

Triterpenoids from the Stem Bark of *Crataeva nurvala*

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ABSTRACT: Two triterpenoids, phragmalin triacetate (**1**) and lupeol (**2**) were isolated from an ethyl acetate extract of the stem bark of *Crataeva nurvala* (Capparidaceae) by repeated chromatography over silica gel. The structures of these compounds were determined by spectroscopic analyses (UV, IR, ¹H NMR, ¹³C NMR and EIMS). This is the first report of the systematic phytochemical investigation and the presence of these compounds **1** and **2** from this plant.

Key words: *Crataeva*, Capparidaceae, Phragmalin triacetate and Lupeol.

INTRODUCTION

The family Capparidaceae comprises about 45 genera and 700 species of trees, which are distributed mainly in the warmer (tropical) parts of the world. The plants occur mostly in dry seasons. Several shrubby species of *Capparis* occur in the Mediterranean region, while few genera, such as *Capparis*, *Gynandropsis*, *Cleome*, *Crataeva* etc are found in Bangladesh.¹ A wide variety of medicinally important compounds including friedelin, diosgenin, sitosterol, butulinic acid and betulinaldehyde have been reported from *C. nurvala*.²⁻⁵ The bark of *C. nurvala* is contraceptive and cytotoxic and is specially useful in urinary disorders, kidney bladder stones, fever, vomiting and gastric irritation.³ Root and bark are laxative and lithontriptic and increase appetite and biliary secretion.⁴ Leaves are externally rubefacient and used in rheumatism; internally they

are given as febrifuge and tonic.^{6,7} Previous phytochemical investigations of different species of *Capparidaceae* resulted in the isolation of essential oils, sugars, alkaloids, steroids and terpenoids.³ So far no detail phytochemical and biological studies have been carried out on *C. nurvala*. Since this plant has good medicinal properties, the present work has been undertaken to isolate and identify its secondary metabolites and in this paper we report isolation and characterization of phragmalin triacetate (**1**)⁸ and lupeol (**2**).

MATERIALS AND METHODS

General. Melting points were determined on a kolfer hot-stage apparatus and are uncorrected. UV spectrum was taken in MeOH solution using a Perkin-Elmer lambda 9UV/Vis./NIR Spectrometer. IR spectra were obtained in CHCl₃ solution on either a Perkin-Elmer 580 or Philips 9800 FTIR instrument. ¹H and ¹³C NMR spectra were acquired on Bruker WP 200 SY and AM 200 SY instruments (¹H, 200.13

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MHz; ^{13}C , 50.32 MHz) using TMS as internal standard and CDCl_3 as solvent. Electron impact mass spectra (EIMS) were recorded using a VG updated MS 12 Spectrometer and optical rotations were measured on AA-100 Polarimeter in CHCl_3 at 20°C . Petroleum ether specifically refers to the bp 40-60° fractions.

Plant Materials. The stem bark of *C. nurvala* was collected from Nasir Nagar of Brahman Baria of Bangladesh. A voucher specimen has been deposited at the Herbarium of the University of Glasgow, Glasgow, U.K.

Extraction and Isolation. The sun-dried stem bark powder (500 g) of *C. nurvala* was extracted in a Soxhlet apparatus for three days with EtOAc. This extract was concentrated *in vacuo* and subjected to flash column chromatography over TLC grade silica gel. Elution of the column first with petroleum ether, increasing amounts of EtOAc in petroleum ether and finally with methanol yielded a number of fractions. The proportion of solvent systems used to obtain **1** (10 mg) and **2** (15 mg) were petroleum ether-EtOAc (90 : 10) from fraction 5 and 6. The compounds were detected on TLC plates by spraying with vanillin- H_2SO_4 reagent.

Phragmalin triacetate (**1**), white crystals, mp. 252°C (reported mp. $252\text{-}254^\circ\text{C}^{11}$) at ν_{max} : 3570, 1748, 1630, 1030, 1010, 880 cm^{-1} ; EIMS m/z (rel;Int.): 686 [M^+] (3), 671 [M^+-15](5), 658 [M^+-CO](10), 643 [$\text{M}^+-\text{CH}_3\text{CO}$](15), 628 [$\text{M}^+-\text{CH}_3\text{CO}-15$] (20), 557 (30), 507 (10), 465 (25), 405 (20), 327 (20), 283 (40), 229 (CO), 182 (40), 121 (30), 95 (10), 43, (CH_3CO)[base peak]; ^1H NMR, δ : 7.50 (1H, s, H-21), 6.42 (1H, d, $J = 1.5$ Hz, H-22), 7.38 (1H, t, $J = 3.38, 1.36$ Hz), 5.53 (1H, s), 6.29 (1H, s), 5.08 (1H, s), 3.68 (3H, s), 1.66 (3H, s), 6.87 (3H, s), 1.12 (3H, s), 1.05 (3H, s), 2.24 (3H, s), 2.13 (3H, s), 1.92 (3H, s). ^{13}C NMR, δ : 86.8 (C-1), 85.3 (C-2), 81.0 (C-3), 46.1 (C-4), 35.5 (C-5), 33.2 (C-6), 172.7 (C-7), 85.9 (C-8), 85.2 (C-9), 45.7 (C-10), 25.38 (C-11), 29.1 (C-12), 34.4 (C-13), 43.1 (C-14), 26.5 (C-15), 171.1 (C-16), 78.6 (C-17), 19.1 (C-18), 16.6 (C-19), 121.07 (C-20), 140.7 (C-21), 109.7 (C-22), 143.0 (C-23), 14.6 (C-28), 40.16 (C-29), 64.3 (C-30). 52.1

(COOMe), 118.9 [O-Me(CO)-O], 21.06 [O-Me(CO)-O], 21.7 (CH_3CO), 21.6 (CH_3CO), 21.1 (CH_3CO), 170.2 (CH_3CO), 170.3 (CH_3CO), 168.6 (CH_3CO).

Lupeol (**2**), white crystals (MeOH), mp $210\text{-}212^\circ\text{C}$, $[\alpha]_{\text{D}} + 30.4^\circ$, (C, 0.58 in CHCl_3); (reported $[\alpha]_{\text{D}} + 27^\circ$, mp $210\text{-}212^\circ\text{C}^8$); IR ν_{max} : 3620, 3070, 3015, 1640, 1520, 1370, 1210, 1020, 888 cm^{-1} ; EIMS m/z (rel. int.): 426 [M^+] (4), 411 [M^+-CH_3] (10), 408 [$\text{M}^+-\text{H}_2\text{O}$] (3), 218 (10), 207 (8), 189 (50), 163 (70), 135 (60), 107 (67), 105 (50), 79 (40), 41 (100); ^1H NMR, δ : 0.74, 0.77, 0.81, 0.90, 0.94, 1.03 (each 3H, s, Me-28, Me-23, Me-24, Me-25, Me-26, Me-27), 1.66 (3H, br s, Me-30), 3.18 (1H, dd, $J = 9.6, 6.2$ Hz, H α -3), 4.57 (1H, d, $J = 0.4$ Hz, H α -29), 4.67 (1H, dq, $J = 0.4, 0.5$ Hz, H β -29); ^{13}C NMR; δ_{C} : 38.0 (C-1), 27.4 (C-2), 78.0 (C-3), 38.7 (C-4), 55.3 (C-5), 55.3 (C-5), 18.3 (C-5), 18.3 (C-6), 34.0 (C-7), 40.1 (C-8), 50.4 (C-9), 37.7 (C-10), 20.9 (C-11), 25.1 (C-12), 38.0 (C-13), 42.8 (C-14), 27.4 (C-15), 35.6 (C-16), 42.8 (C-17), 48.2 (C-18), 48.0 (C-19), 150.8 (C-20), 28.5 (C-21), 40.0 (C-22), 28.1 (C-23), 15.4 (C-24), 16.1 (C-25), 15.9 (C-26), 14.6 (C-27), 18.0 (C-28), 109.3 (C-29), 19.4.(C-30).

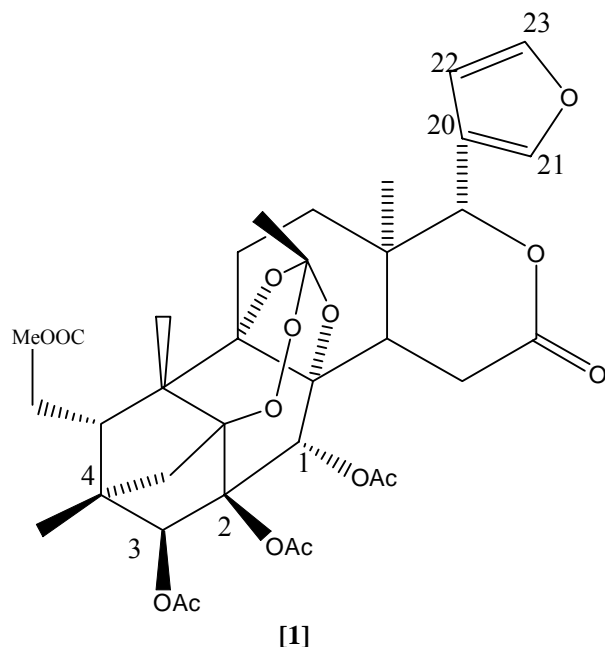
RESULTS AND DISCUSSION

The ethyl acetate extract of the stem bark of *C. nurvala* afforded three triterpenoids which were identified by spectroscopic analysis as well as by comparison of their spectral data with previously reported values.

Compound **1** ($\text{C}_{35}\text{H}_{42}\text{O}_{14}$) was isolated as white crystals from (MeOH) which melted at 252°C . Its IR spectrum exhibited OH, C=O and C=C absorptions at 3570, 1748 and 1630 cm^{-1} . Its mass spectrum displayed the [M^+] peak at m/z 686, and other peaks included 671 [M^+-15], 658 [M^+-CO], 643[$\text{M}^+-\text{CH}_3\text{CO}$], 628 [$\text{M}^+-\text{CH}_3\text{CO}-15$], 557, 507, 465, 405, 327, 283, 229, 182, 121, 95, 43, (CH_3CO , base peak), characteristics of an acetylated phragmalin triterpenoid.

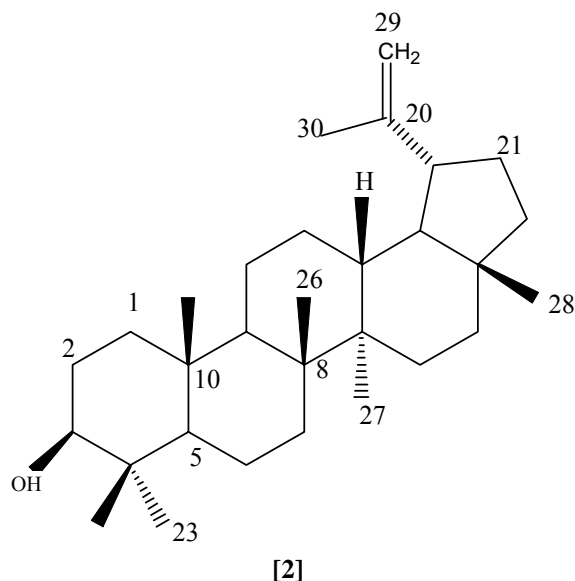
The ^1H NMR spectrum was in close proximity with phragmalin triacetate. Thus it showed signals for five methyl [δ : 3.68, 2.24, 2.13, 1.12 and 1.66]

resonances. Two furan proton signals appeared at δ : 7.5 (H-21), 6.42 (H-22). Characteristic proton signals appeared at δ 6.42 (H-23), 5.53 (H-17), 6.29 (H-30) and 5.08 (H-3). One Me-OOC signal appeared at δ 3.68 and another methyl group of O-MeC(-O)-O appeared at 1.66. Three C-Me groups appeared at δ 0.87, 1.05 and 1.12. The above data suggested that the compound was a triacetylated derivative of phragmalin. Comparison of published data¹⁰ led to the identification of compound **1** as phragmalin triacetate. The ¹³C NMR spectrum confirmed this structure by showing signals for 3 oxygenated carbons at δ 86.8 (C-1), 85.3 (C-2) and 81.0 (C-3). The furan ring carbons appeared at δ 121.07 (C-20), 140.7 (C-21), 109.7 (C-22) and 143.0 (C-23). One deshielded methyl carbon appeared at δ 52.1 corresponding to COOMe group and another carbon appeared at δ 118.9 which was highly deshielded due to three oxygen attached to it [OMeC(-O)-O]. Five-carbonyl carbon of acetyl lactone and MeOOC group appeared at δ 172.6, 171.1, 170.3, 168.6 and 170.2. Seven other methyl carbons appeared at 21.7, 21.6, 21.1, 21.06, 19.1, 16.6 and 14.6.



This data were fully consistent with phragmalin triacetate (**1**). Comparison of this data with published data^{9,10} confirmed the identity of compound **1** as phragmalin triacetate.

Compound **2** was isolated as white crystals, mp 210–212°C, $[\alpha]_D + 30.4^0$ (C, 0.58 in CHCl₃) [lupeol, mp 212°, $[\alpha]_D + 32^0$ (C, 0.50 in CHCl₃)⁹]. Its IR spectrum exhibited hydroxyl (ν_{\max} : 3620, 1030 cm⁻¹) and exomethylene (ν_{\max} : 3060, 1640, 888 cm⁻¹) absorption. The mass spectrum showed the molecular ion peak at m/z 426 corresponding to C₃₀H₅₀O together with fragments at m/z 411 (M⁺-15) and 408 (M⁺-18) and a base peak at m/z 43 (C₃H₇)⁺. The ¹H NMR spectrum revealed signals for six tertiary methyl [δ 0.74, 0.77, 0.81, 0.90, 0.94 and 1.03], a vinyl methyl [δ 1.66 (br d, $J=0.5$ Hz)], a secondary carbinol [δ 3.18 (1 dd, $J=9.6$ and 6.2 Hz)] and an exomethylene group [δ 4.57 (1H, d, $J=0.4$ Hz)] and [δ : 4.67 (1H, d, $J=0.4$ Hz)]. The remaining protons appeared as complex multiplets between δ_H 1.0 to 2.6. These data indicated a pentacyclic triterpenoid of lupane type and comparison of its physical and spectral data with published values confirmed the identity of compound **2** as lupeol.^{8,9}



The ¹³C NMR spectrum of compound **2** showed seven-methyl groups [δ : 28.1, 19.4, 18.0, 16.1, 15.9, 15.4, 14.6] and an exomethylene group [δ : 150.9 (C-20), 109.5 (C-29)] and a secondary hydroxyl bearing carbon [δ_C : 77.0 (C-3)] in addition to ten methylene, five methine and five quaternary carbons. These data were identical to those of lupeol. This is the first report of the isolation of these compounds from *Crataeva nurvala*.

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