
Phytochemical Investigation of the Aerial Parts of *Tribulus terrestris* Linn

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Phytochemical studies on the aerial parts of *Tribulus terrestris* Linn. (Family. Zygophyllaceae) resulted in the isolation of a tetracyclic alkenone, named phenanthroindodecanone and an aliphatic ester. The structures of the new phytoconstituents have been established as cyclopentaperhydro-phenanthranlyl-17-dode-18-ol-20-on-24-ene and trideca-2-oic acid-3,4-diol-8-en-1-decan-10'-oic acid'-1' on the basis of spectroscopic analysis and chemical means.

Tribulus terrestris (F; Zygophyllaceae), a procumbent herb, commonly known as Gokhru, is found throughout India up to 3,600 ft in Kashmir, in Sri Lanka and all warm regions of both hemispheres. The plant possesses diuretic, tonic, cooling and aphrodisiac properties and is used in gleet, gonorrhoea, painful gums, urinary disorders, irregular menstrual flow and impotency¹. Flavonoids², steroids³, steroidal saponins⁴, sugars⁵, carboline alkaloids⁶, steroidal glycosides⁷, flavonoid glycosides⁸, terrestriamide and 7-methyl hydroindanone have been reported from the plant. This communication deals with the isolation and structural elucidation of two new phytoconstituents from the aerial parts of the plant.

MATERIALS AND METHODS

Melting points were determined in a Perfit melting point apparatus in open ended capillary tubes and are uncorrected. UV spectra were recorded on Beckman DU-64 model. IR spectra were taken on Nicolet 5 DX model using KBr pellets. ¹H NMR spectra were scanned on Bruker spectropin 300 MHz in CDCl₃ as a solvent and TMS as internal standard. The chemical shifts are expressed in δ ppm; Mass spectra were taken using a

Jeol-D 300 system equipped with direct inlet probe system. Chemical reagents were of A.R. grade and procured from Qualigens, New Delhi. Their layer chromatographic spots were detected by UV light, iodine chamber and by spraying with ceric sulphate solution.

Extraction and Isolation:

Fresh aerial parts of *T. terrestris* were collected from the Herbal Garden of the Jamia Hamdard. The air-dried, powdered plant material (3 kg) was Soxhlet extracted with ethanol (95%). The ethanolic extract was concentrated under reduced pressure. The concentrated extract (125 g) was dissolved in a minimum amount of methanol, adsorbed on silica gel and subjected to silica gel column chromatography. The column was eluted with petroleum ether, chloroform and methanol in the increasing order of polarity to furnish the following compounds.

Phenanthroindodecanone (1):

Elution of the column with petroleum ether - CHCl₃ (3:1) gave pale yellow coloured product (1): recrystallised from chloroform-methanol (1:15), 0.066 g; R_f 0.71; UV λ_{\max} (MeOH): 206 nm, (log ϵ 4.7); IR ν_{\max} (KBr). 3400, 1720, 1620, 1440, 1356, 1260, 1150 and 715⁻¹; ¹H NMR. δ 5.11 (1H, m, H-24), 5.02 (1H, m, H-25), 3.64 (1H, m, H-18), 2.80 (1H, m, H-17) 2.60 (1H, m, H-14), 2.45 (4H, m,

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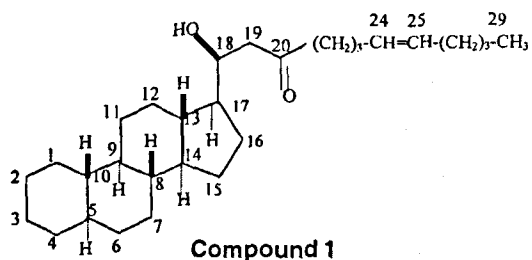
H₂-19, H₂-21), 2.42 (1H, M, H-13), 2.13 (4H, m, H₂, 22, H₂-26), 2.05 (1H, m, H-8), 2.00 (1H, m, H-9), 1.59 (1H, m, H-5), 1.54, (2H, m, H-10, H-17), 1.25 (26 H, brs, 13 x CH₂CH₂), 0.93 3H, t, J = 6.5 Hz, Me-29). EIMS [M]⁺ m/z 428, (C₂₉H₄₈O₂), (3.9), 410 (2.1), 395 (3.6), 293 (6.2), 273 (6.5), 265 (7.1), 264 (20.8), 238 (6.1), 197 (11.0), 167 (7.5), 164 (3.0), 153 (8.3), 150 (3.2), 138 (13.9), 136 (5.4), 125 (125.5), 109 (32.1), 95 (60.6), 83 (66.2), 82 (15.2), 69 (74.7), 57 (100), 55 (72.0). Found C = 81.05, H = 12.31; calcd. C = 81.30, H = 12.21 for C₂₉H₄₈O₂. Acetylation of **1** with a mixture of Ac₂O (3 ml) and pyridine (1ml) yielded a monoacetyl product, m.p. 70-71°, IR γ_{max} 1725 cm⁻¹.

Tetradecanylester (2):

Elution of the column with petroleum ether, chloroform (1:1) afforded orange yellowish crystals, recrystallized from CHCl₃-MeOH, m.p. 55.56°, 0.077g R_f, 0.71; UV λ_{max} 207 (log ε 105). IR γ_{max} (KBr): 3420, 3390, 2930, 2850, 1740, 1628, 1465, 1378, 1180, 730, 710 cm⁻¹. ¹H NMR. δ 5.35 (1H, m, H-8), 5.11 (1H, m, H-9) 4.28 (1H, d, J = 11.5 Hz, H-1'a), 4.15 (1H, d, J = 11.5 Hz, H-1'b), 3.63 (1H, dd J = 6.0, 5.5 Hz, H-3), 3.19 (1H, m, H-4), 2.30 (1H, d, J = 9.0 Hz, H-9'a), 2.28 (1H, d, J=5.5 Hz, H-9'b), 2.03 (1H, d, J = 9.5, H-2), 2.00 (2H, m, H₂-7), 1.67 (2H, brs, H₂-5), 1.59 (2H, m, H₂-10), 1.25 (24 H, brs, 12 x CH₂), 0.87 (3H, t, J = 6.5 Hz Me - 13), EIMS [M]⁺ m/z; 458 (C₂₄H₄₂O₈) (4.0), 440 (3.8), 422 (8.4), 4.05 (18.2), 363 (3.1), 333 (5.6), 271 (5.8), 243 (3.7), 215 (10.4), 187 (5.5), 151 (10.0), 137 (17.7), 125 (12.5), 113 (4.2), 111 (43.5), 97 (84.6), 83 (87.1), 71 (81.0), 69 (97.1), 55 (100), 43 (81.3), Found C = 62.91, H = 9.22 calcd. C = 62.88, H = 9.17 for C₂₄H₄₂O₈. Acetylation of **2** with Ac₂O and pyridine gave a diacetyl product, m.p. 51-52°; IR γ_{max} 1735, 1725 cm⁻¹.

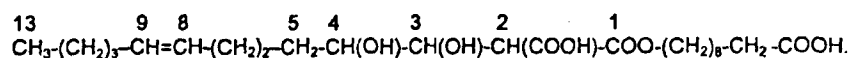
RESULTS AND DISCUSSION

Compound **1**, named phenanthrododecanone was obtained as a pale yellow coloured product from petroleum ether-chloroform (3:1) eluants. Its mass spectrum displayed a molecular ion peak at m/z 428 relating to a tetracyclic branched compound, C₂₉H₄₈O₂. It had six degrees of unsaturation; four of them were adjusted in the



tetracyclic carbon frame work. Its IR spectrum demonstrated the presence of absorption bands for one hydroxyl group (3400 cm⁻¹), carbonyl group (1720 cm⁻¹) and unsaturation (1629 cm⁻¹); The ion fragments at m/z 82 (C_{5,6}-C_{9,10} fission, ion a), 136 (C_{8,14}-C_{9,11} fission, ion b), 293 (M⁺-ion b, ion c), 164 (C_{8,14}-C_{12,13} fission, ion d), 265 (M⁺-ion d, ion e), 238 (C_{14,15}-C_{13,17} fission, ion f) in its mass spectrum supported the presence of cyclopentaperhydrophenanthrene nucleus in the molecule. The location of hydroxyl group at C-18 and carbonyl group at C-20 was inferred from the ion peaks arising of m/z 197 (C₁₇-C₁₈ fission, ion g), 167 (C₁₈-C₁₉ fission, ion h) and 153 (C₂₀-C₂₁ fission, ion i). The existence of the olefinic linkage at C-24 (25) was deduced from the prominent ion fragments appearing at m/z 83 (C₂₃-C₂₄ fission, ion k) and 57 (C₂₅-C₂₆ fission, ion l). The ¹H NMR spectrum of **1** exhibited two one-proton each downfield multiplets at δ 5.11 and 5.02 assigned to H-24 and H-25, respectively. Another one proton multiplet of δ 3.64 was ascribed to C-18 carbinol proton. A four-proton multiplet at δ 2.45 was attributed to C-19 and C-21 methylene protons adjacent to carbinol group. A triplet at δ 0.93 with 6.5 Hz coupling constant, integrated for three protons, was associated with C-29 primary methyl group. The other signals in between 2.80 to 1.25 were due to remaining methine and methylene protons. Acetylation of **1** yielded a monoacetyl product. Based on these accumulated evidence the structure of phenanthrododecanone (**1**) was formulated as cyclopentaperhydrophenanthryl-17-dodec-18-ol-20-on-24-ene.

Compound **2**, named tetradecanylester, was obtained as an orange yellow coloured mass from petroleum ei-



Compound 2

ther-chloroform (1:1) eluants. It responded positively to bromine and tetranitromethane test for unsaturation and acetylating reagents. Its IR spectrum showed absorption bands for hydroxyl (3420 cm^{-1}), carboxyl (3390 cm^{-1}), ester (1740 cm^{-1}) groups, unsaturation (1628 cm^{-1}) and long aliphatic chain ($730, 710\text{ cm}^{-1}$). The mass spectrum of **2** exhibited a molecular ion peak at m/z 458 consistent with the molecular formula $C_{24}H_{42}O_8$. It indicated four degrees of unsaturation, one each was assigned to olefinic linkage, ester group and two carboxyl groups. The spectrum had C_nH_{2n+1} , C_nH_{2n} and C_nH_{2n-1} ions as observed for aliphatic constituents. All the fragments were separated by 14 mass units and decreased in abundance with increasing molecular weight of the long chain hydrocarbon. More intense clusters of peaks corresponding to C_nH_{2n+1} (eg; m/z 69, 83, 97, 111, 125, etc.) in comparison to that relating to C_nH_{2n-1} (eg; m/z 71, 83, 99, 113, 127, 141 etc.) supported unsaturated nature of the molecule. The ion peaks at m/z 440 and 422 generated due to subsequent expulsion of water molecules from $[M]^+$, indicated the presence of two removable hydroxyl groups in the molecule.

The intensity of ion fragments suddenly increased at m/z 215 due to cleavage of C_1 - C_2 bond and at m/z 271 and 187 due to fission of the ester linkage. The appearance of prominent ion peaks of m/z 83 (C_9 - C_{10} fission), 57 ($83\text{-CH}=\text{CH}$)⁺, 333 (C_4 - C_5 fission) and 125 (M^+-333) suggested the existence of C_{14} carboxylic unit esterified with hydroxycapric acid, olefinic linkage at C-8 (9), hydroxyl groups at C-2 and C-3 and carboxylic groups at C-2. The ¹H NMR spectrum of compound **2** displayed two one-proton each multiplets at δ 5.35 and 5.11 assigned to H-8 and H-9, respectively. The doublets at δ 4.28 and 4.11 with coupling constants of 11.5 Hz, integrated one proton each, were ascribed corre-

spondingly to H-1' a and H-1' b of the oxygen substituted methylene group. A one proton multiplet at δ 3.19 was due to H-4 carbinol proton. The H-3 hydroxyl methine proton appeared as a doublet of doublet at δ 3.63 ($J = 6.0, 5.5\text{ Hz}$). A three proton triplet at δ 0.87 ($J = 6.5\text{ Hz}$) was associated with C-13 terminal methyl group. The signals at δ 2.30 (1H, d, $J = 9.0\text{ Hz}$), 2.28 (1H, d, $J = 5.5\text{ Hz}$), 2.03 (1H, d, $J = 9.5\text{ Hz}$), 2.00 (2H), 1.67 (2H) and 1.25 (24H) were ascribed to the remaining methine and methylene protons. Acetylation of **2** yielded a diacetyl product. On the basis of these spectral data analysis and chemical reaction, the structure of tetradecanyl ester was established as trideca-2-oic acid-3,4-diol-8-en-1-yl-decan-10'-oic acid-1'-oate.

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