylation gave a saponin, which upon recrystallization from methanol gave plates $C_{47}H_{76}O_{17}$, mp 255° (dec.), $[\alpha]_D^{21}$ + 20° (MeOH; *c* 0.8). Acid hydrolysis of the saponin with 8% methanolic HCl yielded oleanolic acid, D-glucose and L-arabinose. The glucose–arabinose ratio was found to be 2:1 by GLC



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analysis of their permethylated derivatives [5]. Exhaustive methylation of the saponin by Hakomori's method [6] gave the deca-*O*-methylate which showed ^{1}H NMR signals for ten *O*-methyls (δ3.23–3.94), three anomeric protons (4.20, 1H, $J = 5$ Hz; 4.40, 1H, $J = 6$ Hz; 4.47, 1H, $J = 6$ Hz) and an olefinic proton (5.43, 1H). Hydrolysis of the permethylated saponin gave oleanolic acid, as the aglycone portion, and not the methyl ester suggesting an attachment of a sugar unit at the carboxyl end in the original saponin. GLC analysis of the sugar portion indicated the presence of two sugars in the ratio of 2:1 which were identified as 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3-di-*O*-methyl-L-arabinose (PC and co-PC in three solvent systems and comparison of R_g values) [7, 8]. Partial hydrolysis of the saponin with 5 N NH_4OH for 1 hr [9] and examination of the sugar portion showed the presence of glucose only.

From the above results it was concluded that a disaccharide, 4-(D-glucopyranosyl)-L-arabinose, was attached via the anomeric hydroxyl of arabinose to the C-3 of the aglycone and also that a molecule of glucose was involved in an ester linkage with the -COOH of oleanolic acid. The observation that the saponin was non-reducing and that hydrolysis of the permethylated saponin gave 2 mol of identically methylated glucose molecules confirmed the involvement of the anomeric hydroxyl of glucose in the ester link with the -COOH group.

Information concerning the pyranose form of the sugars and the configuration of the glycosidic linkages was obtained from the coupling constants of the anomeric protons [10] in the ^{1}H NMR spectrum of the permethylated saponin. This was further supported by molecular rotation measurements [9, 11, 12]. The molecular rotation of the saponin $[M]_D$ was observed to be 182.4° showing a difference of 37° from the calculated value of 219.3°. The structure of the saponin was, thus determined to be 3-*O*-[β-D-glucopyranosyl-(1 → 4]-α-L-arabinopyranosyl]-oleanolic acid-(28 → 1)-β-D-glucopyranosyl ester **1**.

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ERIOSIDE, A NEW COUMARIN GLUCOSIDE FROM *LASIOSIPHON ERIOCEPHALUS**

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Key Word Index—*Lasiosiphon eriocephalus*; Thymelaeaceae; 6,8-dihydroxy-7-*O*-β-D-glucosyloxycoumarin.

Lasiosiphon eriocephalus Decen. (Thymelaeaceae) is a small tree or branched bush commonly distributed throughout the Western Ghats and Niligiri [1, 2]. The genus comprises of *ca* 25 species, all endemic to tropical Africa; *L. eriocephalus* is the only species found in India. The genus is reputed for its medicinal and toxic properties [3]. The glycosidic extract of *L. kraussianus* is useful as an antileprosy medicament [4, 5]. Mezerein, a phorbol diterpene ester isolated from *L. bruchelli* [6], has been shown to possess antileukemic activity. The Thymelaeaceae has been found to be rich in bicoumarins and two members of this group, lasiocephalin [7] and lasioerin [8], have been isolated from *L. eriocephalus*. The present studies did not reveal any constituent belonging to the phorbol diterpene ester group in this plant but yielded a

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