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Note

Nonalkaloidal constituents of the seeds of *Gloriosa superba*†

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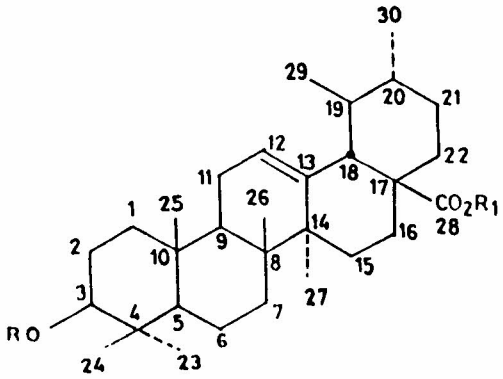
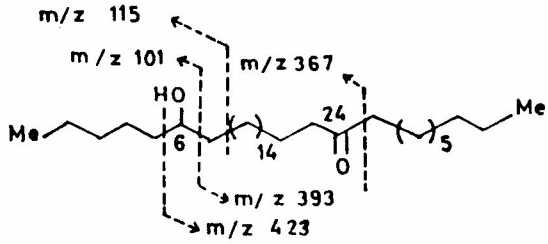
From the seeds of *Gloriosa superba* L. (Liliaceae), two new compounds ursolic acid- 3β-tetracosanoate **1** and 6-hydroxy-24-oxotritriacontane **2**, and the known compounds hentriacontane, nonacosane, palmitic acid, β-sitosterol, β-sitosterol-3β-D-glucoside, β-sitosterol-3β-D-palmitate and stearate, 1-*n*-butyl-β-D-fructopyranoside, luteolin, orcinol and 2-hydorxy-6-methoxybenzoic acid have been isolated and characterized by their spectral and chemical studies.

Gloriosa superba is used in the Ayurvedic system of medicine for a variety of medicinal purposes[1]. Though there are reports of thirty alkaloids from the tuber, bulb, corn, seeds and flowers of *G.superba*[2, 3], no work has been reported on the nonalkaloidal constituents of its seeds. In continuation of our work on phytochemical investigation of medicinal plants[3], the present investigation was carried out on the seeds of this plant leading to the isolation and characterization of known lipids, sterols, terpenoids, phenolics and two new compounds ursolic acid-3β-*O*-tetracosanoate **1** and 6-hydroxy-2-oxotritriacontane **2**. This is the first report of the isolation of nonalkaloidal compounds from the seeds of *G. superba*.

Compound **1**, isolated as an amorphous solid (m.p. 164°) from the hexane-EtOAc fraction, showed its M^+ peak at m/z 806 in its FAB-MS but, no M^+ ion in its EI-MS. Its IR spectrum indicated the presence of ester (1742 cm^{-1}, acid 1708 cm^{-1}) and double bond (1639 cm^{-1}) functions and a long chain moiety (720 cm^{-1}). It was found to be homogeneous on TLC and gave positive LB test



1 · R_1=H; R= $CH_3-(CH_2)_{22}-C-$ (O)
1a · R_1=R=H
1b $CH_3-(CH_2)_{22}-COOH$
1c R_1=Me ; R=H



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for triterpenoid. Its EI-MS exhibited significant peaks at m/z 248, 203 and 133 indicating the presence of a Δ^{12}-amyrin skeleton with a carboxyl group at C-17 position and no OH group on ring D/E[4]. Alkaline hydrolysis of **1** gave an alcohol **1a** (M^+ 456) and a long chain acid **1b** (M^+ 368). Compound **1a** gave positive L-B test and on methylation with diazomethane it furnished a monomethyl ester **1c** (M^+ 470). Hence, compound **1** is a long chain ester of a triterpenoid alcohol having a carboxylic group at C-17. The ^1H NMR of **1** (80 MHz. $CDCl_3$) showed a doublet at δ 2.21 (H-18, *J*=12.2 Hz) indicating the presence of Δ^{12}-ursane skeleton[5, 6]. It also showed the presence of eight methyl groups (δ 0.65-1.10, m), an equatorial C-3 acyloxy group (δ4.51 dd, *J*=3, 7 Hz) and an olefinic proton (δ 5.25, m). The methylene protons appeared in the region δ 1.25 - 1.45 and the signal

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at δ 2.30 (2H, m) was assigned to oxomethylene group of the ester side chain. Compound **1c** was found to be ursolic acid methyl ester by its spectral data and comparison with an authentic sample. Compound **1b** (M^+ 368) was found to be tetracosanoic acid from its spectral data (IR, ^1H NMR and MS). Hence, compound **1** was identified as ursolic acid -3β-*O*-tetracosanoate and this is the first report of its natural occurence.

Compound **2** was isolated from EtOAc-hexane (1:19) eluates as an amorphous solid, m.p. 72° (M^+ at m/z 494). Its IR spectrum showed bands at 3425, 1722, 730 and 725 cm^{-1} due to OH, CO functions and a long chain moiety. The ^1H NMR spectrum of **2** (80 MHz, $CDCl_3$) showed a carbinyl methine proton at δ 3.64 (1H, m, $W_{1/2}$= 14 Hz) and the oxomethylene protons at 2.25 (4H, m). It showed methine and methylene protons at δ 1.62 and 1.27 whereas methyl signals appeared at δ 0.90 (6H, br.t). In its EI-MS, the ion peaks at m/z 101(1.3%), 83(25%) and 393(1.2%) showed the presence of OH at C-6 and the peak at m/z 364 (16%) due to Mclafferty rearrangement involving the carbonyl group was indicative of an oxo group at C-24 position[7]. Thus, compound **2** was identified as 6-hydroxy-24-oxotritriacontane. Other compounds isolated were identified as the known hentriacontane, nonacosane, palmitic acid, stearic acid, β-sitosterol-3β-D-palmitate and stearate, β-sitosterol, β-sitosterol -3β-D-glucoside, 1-*n*-butyl-β-D-fructopyranoside, luteolin, orcinol and 2-hydroxy-6-methoxybenzoic acid from the comparison of their spectral (IR, ^1H NMR and MS) and physical data with those reported in literature[8-10]. Isolation of hentriacontane, nonacosane, palmiic acid, β-sitosterol-3β-D-palmitate and stearate, 1-*n*-butyl-1β-D-fructopyranoside, orcinol and 2-hydroxy-6-methoxybenzoic acid constitutes their first isolation from *G.superba*[2].

Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 1710 FT spectrophotometer, mass spectra on a Jeol D-300 spectrometer and ^1H NMR specta on a Varian FT 80A machine using $CDCl_3$ and DMSO-d_6 as solvents and TMS as internal standard. Column chromatography and TLC were carried out on silica gel (E. Merk, India) and the spots were exposed to I_2 vapour or to 50% H_2SO_4 at 120° for 5 min. for detection.

The seeds of *G. Superba* were collected from New Delhi market as a commercial material and identified by our Botany Division where a voucher specimen has been deposited.

Extraction and isolation. Extraction of the seeds of *G. Superba* L. (1 kg) has been described earlier[3]. Defatted hexane concentrate and acid insoluble material were chromatographed separately on silica gel (60-120 mesh) and 150 fractions of 250 mL each were collected using solvent and solvent mixtures of increasing polarity as eluants. Similar fractions were mixed together according to their TLC behaviour.

Ursolic acid-3β-tetracosanaote 1. EtOAc-hexane fractions on column chromatography and preparative TLC on Si gel ($CHCl_3$-MeOH; 99:1) afforded the compound **1** (0.025 g), R_f 0.40 ($CHCl_3$-MeOH; 49:1).

Hydrolysis of 1. Compound **1** (10 mg) was refluxed with 5% KOH in MeOH for 2 hr and after cooling, the hydrolysate was acidified with 2*N* HCl, and extracted with $CHCl_3$ to afford compounds **1a** and **1b** after prep-TLC.

Compound **1c** was prepared from **1b** by usual diazomethane treatment.

6-Hydroxy-24-oxotritriacontane 2. $CHCl_3$-hexane (1:1) fractions on chromatography and preparative TLC on Si gel ($CHCl_3$) afforded **2** (0.012 g), R_f 0.25 ($CHCl_3$-hexane; 2:1).

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