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New compounds from *Commiphora myrrha* (Nees) Engl.

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Phytochemical investigation of *Commiphora myrrha* (Nees) Engl. has afforded six new compounds identified as cadina-3-en-15-ol (myrracadinol A) (**1**), 7, 8-*seco*-2, 5-dihydroxy-12-acetoxycalam-8-ene (myrracalamene A) (**2**), 7, 8-*seco*-2, 3, 5-hydroxy-12-acetoxycalame-8-ene (myrracalamene B) (**3**), 7, 8-*seco*-cadin-3, 8-dien-2β, 12-diol (myrracadinol B) (**4**), 7, 8-*seco*-12-hydroxycalam-8-ene (myrracalamene C) (**6**), 7, 8-*seco*-cadin-3,7(12)-dien-5α,10α-diol (myrracadinol C) (**7**) along with a known compound triacont-1-ene (**5**). Their structures were elucidated on the basis of spectral and chemical analyses.

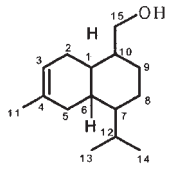
1. Introduction

Myrrh, commonly known as Guggul, is an oleo-gum-resin obtained from *Commiphora myrrha* (Nees) Engl. and other species of *Commiphora* (Goshi 2000). These are small trees of the family Burseraceae, native to Ethiopia, Somalia, and the Arabian peninsula (Khare 2004). In India it's found in the arid and rocky zones in some parts of south-western and north-western regions including Mysore and Rajasthan (Dhiman 2003). Myrrh consists of irregular masses or tear-shaped pieces, dark yellow or reddish brown in colour, that exude naturally or from incisions made in the bark (Prajapati et al. 2003). The different commercial varieties are named according to their source, for example, Somali myrrh and Arabian myrrh. The drug constitute 25–40% resin (containing triterpines, alcohols and esters), 60% gum and up to 14% volatile oil (containing primarily sesquiterpenes and some monoterpines). The presence of isolinalyl acetate, 3-epilupenyl acetate, lupeone, 3-epi-α-amyrin, α-amyrone, β-eudesmol acetate, commiferin and allylcembrol from the plant, monocyclic diterpines such as α-camphorene and cembrene from resin and cholesterol, 4,17(20)-*trans*-pregnadien-3,16-dione, 4,17(20)-*cis*-pregnadien-3,16-dione and three new sterol-guggulsterol I, II, III have been reported from the gum resin (Rastogi and Mehrotra 1999). *Guggul* is one of the constituents in various Ayurvedic preparations like thyrocap, pushkar guggul, rumalya, aryogyavardhini which are used to control simple diffuse goiter, hyperlipidemia, rheumatoid arthritis and hepatic amoebiasis in experimental animals (Wealth of India 2001).

2. Investigations, results and discussion

Compound **1**, named myrracadinol A, was obtained as a colourless amorphous powder from petroleum ether fractions. Its IR spectrum exhibited absorption bands for hydroxyl group (3438 cm^{-1}) and unsaturation (1653 cm^{-1}). The mass spectrum of **1** showed a molecular ion peak at m/z 222 corresponding to cadinene-type sesquiterpene, $C_{15}H_{26}O$. It indicated three degrees of unsaturation, two of them were adjusted in bicyclic carbon framework and one in the olefinic linkage. The ion peak at m/z 154 was generated due to fission of $C_{1,2}$-$C_{5,6}$ bonds indicating vinylic linkage in ring A and hydroxyl group at ring B. The ^{1}H NMR spectrum of **1** showed a one-proton broad multiplet at δ 5.69 assigned to H-3. Two one-proton doublets at δ 3.37 (J = 7.2 Hz) and 3.33 (J = 7.2 Hz) were attributed to the C-15 hydroxymethylene proton. A three-proton broad signal at δ1.68 was assigned to C-11 methyl protons attached to olefinic C-4 carbon. Two three-proton doublets at δ 1.08 (J = 6.9 Hz) and 1.04 (J = 6.9 Hz) were associated with C-13 and C-14 secondary methyl functionalities. The remaining methylene and methine protons resonated in the range δ 2.35–1.17. The ^{13}C NMR spectrum of **1** exhibited important signals for vinylic carbons at δ 121.93 (C-3), 127.19 (C-4), hydroxy methylene carbon at δ 65.13 (C-15) and methyl carbons at δ 7.74 (C-11), 17.18 (C-14) and 14.69 (C-13). The degree of protonation of each carbon was determined by DEPT experiments. Acetylation of **1** with acetic anhydride and pyridine yielded a monoacetyl product. These evidences led to establish the structure of **1** as cadina-3-en-15-ol. This is an unreported sesquiterpene isolated from *C. myrrha* and other plants and is now being reported for the first time.

Compound **2**, named myrracalamene A, was obtained as pale yellow crystals from petroleum ether. It yielded blue colour with ferric chloride. It had a molecular ion peak at m/z 292 (M^+, $C_{17}H_{24}O_4$) and important ion peaks at m/z 249 $[M-Ac]^+$, 233 $[M-OAc]^+$, 191 $[M-C(Me_2)Ac]^+$, 177 $[M-CH_2C(Me_2)Ac]^+$, 122 $[177-C_4H_7]^+$ and 107 $[122-Me]^+$ suggesting the presence of two hydroxyl group in the benzene ring. In addition to the vinylic protons (δ 5.68, H-9; 4.97, 4.71, H_2-8), acetyl protons (δ 1.80, $COCH_3$) and methyl protons (δ 2.59, 1.42, 1.25, 0.87), the ^{1}H NMR spectrum of **2** displayed a one-proton broad signal at δ 7.45 assigned to H-3. The ^{13}C NMR spectrum of **2** showed important carbon signals for aromatic ring (δ 158.61–111.23), acetyl group (δ 171.21, 21.93) and



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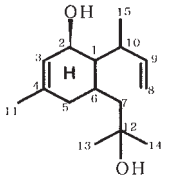

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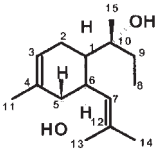

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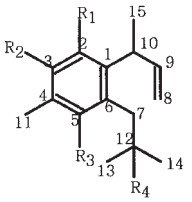
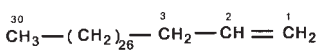


2 = R_1=OH, R_2=H, R_3= OH, R_4= OAc

3 = R_1=OH, R_2=OH, R_3= OH, R_4= OAc

6 = R_1=H, R_2=H, R_3= H, R_4= OH



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vinylic carbons (107.63, 120.39). On the basis of these results the structure of **2** has been formulated as 7,8-seco-2,5-dihydroxy-12-acetoxycalam-8-ene which is a new sesquiterpene.

Compound **3**, named myrracalamene B, was obtained as a pale yellow amorphous powder from petroleum ether. It gave blue colour with ferric chloride and its IR spectrum showed characteristic absorption bands for hydroxyl group (3510 cm^{-1}), ester group (1730 cm^{-1}), unsaturation (1650 cm^{-1}) and aromatic ring (1541, 910 cm^{-1}). The MS of **3** displayed a molecular ion peak at m/z 308 corresponding to a calamene type molecular formula, $C_{17}H_{24}O_5$. The important ion peaks at m/z 265 $[M-COCH_3]^+$, 249 $[M-OCOCH_3]^+$, 176 $[249-73]^+$, 121 $[176\text{-}C_4H_7]^+$, 180 $[M-CH_2\ (CH_3)_2\ OH-C_4H_7]^+$ and 137 $[183\text{-Ac}]^+$ indicated the presence of seco nature and acetyl group in the molecule. The ^{1}H NMR spectrum of **3** displayed one-proton multiplet at δ 5.69 assigned to methine H-9. Two one-proton doublets at δ 4.97 (J = 10.62 Hz) and 4.91 (J = 10.62 Hz) were attributed to unsaturated methylene H_2-8. A three-proton broad signal at δ 1.79 was associated with acetyl protons. A three-proton broad signal at δ 1.68 was due to C-11 methyl group attached to the aromatic ring. A six-proton broad signal at δ 1.26 was assigned to C-13 and C-14 methyl functionalities. The C-15 secondary methyl protons appeared as a three-proton doublet at δ 0.87 (J = 6.69 Hz). The absence of any aromatic proton signal in the spectrum indicated a substituted nature of the aromatic ring. The ^{13}C NMR spectrum of **3** exhibited the signals for aromatic carbons between δ 162.89–111.38, acetyl carbons at δ 171.77 and 24.30, vinylic carbons at δ 103.15 (C-8) and 113.74 (C-9) and oxygenated carbon at δ 77.47 (C-12). On the basis of these results the structure of **3** has been characterized as 7,8-*seco*-2,3,5-hydroxy-12-acetoxycalame-8-ene. This is a new phytoconstituent isolated from *C. myrrha*.

Compound **4**, designated as myrracadinol B, was obtained as a pale yellow amorphous powder from petroleum ether. Its IR spectrum showed absorption bands for hydroxyl groups (3450 cm^{-1}) and unsaturation (1651 cm^{-1}). The MS of **4** displayed a molecular ion peak at m/z 238 (M^+, $C_{15}H_{26}O_2$) and important ion peaks at m/z 220 $[M-H_2O]^+$, 202 $[220\text{-}H_2O]^+$, 187 $[202\text{-Me}]^+$, 183 {238 $[M-C_4H_7]^+$}, 165 $[183\text{-}H_2O]^+$, 150 $[165\text{-Me}]^+$, 129 $[165\text{-}2\times H_2O]^+$ and 114 $[129\text{-Me}]^+$ suggesting the compounds contained a seco cadinol type framework. The ^{1}H NMR spectrum of **4** exhibited deshielded signals as multiplet at δ 5.85 and 5.53 assigned to vinylic H-3 and H-9, respectively. A proton multiplet at δ 4.98 and a doublet at δ 4.73 (J = 6.1 Hz) were attributed to unsaturated C-8 methylene protons. Another one-proton broad multiplet at δ 3.15 with half width of 18.5 Hz was ascribed to carbinol H-2α. A six-proton broad signal at δ 1.26 was accounted to C-13 and C-14 tertiary methyl functionalities. A three-proton broad signal at δ 1.76 was associated with C-11 methyl protons attached to vinylic carbon C-4. A three-proton doublet at δ 0.85 (J = 6.0 Hz) was ascribed to C-15 secondary methyl protons. The ^{13}C NMR spectrum of **4** displayed carbon signals for vinylic carbons at δ 127.23 (C-3), 141.36 (C-4), 111.23 (C-8), 115.37 (C-9) and for carbinol carbons at δ 70.44 (C-2) and 69.36 (C-12). Acetylation of **4** with acetic anhydride and pyridine yielded a monoacetyl product suggesting the existence of one acetylable and one tertiary hydroxyl group. On the basis of these results, the structure of **4** has been established as 7, 8-seco-cadin-3, 8-dien-2β, 12-diol. This is a new phytoconstituent isolated form a natural or synthetic source for the first time.

Compound **5**, an aliphatic constituent, was obtained as a colourless amorphous powder from petroleum ether-chloroform (9 : 1) eluents. It yielded a yellow colour with tetranitromethane and decolourised bromine water indicating unsaturated nature of the molecule. Its IR spectrum displayed absorption bands for unsaturation (1650 cm^{-1}) and long aliphatic chain (735, 715 cm^{-1}). Its MS had a molecular ion peak at m/z 420 ($C_{30}H_{60}$) with one double bond adjustable to the olefinic linkage. The MS displayed ion peaks relating to C_nH_{2n+1}, C_nH_{2n} and C_nH_{2n-1} and most of the fragments were separated by 14 mass units. The intensities of the ion peaks decreased with the increasing molecular weight of the long straight chain hydrocarbon. The absence of (M^+-Me) ions suggested its straight chain nature (Stoianova-Ivanova and Hadijieva 1969). More intense cluster of peaks corresponding to C_nH_{2n-1} (m/z 83, 97, 111, 125, 139, etc) in comparison to that relating to C_nH_{2n+1} (m/z 85, 99, 113, 127, 141, etc) supported the acyclic olefinic nature of the compound (Misra et al. 1989). The ^{1}H NMR spectrum of **5** displayed a one-proton multiplet at δ 5.80 assigned to vinylic H-2. Two one-proton doublets at δ 5.01 (J = 10.34 Hz) and δ 4.94 (J = 10.38 Hz) were attributed to unsaturated C-1 methylene proton. A three-proton triplet at δ 0.87 (J = 7.8 Hz) was associated with C-30 primary methyl functionality. Two one-proton multiplets at δ 2.02 and 2.00 were assigned to C-3 methylene protons attached to unsaturated

C-2. The remaining methylene protons appeared at δ 1.67 ($1 \times CH_2$), 1.58 ($2 \times CH_2$), 1.25 ($22 \times CH_2$) and 1.00 ($1 \times CH_2$). The absence of any signal between δ 4.94 and 2.02 ruled out the location of any carbinol proton in the molecule. On the basis of these results, the structure of **5** has been identified as triacont-1-ene.

Compound **6**, named myrracalamene C, was obtained as a pale yellow crystal from petroleum ether-chloroform (1 : 1 v/v) eluents. It did not respond to ferric chloride test and showed IR absorption bands for hydroxyl (3500 cm^{-1}). Its MS displayed a molecular ion peak at m/z 218 corresponding to *seco*-calamene type diterpene $C_{15}H_{22}O$. The important ion peaks at m/z 145 $[M-CH_2CMe_2OH]^+$, 130 $[145\text{-}Me]^+$, 203 $[M-C_4H_7]^+$, 200 $[M-H_2O]^+$ and 185 $[200\text{-}Me]^+$ suggested the presence of hydroxyl group in the *seco* part of the molecule. The ^1H NMR spectrum of **6** showed three one-proton doublets as a *meta*-coupled doublet at δ 7.07 (J = 2.5 Hz) and as two *ortho*-coupled doublets at δ 5.77 (J = 9.5 Hz, 2.5 Hz) assigned to aromatic H-5, H-2 and H-3, respectively. A two-proton broad signal at δ 4.95 was attributed to unsaturated C-8 methylene protons. A two-proton broad signal at δ 2.49 was ascribed to C-7 methylene protons. A three-proton broad signal at δ 1.86 was assigned to C-11 methyl group attached to C-4 aromatic carbon. A six-proton broad signal at δ 1.25 was ascribed to C-13 and C-14 methyl functionalities. A three-proton doublet at δ 0.87 (J = 6.5 Hz) was due to C-8 primary methyl protons. The ^{13}C NMR spectrum of **6** exhibited signals for aromatic carbons between δ 147.43–119.37, vinylic carbons at δ 129.42 (C-9) and 106.90 (C-8) and carbinol carbon at δ 69.03 (C-12). Acetylation of **6** did not produce any acetyl derivative indicating tertiary nature of the hydroxyl group in the molecule. The spectral data analysis and chemical reactions led to the structure 7,8-*seco*-12-hydroxycalam-8-ene. This is an unreported sesquiterpene.

Compound **7**, designated as myrracadinol C, was obtained from chloroform eluents. Its IR spectrum displayed characteristic absorption bands at 3510 cm^{-1} (OH) and 1651 cm^{-1} (C=C). Its MS showed molecular ion peaks at m/z 238 (M^+, $C_{15}H_{26}O_2$) and important ion peaks at m/z 183 $[M-C_4H_7]^+$, 209 $[M-C_2H_5]^+$, 194 $[209\text{-}Me]^+$, 165 $[238\text{-}C_4H_9O]^+$ and 110 $[165\text{-}C_4H_7]^+$ indicating the existence of one of the hydroxyl group in the seco ring. The ^1H NMR spectrum of **7** displayed two deshielded doublets at δ 5.54 (J = 5.2 Hz) and 4.90 (J = 5.1 Hz) assigned to H-3 and H-7, respectively. A one-proton doublet at δ 3.35 (J = 5.5 Hz) was ascribed to carbinol 5β-H. A two-proton double doublet at δ 2.06 (J = 6.6, 7.5 Hz) was attributed to C-2 methylene protons attached to unsaturated carbon C-3. Three broad signals at δ 1.87, 1.85 and 1.83, integrating three protons each, were accounted to C-11, C-13 and C-14 methyl functionalities attached to olefinic carbons. A three-proton triplet at δ 0.85 (J = 6.6, 6.3 Hz) was due to C-8 primary methyl protons. The remaining methyl, methylene and methine protons appeared at δ 1.25 (Me-15), 1.42 (H_2-9), 2.66 (H-6α) and 0.97 (H-1α). The ^{13}C NMR spectrum of **7** exhibited important signals for vinylic carbons at δ 119.57 (C-3), 146.79 (C-4), 117.16 (C-7) and 135.25 (C-12) and carbinol carbons at δ 71.38 (C-5) and 77.71 (C-10). Acetylation of **7** yielded a monoacetyl product supporting the presence of one acetylable and one tertiary hydroxyl group in the molecule. On the basis of these results the structure of **7** has been established as 7,8-*seco*-cadin-3,7(12)-dien-5α,10α-diol. This is an unreported sesquiterpene alcohol isolated from *C. myrrha* or other species for the first time.

3. Experimental

3.1. Plant material

The oleo-gum-resin of *C. myrrh* was procured from the Khari Baoli market of Delhi and identified by Dr. M. P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard.

3.2. Extraction and isolation

The drug was dried in an oven at a temperature below 45 °C for 2–3 days and coarsely powdered. The pulverised drug (2.5 kg) was extracted exhaustively with ethanol (95%) in a Soxhlet extractor. The ethanolic extract was concentrated under reduced pressure to give a dark brown, viscous mass (460 g, 18.4%). The extract was dissolved in minimum amount of methanol and adsorbed on silica gel (60–120 mesh) for preparation of a slurry. It was dried, packed and chromatographed over silica gel column in petroleum ether. The column was eluted with petroleum ether, chloroform and methanol in the order of increasing polarity. All the solvents were mixed v/v and the eluents were collected as 100 ml fractions.

3.3. General chemical procedure

Melting points were determined on a Perfit apparatus in one end open capillary tube and are uncorrected. UV spectra were recorded on Lamda Bio-20 Spectrophotometer in methanol; IR spectra on Bio-Rad FT Spectrophotometer using KBr pellets; ^1H NMR spectra on Advance DRY 400 Bruker Spectrospin 400-MHz instrument using $CDCl_3$ as solvent and TMS as an internal standard; ^{13}C NMR Spectra on Advance DRY 400 Bruker Spectrospin 100-MHz with TMS as an internal standard in 5 mm spinning tubes at 27 °C; MS by effecting Electron Impact (EI) ionization at 70 eV on a JEOL-JMS-DX 303 instrument, equipped with direct inlet probe system. Silica gel (60–120 mesh) and silica gel-G were used for the column and TLC. Homogeneity of column fractions was controlled by TLC and the spots were visualised in UV light, iodine chamber and by spraying the plates with ceric ammonium sulphate.

3.4. Characterization of the compounds

3.4.1. Myrracadinol A (1)

Elution of the column with petroleum ether (fractions 22–25) yielded a colourless amorphous powder of **1,** which was recrystallized from MeOH, 300 mg (0.01% yield); R_f: 0.25 (pure pet ether); m.p.: 151–152 °C; $[\alpha]_D^{30}$: +79° (C 0.05, $CHCl_3$); UV λ_{max} (MeOH): 202 nm (log ε 3.2); IR υ_{max} (KBr): 3438, 2950, 2845, 1653, 1474, 1360, 1120 cm^{-1}; ^1H NMR ($CDCl_3$): 5.69 (1 H, brm, H-3), 3.37 (1H, d, J = 7.2 Hz, H_2-15a), 3.33 (!H, d, J = 7.2 Hz, H-15b), 2.35 (2 H, brs, H_2-2), 2.29 (6 H, brs, H_2-5, H_2-8, H_2-9), 2.27 (2 H, brs, H-1, H-6), 2.13 (2 H, brs, H-7, H-10), 1.68 (3 H, brs, Me-11), 1.17 (2 H, m, H-12), 1.08 (3 H, d, J = 6.9 Hz, Me-13), 1.04 (3 H, d, J = 6.9 Hz, Me-14); ^{13}C NMR ($CDCl_3$): δ 51.15 (C-1), 28.97 (C-2), 121.93 (C-3), 127.19 (C-4), 26.53 (C-5), 44.01 (C-6), 35.41 (C-7), 20.58 (C-8), 19.18 (C-9), 37.24 (C-10), 7.74 (C-11), 34.10 (C-12), 14.69 (C-13), 17.18 (C-14), 65.13 (C-15); +ve ion FAB MS m/z (rel. int.): 222 $[M]^+(C_{15}H_{26}O)$ (3.6), 154 (100).

Acetylation of **1** Compound **1** (25 mg) was heated with a mixture of Ac_2O (5 ml) and pyridine (1 ml) for 3 h and left overnight. Water (10 ml) was added and the reaction mixture was extracted with $CHCl_3$ (3×5 ml), the organic phase washed with H_2O (1×10 ml), dried with Na_2SO_4 and evaporated to get the product, TLC comparable, IR λ_{max} 1725 cm^{-1}.

3.4.2. Myrracalamene A (2)

Elution of the column with petroleum ether (fractions 26–35) furnished pale yellow crystals of **2**, recrystallized from MeOH, 300 mg (0.01% yield); R_f: 0.48 (Toluene); m.p.: 135–136 °C; $[\alpha]_D^{30}$: −17° (C 0.05, MeOH); UV λ_{max} (MeOH): 217 nm (log ε 4.6); IR υ_{max} (KBr): 3510, 3360, 2955, 2840, 1735, 1650, 1520, 1470, 1365, 1120, 920, 850 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.45 (1 H, brs, H-3), 5.68 (1 H, m, H-9), 4.97 (1 H, d, J = 9.9 Hz, H_2-8a), 4.71 (1 H, brs, H_2-8b), 2.59 (3 H, brs, Me-11), 2.01 (1 H, m, H-10), 1.80 (3 H, brs, $COCH_3$), 1.75 (2 H, brs, H_2-7), 1.42 (3 H, brs, Me-13), 1.25 (3 H, brs, Me-14), 0.87 (3 H, d, J = 6.75 Hz, Me-15); ^{13}C NMR ($CDCl_3$): δ 148.15 (C-1), 159.33 (C-2), 113.60 (C-3), 124.35 (C-4), 158.61 (C-5), 111.23 (C-6), 48.90 (C-7), 107.63 (C-8), 120.39 (C-9), 53.07 (C-10), 7.86 (C-11), 77.28 (C-12), 26.38 (C-13), 24.12 (C-14), 13.87 (C-15), 171.21, 21.93 ($COCH_3$); +ve ion FAB MS m/z (rel. int.): 292 $[M]^+(C_{17}H_{24}O_4)$ (1.3), 249 (22.3), 233 (21.6), 191 (10.3), 177 (12.6), 122 (21.7), 107 (47.3).

3.4.3. Myrracalamene B (3)

Elution of the column with petroleum ether (fractions 26–62) yielded pale yellow amorphous mass of **3**, recrystallized from Me_2CO: $CHCl_3$ 1 : 2, 1.1 g (0.037% yield); R_f: 0.48 (pet. ether : $CHCl_3$ 8 : 2); m.p.: 115–116 °C; UV λ_{max} (MeOH): 217 nm (log ε 5.3); IR υ_{max} (KBr): 3510, 2960, 2845, 1730, 1650, 1541, 1521, 1508, 1457, 1419, 1396, 910 cm^{-1}; ^1H NMR

($CDCl_3$): δ 5.69 (1 H, m, H-9), 4.97 (1 H, d, J = 10.62 Hz, H-8a), 4.91 (1 H, d, J = 10.62 Hz, H-8b), 2.52 (1 H, m, H-10), 2.04 (2 H, brs, H_2-7), 1.79 (3 H, brs, $COCH_3$), 1.68 (3 H, brs, Me-11), 1.26 (6 H, brs, Me-13, Me-14), 0.87 (3 H, d, J = 6.69 Hz, Me-15); ^{13}C NMR ($CDCl_3$): δ 145.03 (C-1), 162.89 (C-2), 148.22 (C-3), 111.38 (C-4), 160.54 (C-5), 128.06 (C-6), 49.11 (C-7), 103.15 (C-8), 113.74 (C-9), 53.45 (C-10), 8.02 (C-11), 77.47 (C-12), 21.05 (C-13), 18.63 (C-14), 16.56 (C-15), 171.77, 24.30 ($COCH_3$); +ve ion FAB MS m/z (rel. int.): 308 $[M]^+(C_{17}H_{24}O_5)$ (18.3), 265 (11.3), 249 (17.16), 180 (9.7), 176 (7.17), 137 (62.5), 121 (15.6), 43(100).

3.4.4. Myrracadinol B (**4**)

Further elution of the column with petroleum ether (fractions 63–80) furnished pale yellow amorphous powder of **4**, recrystallized from $CHCl_3$: MeOH : Me_2CO (0.5 : 1 : 0.5), 400 mg (0.013% yield); R_f: 0.80 (Toluene : $CHCl_3$ 8 : 2); m.p.: 141–142 °C; $[\alpha]_D^{30}$: +87° (C 0.05, $CHCl_3$); UV λ_{max} (MeOH): 203 nm (log ε 4.1); IR υ_{max} (KBr): 3450, 1651, 1521, 1473, 1396, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.85 (1 H, m, H-3), 5.53 (1 H, m, H-9), 4.98 (1 H, m, H_2-8a), 4.73 (1 H, d, J = 6.1 Hz, H_2-8b), 3.15 (1 H, brm, w½ 18.5 Hz, H-2α), 2.29 (2 H, m, H_2-5), 1.94 (1 H, m, H-10), 1.82 (1 H, m, H-1), 1.76 (3 H, brs, Me-11), 1.50 (1 H, m, H-6), 1.50 (2 H, brs, H_2-7), 1.26 (6 H, brs, Me-13, Me-14), 0.85 (3 H, d, J = 6.0 Hz, Me-15); ^{13}C NMR ($CDCl_3$): δ 47.53(C-1), 70.44 (C-2), 127.23 (C-3), 141.36 (C-4), 26.24 (C-5), 40.21 (C-6), 16.79 (C-7), 111.23 (C-8), 115.37 (C-9), 35.20 (C-10), 7.44 (C-11), 69.36 (C-12), 20.26 (C-13), 15.29 (C-14), 28.69 (C-15); +ve ion FAB MS m/z (rel. int.): 238 $[M]^+(C_{15}H_{26}O_2)$ (6.5), 220 (11.9), 202 (23.6), 187 (19.7), 183 (16.1), 165 (22.8), 150 (21.3), 129 (24.6), 114 (37.1).

3.4.5. Triacont-1-ene (**5**)

Elution of the column with petroleum ether : chloroform (9 : 1 v/v) (fractions 81–159) afforded colourless amorphous powder of **5**, recrystallized from MeOH : diethyl ether (1 : 5), 200 mg (0.007% yield); R_f: 0.23 (benzene); m.p.: 110–111 °C; $[\alpha]_D^{30}$: +39° (C 0.05, MeOH UV); λ_{max} (MeOH): 202 nm (log ε 4.7); IR υ_{max} (KBr): 2955, 2845, 1650, 1470, 1310, 1150, 735, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.80 (1 H, m, H-2), 5.01 (1 H, d, J = 10.34 Hz, H_2-1a), 4.94 (1 H, d, J = 10.38 Hz, H_2-1b), 2.02 (1 H, m, H_2-3a), 2.00 (1 H, m, H_2-3b), 1.67 (2 H, m, H_2-4), 1.58 (4 H, brs, 2 × CH_2), 1.25 (44 H, brs, 22 × CH_2), 1.00 (2 H, m, CH_2), 0.87 (3 H, t, J = 7.8 Hz, Me-30); +ve ion FAB MS m/z (rel. int.): 420 $[M]^+(C_{30}H_{60})$ (12.1).

3.4.6. Myrracalamene C (**6**)

Elution of the column with petroleum ether-chloroform (1 : 1 v/v) (fractions 191–239) yielded pale yellow crystals of **7**, recrystallized from MeOH : Diethyl ether (3 : 1), 50 mg (0.0017% yield); R_f: 0.35 (benzene : ethyl acetate : diethyl amine 6 : 3:1); m.p.: 107–108 °C; $[\alpha]_D^{30}$: +69° (C 0.05, MeOH); UV λ_{max} (MeOH): 203 nm (log ε 4.9); IR υ_{max} (KBr): 3500, 2955, 2845, 1636, 1541, 1508, 1473, 1339, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.07 (1 H, d, J = 2.5 Hz, H-5), 5.77 (1 H, d, J = 9.5 Hz, H-2), 5.69 (1 H, dd, J = 9.5, 2.5 Hz H-3), 4.95 (2 H, brs, H_2-8), 2.49 (2 H, brs, H_2-7), 1.86 (3 H, brs, Me-11), 1.73 (2 H, t, J = 6.5 Hz, H_2-9), 1.25 (6 H, brs, Me-13, Me-14), 0.87 (3 H, d, J = 6.5 Hz, Me-8); ^{13}C NMR ($CDCl_3$): δ 147.43 (C-1), 136.42 (C-2), 135.07 (C-3), 143.80 (C-4), 122.82 (C-5), 119.37 (C-6), 42.28 (C-7), 106.90 (C-8), 129.42 (C-9), 34.67 (C-10), 7.42 (C-11), 69.03 (C-12), 19.59 (C-13), 19.13 (C-14), 14.87 (C-15); +ve ion FAB MS m/z (rel. int.): 218 $[M]^+(C_{15}H_{22}O)$ (11.3), 203 (18.6), 200 (22.1), 185 (21.7), 145 (28.9), 130 (33.6).

3.4.7. Myrracadinol C (**7**)

Elution of the column with chloroform (fractions 289–304) furnished pale yellow crystals of **7**, recrystallized from ethanol, 365 mg (0.0122% yield); R_f: 0.83 ($CHCl_3$: MeOH 8.5 : 1.5); m.p.: 225–226 °C; $[\alpha]_D^{30}$: −15° (C 0.05, MeOH); UV λ_{max} (MeOH): 203 nm (log ε 5.3); IR υ_{max} (KBr): 3510, 2965, 2850, 1651, 1490, 1363 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.54 (1 H, d, J = 5.2 Hz, H-3), 4.90 (1 H, d, J = 5.1 Hz, H-7), 3.35 (1 H, d, J = 5.5 Hz, H-5β), 2.66 (1 H, m, H-6α), 2.06 (2 H, dd, J = 6.6, 7.5 Hz, H_2-2), 1.87 (3 H, brs, Me-11), 1.85 (3 H, brs, Me-13), 1.83 (3 H, brs, Me-14), 1.42 (2 H, m, H_2-9), 1.25 (3 H, brs, Me-15), 0.97 (1 H, dd, J = 6.6, 7.5 Hz, H-1α), 0.85 (3 H, t, J = 6.6 Hz, Me-8); ^{13}C NMR ($CDCl_3$): δ 36.09 (C-1), 29.01 (C-2), 119.57 (C-3), 146.79 (C-4), 71.38 (C-5), 34.85 (C-6), 117.16 (C-7), 15.15 (C-8), 17.03 (C-9), 77.71 (C-10), 7.91 (C-11), 135.25 (C-12), 20.96 (C-13), 20.13 (C-14), 22.48(C-15); +ve ion FAB MS m/z (rel. int.): 238$[M]^+(C_{15}H_{26}O2)$ (11.3), 209 (21.3), 194 (16.5), 183 (22.7), 165 (41.6) 110 (100).

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