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New pentacyclic triterpenes from the roots of *Hemidesmus indicus*

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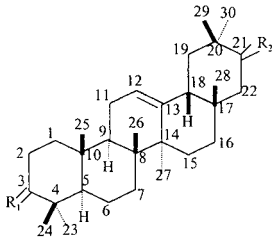
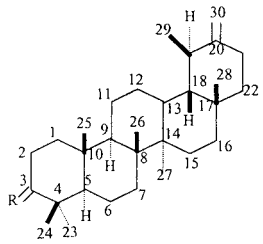
Phytochemical studies on the roots of *Hemidesmus indicus* resulted in the isolation of six new pentacyclic triterpenes including two oleanenes identified as olean-12-en-21β-yl acetate, and olean-12-en-3α-yl acetate, three ursenes characterized as 16(17)-seco-urs-12,20(30)-dien-18αH-3β-yl actetate, urs-20(30)-en-18βH-3β-yl acetate and 16(17)-seco-urs-12,20(30) dien-18-αH-3β-ol and a lupene formulated us lup-1,12-dien-3-on-21-ol including a known compound, β-amyrin acetate, on the basis of spectroscopic techniques and chemical means.

1. Introduction

Hemidesmus indicus R. Br. (Asclepiadaceae), commonly known as Sariva, is found throughout India and Sri Lanka as a twining undershrub [1]. Its tuberous roots possess alterative, aphrodisiac, refrigerant, diuretic, demulcent, blood-purifier and tonic properties and are useful to cure loss of appetite, blood diseases, bronchitis, cough, dysentery, dyspepsia, dysuria, syphilis, ulcers and uterine haemorrhage [2–5]. β-Sitosterol, triterpenes, hexatriacontane, flavonoid glycosides and pregnane glycosides have been reported from various parts of the plant [6]. The present paper describes the isolation and characterization of five new pentacyclic triterpens from the roots of the plant.



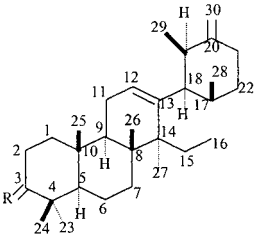
1 $R_1 = H_2$, R_2 = α-H,β-OAc



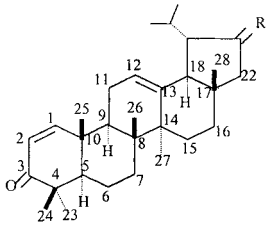
5 R = α-H, β-OAc

3 R_1 = β-H, α-OAc, $R_2 = H_2$

4 R_1 = α-H, β-OAc, $R_2 = H_2$



2 R = α-H, β-OAc
6 R = α-H, β-OH
6a R= 0



7 R = OH

2. Investigations, results and discussion

Compound **1**, named hemidesmusyl acetate, responded positively to the Liebermann-Burchard, TCA and TNM tests suggesting that it was a pentacyclic triterpenoid possessing an olefinic linkage. Its MS showed a molecular ion peak at m/z 468 corresponding to a molecular formula $C_{32}H_{52}O_2$. Its IR spectrum exhibited absorptions for ester group (1736 cm^{-1}) and olefinic linkage (1646 cm^{-1}). The ^1H NMR spectrum of **1** accounts for one H-12 vinylic proton as a triplet at δ 5.17 (J = 9.90 Hz), one H-21 α carbinol proton as a double doublet at δ 4.57 (J = 9.03, 6.00 Hz), eight methyl protons as broad singlets between δ 1.2–0.79 and one acetoxyl group (δ 2.05).

The MS of **1** indicated that the double bond triggered the typical retro – Diels Alder (RDA) fragmentation of ring C resulting in an ion fragment at m/z 192 [ion a]$^+$. The base peak at m/z 276 [ion b]$^+$ was also derived by RDA fragmentation [7]. The fission of $C_{18,19}$–$C_{21,22}$ bonds yielded an ion fragment at m/z 148. Simultaneous cleavage of rings D and E gave a fragment at m/z 234 [ion c]$^+$. Fission of C_8–C_{14}, and C_9–C_{11} bonds and migration of H-9 to H-8 generated an ion peak at m/z 263 [ion d]$^+$. These fragments were characteristics of Δ^{12}-amyrin derivatives containing a hydroxyl group in ring D or E. The ion peaks at m/z 148 [b-$C_7H_{12}O_2$]$^+$, 234 [ion c]$^+$ and 135 [ion d-$C_7H_{12}O_2$]$^+$ indicated the existance of the acetoxyl group in ring E at C-21. The ^{13}C NMR spectrum showed 32 carbon atoms in the molecule containing one ester, two olefinic and one carbinol carbons. Based on these findings the structure of hemidesmusyl acetate (**1**) has been formulated as olean-12-en-21β-yl acetate.

Compound **2**, namely seco-hemidesursenyl acetate, responded positively to the Liebermann-Burchard test and exhibited a molecular ion peak at m/z 468 corresponding to the moleculer formula $C_{32}H_{52}O_2$. Its IR spectrum showed the presence of ester group (1735 cm^{-1}) and unsaturation (1646 cm^{-1}). The ^1H NMR spectrum of **2** displayed signals for olefinic protons at δ 5.17 as a triplet (J = 7.74 Hz) assigned to H-12 and at δ 4.67 and 4.59 as broad singlets for two exocyclic methylene protons, at δ 4.49 as a double doublet (J = 4.4, 9.04 Hz) associated with H-3 axial and a singlet at δ 2.15 ascribed to an acetoxy group. The methyl protons appeared as broad singlets at δ 1.25 (Me-27), 1.06 (Me-23), 1.00 (Me-26), 0.99 (Me-24), and 0.87 (Me-25, Me-27), as doublets at δ 0.91 (J = 6.5 Hz) and 0.83 (J = 6.0 Hz) accounted to Me-29 and Me-28, respectively and as triplet at δ 0.79 (J = 6.0 Hz) for Me-16. The ^{13}C NMR spectrum showed 32 carbon signals including four olefinic and one carbinol signals. The endocyclic olefinic linkage was placed at C-12 in the ursane skeleton on the basis of the appearance of the base peak at m/z 218 [ion b]$^+$ generated due to retro-Diel-Alder fission of ring C [7, 8] followed by the other intensified ion peaks at m/z 250 [ion a]$^+$, 190 [ion a-AcOH]$^+$, 207 [ion a-Ac]$^+$, and 203 [ion b-Me]$^+$. The formation of

ion peaks at m/z 189 [ion b-C_2H_5]$^+$,123 [ion c, $C_{13}-C_{18}$ fission]$^+$, 95 [ion b−ion c]$^+$ and 80 [95-Me]$^+$ supported C-16 (17) seco nature of the molecule was established as 16(17)-seco-urs-12,20(30)-dien-18αH-3β-yl acetate.

Compounds **3** and **4** were identified as 3-epimer β-amyrin acetate and olean-12en-3β-yl acetate by comparing m.p., R_f value and analysis of spectral data.

Compound **5,** named hemidesursenyl acetate, gave positive test with Liebermann-Burchard, TCA and TNM reagents indicating unsaturated triterpenic nature of the compound. It had a molecular ion peak at m/z 468 in its MS corresponding to the molecular formula $C_{32}H_{52}O_2$. Its IR spectrum showed the absorption bands for ester groups (1732 cm^{-1}). The ^{1}H NMR spectrum of **5** displayed broad signals for exocyclic protons at δ 5.07 (H-30 a) and 4.90 (H-30 b), a double doublet at δ 4.60 with coupling interaction of 5.5 and 8.8 Hz were assigned to α-carbinol proton and placed at C-3 on the basis of biogenetic grounds. Four three-proton broad signals at δ 2.04, 1.25, 1.08 and 0.84 were assigned to acetyl, C-23, C-26 and C-24 methyls, respectively. Six-proton each broad signals at δ 1.07 and 0.93 were associated with corresponding to C-25, C-27 methyls and C-28, C-29 methyls. The appearance of all the methyl signals in the range δ 1.25−0.84 suggested the attachment of these functionalities on saturated carbons. A double doublet at δ 2.47 with coupling interactions of 3.9 Hz due to interaction with H-13β and 12.08 Hz due to coupling with H-19 α indicated β-orientation of C-18 proton. The ^{13}C NMR spectrum displayed 32 carbon atoms including one carbinol and one exocyclic methylene carbons. The MS of **5** exhibited diagnostically important ion peaks at m/z 453 [M−Me], 425 [M−Ac], 408 [M−AcOH], and 393 [408-Me] supporting the presence of one removable acetoxyl group in the molecule [10]. The ion fragments at m/z 159 [ion a], 142 [ion b], 139 [ion c-Ac], 122 [ion c-AcOH], 250 [ion d], 207 [ion d-Ac] and 313 [ion k] indicated the location of the acetoxyl group in ring A at C-3. The saturated nature of ring B, C and D and the existence of the olefenic linkage at ring E were deduced from the intensified ion peaks appearing at m/z 218 [ion e], 204 [ion e-CH_2], 277 [ion f], 199 [ion h], 175 [ion h-CH_3], 160 [175-CH_3], 150 [ion e-C_2H_8], 145 [160-CH_3], 150 [ion I], 135 [ion I-CH_3], 121 [135-CH_3], 107 [121-CH_3], 82 [ion j], 69 [ion j-CH_2], 54 [69-CH_2] and 67 [82-CH_3]. Based on these evidences the structure of **5** has been established as urs-20(30)en-18βH-3β-yl acetate. Biogenetic evidence suggesting the structure of **5** is provided by the recent isolation of similar triterpens with 19(29)- and 20(30)-vinylic double bonds [8].

Compound **6**, named seco-hemidesursenol, gave a positive Liebermann-Burchard test and had a molecular ion peak at m/z 426 in its MS consistent with the molecular formula $C_{30}H_{50}O$. Its IR spectrum showed the presence of hydroxyl (3302 cm^{-1}) and unsaturation (1645 cm^{-1}). The ^{1}H NMR spectrum of **6** exhibited signals for vinylic proton as a doublet at δ 5.12 (= 7.36Hz), exocyclic methylene protons as two broad singlets at δ 4.67 (CH_2-30a) and 4.58 (CH_2-30b), a 3-axial carbinol proton as a double doublet at δ 3.21 (J = 9.09, 5.02 Hz), five methyl protons as singlets at δ1.25 (Me-27), 1.07 (Me-23), 1.00 (Me-24) and 0.87 (Me-25, Me-27), two methyl protons as doublets, at δ 0.96 (J = 6.5 Hz, Me-29) and 0.81 (J = 6.0Hz, Me-28) and as triplet at δ 0.79 (J = 6.0 Hz, Me-30). The ^{13}C NMR spectrum displayed 30 carbons including one carbinol and four olefinic carbons. The appearance of a one-proton double doublet at δ 2.20 with coupling interactions of 5.0 and 6.5 Hz and the two methyl signals as doublets suggested that it was a seco-ursane type triterpene. The MS of **6** showed significant peaks at m/z 207 [ion a] and 218 [ion b] corresponding to the typical retro-Diels-Alder cleavage of Δ^{12}-pentacyclic skeleton at C_9-C_{11} and C_8-C_{14} bonds. This was confirmed by the peaks appearing at m/z 189 [ion a-H_2O], 174 [189-Me] and 203 [ion b-Me]. The cleavage of $C_{13}-C_{18}$ bond in the ion b generated important ion fragments at m/z 95 [ion c], 123 [ion d], 68 [ion c-CH_2=CH] and 108 [ion d] supporting $C_{16}-C_{17}$ seco nature of the molecule. The ion peaks at m/z 411 [M−Me], 408 [M−H_2O] and 393 [411-H_2O] supported the presence of one hydroxyl group in the molecule. Treatment of **6** with Jones reagent yielded a 3-oxo derivative (**6a**) which responded positively to the Zimmermann test [9]. These data led to assign the structure of secohemidesursenol (**6**) as 16(17)-seco-urs-12−20(30)-dien-18-αH-3β-ol.

Compound **7**, designated as hemidesmulupenol was, gave a positive Liebermann-Burchard test. Its IR spectrum showed characteristic absorption bands for hydroxyl (3342 cm^{-1}) and carbonyl (1710 cm^{-1}) groups. Its MS showed a molecular ion peak at m/z 438 corresponding to a triterpenic formula $C_{30}H_{46}O_2$. The MS of **7** showed ion peaks at m/z 423 [M−Me]$^+$, 395 [M−C_3H_7]$^+$, 111 [ion a]$^+$, 97 [ion a-CH_2]$^+$, 83 [ion a-C_2H_4]$^+$, 96 [ion b]$^+$, 164 [ion c]$^+$, 150 [ion c-CH_2]$^+$, 136 [150-CH_2]$^+$, 140 [ion d]$^+$, 122 [ion d-H_2O], 298 [M-ion d]$^+$ and 97 [ion d-C_3H_7]$^+$. Retro-Diels-Alder fragmentation of compound **7** generated ion peaks at m/z 203 [ion e]$^+$, 234 [ion f]$^+$, 188 [ion e-Me]$^+$, 219 [ion f-Me]$^+$ and 204 [219-Me]$^+$. The base peak occurred at m/z 191 due to elimination of isopropyl group from the ion f which was regarded as being reasonable indicative of lupane-type carbocyclic skeleton of the molecule [7]. The other important peaks generated at m/z 176 [191-Me]$^+$, 161 [176-Me]$^+$, and 173 [191-H_2O]$^+$. The ^{1}H NMR spectrum of **7** exhibited two downfield doublets at δ 6.84 and 6.22, with coupling constants of 7.08 each, accountable to H-1 and H-2, respectively. Two one-proton each multiplets at δ 5.34 and 3.95 were attributed to H-12 olefinic and H-21 carbinol protons. The methyl protons appeared as singlets at δ 1.25 (Me-23, Me-27), 1.02 (Me-24, Me-26), 0.93 (Me-25, Me-28) and as doublets at δ 0.87 (J = 6.0 Hz, Me-29), and 0.84 (J = 6.0 Hz, Me-30). Based on these observations the structure of hemidesmulupenol (**7**) was formulated as lup-1,12-diene-3-on-21-ol.

3. Experimental

3.1. Extraction procedure

The dried, powdered roots of *H. indicus* were were exhaustively extracted with hot alcohol in a Soxhlet apparatus. The extract was dried under reduced pressure yielding a dark brown coloured viscous mass (265 g; 8.54%). The crude extract was dissolved in minimum amount of MeOH and adsorbed on silica gel to form slurry. The slurry was dried in air and then subjected to silica-gel column chromatography prepared in petroleum-ether. The column was run with petroleum-ether, $CHCl_3$, and MeOH in order of increment of polarity to obtain the following compounds:

3.2. Hemidesmusyl acetate (**1**)

Elution of the column with petroleum ether furnished colourless amorphous powder of **1**, re-crystallised from $CHCl_3$−MeOH (1 : 1), 4.025 g (1.52% yield), R_f 0.796 (petroleum ether−C_6H_6, 1 : 1), m.p. 190–191 °C, $[\alpha]_D^{20}$ +179.48° ($CHCl_3$, C = 1.3). UV λ_{max} (MeOH), 205 nm (log ε 3.5). IR γ_{max} (KBr): 2923, 2852, 1736, 1647, 1458, 1371, 1244, 1143, 1095, 1024, 993, 900, 850 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.17 (1 H, t, J = 8.90 Hz, H-12), 4.57 (1 H, dd, J = 9.03, 6.00 Hz, H-21 α), 2.05 (3 H, brs, $COCH_3$), 1.25 (3 H, brs, Me-27), 1.06 (3 H, brs, Me-23), 1.00 (3 H, brs, Me-26), 0.98 (3 H, brs, Me-30), 0.90 (3 H, brs, Me-29), 0.87 (6 H, brs, Me-24, Me-25), 0.79 (3 H, brs, Me-28). EIMS m/z (rel. int.): 468 [M]$^+$ ($C_{32}H_{52}O_2$)

(15.7), 453 (5.3), 408 (6.5), 393 (5.4), 276 (100), 263 (31.1), 261 (3.9), 248 (28.3), 246 (5.6), 234 (10.0), 233 (10.2), 223 (17.0), 220 (19.0), 218 (92.2), 216 (3.3), 203 (24.7), 192 (5.0), 188 (25.8), 177 (3.7), 148 (11.1), 135 (128.8), 133 (12.7), 95 (15.2), 69 (14.2).

3.3. Seco hemidesursenyl acetate (**2**)

Further elution of the column with petroleum ether-$CHCl_2$ (9 : 1) (fraction 39–51) afforded colourless amorphous powder of **2**, re-crystallised from $CHCl_3$–MeOH (1 : 1), 1.770 g (0.667% yield), R_f 0.567 (petroleum ether-C_6H_6, 1 : 1), $[\alpha]_D^{18}$ + 256.8° ($CHCl_3$, C = 1.35), m.p. 159–160 °C; UV λ_{max} 205 nm (log ε 3.5); IR ν_{max} (KBr); 2926, 2850, 1735, 1646, 1460, 1373, 1246, 1143, 1090, 1025, 990, 880 cm^{-1}. H NMR ($CDCl_3$): δ 5.17 (1 H, t, J = 7.74 Hz, H-12), 4.67 (1 H, brs, H-30a), 4.59 (1 H, brs, H-30b), 4.49 (1 H, dd, J = 4.4, 9.04 Hz, H-3), 2.32 (1 H, dd, J = 4.5, 6.5 Hz, H-18α), 2.15 (3 H, brs, $COCH_3$), 1.25 (3 H, brs, Me-27), 1.06 (3 H, brs, Me-23), 1.00 (3 H, brs, Me-26), 0.99 (3 H, brs, Me-24), 0.91 (3 H, d, J = 6.5 Hz, Me-29), 0.87 (6 H, brs, Me-25, Me-27), 0.83 (3 H, d, J = 6 Hz, Me-28), 0.79 (3 H, t, J = 6.0 Hz, Me-16). EIMS m/z (rel. int.): 468 $[M]^+$ ($C_{32}H_{52}O_2$) (27.1), 454 (12.4), 408 (8.7), 393 (10.7), 280 (7.8), 218 (100), 207 (3.3), 203 (46.3), 190 (19.2), 189 (50.3), 161 (19.2), 148 (13.1), 135 (24.2), 123 (11.6), 121 (12.3), 109 (11.5), 95 (12.5), 80 (10.1), 69 (20.3), 43 (49.2).

3.4. 3-epi-β-Amyrin acetate (**3**)

Further elution of the column with petroleum ether-$CHCl_3$ (3 : 1) (fractions 52–65) yielded colourless amorphous powder of **3**, re-crystallised from $CHCl_3$–MeOH (1 : 1), 2.08 g (0.784% yield). R_f 0.574 (petroleum ether–C_6H_6, 1 : 1); $[\alpha]_D^{18}$ + 164.10° ($CHCl_3$, C = 1.3); m.p. 141–142 °C; UV λ_{max} 208 nm (log ε 3.2); IR ν_{max} (KBr): 2926, 2852, 1736, 1647, 1458, 1373, 1246, 1143, 1097, 1024, 980, 879 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.17 (1 H, t, J = 6.70 Hz, H-12), 4.58 (1 H, dd, J = 6.50, 6.00 Hz, H-3β), 2.04 (3 H, brs, $COCH_3$), 1.32 (3 H, brs, Me-27), 1.25 (3 H, brs, Me-23), 1.06 (3 H, brs, Me-26), 1.00 (3 H, brs, Me-30), 0.97 (3 H, brs, Me-29), 0.87 (6 H, brs, Me-24, Me-25), 0.79 (3 H, brs, Me-28). EIMS m/z (rel. int) : 468 $[M]^+$ ($C_{32}H_{52}O_2$) (11.7), 453 (4.7), 408 (6.0), 393 (3.8), 249 (3.8), 218 (10.0), 203 (30.8), 189 (37.5), 175 (12.5), 161 (18.2), 148 (15.5), 135 (27.2), 133 (24.2), 121 (22.8), 107 (21.6), 95 (28.0), 81 (21.2), 69 (21.9), 43 (73.9).

3.5. β-Amyrin acetate (**4**)

Further elution of the column with petroleum ether–$CHCl_3$ (3 : 1) gave colourless amorphous powder of **4**, re-crystallised from $CHCl_3$–MeOH (1 : 1), 1.43 g (0.539% yield); R_f 0.309 (petroleum ether-C_6H_6, 1 : 1); $[\alpha]_D$ + 79° (C 1.2, $CHCl_3$); m.p. 238–240 °C (lit m.p. 241 °C); UV λ_{max} (MeOH) 209 nm (log ε 3.7); IR λ_{max} (KBr): 2925, 2850, 1735, 1645, 1460, 1375, 1245, 1145, 1096, 1025, 980, 880 cm^{-1} ; ^{1}H NMR ($CDCl_3$): δ 5.12 (3 H, d, J = 7.04 Hz, H-12), 4.49 (1 H, dd, J = 9.30, 6.0 Hz, H-3α), 2.05 (3 H, brs, Me-23), 1.37 (3 H, brs, Me-27), 1.13 (3 H, brs, Me-30), 0.98 (3 H, brs, Me-29), 0.91 (3 H, brs, Me-24), 0.87 (3 H, brs, Me-25), 0.79 (3 H, brs, Me-28). EIMS m/z (rel. int.): 468 $[M]^+$ ($C_{32}H_{52}O_2$) (20.5).

3.6. Hemidesursenyl acetate (**5**)

Elution of the column with petroleum ether–$CHCl_3$ (1 : 1) gave colourless flakes of **5**, re-crystallised from MeOH, 0.295 g (0.111% yield). R_f 0.250 (petroleum ether–C_6H_6, 1 : 1); m.p. 119–120 °C; $[\alpha]_D^{18}$ + 73.3° ($CHCl_3$, C = 0.05); UV λ_{max} (MeOH) 240, 270 nm (log ε 4.5, 4.2); IR λ_{max} (KBr) : 2939, 2858, 1732, 1643, 1460, 1377, 1246, 1141, 1024, 978, 881, 806 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.07 (1 H, brs, H-30 a), 4.90 (1 H, brs, H-18 30 b), 4.60 (1 H, dd, J = 5.5, 8.8 Hz, H-3α), 2.47 (1 H, dd, J = 3.9, 12.08 Hz, H-18 β), 2.04 (3 H, brs, $COCH_3$), 1.25 (3 H, brs, Me-23), 1.08 (3 H, brs, Me-26), 1.07 (6 H, brs, Me-25, Me-27), 0.93 (6 H, brs, Me-28, Me-29), 0.84 (3 H, brs, Me-24). EIMS m/z (rel. int.) 468 $[M]^+$ ($C_{32}H_{52}O_2$) (13.7), 453 (3.6), 425 (13.7), 408 (3.6), 393 (3.7), 313 (6.4), 277 (3.8), 250 (6.7), 218 (76.3), 207 (14.2), 205 (41.2), 204 (36.3), 191 (21.4), 190 (24.1), 189 (63.6), 175 (21.5), 160 (26.3), 159 (10.2), 150 (30.4), 145 (10.1), 142 (3.9), 139 (5.7), 122 (48.3), 121 (77.6), 109 (853), 107 (73.4), 82 (87.2), 69 (100), 67 (63.2), 54 (94.0).

3.7. Seco-Hemidesursenol (**6**)

Further elution of the column with petroleum ether–$CHCl_3$ (1 : 3) (fractions-122–135) furnished colourless amorphous powder of **6**, re-crystallised from $CHCl_3$–MeOH (1 : 1), 0.780 g (0.294% yield). R_f 0.141 (petroleum ether–C_6H_6, 1 : 1); $[\alpha]_D^{18}$ + 346.66° ($CHCl_3$, C = 1.25); m.p. 149–150 °C; UV λ_{max} (MeOH) 211 nm (log ε 3.2); IR λ_{max} (KBr): 3302, 2943, 2858, 1645, 1462, 1383, 1248, 1188, 1097, 1035, 993, 881 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.12 (1 H, t, J = 7.36 Hz H-12), 4.67 (1 H, brs, CH_2-30a), 4.58 (1 H, brs, CH_2-30b), 3.21 (1 H, dd, J = 9.09, 5.02 Hz, H-3α), 2.20 (1 H, dd, J = 5.0, 6.5 Hz, H-18α), 1.25 (3 H, brs, Me-27), 1.07 (3 H, brs, Me-23), 1.00 (3 H, brs, Me-24), 0.96 (3 H, d, J = 6.5 Hz, Me-27), 0.81 (3 H, d, J = 6.0 Hz, Me-28), 0.79 (3 H, t, J = 6.0, Me-16). EIMS m/z (rel. int.) 426 $[M]^+$ ($C_{30}H_{50}O$) (16.6), 411 (8.1), 408 (2.0), 393 (2.4), 218 (100), 207 (26.9), 203 (52.6), 189 (46.6), 174 (14.3), 161 (20.6), 147 (23.7), 135 (30.3), 123 (25.2), 121 (24.8), 108 (22.3), 95 (25.5), 93 (19.2), 68 (31.6).

3.8. Hemidesmulupenol (**7**)

Elution of the column with $CHCl_3$–MeOH (99 : 1) (fractions 196–205) furnished colourless amorphous powder of **7**, re-crystallised from MeOH, 0.075 g (0.028% yield); R_f 0.342 (C_6H_6–EtOAc, 1.3); m.p. 85–86°; $[\alpha]_D^{18}$ + 69.33° ($CHCl_3$, C = +5.2); UV λ_{max} 218, 350 nm. (log ε 3.1, 2.2); IR ν_{max} (KBr): 3342, 2922, 2852, 1710, 1612, 1568, 1510, 1461, 1377, 1292, 1265, 1143, 1105, 1022, 922, 864, 821, 725 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.84 (1 H, d, J = 7.08 Hz, H-1), 6.22 (1 H, d, J = 7.08 Hz, Me-2), 5.34 (1 H, m, H-12), 3.95 (1 H, m, H-21), 1.25 (6 H, brs, Me-23, Me-27), 1.02 (6 H, brs, Me-24, Me-26), 0.93 (6 H, brs, Me-25, Me-28), 0.87 (3 H, d, J = 6.0 Hz, Me-29), 0.84 (3 H, d, J = 6.0 Hz, Me-30). EIMS m/z (rel. int.): 438 $[M]^+$ ($C_{30}H_{46}O_2$) (2.5), 423 (2.4), 395 (5.0), 338 (5.8), 315 (2.8), 313 (6.8), 298 (3.3), 219 (15.3), 204 (6.2), 203 (9.6), 191 (100), 191 (8.1), 188 (12.3), 176 (58.7), 173 (4.0), 164 (28.5), 161 (7.5), 150 (48.5), 146 (10.0), 140 (3.6), 136 (11.2), 126(6.3), 122 (20.6), 111 (8.2), 108 (12.6), 97 (22.3), 96 (9.3), 86 (11.8), 83 (19.8), 81 (16.1), 68 (25.1), 66 (16.3).

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References

1 The Wealth of India, Raw Materials, Council of Scientific and Industrial Research, New Delhi Vol. 5, p. 33, 1959
2 Kirtikar, K. R.; Basu, B. D: Indian Medicinal Plants Vol 3, p. 1596, L. M. Basu, Allahabad 1935
3 Aiyer, K. N.: Pharmacognosy of Ayurvedic Drugs of Travancore-Cochin: University of Kerala, Trivendrum (1): 11–26, 1951
4 Nadkarni, A. K.: Indian Materia Medica, Vol. 1, p. 144, Popular Book Depot, Bombay, 1954
5 Sivarajan, V. V.; Balachandran, I.: Ayurvedic Drugs and their plant sources. Oxford & IBH Publication Co., New Delhi, 1994
6 Rastogi, Ram P.; Mehrotra, B. N.: Compendium of Indian Medicinal Plants (4 Vols). CDRI & PID (CSIR) 1990, 1991 and 1995
7 Budzikiewiecz, H.; Wilson, J. M.; Djerassi, C.: J. Am. Chem. Soc, **85** (22), 3688, (1963)
8 Gupta, D. K.; Ali, M.; Bhutani, K. K.: Indian J. Chem. **35** (B), 1079, (1996)
9 Barton, D. H. R.; Mayo, P. de: J. Chem. Soc. **1 ,** 887 (1954)
10 Das, K. G. and James E. P.: Organic Mass Spectrometry, Oxford and IBH. Publication Ltd., New Delhi, 1976

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