RESEARCH PAPER

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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 pleuchiol. *Momodicaursenol,* 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.

MOMORDICA dioica Roxb. ex Willd (Cucurbitaceae) is a perennial, dioecious climber with tuberous roots found throughout India[1]. Its fruits are used as vegetable[1], in inflammation caused by lizard excretion[2] and to treat discharge from mucous membrane[2]. Vitamins from the fruits[3], fatty acids from the seeds[4,5] and a phytohemagglutinin from the cotyledons[6] 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

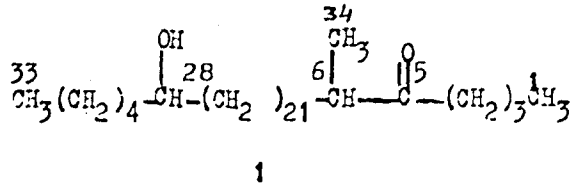
Coarsely powdered fruit rind (1 kg) and defatted seeds (600 g) were Soxhlet extracted separately with EtOH (95%). The concentrated rind extract (50 g) and seed extract (16 g) were chromatographed individually on silica gel columns to separate the following compounds :

6-Methyl tritriacontan-5-on-28-ol (1): Elution of the column of rind extract with petropeum ether furnished colourless crystals of 1, 80 mg, m.p. 56-58°, IR γmax (KBr) 3445 (OH), 2910, 1720, (CO), 1465, 845, 725, 705 cm^{-1} (aliphatic chain). ^1H NMR (100 MHz, $CDCl_3$) δ 4.05 (1 H, br s, H-28), 2.21 (1 H, br s, H-6), 1.75 (2 H, br s, CH_2-4), 1.68 (4 H, br s, CH_2-27, CH_2-29), 1.60 (6 H, br s, 3 x CH_2), 1.55 (8 H, br s, 4 x CH_2), 1.25 (36 H,br s, 18 x CH_2), 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 $[M]^+$ ($C_{34}H_{68}O_2$) (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 Ac_2O-pyridine yielded monoacetyl derivative, m.p. 61-62°, IR γmax 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. 81-82°, IR γmax (KBr) 2940, 2850, 1610 (C=C), 1460, 1355, 985, 740 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$) δ 5.00 (1 H, m, H-4), 4.90 (1 H, m, H-3), 2.08 (4 H, m, 2 x CH_2), 1.25 (48 H, 62 s, 24 x CH_2), 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 $[M]^+$ ($C_{32}H_{64}$) (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).

Pleuchiol : Elution of the column of the rind extract with $CHCl_3$-MeOH (3:1) afforded white amorphous powder of pleuchiol, 40 mg, m.p. 146-147° (lit m.p 144-145°, IR γmax (KBr) 3445 (OH), 1580 (C=C). ^1H NMR (100 MHz, $CDCl_3$) 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=6.5 Hz, Me-21), 0.90 (3 H, d, J=6.00 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 $[M]^+$ ($C_{29}H_{48}O$) (10.8), 397 (7.8), 394 (2.4), 274 (7.0), 271 (26.4), 255 (43.5), 212 (16.4).

Momardicaursenol - (3): Elution of the column of the seed extract with $CHCl_3$-MeOH (9:1) yielded colourless crystalline compound 3, 35 mg, m.p. 263-264°, IR γmax (KBr) 3425 (OH), 1540 (C=C), 1455, 1360, 1265, 1010 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$) δ 5.20 (1 H, m, H-12), 3.40 (1 H, dd, 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 $[M]^+$ ($C_{30}H_{48}O$) (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 Ac_2O-pyridine, TLC comparable.



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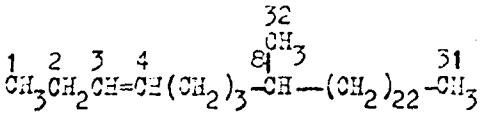

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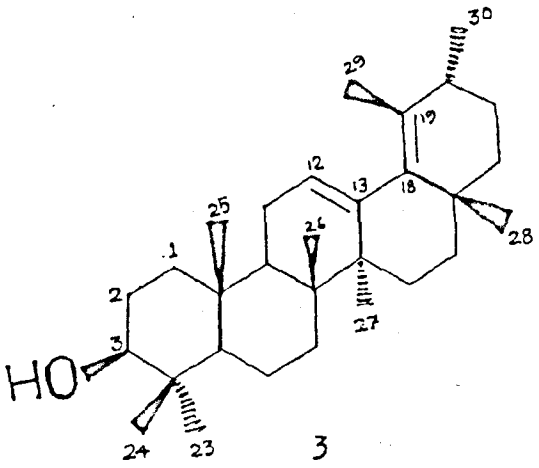
RESULTS AND DISCUSSION

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 $C_{34}H_{68}O_2$ 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 C_nH_{2n+1} in comparison to that relating to C_nH_{2n-1} supported its acyclic and saturated nature[7]. The intensity of ion fragments increased at *m/z* 71 (C_{28}-C_{29} fission), 101, 435 (C_{27}-C_{28} fission) due to the presence of the hydroxyl group at C-28, at *m/z* 395, 113 (C_6-C_7 fission), 423, 85 (C_5-C_6 fission) due to location of the methyl group at C-6 and at *m/z* 451, 57 (C_4-C_5 fission) due to the existence of the carbonyl group[9] at C-5. The ^1H NMR spectrum of 1 displayed one proton broad signal at δ 4.05 assigned to C-28 carbinol 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 tritriacont-5-on-28-ol which is a new natural product.



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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 ($M^+C_{32}H_{64}$) 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 (C_2-C_3 fission) and at 393; 55 (C_4-C_5 fission) suggesting the existence of the olefinic linkage at $\Delta^{3(4)}$ and at *m/z* 351, 97 (C_7-C_8 fission) and 323, 125 (C_8-C_9 fission) due to the location of methyl

group at C-8. The compound resisted reaction with acetylating and oxidizing reagents. These data led to formulate the structure of this new natural product as 8-methyl hentriacont-3-ene.

Pleuchiol was the known sterol, earlier isolated form *Pleuchea lanceolata*[10] 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, $C_{30}H_{48}O$. 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[11] and other important ion fragments at *m/z* 189 [207 - H_2O]$^+$, 174 [189-Me]$^+$ 202 [217-Me]$^+$ and 57 [$C_{1,10}$-$C_{3,4}$ fission]$^+$. The location of another vinylic 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 ^{1}H NMR spectrum the C-12 vinylic 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 carbinol 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),).83 (Me-27),).76 (Me-23, Me-28) and 0.66 (Me-26). These spectral data were compared with that of other relating triterpenes[10,12,13]. The compound formed a monoacetyl derivative. On the basis of these evidences the structure of the new triterpene 3 has been elucidated as urs-12,18-dien-3 β-o1. The ursene-type triterpenes containing olefinic linkages in rings C and E have been earlier reported from *Symplocos racemosa*[14].

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