Characterization of Phytoconstituents of the Fruits of *Momordica dioica*

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Two new aliphatic constituents, characterized as 6-methyl tritriacont-5-on-28-ol and 8-methyl hentriacont-3-ene, have been isolated for the first time form the fruit rind of *Momordica dioica* along with the known sterol plechiol. *Momodica senol*, an unknown pentacyclic triterpene isolated from the seeds, has been identified as urs-12, 18(19)-dien-3β-ol on the basis of spectral data analyses and chemical means.

*Mordica* dioica Roxb. ex Willd (Cucurbitaceae) is a perennial, dioecious climber with tuberous roots found throughout India1. Its fruits are used as vegetable1, in inflammation caused by lizard excretion2 and to treat discharge from mucous membrane3. Vitamins from the fruits4, fatty acids from the seeds4,5 and a phytohemagglutinin from the cotyledons6 have been reported. This paper deals with the isolation and identification of new phytoconstituents from the fruit rind and seeds of this plant.

**EXPERIMENTAL**

**Extraction**

Coarsely powdered fruit rind (1 kg) and defatted seeds (600 g) were Soxhlet extracted separately with EtOH (95%). The concentrated rind extract (50 g) and seed extract (16 g) were chromatographed individually on silica gel columns to separate the following compounds:

6-Methyl tritriacont-5-on-28-ol (1): Elution of the column of rind extract with petroleum ether furnished colourless crystals of 1, 80 mg, m.p. 56-58º, IR vmax (KBr) 3445 (OH), 2910, 1720, (CO), 1465, 845, 725, 705 cm⁻¹ (aliphatic chain). ¹H NMR (100 MHz, CDCl₃) δ 4.05 (1 H, br s, H-28), 2.21 (1 H, br s, H-6), 1.75 (2 H, br s, CH₂-4), 1.68 (4 H, br s, CH₂-27, CH₂-29), 1.60 (6 H, br s, 3 x CH₃), 1.55 (8 H, br s, 4 x CH₃), 1.25 (36 H, br s, 18 x CH₃), 0.93 (3 H, d, J =6.5 Hz, Me-34), 0.88 (3 H, br s, Me-1), 0.83 (3 H, br s, Me-33). EIMS m/z (rel. int.) 508 [M⁺] (C₃₁H₄₅O₂) (6.0), 493 (2.1), 479 (5.6), 451 (14.4), 435 (6.5), 423 (16.3), 395 (10.3), 113 (45.2), 101 (100), 85 (53.2), 71 (65.2), 57 (23.3). Acetylation of 1 with Ac₂O-pyridine yielded monoacetyl derivative, m.p. 61-62º, IR vmax 1725, 1720 cm⁻¹.

8-Methyl hentriacont-3-ene (2): Elution of the column of the rind extract with petroleum ether-chloroform (1:1) afforded colourless crystals of 2, 75 mg, m.p. 81-82º, IR vmax (KBr) 2940, 2850, 1610 (C=C), 1460, 1355, 985, 740 cm⁻¹. ¹H NMR (100 MHz, CDCl₃) δ 5.00 (1 H, m, H-4), 4.90 (1 H, m, H-3), 2.08 (4 H, m, 2 x CH₂), 1.25 (48 H, 62 s, 24 x CH₃), 1.17 (1 H, m, H-8), 0.83 (3 H, d, J=6.5 Hz, Me-32), 0.77 (6 H, br s, Me-1, Me-31). EIMS m/z 448 [M⁺] (C₃₂H₄₄) (5.4), 433 (1.2), 419 (7.9), 393 (2.1), 351 (2.0), 323 (3.5), 125 (43.3), 97 (100), 55 (65.3).

**Plechiol**: Elution of the column of the rind extract with CHCl₃-MeOH (3:1) afforded white amorphous powder of plechiol, 40 mg, m.p. 146-147º (lit m.p. 144-145º). IR vmax (KBr) 3445 (OH), 1580 (C=C). ¹H NMR (100 MHz, CDCl₃) δ 5.37 (1 H, br m, H-6), 5.20 (2 H, m, H-11, H-12), 3.27 (1 H, br s, H-3), 1.00 (3 H, br s, Me-19), 0.97 (3 H, d, J=6 Hz, Me-21), 0.90 (3 H, d, J=6.0 Hz, Me-29), 0.86 (6 H, br s, Me-26, Me-27), 0.76 (3H, br s, Me-18). EIMS m/z (rel. int.) 412 [M⁺] (C₃₁H₄₂O) (10.8), 397 (7.8), 394 (2.4), 274 (7.0), 271 (26.4), 255 (43.5), 212 (16.4).
Momordicauresenol - (3): Elution of the column of the seed extract with CHCl₃-MeOH (9:1) yielded colourless crystalline compound 3, 35 mg, m.p. 263-264°, IR ν max (KBr) 3425 (OH), 1540 (C=C), 1455, 1360, 1265, 1010 cm⁻¹. ¹H NMR (100 MHz, CDCl₃) δ 5.20 (1 H, m, H-12), 3.40 (1 H, d, J=5.5, 9.0 Hz, H-3), 1.55 (3 H, br s, Me-29), 0.97 (6 H, br s, Me-24, Me-25), 0.93 (3 H, d, J=6.0 Hz, Me-30), 0.83 (3 H, br s, Me-27), 0.76 (6 H, br s, Me-23, Me-28), 0.66 (3 H, br s, Me-26). EIMS m/z (rel. int.) 424 [M⁺]⁺ (C₂₆H₆₉O) (1.2), 409 (2.0), 217 (5.2), 207 (12.8), 202 (20.8), 189 (11.1), 174 (5.0), 122 (19.2), 57 (100), 55 (98.1). Monoacetyl derivative with Ac₂O-pyridine, TLC comparable.

RESULTS AND DISCUSSION

Compound 1 showed the presence of hydroxyl and carbonyl groups and long aliphatic chain of the compound in its IR spectrum. Its mass spectrum exhibited a molecular ion peak at m/z 508 consisted with the molecular formula C₂₆H₆₉O, and a large number of fragments with a uniform difference of 14 mass units for a long aliphatic chain. The presence of a peak at m/z 493, generated due to removal of a methyl group from the [M⁺]⁺, confirmed the branched chain nature of the molecule. More intense clusters of peaks corresponding to C₂H₂n⁺ in comparison to that relating to C₂H₂n⁺ supported its acyclic and saturated nature. The intensity of ion fragments increased at m/z 71 (C₂₀-C₂₉ fission), 101, 435 (C₂₀-C₂₅ fission) due to the presence of the hydroxyl group at C-28, at m/z 395, 113 (C₂₅-C₃₀ fission), 423, 85 (C₂₅-C₃₀ fission) due to location of the methyl group at C-6 and at m/z 451, 57 (C₂₅-C₃₀ fission) due to the existence of the carbonyl group at C-5. The ¹H NMR spectrum of 1 displayed one proton broad signal at δ 4.05 assigned to C-28 carbonyl proton. A three-proton doublet at δ 0.93 (J=6.5 Hz) was ascribed to C-34 methyl group. The terminal C-1 and C-33 methyl proton appeared as broad signals at δ 0.88 and 0.83, respectively. The remaining methine and methylene protons resonated in the range δ 2.21-1.25. Acetylation of 1 with acetic anhydride and pyridine formed a monoacetyl derivative. Based on these observations the compound 1 has been identified as 6-methyl trimtiramcont-5-on-28-ol which is a new natural product.

Compound 2 responded positively for TNM and bromine tests for unsaturation. Its IR spectrum was devoid of any functional group absorption band and exhibited an absorption band at 1610 cm⁻¹ for olefinic linkage. The ¹H NMR spectrum of 2 showed two one proton each downfield multiplets at δ 5.00 and 4.90 assigned correspondingly to C-4 and C-3 vinylic protons. A three-proton doublet at δ 0.83 with coupling interaction of 6.5 Hz was associated with C-32 methyl proton signal. The C-1 and C-31 terminal methyl protons appeared as a six-proton broad signal at δ 0.77. The signals at δ 2.08 (4H), 1.25 (48H) and 1.17 (1H) were attributed to the remaining methylene and methine protons. Its mass spectrum displayed a molecular ion peak at m/z 448 (M₂H₂) which indicated one double bond equivalent. The spectrum showed a fragmentation pattern identical to that of 1. The intensities of the ion peaks were suddenly intensified at m/z 419 (C₂₆-C₃₀ fission) and at 393; 55 (C₂₆-C₃₀ fission) suggesting the existence of the olefinic linkage at δ 5.00 and at m/z 351, 97 (C₂₆-C₃₀ fission) and 323, 125 (C₂₆-C₃₀ fission) due to the location of methyl.
The compound resisted reaction with acetylatiing and oxidizing reagents. These data led to formulate the structure of this new natural product as 8-methyl hentriacont-3-ene.

Pleochiolo was the known sterol, earlier isolated form *Plechela lanceolata* and identified as stigmata-5,11 (12)-dien-3β-ol.

Momordicaursenol (3), positive to L.B. test, had molecular ion peak at *m/z* 424 in its mass spectrum corresponding to a pentacyclic triterpene, C₃₀H₄₈O. Its IR spectrum showed characteristic absorption bands for hydroxyl group and olefinic linkage. The mass spectrum of 4 exhibited typical ion peaks at *m/z* 217 and 207, generated due to RDA fragmentation pattern and other important ion fragments at *m/z* 189 [207 - H₂O]⁺, 174 [189-Me]⁺ 202 [217-Me]⁺ and 57 [C_{11}_10-C_{34}_14 fission]⁺. The location of another vinyllic linkage in ring E at C-18-C-19 was inferred from the ion peaks appearing at *m/z* 122 [C_{16}_17-C_{13}_18 fission]⁺ and 55 [C_{19}_20-C_{17}_22 fission]⁺. In the ¹H NMR spectrum the C-12 vinyllic proton appeared as a one proton multiplet at δ 5.30. A one proton double doublet at δ 3.40 was assigned to C-3 carboxin proton and its coupling constants of 5.5 and 9.0 Hz indicated δ-orientation of the proton. A three-proton singlet at δ 1.55 was due to C-29 methyl group attached to the olefinic linkage. Another three-proton doublet at δ 0.93 (J=6.0 Hz) was attributed to C-30 secondary methyl group. The remaining tertiary methyl protons appeared as broad signals at δ 0.97 (Me-24, Me-25), 1.83 (Me-27), 0.76 (Me-23, Me-28) and 0.66 (Me-26). These spectral data were compared with that of other relating triterpenes. The compound formed a monocetyl derivative. The basis of these evidences the structure of the new triterpene 3 has been elucidated as urs-12,18-dien-3β-ol. The ursene-

ACKNOWLEDGEMENTS

Sincere thanks are due to the Head, RSIC, CDRI, Lucknow for screening mass spectra of the compounds and to Dr. M.P. Sharma, Senior Lecturer, Department of Botany, Faculty of Science, Jamia Hamdard, for identification of the plant material.

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