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TETRAHEDRON

Justicia Lignans V. Three New β-Apolignans from *Justicia neesii* Ramamoorthy

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Abstract : The isolation and characterization of three new β-apolignans, namely, 1,4-dihydrotaiwanin C (**3**), jusneesiin (**4**) and jusneesiinol (**5**), in addition to (-) hibalactone (**6**), from *J. neesii* are reported. Compounds **4** and **5** are unprecedentedly angularly fused β-apolignans and the structure of **5** was confirmed by X-ray diffraction data.

The genus *Justicia* (n.o. Acanthaceae) is a rich source of lignans, particularly, arylnaphthalide lignans.[1] Several of these *Justicia* lignans were found to possess antiplatelet,[2] antiviral,[3] antitumor,[4,5] antidipressent,[6] piscidal[7] and insect antifeedant[8] activities. In a continuing study on the chemical constituents of *Justicia* species of the Tirumala Hill Tracts,[9-12] we have investigated *J. neesii* collected from the Tirumala Hills and reported recently, isolation of several arylnaphthalide lignans including two new angularly fused arylnaphthalides (**1**, **2**).[12] Chromatography of the remaining fractions over silica gel yielded three new compounds A, B and C, in addition to a known butyrolactone lignan, (-) hibalactone (**6**). Structure elucidation of compounds A, B and C is presented in this paper.

Compound A was obtained as colourless crystals from chloroform, m.p 248-50°C, $[\alpha]_D^{25}$ +107.4° ($CHCl_3$, c 0.23). Its molecular formula was deduced as $C_{20}H_{14}O_6$ based on high-resolution EIMS (m/z 350.0779, M^+, calcd. 350.0790) and ^{13}C NMR data. Its IR spectrum showed lactone carbonyl at 1745 cm^{-1}. The ^1H NMR spectral data (Table 1) contained five aromatic protons constituted by two singlets (1H each) at δ 6.67 and 6.84 and an ABX system characteristic of 1,2,4-trisubstituted phenyl unit (δ 6.68, 1H, d, J = 1.9 Hz, 6.77, 1H, d, J = 8.3 Hz and 6.68, 1H, dd, J = 1.9, 8.3 Hz), a lactone methylene (δ 3.68, 1H, dd, J = 4.1, 23.0 Hz and 3.95, 1H, dd, J = 4.4, 23.0 Hz) and a methine (δ 4.72, 1H, br.s) in addition to two

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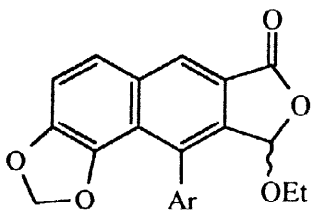

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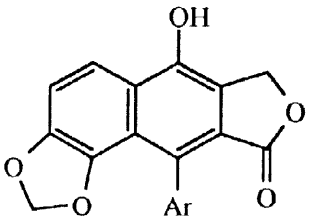

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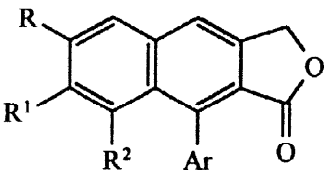
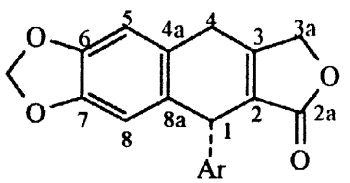


9 R R^1=OCH_2O; R^2=H

10 R=H; R^1 R^2=OCH_2O



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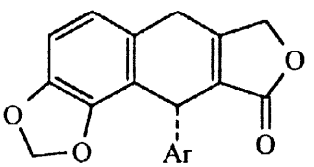

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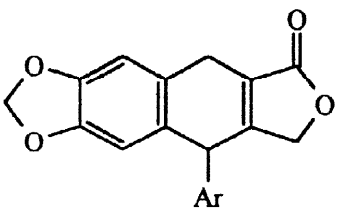

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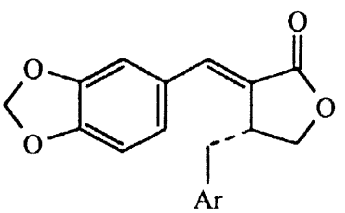

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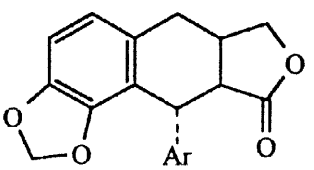

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(Ar = 3,4-methylenedioxyphenyl)

methylenedioxy groups (δ 5.91 - 5.97, 4H). A perusal of above data in comparison with those of other congeneric lignans,[12] revealed that compound A is also an arylnaphthalide type of lignan, but with ring B partially hydrogenated. ^1H - ^1H COSY experiments showed that the methylene protons (H_2-4) and methine (H-1) are coupled by a long range coupling ($^5J_{1,4}$ ~ 4.0 Hz) and such a coupling has been recorded in β-apolignans, earlier.[13] The alternate position for the double bond (between C-1 and C-2), was ruled out based on the observed HMBC correlations of H-1 with C-1′, C-6′, C-8a, C-2, C-3. The position of the lactone carbonyl was deduced as C-2a by the comparison of ^1H and ^{13}C NMR spectral data with those of an isomeric compound **7**.[14] The orientation of lactone was confirmed further by dehydrogenation of compound A with DDQ into taiwanin C (**9**). The configuration at C-1 was assigned tentatively as 1R based on the comparison of optical rotation data with similar compounds.[15] From the foregoing, compound A could be described as (1R) -1,4-dihydrotaiwanin C (**3**).

Compound B was obtained as colourless crystals from ethyl acetate - pet. ether (60- 80 °C), m.p 207-9 °C, $[\alpha]_D^{25}$ + 8.0° (acetone, c 0.1). Its molecular formula was deduced as $C_{20}H_{14}O_6$ by HREIMS (m/z 350.0790, M^+, calcd. 350.0790) and is isomeric with **3**. Its IR spectrum showed

Table 1. NMR spectral data of **3** and **4**[a].

Position	3			4		
	^{1}H NMR δ (500 MHz)[b]	^{13}C NMR δ (125 MHz)[b]	HMBC	^{1}H NMR δ (400 MHz)[c]	^{13}C NMR δ (100 MHz)[c]	HMBC
1	4.72 (1H, br. s)	41.2	C-2, C-3, C-4a, C-8a, C-1′, C-6′	4.98 (1H, m)	37.3	
2		125.3			127.9	
2a		171.9			172.0	
3		160.5			157.9	
3a	4.95 (1H, dd, J = 2.0, 17.3 Hz) 5.03 (1H, d, J = 17.3 Hz)	71.2	C-2, C-3	4.81 (1H, d, J = 17.0 Hz) 4.89 (1H, d, J = 17.0 Hz)	71.1	C-2, C-3
4	3.68 (1H, dd, J = 4.1, 23.0 Hz) 3.95 (1H, dd, J = 4.4, 23.0 Hz)	28.5	C-2, C-4a, C-8a	3.68 (1H, dd, J = 3.0, 22.2 Hz) 3.91 (1H, dd, J = 3.4, 22.2 Hz)	28.4	C-2, C-3
4a		130.1			124.7	
5	6.84 (1H, s)	108.0 (107.97)	C-4, C-4a, C-6	6.78 (1H, d, J = 8.1 Hz)	121.2	C-4
6		146.2		6.75 (1H, d, J = 8.1 Hz)	107.7	
7		146.3			145.8	
8	6.67 (1H, s)	108.8	C-1, C-8a		146.4	
8a		124.0			119.7	
1′		137.7			134.8	
2′	6.68 (1H, d, J = 1.9 Hz)	108.3	C-1, C-6′	6.65 (1H, d, J = 1.7 Hz)	108.5	C-1, C-4′, C-6′
3′		145.8			147.6	
4′		147.3			146.5	
5′	6.77 (1H, d, J = 8.3 Hz)	108.0 (108.02)	C-1′, C-4′	6.69 (1H, d, J = 8.1 Hz)	108.2	C-3′
6′	6.68 (1H, dd, J = 1.9, 8.3 Hz)	121.0	C-1, C-2′	6.75 (1H, dd, J = 1.7, 8.1 Hz)	121.5	C-2′
OCH_2O ring A	5.91 (1H, d, J = 0.8 Hz) 5.97 (1H, d, J = 0.8 Hz)	100.8		5.89 (2H, m)	101.0	
OCH_2O ring C	5.92 (1H, d, J = 1.0 Hz) 5.93 (1H, d, J = 1.0 Hz)	101.0		5.89 (5.892) (2H, m)	101.3	

(a) Assignments are confirmed by ^{1}H - ^{1}H COSY, ^{1}H - ^{13}C COSY and HMBC data.
(b) Solvent : d_6 DMSO, δ values from TMS.
(c) Solvent : $CDCl_3$, δ values from TMS.

lactone carbonyl at 1758 cm^{-1}. Its ^1H NMR spectral data (Table 1) were similar to those of **3**, except for the two doublets at δ 6.78 and 6.75 (1H each J = 8.1 Hz) found in compound B, instead of two singlets at δ 6.67 and 6.84 (1H each) noticed in **3**. These differences could be well accounted for by the change of 6,7-methylenedioxy group present in **3** to 7,8-methylenedioxy group proposed for compound B. Such a change in methylenedioxy substitution is also corroborated by the HMBC correlations of H-5 (δ 6.78, d, J = 8.1 Hz) with C-4 (δ 28.4). As expected, the ^{13}C NMR spectrum of compound B contained only three signals in the region δ 107-109 assigned for C-6, C-2′ and C-5′, consistent with 7,8-methylenedioxy substitution.

The orientation of lactone carbonyl (C-2a) and 7,8-methylenedioxy substitution was finally confirmed by dehydrogenation of compound B with DDQ into retrohelioxanthin (**10**). Hydrogenation of compound B using H_2/Pd-C gave the tetralin, **11**. The configuration at C-1 has been assigned tentatively as 1R by comparison of optical rotation and CD data with those of **3** and other similar lignans.[15]

Based on the above, compound B could be described as (10R)-10-(3,4-methylenedioxyphenyl)-7,10-dihydro-6H-furo[3′,4′:6,7]naphtho[1,2-d][1,3]dioxol-9-one, an unprecedented angularly fused β-apolignan, named Jusneesiin (**4**). It may be noted that β-apopolygamatin was assigned originally as angularly fused β-apolignan,[16] but, revised into a δ-apolignan later.[17]

It is interesting to note that structures **3** and **4** were assigned for the photolysis products of taiwanin A earlier.[18] However, the data reported for a product with a proposed structure of **3** in fact corresponds to **4** and vice-versa. We believe that the erroneous assignments made by the earlier authors were probably due to relying heavily on the splitting of proton signals of methylenedioxy group as an evidence for angularly fused compounds. But it is now known that many compounds having linearly fused methylenedioxy group also show splitting of signals.[13-15,19]

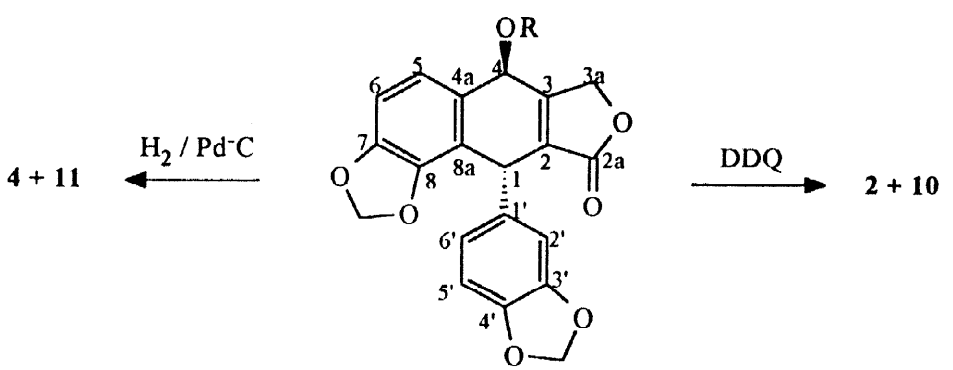
Compound C was obtained as colourless amorphous solid from ethyl acetate - pet. ether (60-80°C), m.p 220-22 °C, $[\alpha]_D^{25}$ +218.4° (acetone, c 0.5) analysed for $C_{20}H_{14}O_7$ by HREIMS (m/z 366.0754, M^+, calcd. 366.0740) and its IR spectrum contained bands due to hydroxyl (3534 br) and lactone carbonyl (1732 and 1261 cm^{-1}). Its ^1H NMR spectral data (Table 2) are similar to those of Jusneesiin (**4**), except for the replacement of two doublet of doublets assigned for 4-CH_2 in **4** by methine proton (δ 5.67, 1H, dd, J = 2.2, 8.1 Hz) and a hydroxyl proton (δ 6.33, 1H, d, J = 8.1 Hz) in compound C. Such a change has been corroborated well by the presence of a signal at δ 62.6 (4-CHOH) in ^{13}C NMR data of compound C. In addition, the signals corresponding to C-3 and C-4a were deshielded to the extent of 6.0 and 7.0 ppm, respectively and C-2, C-3a and C-5 got shielded to the extent of 2.9, 0.7 and 0.7 ppm respectively due to the presence of 4-CHOH.

As expected compound C formed monoacetate **8** with Py / Ac_2O (Scheme 1). In the ^1H NMR spectrum of the acetate, the lactone methylene protons H-3a and H-5 were shielded to the extent of 0.2 ppm and 0.5 ppm, respectively, compared to those of compound C. The homoallylic proton (H-1) was deshielded by 0.2 ppm.

Table 2. NMR spectral data of **5**

Position	^{1}H NMR δ (500 MHz, d_6 DMSO)	^{13}C NMR δ (125 MHz, d_6 DMSO)	HMBC
1	4.79 (1H, br. s)	36.9	C-1′, C-2, C-3, C-4a, C-8a
2		125.0	
2a		171.6	
3		163.9	
3a	5.01 (1H, dd, J = 2.2, 17.6 Hz) 5.15 (1H, d, J = 17.6 Hz)	70.4	C-2, C-3
4	5.67 (1H, dd, J = 2.2, 8.1 Hz)	62.6	C-3, C-4a
4a		131.9	
5	7.20 (1H, dd, J = 0.8, 8.2 Hz)	120.5	C-4, C-8a
6	6.94 (1H, d, J = 8.2 Hz)	107.6	C-4a, C-8
7		146.1	
8		144.5	
8a		118.9	
1′		134.1	
2′	6.64 (1H, d, J = 1.7 Hz)	108.3	C-4′, C-6′
3′		147.2	
4′		146.1	
5′	6.76 (1H, d, J = 7.9 Hz)	108.1	C-1′-C-3′
6′	6.62 (1H, dd, J = 1.7, 7.9 Hz)	121.2	C-1, C-4′, C-5′
OCH_2O	5.93 (1H,d, J = 0.8 Hz)	101.2	
ring A	5.97 (1H, d, J = 0.8 Hz)		
OCH_2O	5.93 (1H, d, J = 1.0 Hz)	100.9	
ring C	5.94 (1H, d, J = 1.0 Hz)		
OH	6.33 (1H, d, J = 8.1 Hz)		C-3, C-4, C-4a

(a) Assignments are confirmed by ^{1}H - ^{1}H COSY, ^{1}H - ^{13}C COSY and HMBC data.



5 R = H

8 R = Ac

Scheme 1

Dehydrogenation of compound C with DDQ gave **10** and **2**. Hydrogenation of compound C using H_2 / Pd-C gave **4** and the tetralin, **11**. The formation of **4** and **11** could be rationalised by initial reduction of the double bond, followed by dehydration and isomerization of the double bond to **4** and then further hydrogenation gave **11**.[20]

The structural features including relative stereochemistry at C-1 and C-4 of compound C were ascertained further by X-ray diffraction data (Fig. 1) on crystal samples obtained by careful crystallization from ethyl acetate solution. The structure refinement led to discrepancy index R=0.040 on 1365 observed reflections and 244 variables. Bond lengths and angles are good agreement with values observed in structurally similar molecules. Torsion angle around C(3)....C(8)

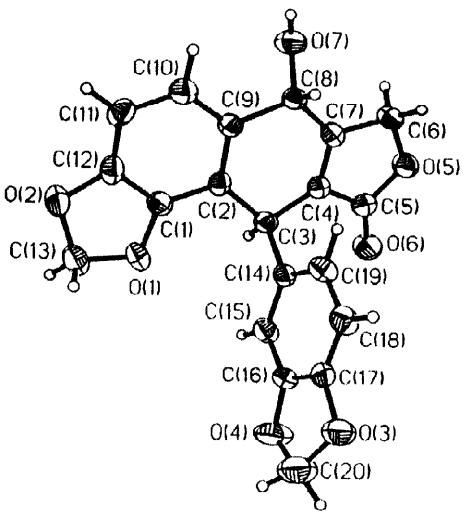


Fig. 1 : ORTEP diagram of jusneesiinol (5)

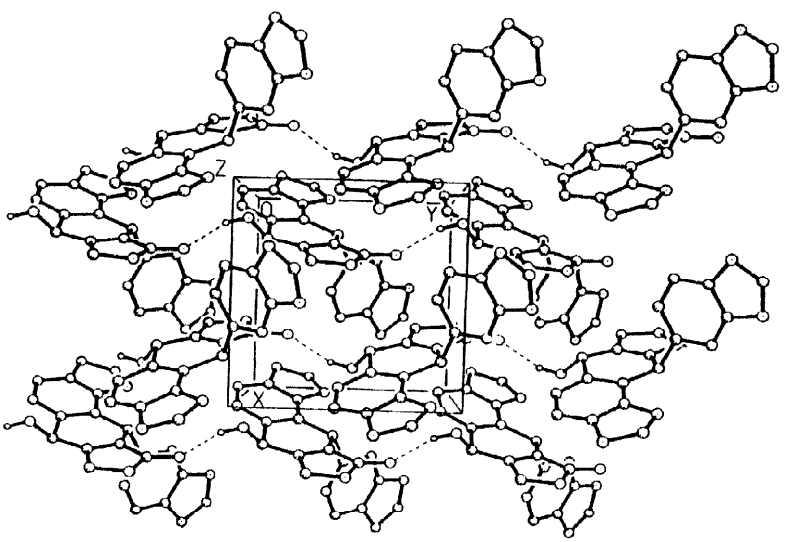


Fig. 2 : Molecular packing of jusneesiinol (5)

[C(14)-C(3)...C(8)-O(7)] is slightly distorted [171.8°] with respect to ideal *trans* conformation. The cyclohexadiene ring is slightly bent and the dihedral angle between the planes, C(8), C(9), C(2), C(3) and C(3), C(4), C(7), C(8) is 13.3°.

The view of the molecular packing is shown in Fig 2. There is a possible H-bonding between the hydroxyl group O(7) and keto oxygen O(6) [O(6)....O(7) 2.8729Å; O(6)...H(7A)-O(7) 151.1°].

Based on the above the structure of compound C could be derived as (6R*, 10R*)-10-(3,4-methylenedioxyphenyl)-7,10-dihydro-6-hydroxy-6H-furo[3',4':6,7]naphtho[1,2-d][1,3]dioxol-9-one. **5** is also a novel angularly fused β-apolignan named Jusneesiinol.

The other lignan was identified as a known butyrolactone, (-) hibalactone (**6**) by comparison with literature data.[21]

Experimental Section

General methods : Melting points were determined on a Mel-Temp apparatus and are uncorrected. UV spectra were recorded on a Shimadzu UV 240 spectrophotometer, IR spectra on a Perkin-Elmer 781 spectrometer, ^{1}H and ^{13}C NMR spectra were recorded on a GE-500 or 400 or 300 MHz or JEOL 400 MHz NMR spectrometers, HREIMS spectra on a VG Autospec spectrometer and EIMS spectra on a VG micromass 70-70H spectrometer. Optical rotations were measured on a Jasco DIP-370 polarimeter. X-ray diffraction data were obtained on a Siemens four circles diffractometer.

Plant material : The plant material was collected from the Tirumala Hills in December 1994 and authenticated as *J. neesii* Ramamoorthy (syn. *J. micrantha* Wall. exCl) by Research and Specimen Cell, NISCOM, CSIR, New Delhi, Voucher Specimens are on deposit at NISCOM (NISCOM field no. 1756) and Department of Chemistry, Sri Venkateswara University, Tirupati.

Extraction and Isolation : The shade dried and milled plant material (ca. 5 Kg) was extracted repeatedly with aq. ethanol (95%). After removal of the solvent, the dark green gummy residue (ca. 340 g) was impregnated on 400 g of silica gel and fractionated with pet. ether, ethyl acetate and methanol. The pet.ether and ethyl acetate extractives shown similar TLC behaviour, and hence combined. Evaporation of the solvent from the combined fraction gave green gummy residue (ca. 107 g). Chromatography of the residue over silica gel (100-200 mesh, 300 g) column using mixtures of pet. ether and ethyl acetate in increasing polarity as eluents yielded six already reported arylnaphthalide lignans and purification of the remaining fractions yielded compound A (**3**, 40 mg), compound B (**4**, 60 mg), compound C (**5**, 500 mg) and (-) hibalactone (**6**, 60 mg).

Compound A : *(1R)-1,4-dihydrotaiwanin C (3)* : Colourless crystals from chloroform, m.p. 248-50°C: $[\alpha]_D^{25}$ + 107.4° ($CHCl_3$, c 0.23) ; IR (KBr) ν_{max} 1745, 1234 and 1040 cm^{-1} ; UV (MeOH) λ_{max} (log ε) 289 nm (3.47) ; ^{1}H and ^{13}C NMR (d_6 DMSO): see Table 1; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 3.65 (1H, dd, *J* = 4.2, 22.5 Hz), 3.86 (1H, dd, *J* = 4.4, 22.5 Hz), 4.81 (1H, d, *J* = 17.1 Hz) 4.88 (1H, d, *J* = 17.1 Hz), 4.76 (1H, br.s), 6.52 (1H, d, *J* = 1.5 Hz), 6.59 (1H, s), 6.69

(1H,s), 6.70 (1H, d, J = 8.0 Hz), 6.73 (1H, dd, J = 1.5, 8.0 Hz), 5.88 (1H, d, J = 1.3 Hz), 5.89 (1H, d, J = 1.3 Hz), 5.91 (1H, d, J = 1.2 Hz) and 5.94 (1H, d, J = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 29.1, 42.2, 71.0, 101.0, 101.2, 107.7, 108.3, 108.5, 109.5, 121.7, 123.4, 128.0, 130.1, 136.6, 146.5, 147.0, 147.3. 147.8, 157.0 and 172.0; high-resolution EIMS: m/z 350.0779 (81.5%, M^+, calcd. for $C_{20}H_{14}O_6$, 350.0790), 348.0634 (21.1%, M^+ - 2H, calcd. for $C_{20}H_{12}O_6$, 348.0634) ; EIMS m/z (%): 350 (M^+, 100), 305 (33), 275 (26), 199 (22), 185 (38), 139 (24) and 122 (53) ; CD (MeOH ; 0.63 mM) Δε : 0 (320) ; - 3.4 (304) ; 0 (296) ; +2.1 (292); 0 (285) ; -2.1 (275) ; 0 (266) and + 75.1 (222).

Dehydrogenation of 3 : A mixture of **3** (10 mg) and DDQ (10 mg) in dry benzene (1 mL) was refluxed for 20 min. After cooling, the reaction mixture was filtered and purified further by column chromatography over silica gel to yield taiwanin C[12] (**9**, 5 mg); m.p. 269-70° (lit.[12] m.p. 265-68°); ^{1}H NMR (400 MHz, d_6 DMSO) : δ 5.43 (2H, s), 6.11, 6.13, 6.17, 6.18 (each 1H, br.s), 6.75 (1H, dd, J = 1.4, 7.9 Hz), 6.87 (1H, d, J = 1.4 Hz), 6.91 (1H, s), 7.03 (1H, d, J = 7.9 Hz) 7.50 (1H, s) and 7.94 (1H, s).

Compound B: Jusneesiin (4) : Colourless amorphous solid from pet. ether - ethyl acetate. m.p. 207-9° ; $[\alpha]_D^{25}$ + 8.0° (acetone, c 0.1) ; IR (Neat) ν_{max} 1758, 1262, 1242 and 1042 cm^{-1} ; UV (MeOH) λ_{max} (log ε) 288 nm (3.88) ; ^{1}H and ^{13}C NMR: see Table 1 ; high-resolution EIMS: m/z 350.0790 (100%, M^+, calcd. for $C_{20}H_{14}O_6$, 350.0790), 348.0658 (8.8%, M^+ - 2H, calcd. for $C_{20}H_{12}O_6$, 348.0634); EIMS m/z (%) : 350 (M^+, 100), 305 (11), 275 (14), 228 (67), 199 (26), 176 (11), 135 (44), 93 (53), 77 (10) and 43 (15) ; CD (MeOH ; 0.7 mM) Δε : 0 (324) , -1.0 (302), 0 (295), + 0.3 (294) , 0 (292), -0.7 (273) , 0 (268) , +13.9 (224) and +16.1 (219)

Dehydrogenation of 4 : Using the procedure described for **3**, **4** (5 mg) was dehydrogenated to give retrohelioxanthin[12] (**10**, 3 mg); m.p 262-64° (lit.[12] m.p. 264-65°); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 5.40 (2H, d, J = 1.0 Hz) 5.93 (1H, d, J = 1.4 Hz), 5.94 (1H, d, J = 1.4 Hz), 6.05 (1H, d, J = 1.4 Hz), 6.09 (1H, d, J = 1.4 Hz), 6.83 (1H, dd, J = 1.7, 7.9 Hz), 6.85 (1H, br.s), 6.90 (1H, d, J = 7.9 Hz), 7.38 (1H, d, J = 8.6 Hz), 7.56 (1H, d, J = 8.6 Hz) and 7.83 (1H, s).

Hydrogenation of 4 : Into a mixture of **4** (5 mg), Pd-C (10%, 20 mg) and ethyl acetate (2 mL) was bubbled hydrogen gas continuously at room temperature overnight. Then the reaction mixture was filtered and purified by chromatography over silica gel to yield **11** (3 mg): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73 (1H, dd, J = 8.8, 15.6 Hz), 2.96 - 3.05 (2H, m), 3.12 (1H, m), 3.44 (1H, t, J = 9.0 Hz), 4.42 (1H, t, J = 9.0 Hz), 4.85 (1H, d, J = 6.4 Hz), 5.91 (1H, d, J = 1.5 Hz), 5.92 (1H, d, J = 1.5 Hz), 5.927 (1H, d, J = 1.5 Hz), 5.933 (1H, d, J = 1.5 Hz), 6.62 - 6.76 (5H, m); EIMS m/z (%): 352 (M^+, 8), 152 (10), 115 (11), 67 (18), 55 (72), 41 (100).

Compound C: Jusneesiinol (5) : Colourless crystals from pet. ether -ethyl acetate m.p. 220-22°C: $[\alpha]_D^{25}$ +218.4° (acetone, c 0.5); IR (KBr) ν_{max} 3534, 1732, 1261, and 1050 cm^{-1}; UV (MeOH)

λ_{max} (log ϵ) 286 nm (3.95) ; ^1H and ^{13}C NMR: see Table 2; high-resolution EIMS: m/z 366.0754 (13.9%, M^+, calcd. for $C_{20}H_{14}O_7$, 366.0740), 348.0630 (100%, M^+ - H_2O, calcd. for $C_{20}H_{12}O_6$, 348.0634); EIMS m/z (%): 366 (M^+, 43), 348 (100), 291 (17), 276 (6), 261 (14), 244 (44), 233 (9), 215 (10), 205 (11), 187 (9), 176 (14), 163 (6), 135 (10), 97 (6), 83 (6), 69 (7), 57 (14) and 43 (8); CD (MeOH;1.17 mM) $\Delta\epsilon$:0 (306) , +6.4 (286) , +4.6 (267) , +10.9 (244) and +14.8 (224).

Dehydrogenation of 5 : Using the procedure described for the dehydrogenation of **3**, **5** (10 mg) was dehydrogenated to give retrohelioxanthin (**10**, 3 mg) and justirumalin[12] (**2**, 4 mg). Data of **2** : m.p. 255-56° (lit.[12] m.p. 258-60°); ^1H NMR (400 MHz, d_6 DMSO): δ 5.33 (1H, s), 5.88 (1H, d, J = 0.9 Hz), 5.89 (1H, d, J = 0.9 Hz), 6.04 (1H,br.s), 6.06 (1H, d, J = 0.5 Hz), 6.67 (1H, dd, J = 1.6, 7.9 Hz), 6.80 (1H, d, J = 1.6 Hz), 6.85 (1H, d, J = 7.9 Hz), 7.45 (1H, d, J = 8.9 Hz), 7.95 (1H, d, J = 8.9 Hz) and 8.27 (1H, s).

Hydrogenation of 5 : Using the procedure described for the hydrogenation of **4**, **5** (10 mg) was hydrogenerated to give **4** (2 mg) and **11** (3 mg).

Acetylation of 5 : **5** (10 mg) was acetylated with pyridine (0.5 mL) and Ac_2O (1.0 mL) at room temperature overnight followed by usual work up gave **8** (5 mg) ; IR (KBr) ν_{max} 1759 and 1234 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$): δ 2.10 (3H, s), 4.78 (1H, dd, J = 2.6, 17.5 Hz), 4.95 (1H, d, J = 17.5 Hz), 4.99 (1H, s), 5.90 (2H, br.s), 5.92 (1H, br.s), 5.93 (1H, br.s), 6.58 (1H, s), 6.64 (1H, br.s), 6.67 (1H, d, J = 8.8 Hz), 6.70 (1H, d, J = 8.8 Hz), 6.85 (1H, m) and 6.93 (1H, d, J = 8.3 Hz); EIMS m/z (%): 408 (M^+, 2), 348 (M^+ - AcOH, 100), 305 (15), 289 (13), 261 (24), 233 (16), 189 (33), 176 (52), 149 (19), 98 (14), 87 (26) and 43 (91).

Crystal data and structure refinement of 5 : Single crystals of 5 were obtained by slow evaporation of ethyl acetate solution in the form of colourless needles.

Crystal data : a = 8.233 (1), b = 7.876(1), c = 12.488 (1) Å, and ß = 91.94(1)°, monoclinic system, space group $P2_1$, z = 2, V = 809.3(1)Å^3, F(000) = 380, $C_{20}H_{14}O_7$, M_w = 366.3, Dc = 1.503 Mg/m^3, μ = 0.12 mm^{-1}.

Accurate cell parameters were obtained by least-squares refinement of the setting angle of 25 reflection at medium θ (6° < θ < 14°), using MoKα radiation at room temperature and SIEMENS four circles diffractometer on line with a MicroVAX 3100 computer. The intensities of two check reflections were monitored every hour and showed a crystal decay ≤ 1% during entire data collection. A total 1886 reflections with $2\theta_{max}$ = 52° were collected and averaged giving 1844 unique reflections, 1365 reflections with I ≥ 3σ(I) were considered observed.

The structure was solved by SHELXTL-Plus package. The refinement was carried out on the positional and anisotropic displacement parmeters of all 27 non-hydrogen atoms using full-matrix least squares method. Hydrogens were located from difference map; they were positioned geometrically and included as riding atoms with fix isotropic temperature factor in the structure factor calculations.

All calculations were performed on a MicroVAX3100 computer using SHELXTL-Plus software.[22] Structure factors, anisotropic displacement parameters and hydrogen atoms coordinates have been deposited.

The final discrepancy index R (on F) was 0.040 on 1365 observed reflections and 244 variabales, R_w = 5.01% with $w = 1/[\sigma^2(F)+0.00265\ F^2]$.

(-) Hibalactone (6)[21] : Pale yellow crystals from pet. ether - ethyl acetate. m.p 148-50° (lit.[21] m.p. 142-43°), $[\alpha]_D^{25}$ -19.6° ($CHCl_3$, c 0.15); IR (KBr) ν_{max} 1744 and 1645 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 292 (4.03) and 330 nm (4.15) ; ^1H NMR (400 MHz, $CDCl_3$): δ 2.59 (1H, dd, *J* = 10.0, 14.3 Hz), 3.00 (1H, dd, *J* = 4.5, 14.3 Hz), 3.74 (1H, m), 4.24 - 4.26 (2H, m), 5.93 (1H, d, *J* = 1.4 Hz), 5.94 (1H, d, *J* = 1.4 Hz), 6.04 (2H, s), 6.64 (1H, dd, *J* = 1.6, 7.9 Hz), 6.66 (1H, d, *J* = 1.6 Hz), 6.73 (1H, d, *J* = 7.9 Hz) 7.04 (1H, d, *J* = 1.7 Hz), 7.08 (1H, dd, *J* = 1.7, 8.1 Hz), 6.88 (1H, d, *J* = 8.1 Hz) and 7.50 (1H, d, *J* = 1.9 Hz).

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References

1. Rao, C.B.S. in *Chemistry of Lignans*, Andhra University Press, Visakhapatnam, **1978.**
2. Chen, C. ; Hsin, W. ; Ko, F. ; Huang, Y. ; Ou, J. ; Teng, C. *J. Nat. Prod.* **1996,** *59,* 1149-1150.
3. Asano, J. ; Chiba, K. ; Tada, M. ; Yoshii, T. *Phytochemistry*, **1996,** *42,* 713-717.
4. Fukamiya, N. ; Lee, K. *J. Nat. Prod.* **1986,** *49,* 348-350.
5. MacRae, W.D. ; Towers, G.H.N. *Phytochemistry*, **1984,** *23,* 1207-1220.
6. Ghosal, S. ; Banerjee, S. ; Frahm, A.W. *Chem. Ind.* (London) **1979,** *23,* 854 - 855.
7. Munakata, K. ; Marumo, S. ; Ohta, K. ; Chen,Y. *Tetrahedron Lett.* **1965,** *47,* 4167 - 4170.
8. Chitra, K.C. ; Reddy, P.V.R. ; Pillai, K.R. ; Subbaraju, G.V. *J. Appl. Zool. Res.* **1995,** *6,* 131-132.
9. Subbaraju, G.V. ; Pillai, K.R. *Indian J. Chem.* **1989,** *28B,* 558-561.
10. Subbaraju, G.V. ; Kumar, K.K.K. ; Raju, B.L. ; Pillai, K.R. *J. Nat. Prod.* **1991,** *54,* 1639 - 1641.
11. Subbaraju, G.V. ; Pillai, K.R. *Indian J. Chem.* **1996,** 35B, 1233 - 1234.
12. Rajasekhar, D. ; Vanisree, M. ; Subbaraju, G.V. *Indian J. Chem.* (in press).
13. Lopez, H. ; Valera, A. ; Trujillo, J. *J. Nat Prod.* **1996,** *59,* 493 - 494.
14. Amer, A. ; Bauer, F. ; Zimmer, H. *J. Nat Prod.* **1993,** *56,* 600 - 605.
15. Kuhnt, M. ; Rimpler, H. ; Heinrich, M. *Phytochemistry,* **1994,** *36,* 485 - 489.
16. Hokanson, G.C. *J. Nat. Prod.* **1979,** *42,* 378 - 384.
17. Stevenson, R. ; Weber, J. V. *J. Nat. Prod.* **1991,** *54,* 310 - 314.
18. Momose, T. ; Kanai, K. ; Hayashi, K. *Chem. Pharm. Bull.* **1978,** *26,* 3195 - 3198.
19. Tanoguchi, M. ; Kashima,T. ; Saika, H. ; Inoue, T. ; Arimoto, M. ; Yamaguchi, H. *Chem. Pharm. Bull.*, **1989,** *37,* 68 - 72.
20. Shashikanth, S. ; Anjanamurthy, C. *Indian J. Chem.* **1997,** *36B,* 572 - 577.
21. Fang, J. ; Jan, S. ; Cheng, Y. *Phytochemistry,* **1985,** *24,* 1863 - 1864.
22. Sheldrick, G.M. SHELXTL-Plus. Revision 4.1 Siemens Analytical X-ray Instr. Inc., Madison, Wisconsin, **1991.**