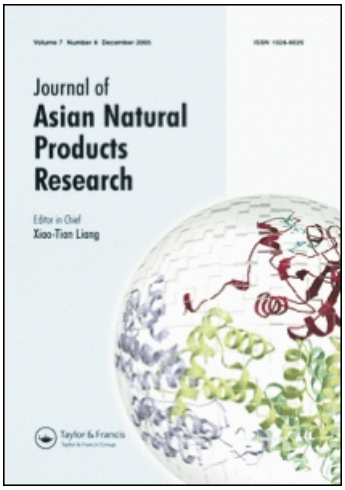

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JUSTICIA LIGNANS VI – PROSTALIDIN D, A NEW ARYLNAPHTHALIDE LIGNAN FROM *JUSTICIA DIFFUSA* VAR. *PROSTRATA* C.B. CLARKE

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A new arylnaphthalide lignan, prostalidin D (**6**) was isolated as a minor metabolite from *Justicia diffusa* var. *prostrata*. **6** contains a rare catechol unit and its structure was confirmed by total synthesis. In addition, seven known lignans, namely, justicidin E (**7**), helioxanthin (**8**), justicidin A (**9**), medioresinol dimethyl ether (**10**), medioresinol (**11**), lariciresinol (**12**) and 8-methoxy-isolariciresinol (**13**) have also been isolated from the same source and identified by direct comparison with authentic samples.

Keywords: *Justicia diffusa* var. *prostrata*; *Justicia prostrata*; Arylnaphthalide lignans; Prostalidin D

INTRODUCTION

Justicia diffusa var. *prostrata* C.B. Clarke (syn. *Justicia prostrata* Gamble n. comb) is a small prostrate plant with long branches which spread diffusely from a root stock and has pale pink flowers [1]. It is used as antidepressant drug in popular medicine [2]. Petrol extractives of this plant showed significant antidepressant actions in laboratory animals. Its chemical examination yielded prostalidin A (**1**), B (**2**), C (**3**), retrocheninsin (**4**) and carpacin (**5**). Prostalidins A–C (**1**–**3**) have shown antidepressant activity and **5** was

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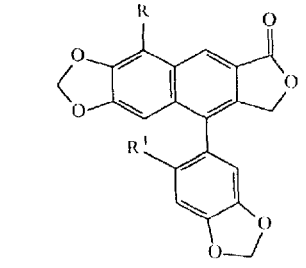
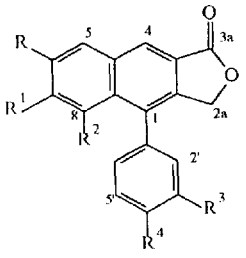
found to potentiate the activity of **1–3** [2]. In a continued study on the *Justicia* species of the Tirumala Hill Tracts [3- 7], we have investigated *J. diffusa* var. *prostrata* and isolated seven known lignans, namely, justicidin E (**7**) [5], helioxanthin (**8**) [8], justicidin A (**9**) [9], medioresinol dimethyl ether (**10**) [5], (+)-medioresinol (**11**) [5], (+)-lariciresinol (**12**) [5] and (+)-8-methoxyisolariciresinol (**13**) [3], in addition to a new 1-arylnaphthalide lignan, named prostalidin D (**6**). The details of structure elucidation and total synthesis of **6** are presented in this paper (Fig. 1).



1 R = OMe; R^1 = H

2 R = R^1 = OMe

3 R = H; R^1 = OH

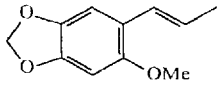


4 RR^1 = OCH_2O; R^2 = H, R^3 = R^4 = OMe

6 RR^1 = OCH_2O; R^2 = H; R^3 = R^4 = OH

7 RR^1 = R^3 R^4 = OCH_2O; R^2 = H

8 R = H; R^{1}R^2=R^{3}R^4 = OCH_2O



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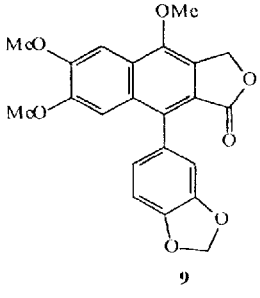

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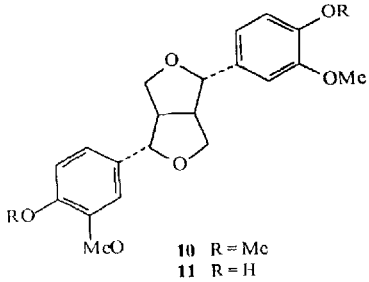
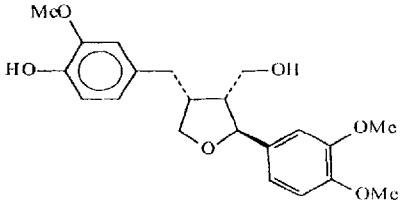


10 R = Me
11 R = H



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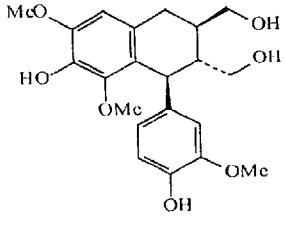

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FIGURE 1

RESULTS AND DISCUSSION

Prostalidin D (**6**) was obtained as pale brown solid, m.p. 230–232°C. Its mass spectrum showed molecular ion at *m/z* 336 (M^+, 100). Its UV spectrum showed bands at 265, 280, 300, 328 (sh) and 340 nm. IR spectrum exhibited bands at 3348 (hydroxyl) and 1748 cm^{-1} (lactone carbonyl). The ^1H NMR spectral data contained six aromatic protons constituted by an ABX system characteristic of a 1,2,4-trisubstituted phenyl unit (δ 6.68–6.76, 2H, m and 6.89, 1H, d, $J = 8.0$ Hz) and three singlets at δ 7.05, 7.61 and 8.31 (1H each), a lactone methylene (δ 5.21, 1H, d, $J = 14.4$ Hz and 5.30, 1H, d, $J = 14.4$ Hz), a methylenedioxy group at δ 6.17 (2H, s), in addition to two phenolic hydroxyls located at δ 9.14 and 9.23 (1H each, s).

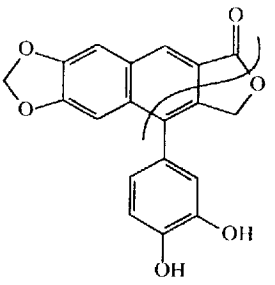
A perusal of the above data in comparison with those of congeneric lignan, justicidin E (**7**), revealed that **6** is also an arylnaphthalide lignan, but, one of the methylenedioxy groups present in **7** is replaced by dihydroxy system in **6**. Further scrutiny of the ^1H NMR data suggested that the chemical shifts of H-2′, H-5′ and H-6′ were shifted upfield to an extent of 0.1–0.2 ppm compared with those of **7**. These variations are indicative of the presence of a 3,4-dihydroxyphenyl unit as the pendent ring in **6** instead of 3,4-methylenedioxyphenyl unit present in **7**.

Based on the above, the structure of prostalidin D could be deduced, tentatively, as 9-(3,4-dihydroxyphenyl)-furo[3′,4′:6,7]naphtho[2,3-d][1,3]-dioxol-6(8H)one (**6**), a new arylnaphthalide lignan.

In view of the rare structural features of prostalidin D (**6**) and also to confirm the structure proposed, we have carried out its total synthesis and details are presented below.

Retrosynthetic analysis of **6** (Scheme 1) revealed that piperonal (**14**) and 3,4-dihydroxybenzaldehyde (**15**) are the suitable starting materials. Condensation of piperonal (**14**) with malonic acid under Knoevenagel–Doebner conditions [10] gave 3,4-methylenedioxycinnamic acid (**18**) in 93% yield. Esterification of **18** with methanol followed by addition of bromine yielded methyl 2,3-dibromo-3-(3,4-methylenedioxyphenyl)propionate (**20**) in 70% yield. Dehydrobromination of **20** with alcoholic KOH gave 3-(3,4-methylenedioxyphenyl)propiolic acid (**16**) in 50% yield (Scheme 2).

3,4-dihydroxybenzaldehyde (**15**) was converted into its dibenzylether (**21**) using $BnBr/K_2CO_3$, in 84% yield. Condensation of **21** with malonic acid under Knoevenagel–Doebner conditions [10] gave 3,4-dibenzyloxycinnamic acid (**22**) in 91% yield. Esterification of **22** with methanol followed by addition of bromine afforded methyl 2,3-dibromo-3-(3,4-dibenzyloxyphenyl)propionate (**24**) in 82% yield. Dehydrobromination of **24** with alcoholic



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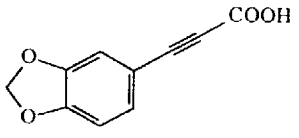

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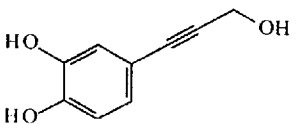

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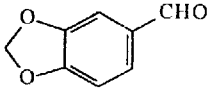

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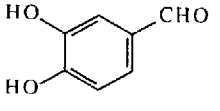

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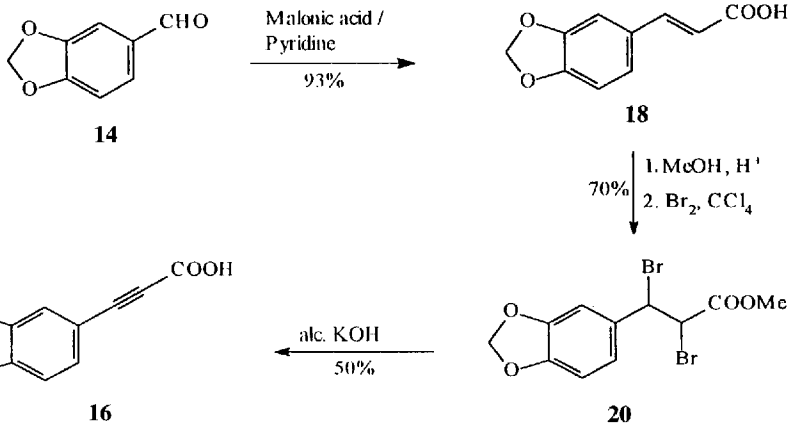
SCHEME 1

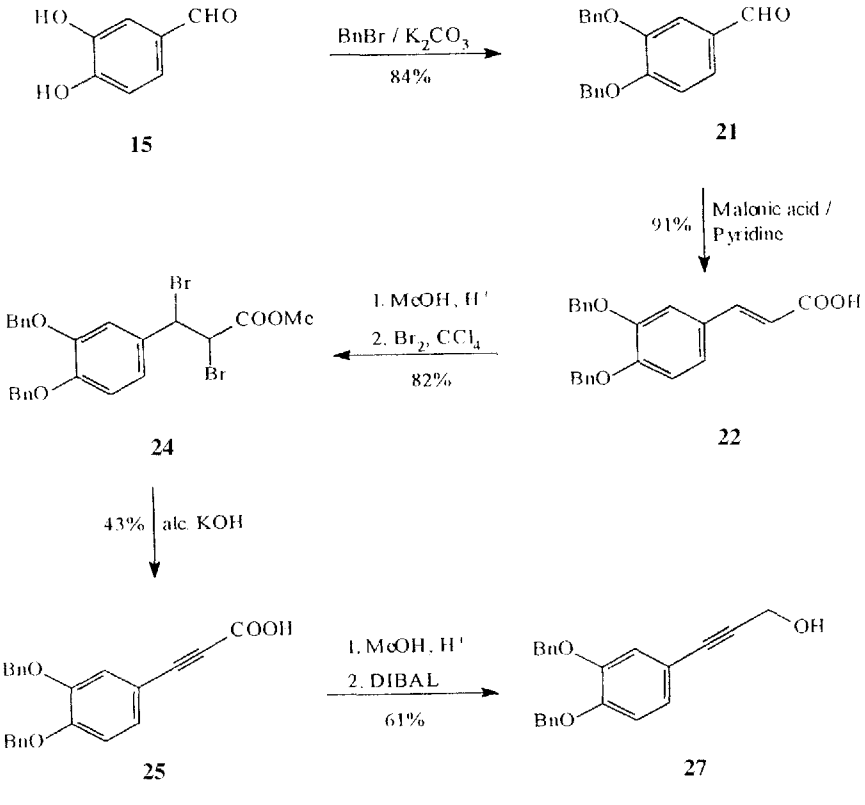


14 **18** **20** **16**

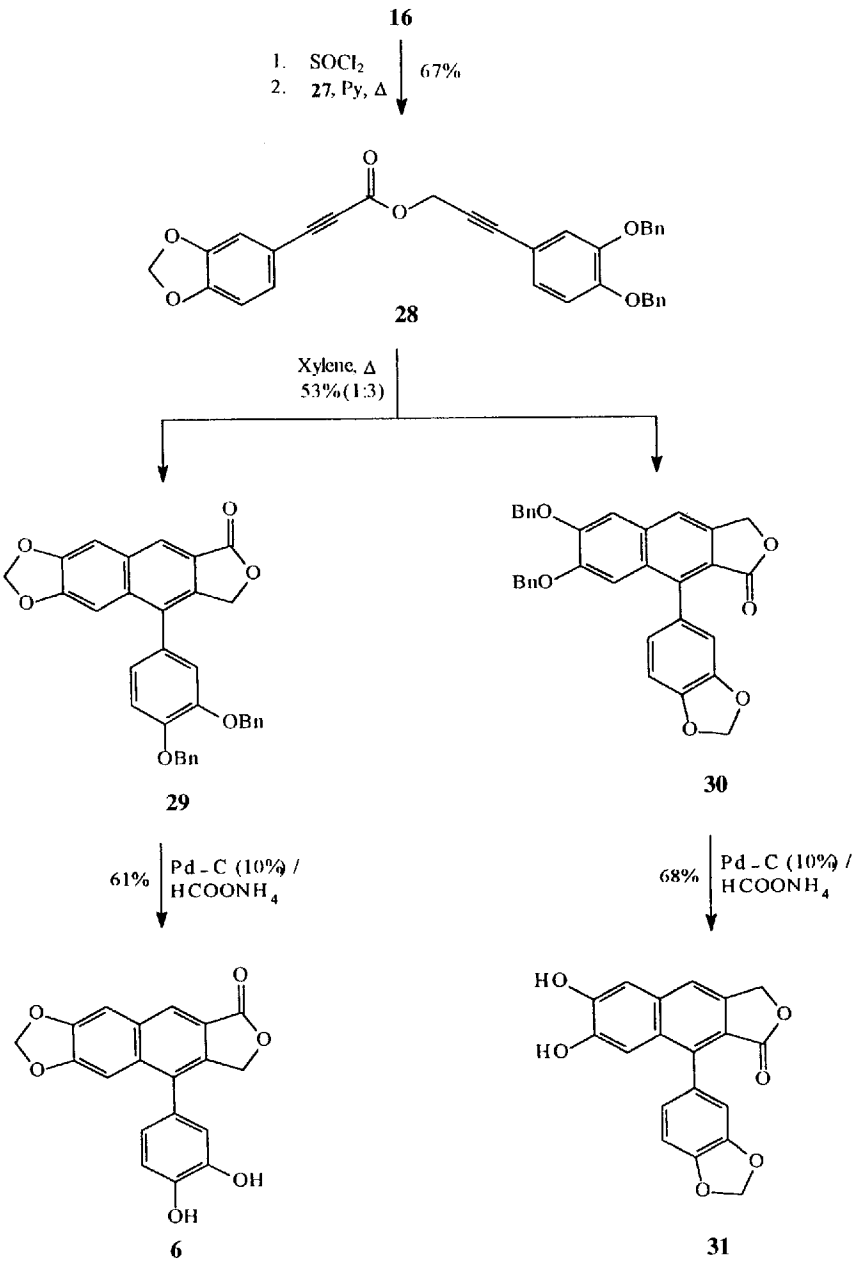
SCHEME 2

KOH under reflux gave 3-(3,4-dibenzoyloxyphenyl)propiolic acid (**25**) in 43% yield. **25** was converted into its methyl ester followed by reduction with DIBAL to give 3-(3,4-dibenzyloxyphenyl)propargyl alcohol (**27**) in 61% yield (Scheme 3).

3-(3,4-Methylenedioxyphenyl)propiolic acid (**16**) was esterified using propargyl alcohol (**27**) in presence of pyridine and DMAP to give the ester **28** in 67% yield. Cyclization of **28** was accomplished by refluxing it in xylene [11] for 5 h to give a mixture of two isomeric products, 9-(3,4-dibenzyloxyphenyl)-furo[3′,4′ : 6,7]naphtho[2,3-d][1,3]dioxol-6(8H)-one (**29**) and 9-(3,4-methylenedioxyphenyl)-6,7-dibenzyloxynaphtho[2,3-c]furan-1(3H)-one (**30**) (1 : 3 ratio) in 53% yield. Debenzylation of **29** and **30** using Pd C (10%) and ammonium formate [12] gave the title compound, prostalidin D (**6**) in 61% yield and its non-natural isomer, **31** in 68% yield (Scheme 4).



SCHEME 3



SCHEME 4

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined in open capillaries and are uncorrected. UV and IR spectra were recorded on a Shimadzu UV 240 spectrophotometer in MeOH and Perkin-Elmer 1600 FTIR spectrometer as KBr pellets, respectively. ^{1}H NMR spectra were recorded on a Bruker 400 MHz or Jeol 90 MHz NMR spectrometers. EIMS were determined on a VG micromass 70-70H mass spectrometer.

Plant Material

The plant material (whole plants) was collected from the campus of Sri Venkateswara University and authenticated as *J. diffusa* var. *prostrata* C.B. Clarke (syn. *J. prostrata* Gamble n. Comb) by Research and Specimen Cell, PID, CSIR, New Delhi. Voucher specimens are on deposit at Department of Chemistry, Sri Venkateswara University, Tirupati.

Extraction and Isolation

The shade dried and milled plant material (*ca.* 2.8 kg) was extracted repeatedly with 95% EtOH in a Soxhlet apparatus. After removal of the solvent, the dark green gummy residue (*ca.* 200 g) was fractionated with hexane and ethyl acetate. Hexane and ethyl acetate solubles were concentrated under reduced pressure, separately. Chromatography of the hexane soluble part (40 g) over silica gel column yielded, justicidin E (**7**, 0.2 g), helioxanthin (**8**, 50 mg), justicidin A (**9**, 40 mg) and medioresinol dimethyl ether (**10**, 40 mg). Chromatography of ethyl acetate soluble part (35 g) yielded (+)-medioresinol (**11**, 60 mg), (+)-lariciresinol (**12**, 30 mg) and (+)-8-methoxy-isolarciresinol (**13**, 40 mg) in addition to a new 1-arylnaphthalide lignan, prostalidin D (**6**, 10 mg). The identification of known compounds was carried out by the spectral data as well as direct comparison with authentic samples (co-TLC and m.m.p.).

Prostalidin D (**6**) Pale brown solid, m.p. 230–232°C; UV (MeOH) λ_{max} 265, 280, 300, 328, 340 nm; IR (KBr) ν_{max} 3348, 1748, 1239 cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ 5.21 (1H, d, $J = 14.4$ Hz, H_a-2a), 5.30 (1H, d, $J = 14.4$ Hz, H_b-2a), 6.17 (2H, s, OCH_2O), 6.68 6.76 (2H, m, H-2′,6′), 6.89 (1H, d, $J = 8.0$ Hz, H-5′), 7.05 (1H, s, H-8), 7.61 (1H, s, H-5), 8.31 (1H, s, H-4), 9.14 (1H, s, OH), 9.23 (1H, s, OH); EIMS *m/z* (%): 336 (M^+, 100), 307 (71), 218 (66), 183 (13), 135 (8), 97 (15) 91 (43), 57 (60).

Justicidin E (**7**) Pale yellow crystals from methanol, m.p. 270–271°C (Ref. [5], m.p. 270–271°C).

Helioxanthin (**8**) Pale yellow crystals from methanol, m.p. 240–241°C (Ref. [8], m.p. 240–241°C).

Justicidin A (**9**) Pale yellow crystalline leaflets from chloroform–methanol m.p. 260–261°C (Ref. [9], m.p. 261–263°C).

Medioresinol dimethylether (**10**) Colourless liquid and its spectral data are identical to those of **10** [5].

(+)-*Medioresinol* (**11**) Pale brown crystals from benzene–hexane m.p. 180–182°C (Ref. [5], m.p. 180–181°C; $[\alpha]_D$ +58.1 (c 0.21, $CHCl_3$)).

(+)-*Lariciresinol* (**12**) Colourless crystals from ethanol m.p. 170–172°C (Ref. [5], m.p. 170–172°C; $[\alpha]_D$ +19.2 (c 0.76, CH_3COCH_3)).

(+)-*8-Methoxyisolariciresinol* (**13**) Colourless crystals from chloroform–methanol m.p. 163–164°C (Ref. [3], m.p. 160–162°C; $[\alpha]_D$ +61.7 (c 0.66, CH_3COCH_3)).

Synthesis of Prostalidin D (6)

3,4-Methylenedioxycinnamic acid (**18**) This was prepared from 3,4-methylenedioxybenzaldehyde (**14**) according to the literature procedure [10] in 93% yield, m.p. 235–237°C (Ref. [10], m.p. 238°C).

Methyl 3,4-methylenedioxycinnamate (**19**) To a solution of 3,4-methylenedioxycinnamic acid (**18**, 5 g, 26 mmol) in dry methanol (13 mL) was added concentrated HCl (2 mL) and the contents were refluxed for 6 h. After this period, the solvent was removed under reduced pressure and extracted with ethyl acetate. The ethyl acetate layer was washed with saturated sodium bicarbonate solution followed by water and the organic layer was dried over anhydrous Na_2SO_4. Removal of solvent followed by recrystallisation of the residue from petroleum ether–ethyl acetate gave methyl 3,4-methylenedioxycinnamate (**19**, 4.6 g, 86%), as colourless crystals, m.p. 78–80°C; UV ($CHCl_3$) λ_{max} 290, 325 nm; IR (KBr): ν_{max} 1707, 1266, 984 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.80 (3H, s), 6.02 (2H, s), 6.27 (1H, d, J = 17.1 Hz), 6.76–7.05 (3H, m), 7.61 (1H, d, J = 17.1 Hz).

Methyl 2,3-dibromo-3-(3,4-methylenedioxyphenyl)propionate (**20**) To a solution of methyl 3,4-methylenedioxycinnamate (**19**, 5 g, 24 mmol) in CCl_4 (25 mL) was added bromine (4.2 g, 1.35 mL, 26 mmol) dropwise at 0°C for 30 min and the reaction was continued at the same temperature for further 2 h. The contents were transferred into an evaporating dish and allowed the solvent to evaporate at room temperature. Recrystallisation of the residue

from petroleum ether–ethyl acetate gave methyl 2,3-dibromo-3-(3,4-methylenedioxyphenyl)propionate (**20**, 7.2 g, 81%) as colourless needles, m.p. 114–116°C, UV (MeOH) λ_{max} 210, 236, 288 nm; IR (KBr) ν_{max} 1743, 1252, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.94 (3H, s), 4.78 (1H, d, J = 7.7 Hz), 5.32 (1H, d, J = 7.7 Hz), 6.01 (2H, s) and 6.82–6.95 (3H, m).

3-(3,4-Methylenedioxyphenyl)propiolic acid (**16**) A mixture of methyl 2,3-dibromo-3-(3,4-methylenedioxyphenyl)propionate (**20**, 2.2 g, 6 mmol), ethanol (6 mL) and KOH (1.1 g, 19.6 mmol) was refluxed for 10 h. After this period, the contents were poured into cold water (50 mL) and acidified with concentrated HCl. The aqueous solution was kept in a refrigerator overnight and the solid precipitated was filtered, dried and recrystallised from CCl_4 to give 3-(3,4-methylenedioxyphenyl)propiolic acid (**16**, 0.57 g, 50%) as colourless solid, m.p. 140–142°C. UV (MeOH) λ_{max} 209, 235, 290, 380 nm; IR (KBr) ν_{max} 3650–5780 (br), 2919, 2215, 1687 cm^{-1}; ^{1}H NMR (d_6-DMSO, 300 MHz): δ 6.14 (2H, s), 7.00–7.23 (3H, m).

3,4-Dihydroxybenzaldehyde (**15**) This was prepared from vanillin according to the literature procedure [13] in 84% yield; m.p. 235–237°C (dec) (Ref. [13], m.p. 238°C).

3,4-Dibenzyloxybenzaldehyde (**21**) A mixture of 3,4-dihydroxybenzaldehyde (**15**, 4 g, 29 mmol), benzyl bromide (8 mL, 67 mmol), potassium carbonate (8 g) and dry acetone (70 mL) was refluxed for 6 h. After this period, K_2CO_3 was filtered off and the solvent was removed. The residue was recrystallised from petroleum ether–ethyl acetate to give 3,4-dibenzyloxybenzaldehyde (**21**, 7.7 g, 84%), m.p. 89–91°C. UV (MeOH) λ_{max} 214, 234, 289, 315 nm; IR (KBr) ν_{max} 2817, 2726, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.20 (2H, s), 5.25 (2H, s), 6.95 (1H, d, J = 8.5 Hz), 7.10–7.45 (12H, m) and 9.70 (1H, s).

3,4-Dibenzyloxycinnamic acid (**22**) A mixture of 3,4-dibenzyloxybenzaldehyde (**21**, 3.2 g, 10 mmol), malonic acid (2.3 g, 22 mmol), dry pyridine (5 mL) and piperidine (0.2 mL) was heated on a water bath for 3 h. Work up as described for 18 gave 3,4-dibenzyloxycinnamic acid (**22**, 3.3 g, 91%) as colourless solid m.p. 197–198°C, UV (MeOH) λ_{max} 230, 274, 305 nm; IR (KBr) ν_{max} 2850, 3050 (br), 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.22 (2H, s), 5.28 (2H, s), 6.26 (1H, d, J = 15.6 Hz), 7.70 (1H, d, J = 15.6 Hz) and 6.88–7.56 (13H, m).

Methyl 3,4-dibenzyloxycinnamate (**23**) To a solution of 3,4-dibenzyloxycinnamic acid (**22**, 3.0 g, 8.3 mmol) in dry methanol (20 mL) was added concentrated HCl (1.5 mL) and the contents were refluxed for 5 h. Work up of the reaction mixture as described for **19** yielded methyl 3,4-dibenzyloxycinnamate (**23**, 2.8 g, 90%), m.p. 70–72°C. UV (MeOH) λ_{max} 295, 320 nm;

IR (KBr) ν_{max} 1713, 1636, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz): δ 3.78 (3H, s), 5.16 (4H, s), 6.62 (1H, d, $J = 17.1$ Hz), 6.85–7.14 (3H, m) and 7.30–7.68 (11H, m).

Methyl 2,3-dibromo-3-(3,4-dibenzyloxyphenyl)propionate (**24**) To a solution of methyl 3,4-dibenzyloxycinnamate (**23**, 1.7 g, 4.55 mmol) in CCl_4 (10 mL) was added bromine (0.3 mL, 0.93 g, 5.8 mmol) dropwise at 0°C for 20 min. Work up as described for **20**, followed by recrystallisation with petroleum ether–ethyl acetate gave methyl 2,3-dibromo-3-(3,4-dibenzyloxyphenyl)propionate (**24**, 2.2 g, 91%) as colourless crystals, m.p. 124–126°C, UV (MeOH) λ_{max} 246, 288 nm; IR (KBr) ν_{max} 1747, 1263 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz): δ 3.90 (3H, s), 4.72 (1H, d, $J = 10.8$ Hz), 5.17 (4H, s), 5.30 (1H, d, $J = 10.8$ Hz), 6.96–7.02 (3H, m) and 7.30–7.52 (10H, m).

3-(3,4-Dibenzyloxyphenyl)propiolic acid (**25**) A mixture of methyl 2,3-dibromo-3-(3,4-dibenzyloxyphenyl) propionate (**25**, 1.4 g, 2.62 mmol), KOH (0.8 g) and ethyl alcohol (4.5 mL) was refluxed for 15 h. Work up as described for **21**, followed by recrystallisation from methanol afforded 3-(3,4-dibenzyloxyphenyl)propiolic acid (**25**, 0.4 g, 43%) as brown solid, m.p. 155–157°C. UV λ_{max} 215, 280, 301 nm; IR (KBr) ν_{max} 1264, 1660, 2342, 3790, 3705 cm^{-1}; ^1H NMR (200 MHz, d_6-DMSO): 5.10 (2H, s), 5.16 (2H, s), 7.02–7.21 (3H, m) and 7.30–7.44 (10H, m).

Methyl 3-(3,4-dibenzyloxyphenyl)propiolate (**26**) To a solution of 3-(3,4-dibenzyloxyphenyl)propiolic acid (**25**, 0.9 g, 2.5 mmol) in methanol (5 mL) was added concentrated HCl (0.2 mL) and the contents were refluxed for 5 h. Work up as described for **23** followed by column chromatography over silica gel with petroleum ether–ethyl acetate (9 : 1) as eluants gave methyl 3-(3,4-dibenzyloxyphenyl)propiolate (**26**, 0.65 g, 70%) as colourless solid m.p. 68–70°C. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.82 (3H, s), 5.14 (2H, s), 5.19 (2H, s), 6.88 (1H, d, $J = 8.3$ Hz), 7.15 (1H, d, $J = 1.8$ Hz), 7.17 (1H, dd, $J = 1.8, 8.3$ Hz) and 7.31–7.46 (10H, m).

3-(3,4-Dibenzyloxyphenyl)propargyl alcohol (**27**) To a solution of methyl 3-(3,4-dibenzyloxyphenyl)propiolate (**26**, 0.2 g, 0.54 mmol) in dry THF (10 mL) at −78°C was added DIBAL (1 M solution in hexane, 2 mL) under nitrogen atmosphere. After the addition, the reaction mixture was allowed to warm up to room temperature. The reaction mixture was then diluted with methanol (20 mL) and dilute HCl (2 N, 2 mL). The resulting solution was extracted with ethyl acetate and the ethyl acetate layer was dried over anhydrous Na_2SO_4 and the solvent was removed. The residue obtained was recrystallised from petroleum ether–ethyl acetate to give 3-(3,4-dibenzyloxyphenyl)propargyl alcohol (**27**, 0.16 g 87%) as colourless solid, m.p. 80–81°C; ^1H NMR ($CDCl_3$, 200 MHz): δ 4.44 (2H, s),

5.12 (2H, s), 5.15 (2H, s), 6.98 (1H, d, $J = 8.8$ Hz), 6.94–7.00 (2H, m), 7.27–7.42 (10H, m).

9-(3,4-Dibenzyloxyphenyl)-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6-(8H)-one (**29**) *and 9-(3,4-methylenedioxyphenyl)-6,7-dibenzyloxynaphtho[2,3-c]furan-1(3H)-one* (**30**) To a solution of 3-(3,4-methylenedioxyphenyl)propiolic acid (**16**, 0.2 g, 0.104 mmol) in dry benzene (2 mL) was added freshly distilled thionyl chloride (0.5 mL, 6.8 mmol). The contents were refluxed for 3 h and excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. The acid chloride was added dropwise to a stirred solution of propargyl alcohol (**27**, 0.30 g, 0.88 mmol) in dry benzene (2 mL) and pyridine (0.1 mL) under stirring. After the addition of acid chloride, the contents were refluxed for 15 h. The reaction mixture was diluted with benzene and passed through a small silica gel column to give the ester (**28**, 0.3 g, 67%, IR (KBr) ν_{max} 2221, 1709, 1231 cm^{-1}) as syrupy liquid. The ester obtained as above was heated under reflux in xylene for 5 h. Usual work up followed by column chromatography over silica gel column gave **29** (40 mg) and **30** (120 mg) (1 : 3 in ratio) in 53% yield. Physical and spectral data of **29**: m.p. 148–150°C, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.85 (1H, d, $J = 15.1$ Hz, H_a-2a), 5.01 (1H, d, $J = 15.1$ Hz, H_b-2a), 5.19 (1H, d, $J = 13.9$ Hz, $PhCH_2$), 5.23 (1H, d, $J = 13.9$ Hz, $PhCH_2$), 5.27 (2H, s, $PhCH_2$), 6.08, 6.09 (each 1H, brs, OCH_2O), 6.83–6.85 (2H, m, H-2',6'), 7.02 (1H, s, H-8), 7.08 (1H, d, $J = 8.3$ Hz, H-5'), 7.30–7.53 (10H, m, 2 × Ph-CH_2), 7.28 (1H, s, H-5), 8.23 (1H, s, H-4).

9-(3,4-Dihydroxyphenyl)-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6-(8H)-one (Prostalidin D, **6**) To a stirred solution of **29** (30 mg, 0.058 mmol) in dry acetone (5 mL) was added ammonium formate (30 mg, 0.48 mmol) and Pd–C (10%, 200 mg). The contents were refluxed for 45 min. The catalyst was filtered off and the solvent was evaporated. The residue obtained was purified further by column chromatography to give 9-(3,4-dihydroxyphenyl)-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(8H)-one (**6**, 12 mg, 61%); Physical and spectral data are identical to those of natural **6**.

9-(3,4-Methylenedioxyphenyl)-6,7-dihydroxy-naphtho[2,3-c]furan-1(3H)-one (**31**) To a stirred solution of **30** (90 mg, 0.174 mmol) in dry acetone (10 mL) was added ammonium formate (100 mg, 1.6 mmol) and Pd–C (10%, 600 mg). The contents were refluxed for 45 min. The catalyst was filtered off and the solvent was evaporated. The residue obtained was purified further by column chromatography to give 9-(3,4-methylenedioxyphenyl)-6,7-dihydroxynaphtho[2,3-c]furan-1(3H)-one (**31**, 40 mg, 68%). Physical and

spectral data of **31**: m.p. 206–208°C; IR (KBr) ν_{max} 3368, 1721, 1233 cm^{-1}; ^1H NMR (d_6-DMSO, 400 MHz): δ 5.38 (2H, s, H-3a), 6.11 (1H, brs, OCH_2O), 6.14 (1H, brs, OCH_2O), 6.74 (1H, brd, $J = 7.9$ Hz, H-6′), 6.87 (1H, brs, H-2′), 6.99 (1H, s, H-8), 7.05 (1H, d, $J = 7.9$ Hz, H-5′), 7.27 (1H, s, H-5), 7.78 (1H, s, H-4), 10.08 (1H, s, OH), 10.07 (1H, s, OH); EIMS *m/z* (%): 336 (M^+, 100), 277 (8), 249 (11), 221 (8), 143 (8), 43 (30).

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