Tetrahedron Vol. 42, No. 10, pp. 2725 to 2730, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
Pergamon Journals Ltd.

SYNTHESIS OF NATURAL POLYHYDROXYSTILBENES[1]

M[a]. LUZ CARDONA, M[a]. ISABEL FERNANDEZ, M[a]. BEGOÑA GARCIA and JOSE R. PEDRO*

Department of Organic Chemistry, Faculty of Chemistry, University of Valencia, Burjassot, Valencia, Spain.

(*Received in UK* 4 *March* 1986)

Abstract.- A synthesis of several natural polyhydroxystilbenes is described.

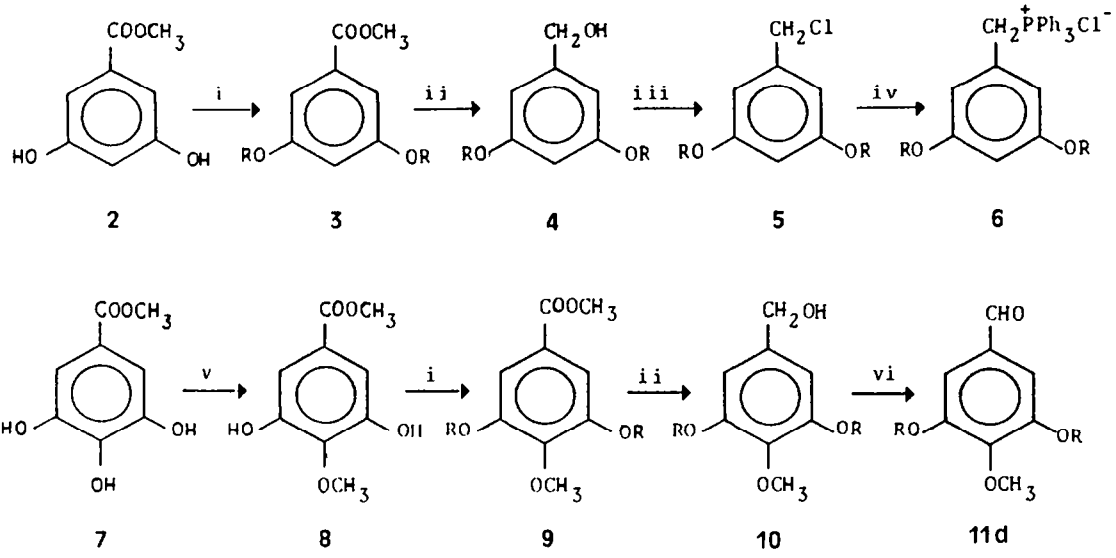
The stilbenes pinosylvin (1a), isorhapontigenin (1b) and piceatannol (1c) have been isolated from wood, bark and leaves of a variety of plants[2] and recently 3,5,3',5'-tetrahydroxy-4'-methoxystilbenes (1d) has been isolated for the first time by us from stems of Phoenix dactylifera[3].The polyhydroxystilbenes are know for having broad spectrum of physiological activities including antifungal, ichthyotoxic and phytogrowth-inhibitory activities[2,4]. Recently the antileukemic activity of piceatannol (1c) has also been reported[5].

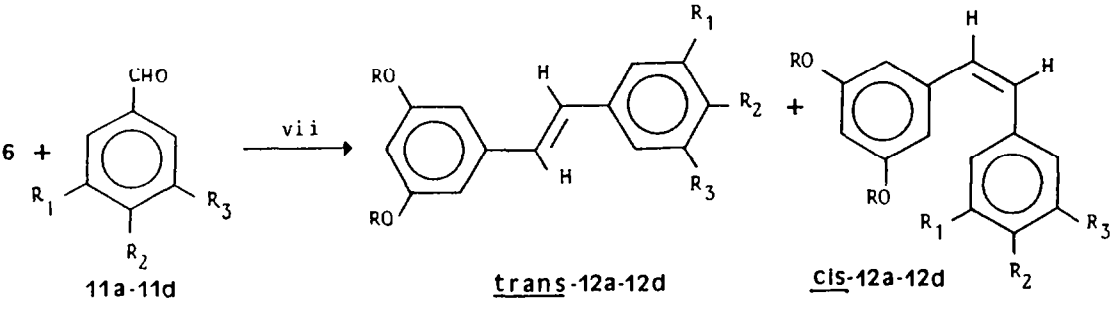
In this paper we describe the synthesis of the cis- and trans-isomers of the stilbenes (1a)-(1d), because of the considerable biological interest of these compounds and as a final proof of the structure of (1d). The syntheses of trans-(1a)[6] trans-(1b)[7] and trans-(1c)[8] has already been reported, however, the synthesis we have achieved is the more general application and sensiblely shorter than those previously reported. The ^{13}C NMR data of the synthesized polyhydroxystilbenes are given, the assignation of signals was made according to the additivity rule and off-resonance decoupled spectra.

Our synthetic route consists essentially in the preparation of the appropriately substituted phosphonium salt which was condensed by a Wittig reaction[9] with aldehydes with a suitable substitution pattern. In both moieties we have protected the phenolic groups as t-butyldimethylsilyl ether[10,11].

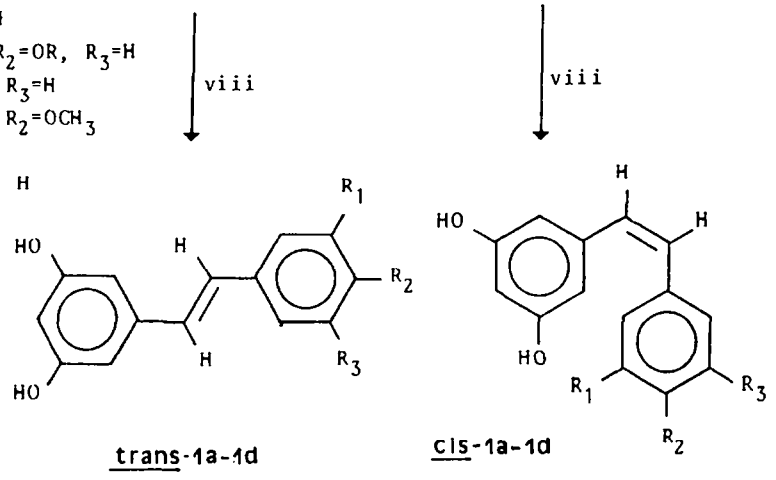
The first step in the preparation of the phosphonium salt 6 was the protection of the phenolic hydroxyl groups of the methyl 3,5-dihydroxybenzoate 2 to give the t-butyldimethylsilylether 3 which was carried out with t-butyldimethylsilyl chloride in DMF/imidazole[12]. Reduction of the ester 3 was carried out with lithium aluminum hydride in anhydrous ether. After the reduction and before the hydrolysis of the metal alkoxide it was necessary to add silica gel[13] to avoid extensive cleavage of the silyl ether. Treatment of the alcohol 4 with triphenylphosphine in CCl_4[14] at 78-80°C led to the substitution of the hydroxyl group by a chlorine atom, giving the chloride 5 with a good yield. Finally, the phosphonim salt 6 was prepared by heating a mixture of chloride 5 and triphenylphosphine in xylene[15] at reflux for 10 h.

The preparation of the aldehyde 11d was made from the methyl 3,4,5-trihydroxy-benzoate 7, by a four steps sequence. The first step was a partial methylation of 7. It is know that an electron withdrawing group in the aromatic ring increases the acidity of phenolic hydroxyls situated in the ortho and para position; however, preliminary experiments carried out with sodium acetate[16] and bicarbonate[17] gave unsuccessful results. The best yield (50%) was obtained in a system with acetone/





11a, 12a, 1a: $R_1=R_2=R_3=H$
11b, 12b, 1b: $R_1=OCH_3$, $R_2=OR$, $R_3=H$
11c, 12c, 1c: $R_1=R_2=OR$, $R_3=H$
11d, 12d, 1d: $R_1=R_3=OR$, $R_2=OCH_3$
R≡ -Si(CH$_3$)$_2$t-Bu,
excepting in 1 where R ≡ H



i) TBDMSCl/DMF, imidazole. ii) $AlLiH_4$/ether. iii) Ph_3P/CCl_4. iv) Ph_3P/xylene. v) Me_2SO_4/acetone, K_2CO_3. vi) PDC/methylene chloride. vii) n-BuLi/benzene. viii) HF/acetonitrile.

methyl sulfate (1.2 eq)/potassium carbonate (1.5 eq) at room temperature for 8 h. The second step was the protection of the hydroxyl groups, which was carried out as in the protection of compound 2. The next step was the reduction of the ester 9 with lithium aluminum hydride in anhydrous ether (silica gel modification). Finally the oxidation of the alcohol 10 with pyridinium dichromate[18] in dichloromethane afforded the aldehyde 11d.

Aldehydes 11b and 11c were prepared by treating vainillin and protocatechuic aldehyde respectively with t-butyldimethylsilyl chloride in DMF/imidazole. The reaction conditions employed in the silylation of 2 (1.2 eq. of silylating reagent)[12] did not give good yields. However in the original conditions of Corey and Venkateswarlu[11] (3.5 eq. of silylating reagent) the protection was complete in 15 min.

The Wittig reaction carried out between the phosphorane generated from the phosphonium salt 6 and n-butyllithium[19] and the aldehydes 11a-11d furnished a mixture (c.a. 3:1 determined by g.l.c.) of trans- and cis- silylated stilbenes 12a-12d. In the cases of 12b and 12c some extension of the cleavage of silyl ether was observed and consequently the last reaction of the sequence was carried out from the crude reaction product. In the case of phenolic hydroxyls, the usual reagent for the cleavage ($n\text{-}Bu_4NF$)[11] gave moderate yields only, as it produced secondary products[20]. However with HF in acetonitrile[21] good yields of polyhydroxystilbenes 12a-12d were obtained. The physical and spectroscopic properties of synthetic stilbenes agree well with those reported for the natural products[3,22].

TABLE 1. ^1H NMR chemical shifts[a] and coupling constants (Hz, in parenthesis) of polyhydroxystilbenes 1a-1d.

Proton	trans-1a	cis-1a	trans-1b	cis-1b	trans-1c	cis-1c	trans-1d	cis-1d
2	6.59d (2.0)	6.51d (2.1)	6.52d (2.2)	6.31d (2.1)	6.51d (2.2)	6.28d (2.1)	6.55d (2.0)	6.28d (2.1)
4	6.31t (2.0)	overlap. CH=CH	6.26t (2.1)	6.22t (2.1)	6.25t (2.2)	6.20t (2.2)	6.30t (2.0)	6.20t (2.1)
6	6.59d (2.0)	6.51d (2.1)	6.52d (2.1)	6.31d (2.1)	6.51d (2.2)	6.28d (2.1)	6.55d (2.0)	6.28d (2.1)
CH=CH	7.09s	6.25s	7.00d(16.2) 6.91d(16.2)	6.40d(12.4) 6.35d(12.4)	6.91d(16.1) 6.80d(16.1)	6.34d(12.4) 6.27d(12.4)	6.85s	6.35[b]s
2'	7.55dd (8.0,1.5)	7.0-7.3m	7.20d (1.9)	6.92d (1.9)	7.05d (1.9)	6.70d (1.9)	6.62s	6.33[b]s
3'	7.34dt (7.9,1.5)	7.0-7.3m	-	-	-	-	-	-
4'	7.23tt (7.4,1.4)	7.0-7.3m	-	-	-	-	-	-
5'	7.34dt (7.9,1.5)	7.0-7.3m	6.79d (8.2)	6.70d (8.2)	6.79d (8.1)	6.60-6.65m	-	-
6'	7.55dd (8.0,1.5)	7.0-7.3m	6.99dd (8.2,1.9)	6.72dd (8.2,1.9)	6.81d (8.1,1.9)	6.60-6.65m	6.62s	6.33[b]s
OCH_3	-	-	3.88s	3.61s	-	-	3.85s	3.78s

[a] 200.1 MHz, CD_3COCD_3, δ-scale, relative to TMS.

[b] Chemical shifts denoted by the same letter in each column may be interchanged.

TABLE 2. ^{13}C NMR Chemical shifts[a] of polyhydroxystilbenes 1a-1d

Carbon	trans-1a	cis-1a	trans-1b	cis-1b	trans-1c	cis-1c	trans-1d	cis-1d
1	140.1s	139.9s	140.8s	140.6s	140.7s	140.6s	140.3s	140.2s
2	105.8d	107.7d	105.7d	107.9d	105.5d	107.8d	105.9d	108.0d
3	159.6s	159.2s	159.5s	159.4s	159.5s	159.4s	159.4s	159.2s
4	103.1d	102.4d	102.6d	102.3d	102.5d	102.1d	102.8d	102.5d
5	159.6s	159.2s	159.5s	159.4s	159.5s	159.4s	159.4s	159.2s
6	105.8d	107.7d	105.7d	107.9d	105.5d	107.8d	105.9d	108.0d
C=C	129.8[b]d	130.0[b]d	129.4d	130.4d	129.6d	130.5d	129.8d	130.7d
	127.3[b]d	127.6[b]d	127.0d	129.0d	126.8d	129.0d	128.5d	130.3d
1'	138.3s	138.0s	130.4s	130.7s	132.9s	132.8s	136.1[b]s	135.5[b]s
2'	129.5[b]d	131.2[b]d	110.1d	113.0d	116.1d	116.8d	106.6d	109.0d
3'	129.0[b]d	130.4[b]d	148.5[b]s	147.6[b]s	146.0[b]s	145.9[b]s	151.3s	150.9s
4'	128.3[b]d	128.8[b]d	147.5[b]s	146.8[b]s	146.2[b]s	146.1[b]s	134.1[b]s	133.8[b]s
5'	129.0[b]d	130.4[b]d	115.8d	115.5d	113.7d	113.5d	151.3s	150.9s
6'	129.5[b]d	131.2[b]d	121.2d	123.4d	119.8d	121.6d	106.6d	109.0d
OCH_3	-	-	56.2q	55.8q	-	-	60.6q	60.6q

[a] 50.3 MHz, CD_3COCD_3, δ-scale, relative to TMS.

[b] Chemical shifts denoted by the same letter in each column may be interchanged.

EXPERIMENTAL

Melting points were determined in capillary tubes with a Buchi melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 281 spectrometer. Mass spectra were performed at 70 eV on a Varian 166 machine. ^1H NMR spectra were determined with a Perkin-Elmer R12B (60 MHz) spectrometer excepting those compounds 1 and 12 that were determined with a Bruker AC-200 spectrometer (200.1 MHz for ^1H and 50.3 MHz for ^{13}C).

Methyl 3,5-di-t-butyldimethylsilyloxybenzoate (3). A solution of 2 (0.859 g, 5.11 mmol), imidazole (1.738 g, 25.57 mmol) and t-butyldimethylsilyl chloride (1.849 g, 12.27 mmol) in DMF (15 mL) was stirred at room temperature for 24 h. The solution was diluted with water and extracted with ether. The combined ether layers were washed with water and brine, dried with $MgSO_4$ and concentrated to give 1.902 g (94%) of 3 as an oil. IR (NaCl): 2950, 2925, 2860, 1728, 1587, 1445, 1340, 1255, 1238, 1165, 1095, 1027, 1010, 925, 825 and 778 cm^{-1}. ^1H NMR (Cl_3CD), δ: 0.19 {s, $2(CH_3)_2Si$}, 0.98 {s, $2(CH_3)_3C$-Si}, 3.85 (s, $COOCH_3$) 6.5 (t, J=2 Hz, H-4) and 7.15 (d, J=2 Hz, H-2, H-6).

3,5-di-t-butyldimethylsilyloxibenzyl alcohol (4). To a mixture of lithium aluminum hydride (0.240 g, 6.32 mmol) in dry ether (5 mL) was added dropwise 1.098 g (2.77 mmol) of 3 in dry ether (5 mL) for 30 min and then refluxed for 1 h. After the mixture had been cooled and quenched with silica gel (1.63 g) and a few drops of saturated aqueous solution of NH_4Cl, the silica gel was filtered off and washed thoroughly with ether. The filtrate and the washings were combined and evaporated in vacuo to give 0.972 g (95%) of 4 as an viscous oil. IR (NaCl): 3600-3150, 2960, 2930, 2860, 1585, 1448, 1335, 1255, 1160, 1028, 1000, 970, 830, 780 and 670 cm^{-1}. ^1H NMR (Cl_3CD), δ: 0.19 {s, $2(CH_3)_2Si$}, 0.95 {s, $2(CH_3)_3C$-Si}, 4.5 (s, CH_2-OH), 6.2 (t, J=2 Hz, H-4) and 6.4 (d, J=2 Hz, H-2, H-6).

3,5-di-t-butyldimethylsilyloxybenzyl choride (5). A mixture of the alcohol 4 (0.368 g, 1 mmol) and Ph_3P (0.314 g, 1.2 mmol) in dry CCl_4 (0.7 mL) was carefully heated (water bath 75-80°) with continous stirring for 2 h. The solvent was then removed in vacuo and the residue filtered on silica gel, from which hexane-ether (9:1) eluted 0.332 g (86%) of 5 as an oil. IR (NaCl): 2955, 2930, 2860, 1590, 1450, 1340, 1255, 1165, 1030, 1005, 825, 777 and 675 cm^{-1}. ^1H NMR (Cl_3CD), δ: 0.19 {s, $2(CH_3)_2Si$}, 0.98 {s, $2(CH_3)_3C$-Si}, 4.4 (s, CH_2Cl), 6.3 (t, J=2 Hz, H-4) and 6.5 (d, J=2 Hz. H-2, H-6).

3,5-di-t-butyldimethylsilyloxybenziltriphenylphosphonium chloride (6). A mixture of chloride 5 (0.332 g, 0.86 mmol) and 0.365 g (1.39 mmol) of Ph_3P in xylene (1.6 mL) was heated at reflux for 10 h. with stirring. The mixture was allowed to cool and the product was filtered, washed with hexane and dried to give 0.471 g (83%) of 6, m.p. 192-195°C. IR (KBr): 3050, 2950, 2930, 2860, 2780, 1595, 1450, 1430, 1330, 1260, 1250, 1155, 1110, 1020, 820, 770, 735, 720 and 690 cm^{-1}. ^1H NMR (CD_3OD), δ: 0.19 {s, $2(CH_3)_2Si$}, 0.98 {s, $2(CH_3)_3C$-Si}, 4.85 (d, J=11 Hz, CH_2P), 6.0 (t, J=2 Hz, H-4), 6.25 (d, J=2 Hz, H-2, H-6) and 7.8-7.4 (m, Ph_3P).

Methyl 3,5-dihydroxy-4-methoxybenzoate (8). A mixture of 7 (1.840 g, 10 mmol) methyl sulfate (1.15 mL, 12.1 mmol) and potassium carbonate (2.073 g, 15 mmol) in

acetone (210 mL) was stirred at r.t. for 8 h and then diluted with water. The acetone was concentrated and the aqueous solution was extracted with ethyl acetate. Working up in the usual way followed by a column chromatography (hexane-ether, 6:4) affording 0.990 (50%) of 8, m.p. 148-149°C (from hexane-ether). IR (KBr): 3500-3100, 3000, 2960, 2850, 1708, 1595, 1508, 1439, 1378, 1290, 1255, 1165, 1060, 1000, 980, 868, 770, 755 and 714 cm^{-1}. ^1H NMR (CD_3COCD_3) δ: 3.80 (s, OCH_3), 3.88 (s, $COOCH_3$), 7.10 (s, H-2, H-6) and 8.20 (br. s, OH).

Methyl 3,5-di-t-butyldimethylsilyloxy-4-methoxybenzoate (9). The same procedure as employed for the preparation of 3. The ester 8 (0.439 g, 2.22 mmol) afforded 0.878 g (93%) of 9 as an oil. IR (NaCl): 2950, 2930, 2860, 1728, 1580, 1490, 1460, 1420, 1345, 1250, 1218, 1080,1000, 930, 868, 820, 775 and 660 cm^{-1}. ^1H NMR (CCl_4), δ: 0.19 {s, $2(CH_3)_2Si$}, 1.0 {s, $2(CH_3)_3C$-Si}, 3.7 (s, OCH_3), 3.8 (s, $COOCH_3$) and 7.04 (s, H-2, H-6).

3,5-di-t-butyldimethylsilyloxi-4-methoxybenzyl alcohol (10). The same procedure as employed for the preparation of 4. The ester 9 (0.878 g, 2.06 mmol) afforded 0.779 g (95%) of 10 as an oil. IR (NaCl): 3600-3100, 2950, 2925, 2855, 1575, 1485, 1428, 1340, 1245, 1220, 1080, 990, 830, 775 and 665 cm^{-1}. ^1H NMR (CCl_4), δ: 0.18 {s, $2(CH_3)_2Si$}, 1.0 {s, $2(CH_3)_3C$-Si}, 3.7 (s, OCH_3), 4.45 (CH_2-OH) and 6.5 (s, H-2, H-6).

3,5-di-t-butyldimethylsilyloxy-4-methoxybenzaldehyde (11d). Pyridinium dichromate (0.635 g, 1.689 mmol) was added to a solution of alcohol 10 (0.455 g, 1.126 mmol) in CH_2Cl_2 (4.2 mL). The reaction mixture was raised at room temperature for 12 h and then was diluted with hexane (15 mL) and filtered on silica gel from which hexane-ether (9:1) eluted 0.392 g (87%) of 11d, m.p. 74-75°C (from hexane-ether). IR (KBr): 2950, 2930, 2855, 1690, 1570, 1480, 1430, 1418, 1380, 1340, 1252, 1208, 1128, 1085, 1000, 820 and 778 cm^{-1}. ^1H NMR (CCl_4), δ: 0.18 {s, $2(CH_3)_2Si$}, 1.0 {s, $2(CH_3)_3C$-Si}, 3.7 (s, OCH_3), 6.8 (s, H-2, H-6) and 9.6 (s, CHO).

Preparation of aldehydes (11b) and (11c). A solution of vainillin or protocatechuic aldehyde (1 mmol), imidazole (0.680 g, 10 mmol) and t-butyldimethylsilyl chloride (0.526 g, 3.50 mmol) in DMF (7.2 mL) was stirred at r.t. for 15 min. The product was worked up in the usual way to give the silylated aldehydes (11b) and (11c) (95%).

Compound (11b): an oil, IR (NaCl): 2950, 2925, 2860, 1690, 1590, 1505, 1450, 1420, 1385, 1295, 1250, 1150, 1120, 1030, 930, 900, 835, 775, 725, 698 and 655 cm^{-1}. ^1H NMR (CCl_4), δ: 0.19 {s, $(CH_3)_2Si$}, 0.95 {s, $(CH_3)_3C$-Si}, 3.85 (s, OCH_3), 6.82 (d, J=8.6 Hz, H-5), 7.23 (dd, J=8.6 and 2.0 Hz, H-6), 7.30 (s, H-2) and 9.75 (s, CHO).

Compound (11c): an oil, IR (NaCl): 2950, 2925, 2860, 1690, 1590, 1520, 1505, 1470, 1425, 1382, 1290, 1250, 1155, 1115, 987, 972, 895, 835 and 778 cm^{-1}. ^1H NMR (CCl_4), δ: 0.19 {s, $2(CH_3)_2Si$}, 0.95 {s, $2(CH_3)_3C$-Si}, 6.87 (d, J=8.6 Hz, H-5), 7.2-7.4 (m, H-2, H-6) and 9.75 (s, CHO).

Cis- and trans-polysilylated stilbenes (12a-12d). To a stirred solution of phosphonium salt 6 (0.389 g, 0.6 mmol) in dry benzene (4 mL) under argon was added a 1.6 M solution (0.6 mL, 0.96 mmol) of n-BuLi in hexane. After stirring for 30 min. aldehyde 11a-11d (0.72 mmol) was added and the reaction mixture stirred for an additional 4 h, after which a few drops of water were added. The benzene layer was separated, dried and concentrated. Dry benzene was added to the residue and evaporated (several times). Filtration of the residue dissolved in hexane through silica gel afforded a mixture of cis- and trans-isomers (80%). In the cases of 12a and 12d both isomers were separated by a careful preparative tlc and in the cases of 12b and 12c the crude reaction mixture was submitted to the cleavage of silyl ether groups.

Compound trans-12a: an oil, HRMS: 440.2550 (M^+), $C_{26}H_{40}O_2Si_2$ requires 440.2556 IR (NaCl) 2950, 2925, 2860, 1580, 1440, 1425, 1335, 1250, 1162, 1025, 1010, 955, 872, 830, 775 and 687 cm^{-1}. ^1H NMR (CCl_4), δ: 0.21 {s, $2(CH_3)_2Si$}, 1.00 {s, $2(CH_3)_3C$-Si} 6.26 (t, J=2.1 Hz, H-4), 6.63 (d, J=2.1 Hz, H-2, H-6), 6.99 (s, CH=CH), 7.24 (tt, J=8.0 and 1.5 Hz, H-4'), 7.35 (dt, J=8.0 and 1.5 Hz, H-3', H-5') and 7.50 (dd, J=8.0 and 1.5 Hz, H-2', H-6'). Compound cis-12a: an oil, IR (NaCl), practically superimposable with that trans-12a excepting the band at 955 cm^{-1}. ^1H NMR (CCl_4), δ: 0.08 {s, $2(CH_3)_2Si$}, 0.92 {s, $2(CH_3)_3C$-Si}, 6.19 (t, J=2.2 Hz, H-4), 6.34 (d, J=2.2 Hz, H-2, H-6), 6.49 and 6.56 (AB system, J=12.2 Hz, CH=CH) and 7.1-7.3 (m, H-4', H-3', H-5', H-2', H-6').

Compound trans-12d: an oil, HRMS: 730.4274 (M^+), $C_{39}H_{70}O_6Si_4$ requires 730.4281, IR (NaCl): 2950, 2925, 2855, 1580, 1493, 1465, 1440, 1365, 1260, 1170, 1090, 1025, 1010, 960, 940, 835, 785 cm^{-1}. ^1H NMR (CCl_4), δ: 0.19 and 0.21 {2s, $4(CH_3)_2Si$}, 0.99 and 1.02 {2s, $4(CH_3)_3C$-Si}, 3.72 (s, OCH_3), 6.23 (t, J=2.1 Hz, H-4), 6.58 (d, J=2.1 Hz, H-2, H-6), 6.64 (s, H-2', H-6') and 6.74 and 6.80 (AB system, J=16.3 Hz, CH=CH). Compound cis-12d: and oil, IR (NaCl), practically superimposable with that trans-12d, excepting the band at 960 cm^{-1}. ^1H NMR (CCl_4), δ: 0.07 and 0.11 {2s, $4(CH_3)_2Si$}, 0.93 and 0.95 {2s, $4(CH_3)_3C$-Si}, 3.67 (s, OCH_3), 6.15 (t, J=2.3 Hz, H-4), 6.33 (d, J=2.3 Hz, H-2, H-6) and 6.37 and 6.38 (2s, H-2', H-6' and CH=CH).

Cis- and trans-polyhydroxystilbenes (1a-1d). The polysilylated stilbenes 12a-

12d (0.25 mmol) was dissolved in acetonitrile (1 mL) containing a 5% of a 40% aqueous solution of HF. The mixture was stirred at room temperature for 4 h after which was worked up in the usual way to give the polyhydroxystilbenes 1a-1d (80% yield for 1a and 1d, and 55% yield for the two reactions of preparation of 1b and 1c).

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