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TRITERPENOIDS FROM *RANDIA DUMETORUM*

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Abstract—A new triterpene having an oleanane skeleton was isolated from the root bark of *Randia dumetorum*. Its structure was established by chemical and spectroscopic data as 1-keto-3α-hydroxy oleanane. In addition, three known triterpenes, α- and β-amyrin and oleanolic acid were isolated, besides β-sitosterol.

INTRODUCTION

Randia dumetorum Lamk. [1], known in Telugu as Manga, is a large shrub found in the dry ever-green forests of India. The root bark and the fruits are good detergents. The fruit is an effective fish poision.

The fruits and other parts of the plant contain oleanolic acid saponins besides other known compounds [2–4]. Another saponin, D_1 randinin [5] was reported from the fruits, the carbohydrate moiety being L-fucose, D-glucose and D-glucuronic acid in the ratio, 1 : 3 : 3. The presence of D-mannitol [6] was also reported from the root bark. The bark also gave two new ursolic acids [7], Randialic acid A and Randialic acid B. Pomolic acid, isolated from apple peel [8] and *Micromeria benthami* [9], was assigned the structure of randialic acid A, the two acids differing only in their physical constants. In our Laboratories [10], the presence of D-mannitol, oleanolic acid saponins and two minor crystalline constituents were reported from the methanolic extract of the root bark, besides the presence of β-sitosterol, stigmasteryl glucoside and two oleanolic acid saponins in the fruits.

To characterize the minor crystalline constituents, the plant was reinvestigated and was shown to contain β-sitosterol, α-amyrin, β-amyrin, oleanolic acid and a new triterpene identified as 1-keto-3α-hydroxy oleanane (**1**).

RESULTS AND DISCUSSION

The root bark powder was thoroughly extracted with methanol. The methanol extract on concentration afforded a brown crystalline mass, which on purification gave colourless crystals of a compound, mp 120–121°, identified as D-mannitol by comparison with an authentic sample. The filtrate failed to yield any further solid, so it was adsorbed on spent powder and fractionated with hexane, chloroform and methanol. The hexane extract on column chromatography on silica gel gave three compounds, A–C. Compound A, colourless shining needless from methanol, mp 186–187°, $[\alpha]_D$ +90°, was identified as α-amyrin by comparison with an authentic sample [11] (mmp, coTLC and IR). Compound B, mp 198–199°, $[\alpha]_D$ +94°, was identified as β-amyrin [11] by comparison with an authentic sample. Compound C gave positive Liebermann–Burchard test and was identified as β-sitosterol, mp 136–137°, $[\alpha]_D$ −35°, by comparison with an authentic sample.

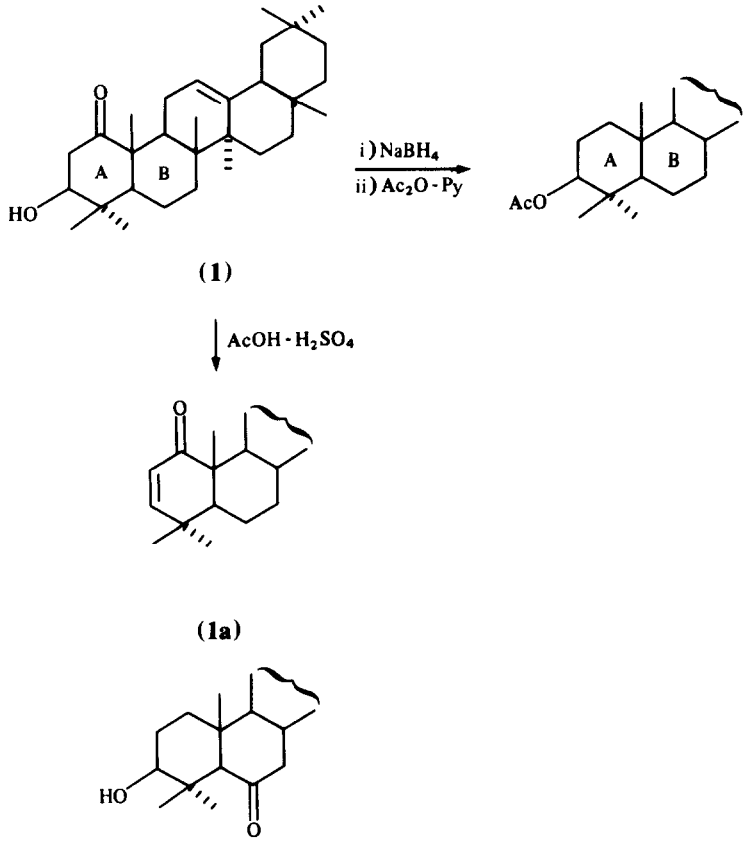
The chloroform extract contained two compounds, D and E (TLC, benzene–acetone, 4:1, compound D, R_f 0.76, pink and E, R_f 0.61, violet). The major compound (E), colourless needles from methanol, mp 300–302° $[\alpha]_D$ +78°, formed an insoluble sodium salt. It was identified as oleanolic acid by direct comparison with an authentic sample [11], and by derivatization. Compound D (**1**), colourless needles from methanol, mp 268–270° $[\alpha]_D$ +68°. IR ν_{max}^{KBr} cm^{-1}: 1710 (–C=O), 3450 (–OH), 1660 and 830 (–C=CH); ^1H NMR $CDCl_3$ (TMS): δ 0.75–1.15 (*s*, 8 tertiary methyls), 5.3 (*m*, olefinic proton) 2.8 (*m*, α-methylene to carbonyl), 3.6 (*b*, α-hydroxyl proton); MS *m/z* (rel. int.): 440 $[M]^+$ (15) 221 (10) 218 (35), 203 (52) 189 (55), 188 (30), 175 (26), 166 (21).

The above data suggested that compound D was a new triterpene with a hydroxyl and a carbonyl function. Compound D underwent facile acetylation with pyridine and acetic anhydride to give a monoacetate mp 220–222° $[\alpha]_D$ +54° IR ν_{max}^{KBr} cm^{-1}: 1710, 1740, 1660 and 830; ^1H NMR $CDCl_3$ (TMS): δ 0.75–1.15 (*s*), 8 tertiary methyls), 2.1 (*s*), –COMe), 4.63 (*t*, geminal β-proton to the acetoxyl), 2.8 (*m*, α-methylene protons to carbonyl), 5.3 (*m*, olefinic proton).

These results clearly indicated compound D to be a monoketo alcohol. The NMR and MS data established that compound D had a β-amyrin skeleton. This was confirmed by reduction of compound D with $NaBH_4$ under basic conditions, and the subsequent characterization of the acetate of the reduction product, mp 243°, $[\alpha]_D$ +91.6°, as β-amyrin acetate by comparison with an authentic sample [11], (mmp, coTLC and IR). The hydroxyl was fixed at C-3 as in β-amyrin on biogenetic grounds and the carbonyl was assumd to be either at C-1 or C-6, both cases yielding only β-amyrin on reduction. To fix the position of the carbonyl, compound D was dehydrated using acetic acid containing a drop of H_2SO_4. The dehydration product was obtained as a gum (UV 229 nm $\log \varepsilon$ 11450). The UV data showed the presence of an α,β-unsaturated ketone system in the reduction product. This was further confirmed by the ^1H NMR spectrum of the reduction product in $CDCl_3$ (TMS), the two olefinic protons appearing at δ 5.85 (*d*, 1H) and 6.49 (*d*, 1H). This is only possible if the carbonyl is located at C-1 in compound. D.

Thus compound D was confirmed as 1-keto-3α-hydroxy oleanane (**1**).

The methanol extract yielded a crude hygroscopic



mixture of saponins and its study was not pursued. As reported earlier [10], hydrolysis of the saponin mixture afforded oleanolic acid as the major sapogenin, and the sugars D-glucuronic acid, D-glucose, L-rhamnose, D-xylose and D-glucuronolactone. This is a first report of the presence of 1-keto-3α-hydroxy oleanane in this plant.

EXPERIMENTAL

The root bark powder (1 kg) was extracted repeatedly with MeOH (1.5 l). The MeOH extract on concentration and leaving overnight afforded D-mannitol (3.0 g). The residual viscous filtrate was adsorbed on spent powder and was fractionated with hexane (2.0 l), $CHCl_3$ (2.0 l) and MeoH (2.0 l). The crude hexane extract (15.0 g) was adsorbed on silica gel and subjected to CC using hexane, hexane–C_6H_6 mixtures and C_6H_6 as elutant, collecting 150 ml fractions. The first 15 fractions afforded compound A. Compound B was obtained from fractions 16–25 and compound C from fractions 30–35.

The $CHCl_3$ extract resisted crystallization and was adsorbed on silica gel and chromatographed using C_6H_6 as elutant, collecting 100 ml fractions each time. Compound D was obtained from the first seven fractions and compound E from fractions 15–25.

Compound D was crystallized (×2) from MeOH to give colourless shining needles, mp 268–270°: $[\alpha]_D$ + 68°. [C, 81.78; H, 10.86: $C_{30}H_{48}O_2$ requires C, 81.81; H, 10.9%.] Compound D (50 mg) was acetylated using pyridine (3.0 ml.) and Ac_2O (5.0 ml). The acetate was obtained as colourless needles from MeOH, mp 220–222°; $[\alpha]_D$ + 54°. [C, 79.60; H, 10.32: $C_{32}H_{50}O_3$ requires C, 79.67; H, 10.37%.]

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