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TRITERPENES, A STEROL AND A MONOCYCLIC ALCOHOL FROM *MOMORDICA CHARANTIA*

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Key Word Index—*Momordica charantia*; Cucurbitaceae; pentacyclic triterpenes; sterol; monocyclic alcohol.

Abstract—Five new compounds have been isolated from the fresh fruits of *Momordica charantia* and their structures elucidated through spectroscopic studies. These include three pentacyclic triterpenes 13-hydroxy-28-methoxy-urs-11-en-3-one (momordicin), 13β,28-epoxy-urs-11-en-3-one (momordicinin), 24-[1′-hydroxy,1′-methyl-2′-pentenyloxyl]-ursan-3-one (momordicilin), a sterol 3β-hydroxy-stigmasta-5,14-dien-16-one (momordenol) and a monocyclic alcohol 1-hydroxy-1,2-dimethyl-2-[8′,10′-dihydroxy-4′,7′-dimethyl-11′-hydroxy methyl-trideca]-3-ethyl-cyclohex-5-en-4-one (momordol). Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Momordica charantia L. is found in the tropics and is widely cultivated as a vegetable crop. The fruits, leaves and roots of *M. charantia* have been used in Ayurveda for a number of diseases, as a bitter stomachic, laxative and anthelmintic [1]. An active principle from this plant has been used in diabetes mellitus [2]. The whole extract of the fruit is also advocated in diseases of spleen, liver, rheumatism, gout etc [3]. In view of the reported pharmacological significance of this plant, studies were undertaken on the chemical constituents of the methanolic extract of the fruits. As a result, five new compounds have been isolated and their structures elucidated through spectroscopic studies. These include three pentacyclic triterpenes momordicin (**1**), momordicinin (**2**), momordicilin (**3**), a sterol momordenol (**4**) and a monocyclic alcohol momordol (**5**).

RESULTS AND DISCUSSION

The HR-mass spectrum of **1** showed the molecular ion peak at *m/z* 470.3748 corresponding to the molecular formula $C_{31}H_{50}O_3$. The IR spectrum showed diagnostic absorptions at 3650 (–OH), 1710 (C=O), and 1600 (C=C) cm^{-1}. The ^1H NMR spectrum (see Experimental) showed two doublets for tertiary methyls at δ0.89 (J = 6.2 Hz) and 0.87 (J = 7.4 Hz) and five singlets of three-protons each at δ1.24, 1.19, 0.88, 0.86 and 0.85 along with a doublet at δ1.72 (J = 10.9 Hz) for H-18. These data showed that **1** belonged to the ursane series of triterpenoids with one methyl group functionalized. The ^1H NMR spectrum further showed a three-proton singlet at δ3.14 attributable to a methoxy group and a set of mutually coupled doublets at δ3.39 and 3.97 (J = 10.1 Hz).

The mass fragments at *m/z* 205.1643 ($C_{14}H_{21}O$), 263 (in the EI-mass spectrum) and 213.1589 ($C_{16}H_{21}$) resulting through the cleavage of ring C and losses of methanol and water molecules (see structure) were indicative of two oxygen functions and a double bond in rings C–E and an oxygen function in ring A/B. Seven unsaturations were evident from the molecular formula, five of which were accounted for by the pentacyclic rings and one by a disubstituted double bond (δ6.03, *dd*, J = 9.8, 2.1 Hz, H-12; δ5.62, *dd*, J = 9.8, 3.7 Hz, H-11). The oxygen function in ring A/B was placed at C-3 on biogenetic grounds [4] and the absence of a carbinylic H-3, the requirement of one more double bond equivalence and the IR band at 1710 cm^{-1} identified it as a ketone. Two mutually coupled doublets at δ3.97 and 3.39 and the singlet at δ3.14 suggested a methoxy group on one of the skeletal methyl carbons. Since the doublets of H-29 and H-30 were recognized this might be placed at either C-27 or C-28 and the mass fragments (*vide* structure) supported its location at C-28. The third oxygen function was taken to be a hydroxyl function at a quaternary carbon as no carbinylic proton was present. It was placed at C-13 as H-18 gave a doublet. The double

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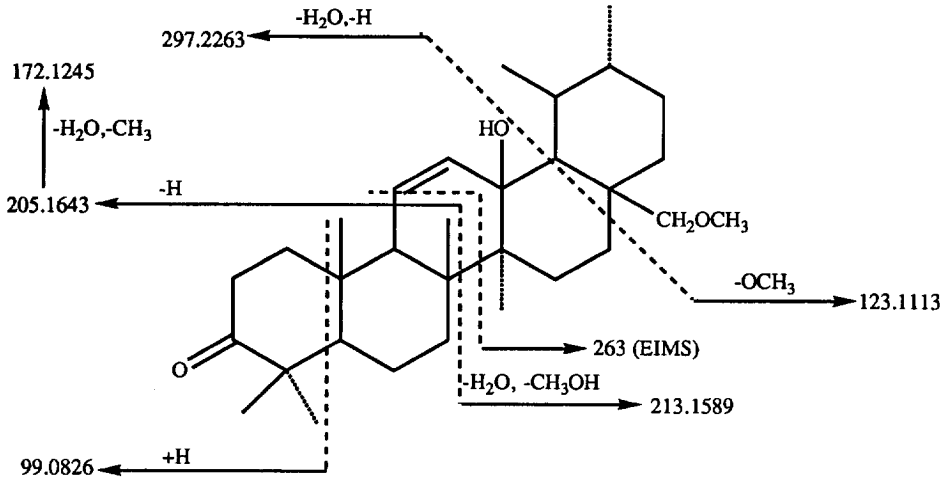

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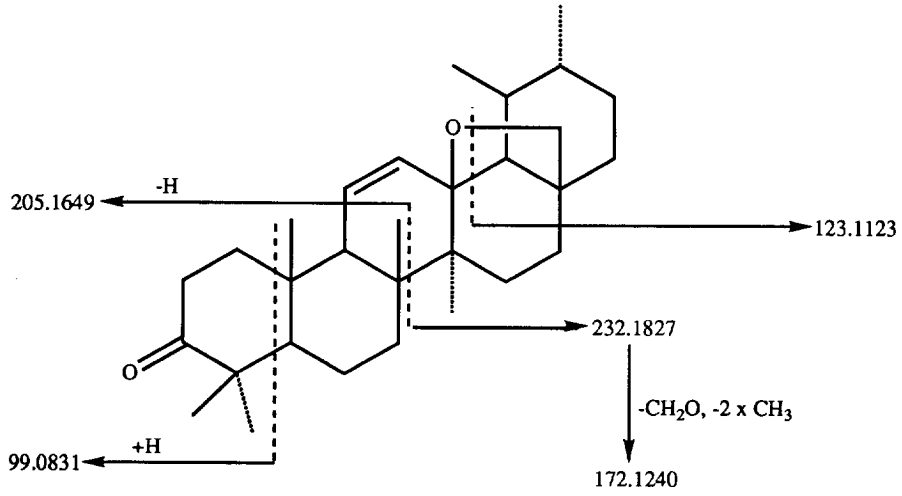

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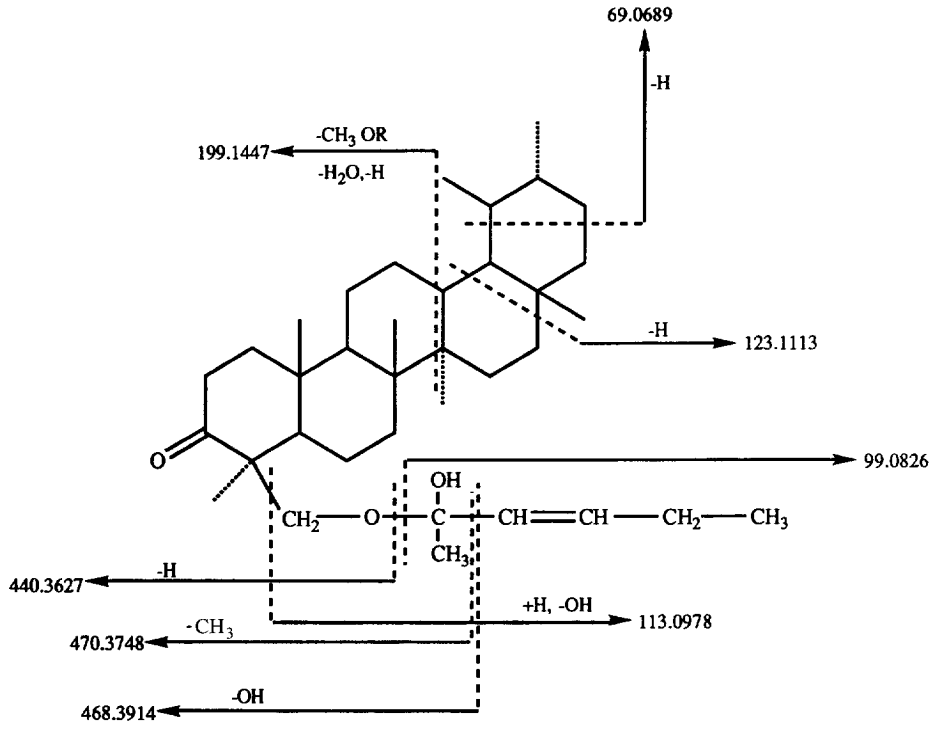
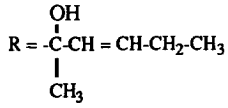
bond could therefore be placed at C-11 and supported by the chemical shifts and coupling constants of H-11 and H-12. On the basis of the spectral evidence, the structure of momordicin was decided to be 13-hydroxy-28-methoxy-urs-11-en-3-one (**1**).

Compound **2** has the molecular formula $C_{30}H_{46}O_2$ (HR-mass spectrum, 438.3503). The spectral data (see Experimental) of **2** were very similar to those of **1** except that the molecular formula now showed eight unsaturations instead of seven and the doublets of H-28a and H-28b now shifted to δ3.65 and 3.50 with a coupling constant of 8.4 Hz. This was suggestive of a 13β-28 epoxy bridge and the relatively downfield shifts of H-28a and H-28b favoured the double bond at C-11 [5] since in the compounds lacking this double bond these protons resonated upfield (*ca* δ3.2 and 3.5) [6]. The mass fragments (*vide* structure) substantiated the structure of momordicinin as 13β,28-epoxy-urs-11-en-3-one.

The triterpene **3** had the molecular ion peak at *m/z* 540 in the EI-mass spectrum corresponding to $C_{36}H_{60}O_3$. The ^{1}H NMR spectrum displayed nine methyl signals, six located on quaternary carbons at δ0.85, 0.86, 0.88, 0.90, 1.19, 1.32, two as doublets at δ0.87 (J = 7.4 Hz) and 0.89 (J = 6.29 Hz) and one as a triplet at δ1.20 (J = 7.36 Hz, Me). The downfield singlet (δ1.32) indicated that this methyl (Me-6′) was located on a carbon carrying an oxygen atom. The two methyl doublets indicated the compound to be related to the ursane series of triterpenoids. The molecular formula showed seven double bond equivalents, five of which adjusted in five rings, one was accounted for by a ketone group (IR: 1715 cm^{-1}) placed at C-3 on the basis of biogenetic analogy [4] and one could be justified by a *trans*-disubstituted double bond in the open chain. The existence and *trans*-nature of the C=C bond was demonstrated by the IR spectrum (1610 cm^{-1}) and the resonances at





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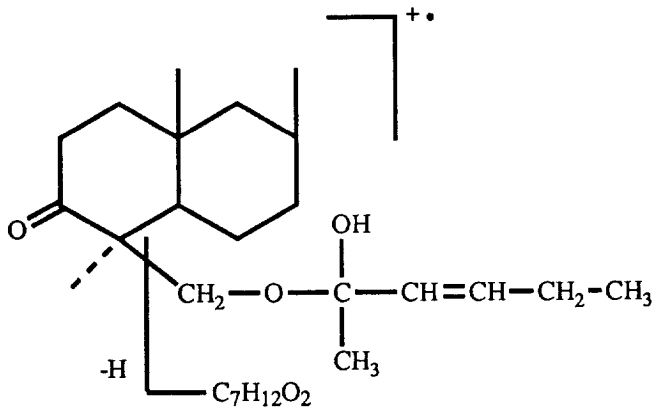
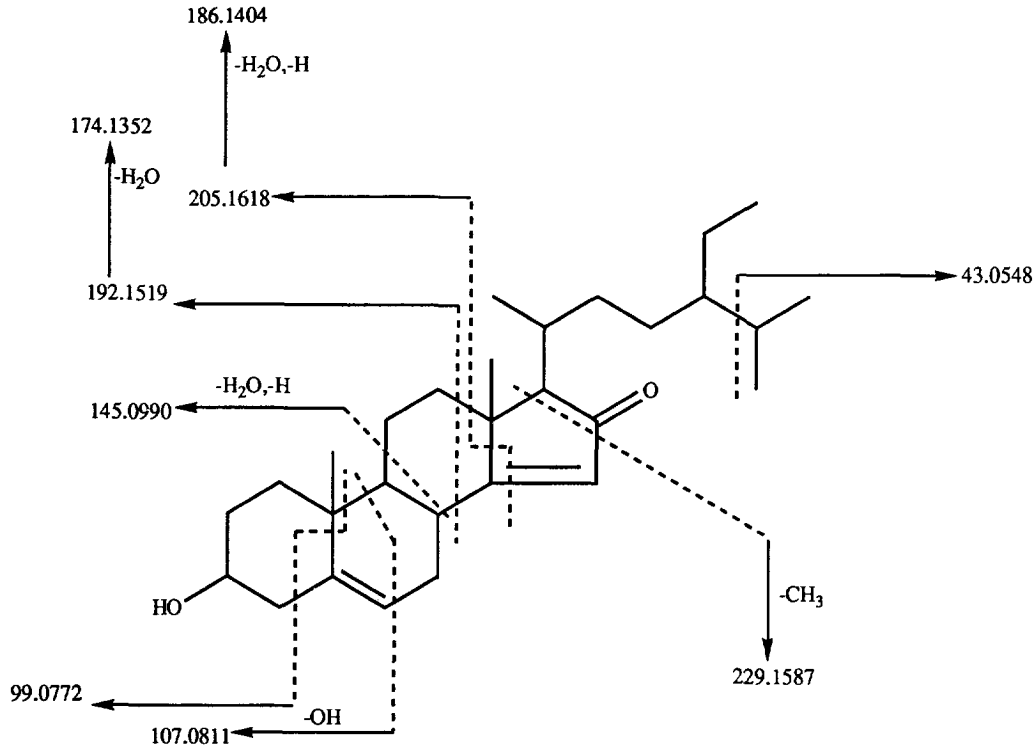


3a

$3a\text{-}C_7H_{12}O_2 = C_{13}H_{20}O = 192.1517$

$192.1517\text{-}H_2O\text{-}H = 173.1300 = C_{13}H_{17}$

δ5.53 (*ddd*, J = 16.2, 8.1, 5.3 Hz, H-3′) and 5.39 (*dd*, J = 16.2, 0.9 Hz, H-2′). These data suggested the saturated nature of the pentacyclic skeleton. Apart from these signals, the ^{1}H NMR spectrum showed two one-proton AB doublets at δ3.97 and 3.39 each with a coupling constant of 10.1 Hz indicating an oxygen substituted methylene group. A methyl triplet, a downfield methyl singlet and the disubstituted double bond carbons, one being attached to a fully substituted carbon led to the structure of the side chain



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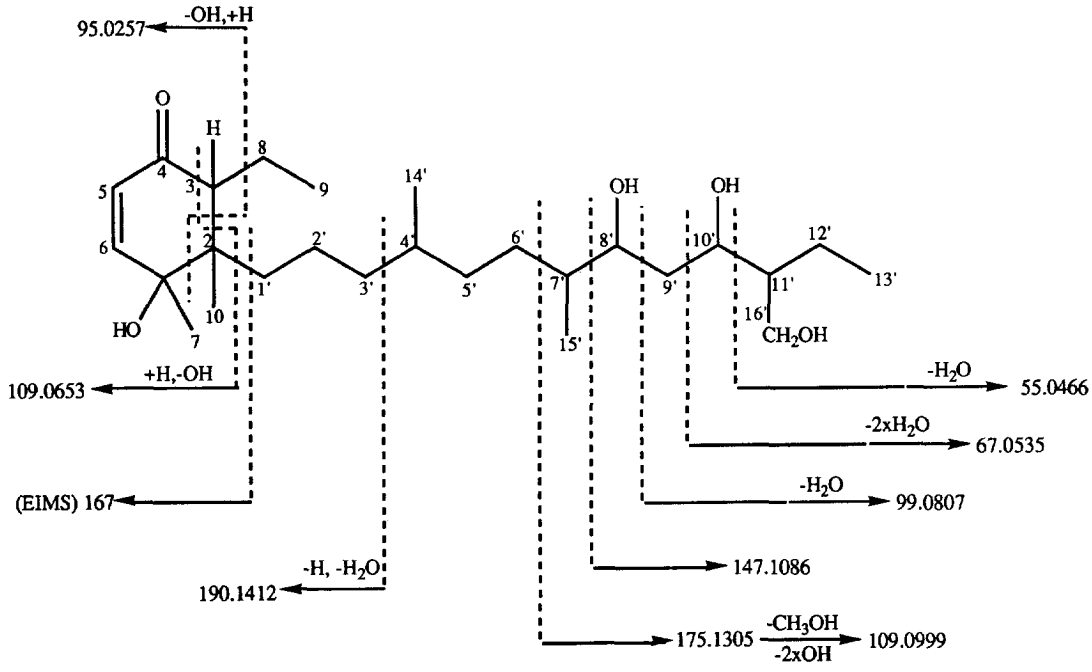


5

as a hemiacetal on one of the ring methyls as O–C(OH)–(CH_3)–CH:CH–CH_2–CH_3 which was supported by fragments at *m/z* 99.0826 $[C_6H_{11}O]^+$, 468.3914 $[C_{32}H_{53}O_3-OH,\ C_{32}H_{25}O_2]^+$, 470.3748 $[C_{31}H_{50}O_3]^+$, 440.3627 $[C_{30}H_{48}O_2]^+$ and 113.0978 $[C_7H_{13}O]^+$, 100% (*vide* structure). Fragments at *m/z* 69.0689 $[C_5H_9]^+$, 123.1113 $[C_9H_{15}]^-$ and 199.1447 $[C_{15}H_{19}]^+$ further displayed that this hemiacetal side chain was in ring A/B. Although no peak corresponding to the fragment **3a** was observed in the

mass spectrum of **3**, peaks at 192.1517 [**3a**-$C_7H_{12}O_2$ (side chain)] and 173.1300 (192.1517 − H_2O − H)$^+$ further supported this side chain to be situated on the A/B rings. The spatial interaction of the protons at δ3.39 (H-24a) and 3.97 (H-24b) with the protons at δ1.19 (H-23), 0.88 and 0.86 (H-25 and H-26) suggested that this side chain was located on C-24. The methyl protons could be assigned by comparison with the published data [7, 8]. Hence the structure of momordicilin was determined as 24-[1′-hydroxy,1′-methyl-2′-pentenyloxy]-ursan-3-one (**3**).

The HR-mass spectrum of **4** showed the molecular ion peak at *m/z* 426.3474 corresponding to $C_{29}H_{46}O_2$ showing seven double bond equivalence. The IR spectrum showed the presence of a hydroxyl group (3400 cm^{-1}), a ketone function (1700 cm^{-1}) and C=C (1595 cm^{-1}). The UV maxima were observed at 203 and 220 nm. Compound **4** gave positive tests of sterols (Liebermann–Burchard and Salkowski). The ^{1}H NMR spectrum had six methyl signals, two as singlets at δ0.99 (Me-19) and 0.88 (Me-18), three as doublets at δ1.07 (J = 6.8 Hz), 0.86 (J = 6.4 Hz) and 0.79 (J = 5.7 Hz) attributable to Me-21, Me-26 and Me-27, respectively [9], and one as a triplet at δ0.84 (J = 7.3 Hz) which was ascribed to Me-29. Two olefinic protons appeared at δ5.37 (*m*, H-6) and 5.57 (*br*, *s*); the former led to placement of one C=C bond at C-5, a position normally encountered in sterols and supported by the mass fragments at *m/z* 69 and 83 in the EI-mass spectrum, and *m/z* 99.0772 $[C_6H_{11}O]^+$ and 107.0811 $[C_8H_{11}]^+$ in the HR-mass spectrum. The chemical shift (δ5.57) and shape (*br*, *s*) of the second olefinic proton suggested that it was located on the α-carbon of a trisubstituted double bond conjugated with a carbonyl group. The IR band (1700 cm^{-1}) was suggestive of this α,β-unsaturated carbonyl system in a five membered ring (ring D), hence the double bond was placed at C-14 and the ketonic carbon was at C-16. This was substantiated by the fragment ions at *m/z* 192.1519 ($C_{13}H_{20}O$), 205.1618 $[C_{14}H_{21}O]^+$, 229.1587 $[C_{16}H_{21}O]^+$ and 285 ($[C_{19}H_{25}O_2]^+$ (*vide* structure). A carbinylic proton resonated at δ3.33 as a multiplet which supported the presence of a hydroxyl group indicated by the IR spectrum. It was placed at C-3 on biogenetic grounds with β-disposition considering the half width of the axial H-3 [21.5 Hz). Thus the four rings of the nucleus, two C=C bonds and one carbonyl function fully justified the seven unsaturations of the molecule, and left a C-10 saturated side chain which was also indicated by the ions at *m/z* 285 [M]$^+$- side chain) and 141 (side chain) in the EI-mass spectrum. The multiplicities of various methyl signals suggested an ethyl and an isopropyl moiety in the side chain. The ethyl group was placed at C-24 on biogenetic grounds [9] and the 24*R*-configuration was decided by comparison of the side chain carbons/protons chemical shifts with the reported values of this series [8]. In the light of these observations the structure of momordenol has been established as 3β-hydroxy-stigmasta-5,14-dien-16-one (**4**) which was fully supported by the

Table 1. ^{13}C NMR spectral data of compounds **4** and **5** [δ (ppm), $CDCl_3$]

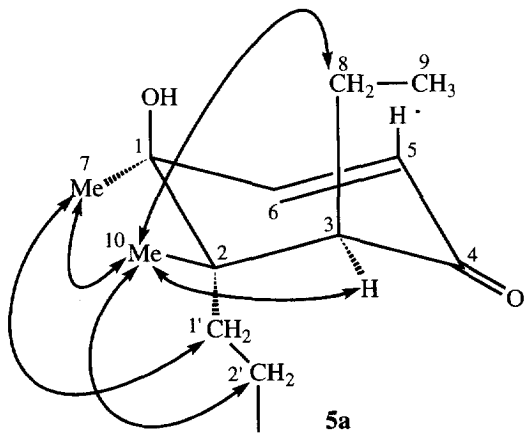
4		**5**	
C	δ	C	δ
1	38.6	1	76.4
2	31.9	2	45.2
3	70.9	3	38.0
4	41.5	4	198.0
5	142.0	5	131.6
6	121.4	6	148.5
7	29.9*	7	24.4
8	34.1	8	27.2
9	50.2	9	14.0*
10	36.1	10	16.7
11	25.8	1′	33.4
12	30.0*	2′	24.7
13	43.2	3′	38.2
14	194.5	4′	32.0
15	123.9	5′	30.5
16	207.1	6′	31.9
17	57.9	7′	43.0
18	14.1	8′	76.2**
19	19.5	9′	39.3
20	36.0	10′	76.1**
21	18.7	11′	50.2
22	39.4	12′	21.6
23	26.1	13′	15.0*
24	45.1	14′	19.9***
25	29.3	15′	20.6***
26	19.1	16′	65.6
27	19.4		
28	22.6		
29	14.9		

*, **, *** = values may be interchanged.

^{13}C NMR data (Table 1) which showed 29 carbons in the molecule including the carbinylic carbon (C-3) at δ70.5, four unsaturated carbons at δ142.0, 121.4, 194.5 and 123.9 (C-5, C-6, C-14 and C-15, respectively) and a carbonyl carbon (C-16) at δ207.1. The carbons were assigned through comparison with the values of compounds with similar partial structures [10, 11].

The HR-mass spectrum of **5** gave the molecular formula $C_{26}H_{48}O_5$ [M]$^+$ at *m/z* 440.3558) indicating three degrees of unsaturation. The IR spectrum showed bands characteristic of hydroxyl (3400, 1150 cm^{-1}), carbonyl (1690, cm^{-1}) and C=C (1600 cm^{-1}) groups. The ^{1}H and ^{13}C NMR (Table 1) spectra revealed the presence of one carbonyl and one C=C double bond so that **5** was considered a monocyclic compound. The ^{13}C NMR and DEPT experiments further showed that **5** possessed six methyls, nine methylenes, eight methines and three quaternary carbons. One methylene (δ_c65.6), two methines (δ_c76.1, 76.2) and one quaternary carbon (δ_c76.4) could be assigned to carbons bearing the hydroxyl groups. The

IR and NMR data (δ_{C-4} = 198.0; δ_{H-5} = 5.65, *d*, J = 9.7 Hz, δ_{C-5} = 131.6; δ_{H-6} = 6.06, *d*, J = 9.7 Hz, δ_{C-6} = 148.5) displayed a cyclohexenone moiety in the molecule. The ^{1}H NMR spectrum further showed two double doublets at δ3.45(J = 10.0, 7.1 Hz) and 3.71 (J = 10.0, 7.1 Hz) pointing the —CH_2OH group on a secondary carbon. Six overlapped methyl signals were identified from the 2D J resolved spectrum, two as singlets at δ0.84 and 1.20, two as doublets at δ0.89 (J = 6.6 Hz) and 0.97 (J = 6.6 Hz), and two as triplets at δ0.86 (J = 6.8 Hz) and 0.87 (J = 6.9 Hz) which pointed a highly branched carbon side chain. A fragment at *m/z* 167 in the EI-mass spectrum corresponding to $C_{10}H_{15}O_2$ and ions at *m/z* 135.0742 [$C_9H_{11}O$, 167−CH_3−OH]$^+$, 121.0996 [C_9H_{13}, 167−CO−H_2O]$^+$, 107.0831 [C_8H_{11}, 167−CO−H_2O−CH_3+H]$^+$ and 105.0713 [C_8H_9, 167−CO−H_2O−CH_3−H]$^+$ in the HR-mass spectrum suggested a 16 carbon side chain linked to the cyclohexenone ring bearing a hydroxyl function and four additional carbons. A methyl singlet at δ1.20 was attributable to the methyl group, geminal to the tertiary hydroxyl group. Since the β-proton (δ6.06) of the α,β-unsaturated ketone system showed coupling with the α-proton only its adjacent C must be fully substituted and hence the methyl and the hydroxyl functions were placed on this carbon (C-1) and supported by fragments at *m/z* 109.0653 (C_7H_9O) and 95.0257 (C_6H_7O) (*vide* structure). A one-proton triplet at δ2.46 (J = 8.6 Hz) was assignable to the proton on the carbon (C-3) next to the carbonyl group. The triplet showed that C-3 possessed a CH_2- and a quaternary carbon on its neighbour. Hence the remaining quaternary methyl and one of the side chains was placed on its adjacent carbon (C-2). The ^{1}H–^{1}H interactions in the COSY-45 spectrum were observed between the protons at δ2.46 (H-3) and δ1.21 (*m*, H-8), and between H-8 and H-9 (δ0.86, *t*). On this account the ethyl side chain was placed at C-3 justifying one methyl triplet and the upfield methyl shift [δ14.0/15.0) [12]. The $C_{16}H_{33}O_3$ side chain was therefore placed at C-2. Three remaining methyls and the —CH_2OH group indicated that this chain might be composed of three isoprenoid units linked to C-1′. A fragment at *m/z* 147.1086 [$C_7H_{15}O_3$]$^+$ was indicative of the three hydroxyl groups distributed between the seven terminal carbons. The methyl protons triplet at δ0.87 and its connected carbon (δ_c14.0/15.0) suggested that the terminal end is –CH_2CH_3 instead of an isopropyl moiety [12, 13]. Hence the head of the terminal isoprenoid is linked with the next isoprenoid unit and the –CH_2OH is at C-11′. This was supported by the following fragments (*vide* structure) which also exhibited the positions of the remaining hydroxyl groups at C-8′ and C-10′, *vis á vis*: *m/z* 73 [C_4H_9O]$^+$, 55.0466 [C_4H_7]$^+$, 103 [$C_5H_{11}O_2$]$^+$, 69.0651 [C_5H_7]$^-$, 117 [$C_6H_{13}O_2$]$^+$, 99.0807 [$C_6H_{11}O$]$^+$, 147.1086 [$C_7H_{15}O_3$]$^+$ and 175.1305 [$C_9H_{19}O_3$]$^+$. These fragments also showed the linkage of the terminal isoprenoid unit with the next unit in head to tail fashion. The head to head joining of the mid unit with the next isoprenoid moiety was concluded from the ^{13}C NMR shifts. The shift of C-1′ is close to that of C-1′ of iristectorene B, and its derivatives [11] while those of C-2′ and C-3′ are comparable with the partial structures of similar compounds [13, 14]. The remaining carbons were assigned following the additivity rules [15] and comparison with similar partial structures [12, 14, 16]. These assignments fit best with the head to head (C-5′/C-6′) and tail-to-head (C-9′/C-10′) linkages than in any other arrangement. These observations led to the assignment of the structure of momordol as 1-hydroxy, 1-2-dimethyl,2-[8′,10′-dihydroxy-4′,7′-dimethyl-11′-hydroxymethyl-trideca]-3-ethyl-cyclohex-5-en-4-one (**5**) which was substantiated by further mass spectral fragments (*vide* structure). The stereochemistry of the ring system was deduced by a NOESY experiment which showed the correlation of H-7 with H-10 as well as H-1′ suggesting the equatorial orientation of the methyl at C-1. Furthermore, H-10 was correlated with H-3 as well as H-8 and H-2′ pointing to the equatorial disposition of H-10 (2-CH_3). Hence the relative stereochemistry of the ring system of **5** is as shown in **5a**. The NOESY experiment, however, proved of no help in assigning the configurations of the asymmetric centres at C-4′, C-7′, C-8′, C-10′ and C-11′, and other methods [17] could not be applied in the present studies due to the limited quantity of the compound available.



5a

EXPERIMENTAL

General. Mps: uncorr. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz): $CDCl_3$ with the spectra reference to residual solvent signals; EI-MS (probe): 70 eV; HREI-MS (probe): 70 eV; VLC: silica gel GF_{254}; FCC (Model Eyela, E-10, silica 9385, E. Merck).

The fresh fruits (20 kg) of *M. charantia* obtained from the local market of Karachi were cut into small pieces and repeatedly (× 5) extracted with MeOH at room temp. After removal of the solvent under vacuum, the syrupy residue was partitioned between EtOAc and H_2O. The EtOAc phase was treated with 4% aq. soln of Na_2CO_3 to remove the acidic com-

ponents. The neutral constituents obtained on washing (H_2O), drying (dry Na_2SO_4), decolourizing (activated charcoal bed) and removal of the solvent from the EtOAc layer was divided into petrol soluble and petrol insoluble frs. The latter fr. was separated by VLC using $CHCl_3$, $CHCl_3$–MeOH (increasing polarity) as eluents, successively. The fr. eluted with $CHCl_3$ yielded a mixt. of triterpenes which on prep. TLC ($CHCl_3$–MeOH, 99:1) afforded **1**, **2** and **3** in order of polarity. The $CHCl_3$–MeOH, (24:1) eluate of VLC furnished **4** on purification over prep. TLC ($CHCl_3$–MeOH, 49:1). The $CHCl_3$–MeOH (97:3) eluate was subjected to FCC ($CHCl_3$, $CHCl_3$–MeOH, increasing polarity) followed by prep. TLC ($CHCl_3$–MeOH, 97:3) affording the monocyclic alcohol (**5**).

Momordicin (**1**). Fine needles (3.6 mg), mp 121–122°; $[\alpha]_D^{27} = +62°$ ($c = 0.12$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3650 (–OH), 2910 (C–H), 1710 (C=O), 1600 (C=C). HREI-MS *m/z* (rel. int.): 470.3748 $[M]^+$ (calcd for $C_{31}H_{50}O_3$ *m/z* 470.3759) (18), 297.2263 $[C_{21}H_{29}O]^+$ (15), 263 (EI-MS) 213.1589 $[C_{16}H_{21}]^+$ (100), 205.1643 $[C_{14}H_{21}O]^+$ (33), 187.1433 $[C_{14}H_{19}]^+$ (15), 172.1245 $[C_{14}H_{21}O-H_2O-CH_3, C_{13}H_{16}]^+$ (30), 135.1131 $[C_{10}H_{15}]^+$ (27), 123.1113 $[C_9H_{15}]^+$ (31), 121.0969 $[C_9H_{13}]^+$ (21), 107.0843 $[C_8H_{11}]^+$ (32), 99.0826 $[C_6H_{11}O]^+$ (39). ^1H NMR: δ6.03 (1H, *dd*, $J = 9.8$, 2.1 Hz, H-12), 5.62 (1H, *dd*, $J = 9.8$, 3.7 Hz, H-11), 3.97 (1H, *d*, $J = 10.1$ Hz, H-28a), 3.39 (1H, *d*, $J = 10.1$ Hz, H-28b), 3.14 (3H, *s*, OCH_3), 1.72 (1H, *d*, $J = 10.9$ Hz, H-18), 1.24, 1.19, 0.88, 0.86, 0.85 (each 3H *s*, $5 \times CH_3$), 0.89 (3H, *d*, $J = 6.2$ Hz, CH_3), 0.87 (3H, *d*, $J = 7.4$ Hz, CH_3).

Momordicinin (**2**). Irregular plates (4.0 mg), mp 146–147°; $[\alpha]_D^{27} = +54$ ($c = 0.14$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 2900 (CH), 1710 (C=O), 1600 (C=C), 1080 (C–O–). HREI-MS *m/z* (rel. int.): 438.3503 $[M]^+$ (calcd for $C_{30}H_{46}O_2$ *m/z* 438.3497) (37), 423.3337 $[C_{29}H_{43}O_2]^+$ (16), 403.3036 $[C_{29}H_{39}O]^+$ (20), 297.2265 $[C_{21}H_{29}O]^+$ (13), 232.1827 $[C_{16}H_{24}O]^+$ (100), 205.1649 $[C_{14}H_{21}O]^+$ (11), 187.1438 $[C_{14}H_{19}]^+$ (19), 172.1240 $[C_{13}H_{16}]^+$ (27), 157.1032 $[C_{12}H_{13}]^+$ (33), 123.1121 $[C_9H_{15}]^+$ (33), 121.0971 $[C_9H_{13}]^+$ (32), 99.0831 $[C_6H_{11}O]^+$ (49). ^1H NMR: δ6.08 (1H, *dd*, $J = 10.0$, 2.5 Hz, H-12), 5.63 (1H, *dd*, $J = 10.0$, 3.5 Hz), 3.65 (1H, *d*, $J = 8.4$ Hz, H-28a), 3.50 (1H, *d*, $J = 8.4$ Hz, H-28b), 2.10 (1H, *m*, H-9), 1.74 (1H, *d*, $J = 10.8$ Hz, H-18), 1.22, 1.12, 0.88, 0.86, 0.85 (each 3H *s*, $5 \times CH_3$), 0.89 (3H, *d*, $J = 6.3$ Hz, CH_3), 0.87 (3H, *d*, $J = 7.5$ Hz, CH_3).

Momordicilin (**3**). Needles (3.0 mg), mp 170–171°; $[\alpha]_D^{27} = +42°$ ($c = 0.19$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2910 (CH), 1715 (C=O), 1610 (C=C), 1080 (C–O). FD-MS *m/z*; 540 $[M]^+$ ($C_{36}H_{60}O_3$); HREI-MS *m/z* (rel. int.): 484.3928 (calcd for $C_{32}H_{52}O_3$ *m/z* 484.3916) $[M-C_4H_8]^+$ (15), 470.3745 $[C_{31}H_{50}O_3]^+$ (18), 468.3914 $[C_{32}H_{52}O_2]^+$ (21), 440.3627 $[C_{30}H_{48}O_2]^+$ (38), 309.2543 $[C_{19}H_{33}O_3]^+$ (57), 213.1589 $[C_{16}H_{21}]^+$ (10), 199.1447 $[C_{15}H_{19}]^+$ (10), 192.1517 $[C_{13}H_{20}O]^+$ (13), 173.1300 $[C_{13}H_{17}]^+$ (29), 123.1113 $[C_9H_{15}]^+$ (32), 113.0978 $[C_7H_{13}O]^+$ (100), 99.0826 $[C_6H_{11}O]^-$ (50), 69.0689 $[C_5H_9]^+$ (35). ^1H NMR: δ5.53 (1H, *ddd*, $J = 16.2$, 8.1, 5.3 Hz, H-3′). 5.39 (1H, *dd*, $J = 16.2$, 0.9 Hz, H-2′), 3.97 (1H, *d*, $J = 10.1$ Hz, H-24a), 3.39 (1H, *d*, $J = 10.1$ Hz, H-24b), 1.32 (3H, *s*, H-6′), 1.20 (3H, *t*, $J = 7.4$ Hz, H-5′), 1.19, 1.09, 0.88, 0.86, 0.85 (each 3H, *s*, $5 \times CH_3$), 0.89 (3H, *d*, $J = 6.3$ Hz, CH_3), 0.87 (3H, *d*, $J = 7.4$ Hz, CH_3).

Momordenol (**4**). Fine needles (6.0 mg), mp 160–161°; $[\alpha]_D^{27} = -62.9°$ ($c = 0.1$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2930 (CH), 1700 (C=O), 1595 (C=C); UV λ_{max}^{EtOH} nm: 225. HREI-MS *m/z* (rel. int.): 426.3474 $[M]^+$ (calcd for $C_{29}H_{46}O_2$ *m/z* 426.3497) (30), 411.3259 $[C_{28}H_{43}O_2]^+$ (26), 408.3389 $[C_{29}H_{44}O]^+$ (28), 393.3155 $[C_{28}H_{41}O]^+$ (33), 229.1587 $[C_{16}H_{21}O]^+$ (15), 205.1618 $[C_{14}H_{21}O]^+$ (21), 192.1519 $[C_{13}H_{20}O]^+$ (34), 186.1404 $[C_{14}H_{18}]^+$ (29), 174.1352 $[C_{13}H_{18}]^+$ (43), 145.0990 $[C_{11}H_{13}]^+$ (75), 119.0852 $[C_9H_{11}]^+$ (100), 107.0811 $[C_8H_{11}]^+$ (54), 99.0772 $[C_6H_{11}O]^+$ (23), 43.0548 $[C_3H_7]^+$, (68). ^1H NMR: δ5.57 (1H, *br*, *s*, H-15), 5.37 (1H, *m*, H-6), 3.33 (1H, *m*, $W1/2 = 21.5$ Hz, H-3), 1.07 (3H, *d*, $J = 6.83$ Hz, H-21), 0.96 (3H, *s*, H-19), 0.86 (3H, *d*, $J = 6.4$ Hz, H-26), 0.85 (3H, *t*, $J = 7.32$ Hz, H-29), 0.79 (3H, *d*, $J = 5.7$ Hz, H-27), 0.68 (3H, *s*, H-18). ^{13}C NMR: Table 1.

Momordol (**5**). Oil (8.0 mg), $[\alpha]_D^{27} = +37°$ ($c = 0.15$, $CHCl_3$). IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1690 (α, β unsat C=O), 1600 (C=C), 1150 (C–O); UV λ_{max}^{EtOH} nm; 215. HREI-MS *m/z* (rel. int.): 440.3558 $[M]^+$ (calcd for $C_{26}H_{48}O_5$ *m/z* 440.3501) (43), 239.2042 $[C_{15}H_{27}O_2]^+$ (19), 192.1525 $[C_{18}H_{20}O]^+$ (26), 190.1412 $[C_{13}H_{18}O]^+$ (19), 175.1305 $[C_9H_{19}O_3]^+$ (19), 174.1367 $[C_{13}H_{18}]^+$ (20), 161.1198 $[C_8H_{17}O_3]^+$ (19), 147.1086 $[C_7H_{15}O_3]^+$ (25), 135.0742 $[C_9H_{11}O]^+$ (9), 123.1101 $[C_9H_{15}]^+$ (11), 121.0996 $[C_9H_{13}]^+$ (12), 109.0999 $[C_8H_{13}]^+$ (100), 109.0653 $[C_7H_9O]^+$ (33), 107.0831 $[C_8H_{11}]^-$ (26), 105.0713 $[C_8H_9]^+$ (28), 99.0807 $[C_6H_{11}O]^+$ (22), 95.0257 $[C_6H_7O]^+$ (20), 67.0535 $[C_5H_7]^+$ (17), 55.0466 $[C_4H_7]^+$ (28). ^1H NMR: δ6.06 (1H, *d*, $J = 9.7$ Hz, H-6), 5.65 (1H, *d*, $J = 9.7$ Hz, H-5). 3.71 (1H, *dd*, $J = 10.0$, 7.1 Hz, H-16′a), 3.45 (1H, *dd*, $J = 10.0$, 7.1 Hz, H-16′b), 3.35–3.55 (2H, *m*, H-8′, H-9′), 2.46 (1H, *t*, $J = 8.5$ Hz, H-3), C-methyls: 1.20 (*s*), 0.97 (3H, *d*, $J = 6.6$ Hz), 0.89 (3H, *d*, $J = 6.6$ Hz), 0.87 (3H, *t*, $J = 6.9$ Hz), 0.86 (3H, *t*, $J = 6.8$ Hz), 0.84 (*s*). ^{13}C NMR: Table 1.

REFERENCES

1. Kritikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, The Indian Press, Allahabad, 1918, p. 590.
2. Baldwa, V. S., Bhandari, C. M., Pangaria, A. and Goyal, R. K., *Upsala Journal of Medical Science*, 1977, **82**, 39.
3. Chopra, R. N., Chopra, I. C., Handa, K. L. and Kapoor, L. D., *Indigenous Drugs of India*, U.N. Dhur and Sons Pvt., Calcutta, 1958.
4. Kojima, H. and Ogura, H., *Phytochemistry*, 1989, **28**, 1703.
5. Yamamoto, A., Suzuki, H., Miyase, T., Ueno, A. and Maeda, T., *Phytochemistry*, 1993, **34**, 485.

6. Bloor, S. J. and Qi, L., *Journal of Natural Products*, 1994, **57**, 1354.
7. Jimeno, M. L., Rumbero, A. and Vázquez, P., *Magnetic Resonance in Chemistry*, 1995, **33**, 408.
8. Yamamoto, A., Miyase, T., Ueno, A. and Maeda, T., *Chemical and Pharmaceutical Bulletin*, 1993, **41**, 1270.
9. Rubinstein, I., Goad, L. J., Clague, A. D. H. and Mulheirn, L. J., *Phytochemistry*, 1976, **15**, 195.
10. Breitmaier, E., Haas, G. and Voelter, W., *Atlas of Carbon*-13 *NMR Data*, Compound No. 882, Vol 1. Heyden and Son, London, 1979.
11. Alam, M. S., Chopra, N., Ali, M., Niwa, M. and Sakae, T., *Phytochemistry*, 1994, **37**, 521.
12. Seiki, K. Tomihara, T., Haga, K. and Kaneko, R., *Phytochemistry*, 1994, **36**, 433.
13. Matsuo, M. and Uraano, S., *Tetrahedron*, 1976, **32**, 229.
14. Johnson, L. F. and Jankowski, W. C. *Carbon*-13 *NMR spectra. A Collection of Assigned, Coded and Index Spectra*, Compounds 325, 445. Robert E. Krieger, Huntington, N.Y., 1978.
15. Stothers, J. B. *Carbon*-13 *NMR Spectroscopy*, Vol. 24, Organic Chemistry. Academic Press, New York, 1972.
16. Siddiqui, S., Siddiqui, B. S., Mahmood, T. and Faizi, S. *Heterocycles*, 1989, **29**, 87.
17. Fiaud, J. C., Horeau, A. and Kagan, H. B. in *Stereochemistry Fundamentals and Methods*, Vol. 3, Determination of configuration by Chemical Methods. ed. H. B. Kagan. Georg Thieme, Stuttgart, Germany, 1977.