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Phytochemistry 62 (2003) 579–584
PHYTOCHEMISTRY
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Quassinoids from *Ailanthus excelsa*

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Received 8 May 2002; received in revised form 8 October 2002

Abstract

Three quassinoids, **1**, **2** and 3, 4-dihydro excelsin **3** were isolated from the stem bark of *Ailanthus excelsa*, along with five known quassinoids excelsin, glaucarubine, ailanthinone, glaucarubinone and glaucarubolone. The glaucarubolone has been isolated for the first time from this plant. The structural elucidation is based on the analysis of spectroscopic data.

Keywords: *Ailanthus excelsa*; Simaroubaceae; Stem-bark; Quassinoids; Excelsin; 3.4-Dihydroexcelsin; Glaucarubine; Ailanthinone; Glaucarubinone; Glaucarubolone

1. Introduction

The plants of the Simaroubaceae family contain the bitter principles known as quassinoids which are degraded triterpenes and are highly oxygenated. Some of these plants are used in folk medicine for anthelmintic and antiamoebic properties (Polonsky, 1973). In recent years attention has been focused on quassinoids as several of them have shown promising antitumor, antiviral, antimalarial, antileukemic and antifeedant properties (Polonsky, 1985).

Chemical examination of *Ailanthus excelsa*, a Simaroubaceous plant, has been carried out by several workers resulting in the isolation of quassinoids (Ogura et al., 1977; Khan and Shamsuddin, 1978; Khan et al., 1980; Khosa et al., 1985; Bhatia et al., 1985) alkaloids (Ogura et al., 1978) and terpenoids (Sherman et al., 1980). In this paper we report the isolation of three new C_{20} quassinoids.

2. Results and discussion

The $CHCI_3$ fraction of the MeOH extract of the stem bark of *A. excelsa* afforded **1**, **2** and **3** (see Section 3) after column chromatography.

Compound **1** as an oil, possessed a molecular formula of $C_{25}H_{32}O_7$ as indicated by El and ES mass spectra. The IR spectrum showed the presence of hydroxyl (3450 cm^{-1}), δ-lactone (1724 cm^{-1}) and an aromatic (1600 cm^{-1}) moiety. The ^1H NMR spectrum of **1** revealed the presence of two aromatic protons at δ 7.03 and a doublet at δ 5.30 ($J = 10$ Hz) which was characteristic of the ester function at C-15. H-20 appeared as an AB system as two doublets ($J = 8.4$ Hz) at δ 4.02 and 3.66 and H-12 appeared as a broad singlet at δ 3.85. The two methyl groups on the aromatic ring appeared as singlets at δ 2.22 and δ 2.33. A doublet at δ 1.21 ($J = 7$ Hz) for six protons was assigned to H-5′ and H-21, and H-4′ appeared as a triplet at δ 0.97 ($J = 7.4$ Hz).

The ^{13}C NMR spectrum revealed the presence of 25 carbon atoms including six aromatic carbons. The DEPT spectrum indicated the presence of five methyls, three methylene, nine methines as well as eight quatemary carbons. The signals at δ 71.2 (C-20) and 108.9 (C-11) in the ^{13}C NMR spectrum were characteristic of an 11 β, 20-hemiketal moiety. On the basis of above spectral data structure **1** was proposed for this compound which was further confirmed by the spectral data of its triacetate **4**.

Compound **4** solid, mp. 230 °C showed absorption bands at 1740, 1724, 1650 and 1600 cm^{-1} in the IR spectrum. In ES–MS the highest peak was observed at m/z 593 $[M+Na]^+$ which corresponded to the molecular formula $C_{31}H_{38}O_{10}$ for compound **4**. El–MS showed a peak at m/z 528 $[M^+-42]$. All the signals in ^1H NMR spectrum of the triacetate **4** were completely resolved. H-2 and H-3 appeared as a singlet at δ 7.01, H-20 as an AB system at δ 4.28 and 3.64 as two doublets ($J = 12$ Hz), the doublet ($J = 2$ Hz) at δ 5.66 was assigned to H-12 and H-15 appeared as a doublet ($J = 12$ Hz) at δ 6.05.

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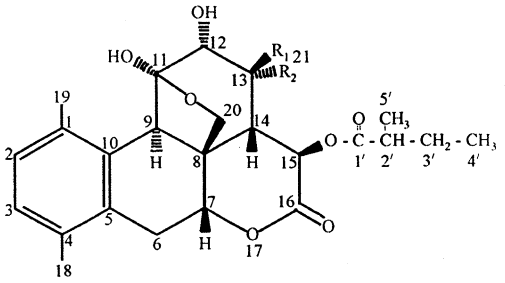
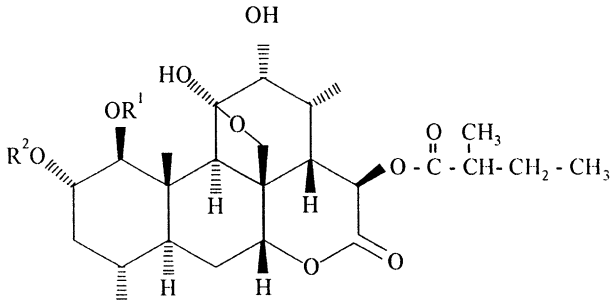
PII: S0031-9422(02)00493-4



1 $R_1 = H$, $R_2 = CH_3$

2 $R_1 > = R_2 = CH_2$

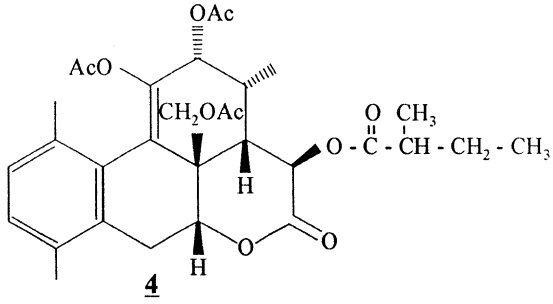


3 $R^1 = R^2 = H$

5 $R^1 = H$, $R^2 =$ H and 3, 4 double bond

8 $R^1 = H$, $R^2 = CH_3$ and 3, 4 double bond

10 $R^1 = CH_3$, $R^2 = CH_3$ and 3, 4 double bond



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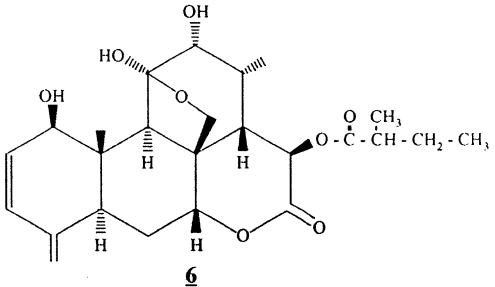

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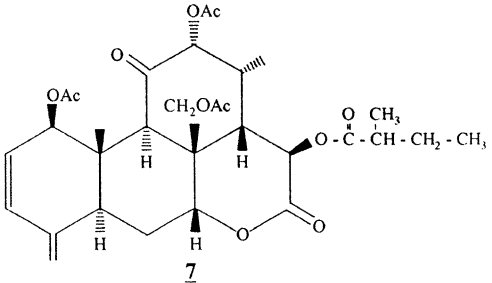

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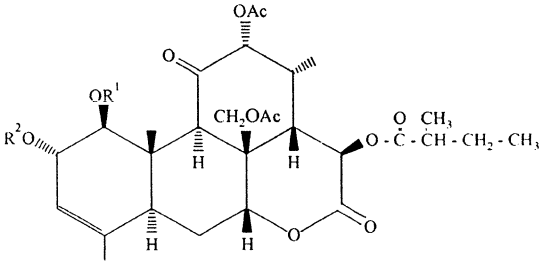
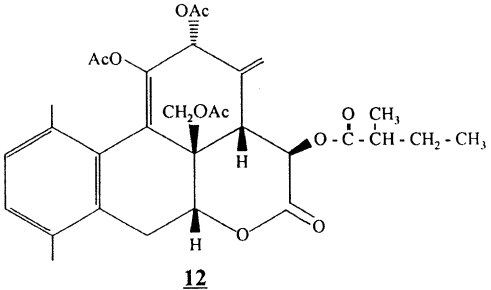


9 $R^1 =$ Ac; $R^2 = CH_3$

11 $R^1 = CH_3$; $R^2 = CH_3$



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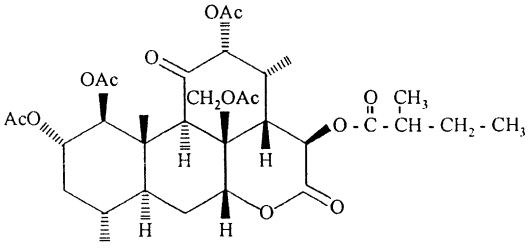

13

14 3, 4 double bond

Finally the structure of **1** was proved by the transformation of excelsin **5** (Khan et al., 1980) into **1**. The reaction of excelsin with 1 N HCI in DMF gave two products. The major product was identified as **1** by direct comparison (IR, ^{1}H NMR and mass spectra) with that isolated compound. The minor product was assigned structure **6** on the basis of spectral data (Polonsky, 1973). In the ^{1}H NMR spectrum of compound **6**, H-3 appeared as a doublet at δ 6.20 ($J=9$ Hz) and H-1, H-7 overlapped at δ 4.60. Acetylation of **6** gave the triacetate **7** whose ^{1}H NMR spectrum was consistent with its structure.

During our attempts to synthesize **1** from excelsin **5**, we treated excelsin with p-TsOH in MeOH at room temp. for 43 h which resulted in the formation of one major product identified as the 2-methyl ether **8** on the basis of spectral data. Acetylation of **8** gave the triacetate **9**. Compound **8** on treatment with diazomethane (Khan and Shamsuddin, 1980) furnished the 1,2-dimethyl ether **10**. Acetylation of **10** gave the diacetate **11**.

Compound **2** was obtained as an oil and analysed for $C_{25}H_{30}O_7$ by El and ES mass spectrometry. The ^{1}H NMR spectrum of **2** was very similar to that of **1**. In the ^{1}H NMR spectrum the presence of two singlets at δ 5.45 and δ 5.27 each for one proton and the absence of three proton doublet at δ 1.21 suggested that the C-13 methyl in **1** has been replaced by an exomethylene group which was fully supported by MS [442 $(M)^+$, two mass unit less than compound **1**] and further confirmed by ^{13}C NMR which displayed signals at δ 141.9 and 124.0 for the exomethylene carbons. Consequently **2** was deduced as 13,21-dehydro analogue of **1**. The structure of **2** was further confirmed by synthesis of its acetate **12**.

Compound **3** could not be isolated in the pure form, therefore it was identified only as its acetate **13**, mp. 201 °C (see Section 3). The ESMS of **13** showed a strong peak at m/z 673 $[M+Na]^+$ and ElMS showed a molecular ion peak at m/z 650 $[M]^+$. These observation suggested the molecular formula as $C_{33}H_{46}O_{13}$ for compound **13**. A comparison of the ^{1}H NMR spectrum of **13** with that of the tetra acetate of excelsin **14** (Khan et al., 1980) revealed that the two spectra were strikingly similar with respect to the BCDE rings and ester side chain except the signal due to H-3 in **14** was absent in **13** and an extra doublet at δ 1.04 ($J=8$ Hz) for three protons was present. The mass spectrum gave a molecular ion peak at m/z 650 which was two mass units more than that of **14** ^{13}C NMR spectrum of **13** confirmed the presence of 33 carbons [9×Me, 4×CH_2, 11×CH and 9×C as determined from the DEPT spectrum] including a δ-lactone (δ 167.9), carbonyls (δ 170.0, 170.4, 170.6, 171.8, 176.1, 204.9) and six oxygen bearing carbons (δ 62.0, 68.4, 69.1, 78.2, 80.8, 81.4). On the basis of above observations compound **13** was identified as 3,4 dihydro excelsin tetra acetate. Therefore the naturally occurring compound was assigned structure **3**. Since no NOE was observed between C-10 and C-4 methyls, therefore α-stereochemistry was assigned to C-4 methyl. Table 1 shows the comparison of ^{13}C NMR spectrum of **13** and **14** and the latter is being reported for the first time.

Five known compounds were identified as excelsin **5** (Khan et al., 1980); glaucarubine (Khan and Shamsuddin, 1980); ailanthinone, glaucarubinone (Ogura et al., 1977); and glaucarubolone (Gaudemer and Polonsky, 1965) by comparing their physical and spectral data with those reported in the literature. Glaucarubolone has been isolated for the first time from this plant.

3. Experimental

3.1. General

Mp. uncorr. ^{1}H and ^{13}C NMR were recorded at 300 MHz instrument using TMS as int. standard. The electrospray mass spectra (ESMS) were recorded on a MICROMASS QUATTRO II Triple Quadrupole Mass Spectrometer. The samples (dissolved in appropriate solvent) were introduced into the ESI source through a syringe pump at the rate of 5 μl per min. The ESI capillary was set at 3.5 kV and the cone coltage was 40

Table 1
^{13}C NMR spectral data for compounds **13** and **14** (in $CDCl_3$)

Carbon	**13**	**14**
1	81.4a	80.9a
2	69.1b	73.8
3	37.1	120.7
4	33.2	138.0
5	39.1	40.2
6	26.9	25.1b
7	78.2	77.7
8	47.9	47.6
9	51.4	49.5
10	43.1	42.9
11	204.9	200.4
12	80.8a	80.2a
13	35.0	35.4
14	41.2c	41.6c
15	68.4b	68.3
16	167.9	167.7
18	15.6d	21.0
19	15.2d	11.8
20	62.0	62.1
21	16.4d	16.5
1′	176.1	176.1
2′	41.6c	41.2c
3′	28.9	27.0b
4′	11.8	12.2
5′	16.4d	15.7
1-OAc	171.8e, 21.4f	171.7d, 21.4e
2-OAc	170.6e, 21.3f	171.3d, 21.1e
12-OAc	170.4e, 21.0f	170.4d, 21.1e
20-OAc	170.0e, 20.8f	170.2d, 21.1e

a–f: Signals within any vertical column may be interchanged.

V unless stated otherwise. The spectra were collected in 6-s scans and the print out are averaged spectra of 6–8 s > cans. TLC was performed on silica gel-G (Qualigen). The solvent system used for TLC was various proportions of MeOH (1–10%) in $CHCI_3$ and spots were revealed by spraying with 50% sulfuric acid. The column chromatography (cc) was performed on silica gel 60-120 (Qualigen).

3.2. Plant material

The stem-bark of *A. excelsa* was collected in August 1999 from Kukrail Reserve Forest, Lucknow. The identification of the plant was carried out by Dr. S.P. Jam, Botany Department, CIMAP, Lucknow, where a voucher specimen has been deposited.

3.3. Extraction and isolation

Ten kilograms of the dried bark of *A. excelsa* were exhaustively extracted with cold MeOH. The MeOH extract was concentrated, diluted with equal amount of water and left overnight. The ppt. was filtered off and the filtrate was extracted first with $CHCI_3$ and then ethyl acetate. The chloroform fr. (15 g) was chromatographed on a column of silica gel with stepwise increases of MeOH content (1–10%) in $CHCI_3$. The 1.5% MeOH eluate was purified by prep. TLC (silica gel, $CHCl_3$:MeOH, 98:2) to give compound **1** (25 mg) as an oil. The fractions eluated with 2, 5, 5.5, 6, 6.5% MeOH in $CHCI_3$ gave compounds **2**, **3**, excelsin **5**, glaucarubine and ailanthinone, respectively. The ethyl acetate fr. was subjected to a column chromatography on a silica gel affording compounds glaucarubinone and glaucarubolone in 5 and 7% MeOH in $CHCI_3$, respectively.

3.4. Compound *1*

Oil, IRυ_{max}^{KBr} cm^{-1}: 3450 (broad), 1724 (broad), 1600, 1458, 1220, 1147, 1024, 759. ^{1}H NMR ($CDCl_3$, δ): 7.03 (2H, centre of AB system, H-2 and H-3), 4.94 (1H, *m*, H-7), 2.99 (1H, *s*, H-9), 3.85 (1H, *brs*, H-12), 5.30 (IH, *d*, $J=10$ Hz, H-15), 2.33 (3H, *s*, H18), 2.22 (3H, *s*, H-19). 4.02 and 3.66 (2H, *d* each, $J=8.4$ Hz. H-20a and H-20b), 1.21 (3H, *d*, $J=7$ Hz, H-21), 0.97 (3H, *t*, $J=7.4$ Hz, H-4′), 1.21 (3H, *d*, $J=7$Hz, H-5′). ^{13}CNMR ($CDCI_3$, δ): 135.5, 134.9 130.9, 127.3 (*s* each, C-1, C-4, C-5, C-10), 129.5[a] (C-2), 129.0[a] (C-3), 26.4 (C-6), 74.4 (C-7), 47.5 (C-8), 46.6 (C-9), 108.9 (C-11), 78.1 (C-12), 32.3 (C-13), 40.8 (C-14), 69.5 (C-15), 168.2 (C-16), 19.4[b] (C-18), 20.6[b] (C-19), 71.2 (C-20), 13.6 (C-21), 176.2 (C-1′), 37.4 (C-2′), 30.5 (C-3′). 11.5 (C-4′), 16.0 (C-5′). * 'a' and 'b' interchangeable. EI–MS *m/z*: 444 $[M]^+$, $C_{25}H_{32}O_7$, 428, 414, 385, 360, 342, 324, 296, 267, 239, 213, 188, 169, 157, 143, 119, 105, 85, 69, 57,44.

3.5. Acetylation of *1*

A solution of 20 mg of **1** in l ml of pyridine was treated with 2 ml of Ac_2O at room temp. for 36 h. Dilution with H_2O and extraction with $CHCI_3$ yielded triacetate **4** as a solid, mp. 230 °C, $[\alpha]_D^{23}$ +84° ($CHCl_3$; *c* 0.70), IR υ_{max}^{KBr} cm^{-1}: 1740, 1724, 1650, 1600. ^{1}H NMR ($CDCI_3$, δ): 7.01 (2H, centre of AB system, H-2 and H-3), 4.39 (1H, *dd*, $J=12$, 4 Hz, H-7), 5.66 (1H, *d*, $J=2$ Hz, H-12), 6.05 (1H, *d*, $J=12$ Hz, H-15), 2.26 (3H, *s*, H-18), 2.15 (3H, *s*, H-19), 4.28, 3.64 (2H, *d* each, $J=12$ Hz, H-20a and H-20b), 1.29 (3H, *d*, $J=6$ Hz, H-21), 1.03 (3H, *t*, $J=8$ Hz, H-4′), 1.21 (3H, *d*, $J=8$ Hz, H-5′), 1.76, 1.95, 2.03 (3H, each, *s*, acetates). ^{13}C NMR ($CDCI_3$, δ): 143.4, 132.8, 132.1, 129.3, 130.9, 124.6 (*s* each, C-1, C-4, C-5, C-9, C-10, C-11), 130.4[a] (C-2), 128.6[a] (C-3), 26.6 (C-6), 68.2[b] (C-7), 46.7 (C-8), 78.7 (C-12), 31.9 (C-13), 40.7 (C-14), 68.0[b] (C-15), 166.9 (C-16), 18.8[c] (C-18), 19.0[c] (C-19), 66.8 (C-20), 15.6 (C-21). 174.6 (C-1′), 39.6 (C-2′), 33.3 (C-3′), 11.2 (C-4′). 16.0 (C-5′), 20.7, 20.6, 20.1 (acetate–CH_3), 170.7, 170.7,168.9 (acetate–carbonyl). 'a' 'b' and 'c' are interchangeable.

ES–MS *m/z*: 593$[M+Na]^+$ 609 $[M+K]^+$, $C_{31}H_{38}O_{10}$ EI–MS *m/z*: 528 $[M^+-42]$, 511, 468, 426, 409, 366, 324, 308, 293, 278, 265, 237, 212, 169, 85, 57, 42.

3.6. Transformation of excelsin *5* into *1*

To a solution of 20 mg of excelsin **5** in 0.5 ml of DMF was added 0.5 ml of 1N HCl and the reaction mixture was heated at 100 °C for 1 h. It was diluted with H_2O and extracted with $CHC1_3$. The washed and dried extract was evaporated to furnish 18 mg of crude material, which was separated by prep. TLC ($CHCI_3$: MeOH; 9:1)to furnish **1** 12 mg and **6** 5 mg.

3.7. Compound *6*

Oil, ^{1}H NMR ($CDCl_3$, δ): 4.60 (2H, *brs*, H-l, overlapping with H-7), 5.50 (1H, *d*, $J=9$ Hz, H-2), 6.20 (1H, *d*, $J=9$ Hz, H-3), 4.60(2H, *brs*, H-7, overlapping with H-1), 4.06 (1H, *d*, $J=4$ Hz, H-12), 5.67 (1H, *d*, $J=12$ Hz, H-15), 4.88 and 5.04 (2H, *brs* each, H-18a and H18b), 1.25 (3H, *s*, H-19), 4.06 and 3.79 (2H, *d* each, $J=8$ Hz, H-20a and H-20b), 1.14 (3H, *d*, $J=7$ Hz, H-21), 1.01 (3H, *d*, $J=7$ Hz, H-5′), 0.96 (3H, *t*, $J=7$ Hz, H-4′). ES–MS *m/z* :485 $[M+Na]^+$, $C_{25}H_{34}O_8$. ElMS *m/z*: 444 (M^+-H_2O).

3.8. Acetylation of *6*

A solution of 5 mg of **6** in 0.5 ml of pyridine was treated with 1 ml of Ac_2O at room temp. for 24 h. The reaction mixture was evaporated with the help of toluene to afford triacetate **7** as an oil, IR υ_{max}^{KBr} cm^{-1}: 3393, 2930, 1752, 1631, 1222, 1032, 768. ^{1}H NMR ($CDCI_3$, δ):

5.56 (1H, *d*, *J* = 2 Hz, H-1), 6.20 (1H, *d*, *J* = 9 Hz, H-3), 4.88 (1H, *brs*, H-7), 3.44 (1H, *s*, H-9), 5.11 (1H, *d*, *J* 2Hz, H-i2), 5.78–5.88 (2H, overlapping signal of H-2 and H-15). 5.28 and 5.46 (2H, *brs* each, H-18a and H-18b), 1.49 (3H, *s*, H-19), 3.90 and 4.57 (2H, *d*, *J* 12 Hz, H-20a and H-20b), 1.15 (3H, *d*, *J* = 7 Hz, H-21), 0.95 (3H, *t*, *J* = 7 Hz, H-4′), 1.11 (3H, d, *J* = 7 Hz, H-5′). ES–MS *m*/*z*: 611 $[M+Na]^+$ $C_{31}H_{40}O_{11}$, EI–MS *m*/*z*: 588 $[M]^+$, 485, 442, 398, 85, 56, 43.

3.9. Reaction of excelsin **5** with p-TsOH in MeOH

To a solution of 30 mg of excelsin **5** in 1 ml of dry-MeOH was added 10 mg p-TsOH and the reaction mixture left at room temp. for 43 h. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. It was purified by prep TLC ($CHCl_3$:MeOH, 4:1) to furnish compound **8** 26 mg as an oil, IRυ_{max}^{KBr} cm^{-1}: 3386, 1737, 1600, 1458, 1213, 1151, 1045, 759. ^1H NMR ($CDCl_5$, δ): 3.5–4.2 (overlapping signals of H-1, H-2, H-12, H-20), 5.57 (1H, *brs*, H-3), 4.52 (1H, *brs*, H-7), 2.50 (1H, *s*, H-9), 5.63 (1H, *d*, *J* = 12 Hz, H-15), 1.70 (3H, *s*, H-18), 1.27 (3H, *s*, H-19), 1.17 (3H, *d*, *J* = 7 Hz, H-21), 0.96 (3H, *t*, *J* = 7 Hz, H-4′), 1.08 (3H, *d*, *J* = 7 Hz, H-5′), 3.40 (3H, *s*, 2-OMe). ^{13}C NMR (pyridine-d_5, δ): 80.8 (C-1), 82.8 (C-2), 122.3 (C-3), 137.0 (C-4), 41.6 (C-5), 26.1[a] (C-6), 79.2[b] (C-7), 48.3 (C-8), 45.6 (C-9), 42.3 (C-10), 111.1 (C-11), 80.2[b] (C-12), 33.2 (C-13), 46.4 (C-14), 70.6 (C-15), 168.6 (C-16), 21.5 (C-18), 11.2 (C-19), 71.9 (C-20), 15.9 (C-21), 75.8 (C-1′), 41.6 (C-2′), 27.3[a] (C-3′), 12.0 (C-4′), 16.6 (C-5′), 56.7 (2-OMe). 'a' and 'b' are interchangeable. EI–MS *m*/*z*: 458 $[M^+-2H_2O]$ $C_{26}H_{38}O_9$, 442, 427, 374, 359, 341, 230, 212, 184, 168, 156, 137, 118, 104, 85, 57.

3.10. Acetylation of **8**

A solution of 15 mg of **8** in 1 ml pyridine was treated with 2 ml of Ac_2O and the reaction mixture left at room temp. for 48 h. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$, yielded an oily compound **9**, IRυ_{max}^{KBr} cm^{-1}: 1747 (broad), 1216, 1030. ^1H NMR ($CDCl_3$, δ): 4.96 (1H, *d*, *J* = 8 Hz, H-1), 3.75 (1H, *m*, H-2), 5.52 (1H, *m*, H-3), 4.73 (1H, *m*, H-7), 5.09 (1H, *d*, *J* = 1.5 Hz, H-12), 6.06 (1H, *d*, *J* = 10 Hz, H-15), 1.70 (3H, *brs*, H-18), 1.38 (3H, *s*, H-19), 4.68 and 3.88 (each 1 H, *d*, *J* = 15 Hz, H-20a and H-20b), 1.19 (3H, *d*, *J* = 6 Hz, H-21); 0.95 (3H, *t*, *J* = 8Hz, H-4′); 1.05 (3H, *d*, *J* = 6 Hz, H-5′); 3.25 (3H, *s*, 2-OMe); 2.26, 2.09, 1.87 (each 3H, *s*, acetate-methyls). ^{13}C NMR ($CDCI_3$, δ): 79.2[a] (C-1), 80.4 (C-2), 121.6 (C-3), 136.6 (C-4), 39.8 (C5), 26.5[b] (C-6), 77.4 (C-7), 47.1 (C-8), 49.2 (C-9), 42.1 (C-10), 204.4 (C-11), 78.6[a] (C-12), 34.8 (C-13), 40.7[c] (C-14), 68.0 (C-15), 167.5 (C-16), 21.1 (C-18), 11.4 (C-19), 61.7 (C-20), 16.1 (C-21), 175.6 (C-1′), 41.14[c] (C-2′), 24[b] (C-3′), 11.7 (C-4′), 15.2 (C-5′), 171.3, 170.0, 169.9 (acetate–carbonyls) 54.8 (2-OMe), 21.0, 20.8, 20.8 (acetate–CH_3). 'a', 'b' and 'c' interchangeable. ESMS *m*/*z*: 643 $[M+Na]^+$, 659 $[M+K]^+$, $C_{32}H_{44}O_{12}$. ElMS *m*/*z*: 560 $[M^+-60]$, 545, 503, 485, 469, 425, 85, 57.

3.11. Reaction of **8** with diazomethane

Fifteen milligrams of **8** was treated with an excess of etherial solution of CH_2N_2 for 12 h at room temp. Evapn. of the solvent gave a residue which was chromatographed on a column of silica gel. Elution with $CHC1_3$ furnished oily compound **10**. which was identified as its acetate **11**. IRυ_{max}^{KBr} cm^{-1}: 1740,1410,1210. ^1H NMR ($CDCl_3$, δ): 3.80 (1H, *m*, H-2), 5.55 (1H, *m*, H-3), 4.74 (1H, *m*, H-7), 3.21 (1H, *s*, H-9), 5.14 (1H, *d*, *J* = 2Hz, H-12), 6.07 (1H, *d*, *J* = 10 Hz, H-15), 1.68 (3H, *brs*, H-18), 1.30 (3H, *s*, H-19), 4.65 and 3.93 (each 1H, each *d*, *J* = 14 Hz, H-20a and H-20b), 1.18 (3H, *d*, *J* = 6Hz, H-21), 0.98 (3H, *t*, *J* = 7 Hz, H-4′), 1.07 (3H, *d*, *J* = 7H, H-5′), 3.36 (3H, *s*, 2-OMe) and 3.54 (3H, *s*, 1-OMe), 2.23 and 2.09 (each 3H, *s*, acetate–CH_3). EI–MS *m*/*z*: 592 $[M]^+$, 572, 556, 529, 516, 498, 469, 456, 427, 414, 390, 355, 337, 324, 311, 279, 263, 251, 182, 148, 127, 110, 97, 84, 68, 57, 44.

3.12. Compound **2**

Oil, IRυ_{max}^{KBr} cm^{-1}: 3450 (broad), 1735 (broad), 1600, 1456, 1218, 1145, 1022, 758. ^1H NMR ($CDCI_3$, δ): 7.05 (2H, centre of AB system, H-2 and H-3), 4.82 (1H, *d*, *J* = 2 Hz, H-7), 3.03 (1H, s, H-9), 4.38 (1H, *s*, H-12), 5.58 (1H, *d*, *J* = 10 Hz, H-15), 2.42 (3H, *s*, H-18), 2.22 (3H, *s*, H-19), 3.98, 3.54 (2H, each *d*, *J* = 8 Hz, H-20a and H-20b), 5.45, 5.27 (2H, each *s*, H-21a and H-21b), 0.98 (3H, *t*, *J* = 8 Hz, H-4′), 1.20 (3H, *d*, *J* = 8 Hz, H-5′). ^{13}C NMR ($CDCI_3$, δ): 136.2, 135.1, 130.9, 127.0 (each *s*, C-1, C-4, C-5, C-10), 130.0[a] (C-2), 129.5[a] (C-3), 30.8 (C-6), 75.2 (C-7), 47.4 (C-8), 52.4 (C-9), 109.0 (C-11), 79.6 (C-12), 141.9 (C-13), 41.2 (C-14), 70.3 (C-15), 167.6 (C-16), 19.8[b] (C-18), 21.0[b] (C-19), 71.0 (C-20), 124.0 (C-21), 176.7 (C-1′), 38.0 (C-2′), 27.0 (C-3′) 11.9 (C-4′), 16 8 (C-5′). 'a' and 'b' interchangeable. ES–MS *m*/*z*: 465 $[M+Na]^+$, $C_{25}H_{30}O_7$. EI–MS *m*/*z*: 442 $[M^+]$, 342, 309, 282, 253, 237, 213, 183, 169, 142, 105, 85, 59, 56, 43.

3.13. Acetylation of **2**

A solution of 10 mg of **2** in 0.5 ml of pyridine was treated with 1 ml of Ac_2O at room temp. for 24 h, the usual workup provided an oily triacetate **12**, $[\alpha]_D^{23}$ + 32° ($CHCl_3$, *c* 0.70), ^1H NMR ($CDCl_3$, δ): 7.01 (2H, centre of AB system, H-2 and H-3), 4.43 (1H, *dd*, *J* = 12, 4 Hz, H-7), 6.03 (1H, *s*, H-12), 5.88 (1H, *d*, *J* = 12.5 Hz, H-15), 2.27 (3H, *s*, H-18), 2.14 (3H, *s*, H-19), 3.99, 3.71 (2H, each *d*, *J* = 12 Hz, H-20a and H-20b), 5.68, 5.45 (2H, each *s*, H-21a and H-21b), 0.96 (3H, *t*, *J* = 8 Hz,

H-4′), 1.15 (3H, *d*, $J=8$ Hz, H-5′), 1.99, 1.93, 1.79 (3H each, *s*, acetate). ES–MS *m/z*: 591 $[M+Na]^+$, 607 $[M+K]^+$ $C_{31}H_{36}O_{10}$. EI–MS *m/z*: 467 $[M^+-C_5H_9O_2]$; 452, 439, 292, 264, 208, 170, 156, 130, 99, 83, 77, 69, 57, 44.

3.14. Compound 3

Repeated column chromatography and prep TLC of the mixture containing compound **3** did not yield pure compound (vide ^{1}H NMR, ^{13}C NMR). Therefore the crude was acetylated as usual, which was separated by prep. TLC ($CHCl_3$:MeOH, 99:1) to furnish pure compound **13** as crystalline. Mp. 201°, $[\alpha]_D^{23}+11°$ ($CHC1_3$, *c* 0.70) ^{1}H NMR ($CDCl_3$, δ): 5.05 (1H, *brs*, H-1), 5.15 (1H, *m*, H-2), 4.70–4.75 (2H, overlapping signals of H-7 and H-12), 3.17 (1H, *s*, H-9), 5.98 (1H, *d*, $J=10$ Hz, H-15), 1.04 (3H, *d*, $J=8$ Hz, H-18), 1.55 (3H, *s*. H-19), 0.96 (3H, *t*, $J=8$ Hz, H-4′), 1.03 (3H, *d*, $J=8$ Hz, H-5′), 2.08, 2.08 1.96, 1.83 (each *s*, acetate methyl). ES–MS *m/z*: 673 $[M+Na]^+$, 689 $[M+K]^+$ $C_{33}H_{46}O_{13}$, EI–MS *m/z*: 650 $[M]^+$, 565 $[M^+-C_5H_9O)$, 549 $[M^+-C_5H_9O_2]$, 85.

Acknowledgements

The authors are grateful to the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for providing spectral facilities. Thanks are also due to CSIR, New Delhi, for providing an Emeritus grant to R.P.S. and fellowship to B.C.J.

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