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SALACIANONE AND SALACIANOL, TWO TRITERPENES FROM *SALACIA BEDDOMEI*

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Key Word Index—*Salacia beddomei*; Celastraceae; new triterpenoids; salacianone; salacianol.

Abstract—Two new lupane triterpenes, salacianone (lup-20(29)-en-3,21-dione) and salacianol (21β-hydroxylup-20(29)-en-3-one), have been isolated from the hexane extract of the stem bark of *Salacia beddomei* together with the known compounds lup-20(29)-en-3-one, friedelan-3-one, 15α-hydroxyfriedelan-3-one, 15α-hydroxyfriedelane-1,3-dione, pristimerin and sitosterol. Their structures have been elucidated with the aid of IR, NMR and mass spectroscopic techniques.

INTRODUCTION

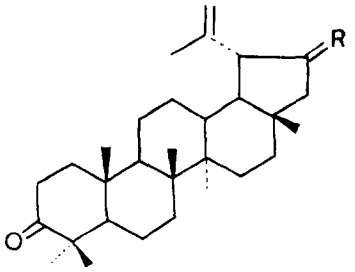
Reviews on the chemistry and biology of Celastraceae plants have been published [1, 2]. *Salacia beddomei* (Gamble), a woody climber belonging to the family Celastraceae, is hitherto an uninvestigated species. As part of our studies on Keralan medicinal plants, we have investigated the stem bark of *S. beddomei* and isolated several compounds. In this paper we report the isolation and characterization of two new lupane triterpenoids, together with six other known compounds.

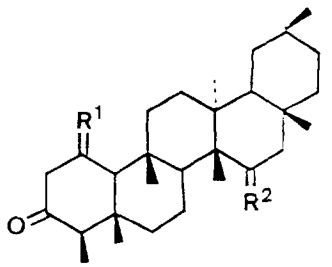
RESULTS AND DISCUSSION

The concentrated hexane extract of the stem bark of *S. beddomei* was repeatedly chromatographed over silica gel columns, and compounds **1**–**8** were eluted in the order of their increasing polarity. The ^{1}H and ^{13}C NMR spectral data for these compounds revealed that **1**, **3** and **5** belong to the lupane group, and **2**, **4** and **7** belong to the friedelane group. Compound **6** was identified as sitosterol from its physical constants, spectral data and by a direct comparison with an authentic sample. Compound **8** was isolated as an orange–red amorphous solid. The ^{1}H NMR spectrum (270 MHZ, $CDCl_3$) showed the presence of six tertiary methyl singlets at δ0.54, 1.10, 1.18, 1.27, 1.43 and 2.21 and a methoxyl methyl singlet at δ3.55. In addition, the presence of three aromatic protons were visible at δ6.34, 6.53 and 7.01. This compound was identified as pristimerin, a quinonemethide nortriterpenoid found in *Salacia* species such as *S. crassifolia* [3] and *S. macrosperma* [4], based on its identical spectral data (IR, ^{1}H NMR, EI mass spectra) with the reported values [5, 6].

Among the compounds **2**, **4** and **7**, compound **2** could be easily identified as friedelan-3-one from its identical ^{1}H and ^{13}C NMR data and physical constants reported in the literature [7]. The ^{1}H and ^{13}C NMR spectral data for **4** were very similar to those for **2** except the changes due to the presence of an additional seondary hydroxyl group. This compound was identified as 15α-hydroxyfriedelan-3-one from its identical ^{1}H and ^{13}C NMR spectral data and physical constants reported in the literature [7]. In comparison with the NMR spectral features of **2** and **4**, compound **7** showed the spectral properties of a 1,3-diketo-friedelane with a secondary hydroxyl group. This compound was identified as 15α-hydroxyfriedelane-1,3-dione based on its identical ^{1}H and ^{13}C NMR data and physical constants reported in the literature [7]. Compounds **2** and **7** were recently reported from *Peritassa compta* (Celastraceae) by Klass *et al.* [7] and this seems to be the second report on the isolation of these compounds. Among the compounds **1**, **3** and **5**, compound **1** was identified as lup-20(29)-en-3-one from its identical ^{1}H and ^{13}C NMR spectral data and physical constants reported in the literature [8, 9].

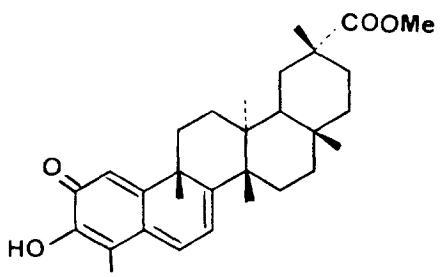
Salacianone (**3**), a new lupane triterpenoid, was obtained as needle like crystals, mp 215–18°, and was positive to the Liebermann–Burchard colour reaction. Its IR spectrum showed bands for carbonyl groups at 1740 (five membered ring ketone) and 1710 cm^{-1} and no absorption bands due to hydroxyl groups were observed. The ^{13}C NMR (67.9 MHz, $CDCl_3$, INEPT) spectrum showed the presence of 30 carbons including 10 CH_2 carbons, five CH carbons, seven CH_3 carbons and eight quarternary carbons. The presence of two carbonyl groups was evident in the ^{13}C NMR spectrum from the appearance of two carbonyl carbon signals at δ217.8 and 217.7. The EI mass spectrum showed a $[M]^+$ ion peak at *m/z* 438





	R
1	H_2
3	O
5	H, ß OH

	R^1	R^2
2	H_2	H_2
4	H_2	H, ∝OH
7	O	H, α OH



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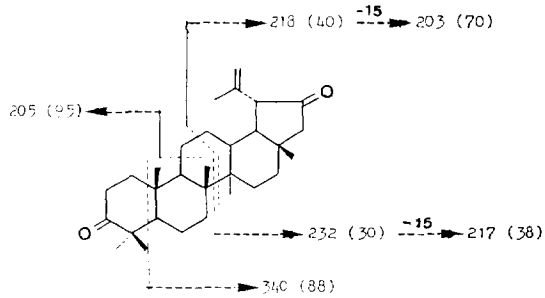
(100%), which was consistent with a molecular formula $C_{30}H_{46}O_2$ which was supported by its IR and NMR data. The EI mass spectrum showed fragment ions characteristic for the cleavages of the C ring in lupane skeletons, giving three important fragment ions at *m/z* 232 (30), 218 (40) and 205 (95) from which subsequent loss of methyl radicals were observed (Scheme 1). The intense peak at *m/z* 205 (95%) in the EI mass spectrum of **3** was indicative of a fragment ion composed of rings A and B with a C-3 ketone function in lupane triterpenoids [10]. The ions at *m/z* 232 and 218 formed by the C-ring cleavages indicated that the second carbonyl group was in the fragment ions constituting the rings D and E as shown in Scheme. 1. The ^1H and ^{13}C NMR spectral data for **3** was very similar to those for **1** except the changes in the chemical shifts due to the additional keto group. In order to locate the position of keto groups in **3**, we have made a careful comparison of its ^1H and ^{13}C NMR spectral data with those of **1**. The ^{13}C NMR chemical shifts in both **1** and **3** were found to be identical for the carbon atoms up to ring D, while considerable differences in the chemical shifts could be observed for the carbons in ring E and the adjacent isopropenyl group. These data indicated that the structural features of both molecules are identical up to ring D and consequently the second carbonyl function in **3** must be in ring E. The ^{13}C NMR signals of the isopropenyl group in **1** at δ19.3



Scheme 1. EI-mass spectral fragmentation of **3**. Relative intensities are given in parentheses.

(C-30), 109.4 (C-29) and 150.8 (C-20) were shifted to δ20.8 (C-30), 115.0 (C-29) and 143.4 (C-20) in **3**. The CH_2 carbon signal at δ29.8 (C-21) in **1** was absent in **3** and the CH_2 carbon shift at δ40.0 (C-22) was replaced by a CH_2 carbon shift at δ55.4 in **3**. In addition, the CH carbon shifts at δ47.9 (C-19) and 48.3 (C-18) in **1** were replaced by CH carbon signals at δ59.0 and 47.0 in **3**. These data clearly indicated that the carbonyl function is either at C-21 or at C-22. The exact position of the carbonyl group in the ring E was assigned at C-21 from a comparison of its ^{1}H NMR data with that of **1**. In the ^{1}H NMR spectrum of **1**, the H-19 proton signal was found to be merged with the H-2 proton multiplets at δ2.40, while in the ^{1}H NMR spectrum of **3**, the H-19 signal was shifted to lower field and appeared as a doublet at δ2.68 with a coupling constant of 10.8 Hz due to the axial–axial interaction between H-19 and H-18. These data indicated the absence of H-21 protons in **3** due to the keto group substitution. Further, the appearance of the isolated H-22 protons in **3** as a typical AB system at δ2.17 (J = 16.2 Hz) and 1.92 (J = 16.2 Hz) substantiated the assignment and confirmed the structure of salacianone as lup-20(29)-en-3,21-dione.

Salacianol (**5**), a new compound, obtained as white crystals was also positive to the Liebermann–Burchard colour reaction for triterpenoids. The ^{1}H and ^{13}C NMR spectral data showed that it is a lupane compound similar to **1** and **3**. The IR spectrum showed absorption bands for both hydroxyl (3450 cm^{-1}) and keto group (1700 cm^{-1}). The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) showed the presence of seven tertiary methyls including a vinyl methyl group. In addition, the spectrum revealed the presence of a carbinol proton at δ3.95 as a narrow triplet and a pair of exomethylene protons at δ4.65 and 4.85 as broad singlets. The ^{13}C NMR spectrum (100 MHz, $CDCl_3$, INEPT) showed the presence of seven CH_3 carbons, 10 CH_2 carbons, seven quaternary carbons and five CH carbons. The remaining carbinol methine carbon appeared as a weak and broad signal at δ77.7, thus accounting for a total of 30 carbons. The EI mass spectrum showed an intense $[M]^+$ ion at m/z 440 (100%) in agreement with a molecular formula of $C_{30}H_{48}O_2$ in corroboration with the other spectroscopic data. The EI mass spectrum showed fragment ions at m/z 422 $[M - H_2O]^+$ (65%), 425 $[M - Me]^+$ (30%) and 407 $[M - Me - H_2O]^+$ (15%). The other features of the fragmentation pattern in the EI mass spectrum of **5** were characteristic ions at m/z at 205 (75%) and 220 (33%) due to the cleavages of the C ring in a lupane skeleton [10]. The ion at m/z 205 was indicative of the fragment constituting rings A and B with a C-3 keto function as in the previous case, and an ion at m/z 220 (33%) was indicative of the fragment constituting rings D and E with the hydroxyl function. The exact location of the hydroxyl group was made by a comparison of the ^{1}H and ^{13}C NMR spectral data for **5** with those for **1** and **3**. The ^{13}C NMR chemical shifts for the carbon atoms up to ring D in **5** were identical to those in **1** and **3**, indicating their identical structural features. The differences in the ^{1}H and ^{13}C NMR chemical shifts for the atoms in the E ring and the isopropenyl group in **5** with respect to the corresponding shifts in **1** and **3** pointed to the hydroxyl group substitution being in ring E, either at C-21 or at C-22. The position of the hydroxyl group in **5** was assigned at C-21 from the following observations. The ^{13}C NMR signals at δ20.8 (C-30), 115.0 (C-29) and 143.4 (C-20) in **3** were shifted to δ19.7 (C-30), 111.3 (C-29) and 148.3 (C-20) in **5**, which were quite different from the corresponding shifts in **1**. These data indicated that the hydroxyl group was in the vicinity of the isopropenyl group. The H-19 proton, which appeared as a doublet at δ2.68 in **3**, was replaced in **5** by a multiplet at δ2.35 partially merged with the H-2 proton multiplet at δ2.50. In addition, the H-22 protons that appeared as an AB quartet at δ2.17 and 1.92 in **3**, were replaced by a multiplet at δ1.60–1.70 in **5**. The assignment of the hydroxyl group substitution at C-21 was verified from the ^{1}H–^{1}H COSY spectrum of **5** in which the coupling interaction between the carbinol methine proton at δ3.95 (H-21) and the H-19 proton at δ2.35 were clearly visible. Jones oxidation of **5** yielded a diketone, which was found to be identical with **3**, confirming that **5** was a 21-hydroxyl derivative of **3**. The orientation of the hydroxyl group was clarified with the aid of NOE difference spectroscopy. The irradiation of the H-21 proton triplet at δ3.95 enhanced the H-30 methyl resonance at δ1.71, and vice versa, but did not affect the H-28 resonance, which clearly indicated the β-orientation of the hydroxyl.

Even though the keto/hydroxyl group substitutions at various positions in rings A, B, C and D in lupane skeletons have been frequently encountered in nature, the substitution in ring E seems relatively rare. Ochraceolides A–E, the first group of lupane r-lactones formed by oxidative carboxylation of the C-30 methyl group followed by lactonization with the 21α-hydroxyl group have been reported from *Kokoona ochracea* (Celastraceae) by Nagassappa *et al.* [11]. The orientation of the r-lactone ring in the above compounds was found to be α. However, the 21 β-hydroxy substitution in **5** and the 21-keto substitution in **3** may be rationalized from the chemotaxonomic point of view.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 270 and 400 MHz in $CDCl_3$ using TMS as int. standard. ^{13}C NMR spectra were recorded at 67.9 and 100 MHz in $CDCl_3$ using TMS as int. standard and multiplicities were determined by INEPT techniques. TLC was performed on 0.2 mm silica gel plates and the spots were detected by spraying with vanilline–H_2SO_4 followed by heating at 110° until the visualization of a characteristic colour.

Plant material. Stem bark of *S. beddomei* was collected in November 1993 from Vittalapacha, palode, Kerala, and was identified by Dr. A. Nazarudeen, Tropical Botanical Garden & Research Institute, Palode, Kerala, where a voucher specimen has been deposited.

Extraction and isolation. The shade dried stem bark powder (500 gm) was repeatedly extracted several times with hexane at room temp. The combined extract (8 l.)

was concd under red. pres. to obtain 19 g of a dark brown resinous solid, which was chromatographed on silica gel column and eluted with hexane, mixts of hexane–C_6H_6, C_6H_6, mixts of C_6H_6–$CHCl_3$, $CHCl_3$ and $CHCl_3$–EtOAc mixts. Compounds **1** and **2** were obtained from the hexane–C_6H_6 fr. and **3** from the C_6H_6–$CHCl_3$ frs. The rest of the frs were not homogeneous and were pooled together and rechromatographed repeatedly in either silica gel or alumina columns and eluted with the above solvents to obtain compounds **4**–**8**.

Lup-20(29)-*en*-3-*one* (**1**). Crystals ($CHCl_3$–MeOH) (80 mg), mp 170–72° (lit. [9] mp 174°). ^{1}H NMR (270 MHz, $CDCl_3$): δ0.80 (3H, *s*, H-28), 0.94 (3H, *s*, H-25), 0.96 (3H, *s*, H-27), 1.04 (3H, *s*, H-24), 1.08 (6H, *s*, H-23 and H-26), 1.68 (3H, *s*, H-30), 1.90–2.0 (2H, *m*, H-1a, H-21a), 2.40 (3H, *m*, H-2, H-19), 4.58 (1H, *br s*, H-29a), 4.63 (1H, *br s*, H-29b), ^{13}C NMR (67.9 MHz, $CDCl_3$): Table 1.

Friedelan-3-*one* (**2**). Crystals ($CHCl_3$–MeOH) (30 mg), mp 262–264 (lit. [7] mp 260–263°). IR γ_{max}^{KBr} cm^{-1}: 1720 (CO). ^{1}H NMR (270 MHz, $CDCl_3$): δ0.71 (3H, *s*, H-24), 0.86 (3H, *d*, J = 7.8 Hz, H-23), 0.85 (3H, *s*, H-25), 0.95 (3H, *s*, H-30), 1.00 (6H, *s*, H-26 and H-27), 1.05 (3H, *s*, H-27), 1.17 (3H, *s*, H-28), 1.96 (1H, *m*, H-1a), 2.28 (2H, *m*, H-2b, H-4), 2.39 (1H, *m*, H-2a), 1.2–1.8 (*m*, rest of the protons). ^{13}C NMR (67.9 MHz, $CDCl_3$): (C-1–C-30): δ22.28, 41.53, 213.17, 58.24, 42.14, 41.30, 18.24, 53.12, 37.45, 59.50, 35.64, 30.50, 39.71, 38.31, 32.78, 36.01, 29.99, 42.81, 35.35, 28.18, 32.44, 39.24, 6.81, 14.65, 17.94, 20.25, 18.65, 32.09, 31.77, 35.01. EIMS: see ref. [7].

Table 1. ^{13}C NMR data for compounds **1**, **3** (67.9 MHz, $CDCl_3$) and **5** (100 MHz, $CDCl_3$, TMS)

C	1	3	5
1	39.6	39.5	39.6
2	34.1	34.1	34.1
3	217.9	217.8	218.1
4	47.3	47.3	47.3
5	54.9	54.9	54.9
6	19.7	19.6	19.6
7	33.6	33.2	33.4
8	40.8	40.9	40.8
9	49.8	49.6	49.7
10	36.9	36.8	36.8
11	21.5	21.2	21.4
12	25.1	25.3	24.7
13	37.4	37.3	37.6
14	42.8	42.7	42.6
15	27.4	26.9	27.1
16	35.6	34.8	35.6
17	43.0	37.8	41.9
18	48.3	47.0	48.0
19	47.9	59.0	59.8
20	150.8	143.4	148.3
21	29.8	217.7	77.7
22	40.0	55.4	49.3
23	26.6	26.6	26.6
24	21.0	21.0	21.0
25	15.9	15.9	15.9
26	15.8	15.7	15.8
27	14.5	14.5	14.4
28	18.0	18.7	19.7
29	109.4	115.0	111.3
30	19.3	20.8	19.7

Salacianone (*lup*-20(29)-*en*-3,21-*dione*) (**3**). Crystals ($CHCl_3$–MeOH) (80 mg), mp 215–218°. IR γ_{max}^{KBr} cm^{-1}: 2930, 2850, 1740, 1700, 1460, 1380, 880. ^{1}H NMR (270 MHz, $CDCl_3$): δ0.92 (3H, *s*, H-28), 0.95 (3H, *s*, H-25), 1.04 (3H, *s*, H-28), 1.05 (3H, *s*, H-24), 1.12 (3H, *s*, H-26), 1.65 (3H, *s*, H-30), 1.90 (1H, *m*, H-la), 1.98 (1H, *d*, J_{ab} = 16.2 Hz, H-22b), 2.19 (1H, *d*, J_{ab} = 16.2 Hz, H-22a), 2.42 (2H, *m*, H-2), 2.68 (^{1}H, *d*, J = 10.8 Hz, H-19), 4.80 (1H, *br s*, H-29b), 4.87 (1H, *br s*, H-29a), 1.10–1.90 (*m*, rest of the protons). ^{13}C NMR (67.9 MHz, $CDCl_3$): Table 1. EIMS (70eV) *m/z* (rel. int.): 438 $[M]^+$ (100) 423 $[M - Me]^+$ (33), 395 (15), 353 (15), 340 (88), 245 (28), 232 (33), 219 (41), 205 (95), 203 (72), 161 (47), 120 (61), 121 (75), 96 (90).

15α-*Hydroxyfriedelan*-3-*one* (**4**). Crystals ($CHCl_3$–MeOH) (90 mg), mp 273.74 (lit. [7] mp 275–276). ^{1}H NMR (270 MHz, $CDCl_3$): δ0.72 (3H, *s*, H-24), 0.87 (3H, *d*, J = 7.8 Hz, H-23), 0.88 (3H, *s*, H-25), 0.94 (3H, *s*, H-30), 0.99 (3H, *s*, H-27), 1.01 (3H, *s*, H-29), 1.06 (3H, *s*, H-26), 1.29 (3H, *s*, H-28), 1.95 (3H, *m*, H-1a), 2.15 (1H, *t*, H-16a), 2.20–2.28 (2H, *m*, H-2b, H-4), 2.40 (1H, *m*, H-2a) 3.73 (1H, *d*, J = 8.5 Hz, H-15β). ^{13}C NMR (67.9 MHz, $CDCl_3$) (C-1–C-30): δ22.32, 41.48, 213.00, 58.17, 42.00, 41.27, 19.96, 53.46, 37.79, 59.39, 35.63, 31.16, 40.56, 44.08, 74.57, 48.38, 30.19, 41.60, 35.58, 28.12, 31.89, 38.71, 6.78, 14.47, 17.95, 14.02, 18.71, 32.58, 30.89, 35.64. EIMS: see ref. [7].

Salacianol (21β-*hydroxylup*-20(29)-en-3-*one*) (**5**). Crystals ($CHCl_3$–MeOH) (80 mg), mp 195–198°. IR γ_{max}^{KBr} cm^{-1}: 3560 (OH), 1720 (CO), 900 (>C=CH_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ0.94 (3H, *s*, H-25), 0.95 (3H, *s*, H-27), 1.03 (6H, *s*, H-24, H-28), 1.07 (3H, *s*, H-23) 1.08 (3H, *s*, H-26), 1.71 (3H, *s*, H-30), 1.80–1.90 (2H, *m*, H-1a and H-22a), 2.35 (1H, *m*, H-19), 2.40 (2H, *m*, H-2), 3.95 (1H, narrow *t*, H-21β), 4.69 (1H, *br s*, H-29b), 4.82 (1H, *br s*, H-29a). ^{13}C NMR (100 MHz, $CDCl_3$): Table 1. EIMS (70eV) *m/z* (rel. int.): 440 $[M]^+$ (100), 425 $[M - Me]^+$ (28), 422 $[M - H_2O]^+$ (60), 407 (13), 396 (48), 357 (30), 341 (15), 313 (10), 273 (22), 245 (68), 232 (18), 220 (32), 205 (75), 203 (42), 48 (175), 163 (43), 121 (63), 109 (73).

Jones oxidation of salacianol (**5**) *to salacianone* (**3**). Compound **5** (15 mg) was dissolved in aldehyde free Me_2CO (2 ml) and titrated with Jones reagent at 20°. The excess of acid was decomposed with $NaHSO_3$ and the mixt. worked up in the usual way. The product was purified by prep. TLC to yield 8 mg **3** (identical TLC, ^{1}H NMR).

Sitosterol (**6**). Compound **6** was identified by ^{1}H and ^{13}C NMR spectral data and by direct comparison with an authentic sample.

15α-*Hydroxyfriedelane*-1,3-*dione* (**7**). Crystals ($CHCl_3$–MeOH) (40 mg), mp 250° (lit. [7] mp 245–248°). IR γ_{max}^{KBr} cm^{-1}: 3520 (OH), 1735 (CO), 1710 (CO). ^{1}H NMR (400 MHz, $CDCl_3$): δ0.69 (3H, *s*, H-24), 0.94 (3H, *s*, H-30), 0.96 (3H, *s*, H-27), 1.02 (3H, *s*, H-29), 1.05

(3H, *s*, H-23), 1.09 (3H, *s*, H-26), 1.22 (3H, *s*, H-25), 1.29 (H-28), 1.15 (1H, *m*, H-19b), 1.25 (*m*, H-16a), 1.38–1.45 (*m*, H-6b, H-21a, H-22a), 1.50–1.60 (2H, *m*, H-12a, H-7b), 1.92–97 (*m*, H-6a, H-7a, H-22b), 2.16–2.22 (2H, *m*, H-16a, H-11a), 2.38 (1H, *s*, H-9), 2.58 (1H, *q*, $J = 6.7$ Hz) 3.25 (1H, *d*, $J_{ab} = 18$ Hz), 3.46 (1H, *d*, $J_{ab} = 18$ Hz), 3.70 (1H, *d*, $J = 8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) (C-1–C-30): δ202.68, 60.67, 204.01, 59.02, 37.70, 40.64, 19.65, 52.55, 37.57, 71.82, 34.63, 30.79, 40.33, 43.99, 74.64, 48.60, 30.20, 41.54, 35.49, 28.12, 31.92, 38.85, 7.25, 15.79, 18.02, 14.03, 18.81, 32.65, 30.93, 35.58. EIMS: see ref. [7].

Pristimerin (**8**). Orange–red amorphous solid (15 mg). IR γ_{max}^{KBr} cm^{-1}: 3360 (OH), 1720 (ester CO), 1620 (CO). ^{1}H NMR (270 MHz, $CDCl_3$): δ0.54 (3H, *s*), 1.10 (3H, *s*), 1.27 (3H, *s*), 1.43 (3H, S), 2.47 (1H, *d*, $J = 16.7$ Hz), 3.55 (3H, *s*, OMe), 6.34, 653, 7.01 (each 1H, *br s*, H-1, H-6, H-7), 0.90–2.10 (*m*, rest of the protons). EIMS (70 eV) *m/z*: 464 $[M]^+$ (75), 386 (18), 241 (53), 229 (29), 203 (100), 202 (68), 201 (80).

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