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THREE STILBENOIDS FROM THE ORCHID *AGROSTOPHYLLUM CALLOSUM*

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Key Word Index—*Agrostophyllum callosum*; Orchidaceae; callosumin, 9,10-dihydrophenanthrene; callosuminin, phenanthrene; callosumidin, 9,10-dihydrophenanthropyran derivative.

Abstract—Callosumin, callosuminin and callosumidin, three new stilbenoids, were isolated from the orchid *Agrostophyllum callosum* which earlier afforded, besides 4-hydroxy-3,5-dimethoxybenzoic acid, 10 other structurally related stilbenoids, viz. orchinol, 6-methoxycoelonin, imbricatin, flaccidin, oxoflaccidin, isooxoflaccidin, flaccidinin, agrostophyllin, callosin and callosinin. The structures of callosumin, callosuminin and callosumidin were established as 2,4,6,7-tetramethoxy-9,10-dihydrophenanthrene, 2,4,6,7-tetramethoxyphenanthrene and 2,7-dihydroxy-5-ethoxy(*ax*)-6-methoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran, respectively, from spectral and chemical evidence. Although in naming callosumidin the systematic numbering system has been adopted, for ease of comparison of the spectral results the phenanthrene numbering system for the compound and its structural analogues is used.

INTRODUCTION

We reported earlier the isolation of a number of stilbenoids of diverse structural types [1–7], a number of simple aromatic compounds and other polyphenolics [8–11], several triterpenoids [12] and steroids of biogenetic importance [13] from a series of Indian orchids. As part of this general programme of research, we investigated the orchid *Agrostophyllum callosum* which earlier afforded, besides 4-hydroxy-3,5-dimethoxybenzoic acid, 10 stilbenoids, viz. orchinol (**1a**) [14, 15], 6-methoxycoelonin (**1b**) [16], callosin (**1c**) [17], imbricatin (**2a**) [18], flaccidin (**2c**) [19], oxoflaccidin (**2d**) [20], isooxoflaccidin (**2e**) [4], callosinin (**2f**) [17], flaccidinin (**3a**) [20] and agrostophyllin (**3b**) [21]. Further chemical investigation of this orchid has now resulted in the isolation of three new stilbenoids, designated callosumin, callosuminin and callosumidin, which were shown to have the structures **1d**, **4a** and **2g**, respectively, from spectral and chemical evidence.

RESULTS AND DISCUSSION

Compound **1d**, $C_{18}H_{20}O_4$ ($[M]^+$ *m/z* 300) showed UV absorptions, λ_{max}^{EtOH} 221, 278, 302 and 316 (sh) nm (log ε 4.47, 4.21, 4.19 and 2.39), which are typical of 9,10-dihydrophenanthrene derivatives. Compound **4a**, $C_{18}H_{18}O_4$ ($[M]^+$ *m/z* 298), on the other hand, exhibited UV absorbtions, λ_{max}^{EtOH} 209, 260, 343 and 360 nm (log ε 4.39, 4.46, 3.35 and 3.36), which are strikingly similar to those of polyoxygenated phenanthrenes. Both **1d** and **4a** are devoid of any phenolic hydroxyl function as evident from their IR spectra and also from their isolation from the neutral fraction of a methanolic extract of *A. callosum*.

The ^{1}H NMR spectrum of **1d** showed signals for four aromatic methoxyl groups [δ 3.83, 3.89, 3.90 and 3.92 (each 3H, *s*)], four aromatic protons [δ 7.92 (1H, *s*), 6.74 (1H, *s*), 6.47 and 6.44 (each 1H, *d*, J = 2.4 Hz) and a four-proton singlet at δ 2.77, which is typical of the H_2-9 and H_2-10 of a 9,10-dihydrophenanthrene derivative, indicating an identical skeletal structure also for **1d**. This was also supported by the lowfield aromatic proton signal at δ 7.92, which is characteristic of H-4 or H-5 of a 9,10-dihydrophenanthrene derivative. If the above signal is assigned to H-5 of **1d**, C-4 of the compound must contain one of its aromatic methoxyl groups. Again, the appearance of the signal at δ 7.92 as a sharp singlet implies that both C-6 and C-7 of **1d** must also be substituted and contain two of the remaining three methoxyl groups. Consequently, the singlet at δ 6.74 may be attributed to H-8 of **1d**. The splitting pattern of the remaining two aromatic proton signals of **1d** at δ 6.47 and 6.44 (each 1H, *d*, J = 2.4 Hz) corresponded to two *meta*-coupled protons, which could then be attributed to H-1 and H-3, respectively, flanked by its fourth aromatic methoxyl group at C-2. The above spectral data for **1d** are thus intelligible in terms of a 2,4,6,7-tetramethoxy-9,10-dihydrophenanthrene formulation for the compound.

The ^{1}H NMR spectrum of **4a** also showed signals for four aromatic methoxyl groups [δ 3.97, 4.03, 4.08 and

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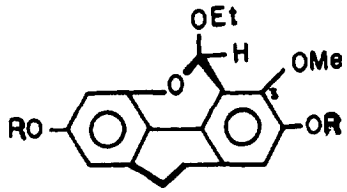
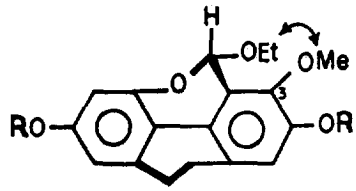


5a



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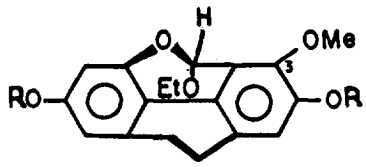

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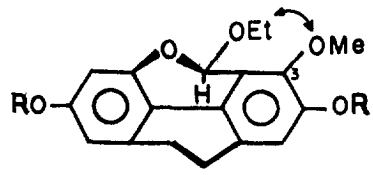

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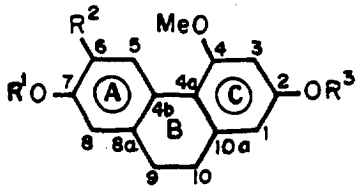
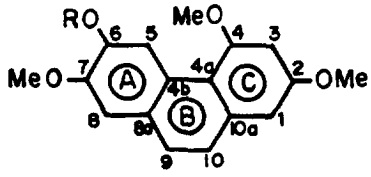
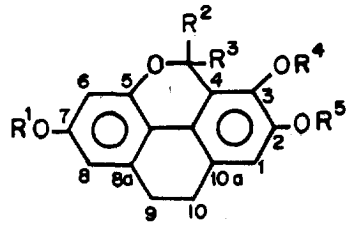


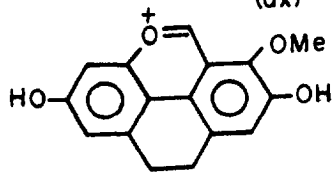
	R^1	R^2	R^3
1a	H	H	Me
1b	H	OMe	H
1c	Me	OH	H
1d	Me	OMe	Me



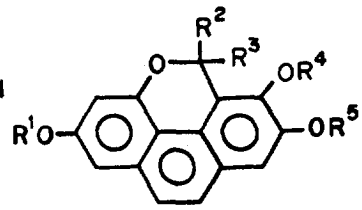
	R
4a	Me
4b	H



	R^1	R^2	R^3	R^4	R^5
2a	H	H	H	Me	H
2b	Ac	H	H	Me	Ac
2c	H	H	H	H	Me
2d	H	—O—		H	Me
2e	H	—O—		Me	H
2f	Me	H	H	Me	Me
2g	H	OEt (ax)	H	Me	H
2h	Ac	OEt (ax)	H	Me	Ac



a (m/z 269)



	R^1	R^2	R^3	R^4	R^5
3a	H	—O—		H	Me
3b	Me	H	H	Me	H

4.09 (each 3H, *s*)] and differed from that of **1d** by the appearance of two additional aromatic proton signals at δ 7.53 and 7.62 (each 1H, *d*, $J = 9$ Hz) in place of the signal at δ 2.77 (4H, *s*) for H_2-9 and H_2-10 of the latter, and also by the overall lowfield shifts of the remaining four aromatic proton signals of the former [δ 9.11 (1H, *s*), 7.21 (1H, *s*) and 6.88 and 6.74 (each 1H, *d*, $J = 3$ Hz)] compared to those of the latter. The signals at δ 7.59 and 7.62 corresponded to H-9 and H-10 of a phenanthrene derivative and that at δ 9.11 is again typical of H-4 or H-5 of the same type of compound. If the above lowfield signal of **4a** is assigned to H-5, C-4 of the compound must contain one of its methoxyl groups. Again the appearance of the

Table 1. ^{13}C NMR spectral data for compounds **1b**, **1c**, **1d**, **2b**, **2h**, **4a** and **4b**

C	1d*	1b†	1c†	4a*	4b*	2h*	2b*
1	106.9	108.5	107.3	108.9	109.1	123.1	121.5
2	157.8	157.4	154.9	160.5	160.3	142.7	142.2
3	98.3	99.4	99.1	99.1	99.6	146.1	145.2
4	159.0	158.7	158.0	158.0	158.6	121.9	122.2
4a	117.0	115.3	117.8	116.0	115.9	123.9	124.5
4b	125.7	125.6	124.0	126.9[a]	126.4	114.9	116.3
5	111.6	113.4	114.5	112.1	113.4	151.1	152.9
6	147.2[a]	146.1[a]	145.7	148.5[b]	147.4[a]	108.8	107.8
7	146.9[a]	145.3[a]	143.3	148.0[b]	147.1[a]	150.3	150.6
8	113.1	114.9	110.1	101.2	102.2	114.4	114.1
8a	130.7	131.7	129.9	126.5[a]	127.6	135.8	136.6
9	31.1[b]	31.6[b]	29.6[b]	127.3[c]	128.5[b]	27.4[a]	27.1[a]
10	29.3[b]	30.1[b]	29.5[a]	124.9[c]	125.2[b]	26.9[a]	26.4[a]
10a	140.8	141.4	141.2	134.7	135.8	129.4	128.9
OMe	55.2	55.9	55.5	55.3	55.6	61.7	61.0
	55.8	56.6	56.0	55.6	2 × 56.0		
	2 × 56.1			55.8			
				56.0			
OCOMe	—	—	—	—	—	168.9	168.9
						168.8	168.7
						20.6	20.6
						21.0	20.3
Ar–OCH$_2$Ar	—	—	—	—	—	—	63.1
Ar–OCH(OEt)–Ar	—	—	—	—	—	94.0 (O–CH–O)	—
						64.0 (O–CH$_2$–)	
						15.0 (–CH$_3$)	

*Spectra run in $CDCl_3$ and chemical shifts measured with δ (TMS) = δ ($CDCl_3$) + 76.9 ppm.
†Spectra run in acetone-d_6 and chemical shifts measured with δ (TMS) = δ (acetone-d_6) + 29.6 ppm.
[a–c]Values interchangeable within the same column.

signal at δ 9.11 as a sharp singlet confirmed the presence of a methoxyl group at C-6 and C-7 of **4a**. The signal at δ 7.21 could then be attributed to H-8 of the compound. The remaining two aromatic proton signals of **4a**, at δ 6.88 and 6.74, corresponded to two *meta*-coupled protons, which were assigned to H-1 and H-3, respectively, of the compound separated by its fourth aromatic methoxyl group located at C-2, as in **1d**. The above ^1H NMR spectral data for **4a** would thus suggest it to be the corresponding phenanthrene derivative of **1d**.

The proposed structures of **1d** and **4a** were also supported by the ^{13}C NMR spectral data (Table 1). The degree of protonation of each carbon atom of both the compounds (as well as those of **2h**) were confirmed by APT experiments, and the carbon chemical shifts were assigned by comparison with the δ_c values of the structurally related compounds, taking into consideration the additive parameters of the functional groups. Thus, the δ_c values of **1d** are comparable with those of **1b** [16] and **1c** [17]; the marginal differences may be attributed to replacement of the hydroxyl groups of **1b** and **1c** by methoxyl groups in **1d**. Again, the virtually identical δ_c values of the ring-C carbon atoms of **4a** and batatasin-I (**4b**) [22] confirmed the placement of two aromatic methoxyl groups at C-2 and C-4 in both the compounds. The δ_c values of C-9, C-10, C-8a and C-10a of **4a** are also comparable with those of the corresponding carbon atoms of **4b**, corroborating the phenanthrene skeletal structure of the compound. The marginal differences in the δ_c values of the ring-A carbon atoms of **4a** and **4b** may be attributed to the replacement of the hydroxyl group at C-6 of the latter by a methoxyl group at the same position in the former.

The structures of **1d** and **4a** were finally confirmed by the formation of the former by methylation of both **1b** and **1c** by the action of diazomethane and by the dehydrogenation of **1d** to **4a** with DDQ in dry benzene.

Compound **2g** was isolated as its diacetyl derivative (**2h**), $C_{22}H_{22}O_7$ ($[M]^+$ *m/z* 398). The UV spectrum of **2h**, λ_{max}^{EtOH} 216, 275, 298 and 309 nm (log ε 4.10, 3.66, 3.57 and 3.59), showed striking resemblance to those of 9,10-dihydrophenanthrene derivatives. The formation of the diacetyl derivative **2h** indicated the presence of two phenolic hydroxyl groups in the parent compound **2g**.

The ^1H NMR spectrum of **2h** showed signals for an aromatic methoxyl group (δ 3.79, 3H, *s*), two acetate methyls (δ 2.27 and 2.34, each 3H, *s*), three aromatic protons [δ 6.89 (1H, *s*) and 6.58 and 6.61 (each 1H, poorly resolved *meta*-coupled doublet)], a methine proton attached to a carbon atom bearing two oxygen atoms (δ 6.26, 1H, *s*), an ethoxyl group [δ 3.83 (2H, *m*)

and 1.15 (3H, *m*)] and a four-proton multiplet at δ 2.81, which is typical of H_2-9 and H_2-10 of a 9,10-dihydrophenanthrene derivative, rendered non-equivalent presumably by a neighbouring chiral centre. The signal at δ 2.81 in the ^{1}H NMR spectrum of **2h** thus indicated it to be also a 9,10-dihydrophenanthrene derivative. The absence of any relatively downfield signal at *ca* δ 8.0 characteristic of H-4 and H-5 of a 9,10-dihydrophenanthrene in the ^{1}H NMR spectrum of **2h** implies that both C-4 and C-5 of the compound are substituted. The signal at δ 6.26 and those for the ethoxyl group may then be attributed to the presence of an ethyl ether of a lactol bridge joining the C-4 and C-5 of **2h** as represented by the moiety C_5-O-CH(OEt)-C_4. The placement of the lone methoxyl group at C-3 and the two acetoxy functions at C-2 and C-7 of **2h** was based on the striking similarities of the chemical shifts and the splitting patterns of the aromatic proton signals of **2h** with those of imbricatin diacetate (**2b**). The three aromatic proton signals of **2h** at δ 6.89, 6.58 and 6.61 may then be altributed to H-1, H-6 and H-8, respectively. The spectra of **2h** thus differ essentially from those of **2b** by the replacement of the signal for the oxymethylene protons of the latter (δ 5.22) by the methine proton signal (δ 6.26) and those of the ethoxyl group of the ethyl ether of the lactol bridge of the former. Callosumidin diacetate is, therefore, a derivative of imbricatin diacetate, in which one of the oxymethylene protons of the latter is replaced by an ethoxyl group. The structure of callosumidin was also in conformity with its mass spectral fragmentations, exhibiting a very intense peak at *m/z* 269, which may be attributed to the highly stabilized oxonium ion-fragment **a** formed by sequential loss of two ketene molecules from the $[M]^+$ followed by the expulsion of an ethoxyl radical.

The proposed structure of **2h** was also corroborated by its ^{13}C NMR spectral data (Table 1). The carbon chemical shifts of **2h** were virtually identical to those of the corresponding carbon atoms of **2b** except that the signal for the oxymethylene carbon in the spectrum of the latter (δ_c 63.1) is replaced by a lowfield methine carbon signal at δ_c 94.0 and a methylene (δ_c 64.0) and a methyl carbon (δ_c 15.0) signal in the spectrum of the former owing to the structural change C_5-O-CH_2-C_4 in **2b** to C_5-O-CH(OEt)-C_4 in **2h**. The placement of the methoxy group at C-3 in both **2h** and **2b** was affirmed by the lowfield shifts of their methoxyl carbons appearing in the region at *ca* δ_c 61–62, which are characteristic of the carbon atoms of methoxyl groups having no *ortho*-hydrogen atom. The carbon atoms of methoxyl groups having *ortho*-hydrogen atom(s) normally resonate at *ca* δ_c 55–56. The placement of the methoxyl group at C-3, in turn, also confirmed the location of the two acetoxy groups at C-2 and C-7 in **2h**.

Having established the gross structure of **2h** and, hence, **2g** itself, it now remained to ascertain the stereochemistry of the ethoxyl group at the chiral centre of the oxymethine carbon. Since callosumidin is optically inactive, it must be a *dl*-pair. Construction of the Dreiding models of the possible conformers of **2h** shows that it may either be the *dl*-pair of the enantiomers **5a** and **5b** [R = Ac], in which the ethoxyl group is axial or the *dl*-pair of the enantiomers **6a** and **6b** [R = AC], which have the ethoxyl function equatorially oriented. In **6a** and **6b**, the ethoxyl group is so close to the methoxyl group at C-3 that they produce severe steric interaction which renders them too unstable to exist. Compounds **5a** and **5b**, on the other hand, having the ethoxyl function far away from the methoxyl group at C-3, are free from such steric interaction. Based on this assumption callosumidin diacetate is believed to exist exclusively as an equimolecular mixture of **5a** and **5b** [R = Ac]. The energy barrier for the apparently expected flipping of **5a** to **6b** and of **5b** to **6a** becomes so high due to the aforesaid steric interaction that callosumidin diacetate exists exclusively as the *dl*-pair of **5a** and **5b** [R = Ac] even at elevated temperature. The parent **2g** is thus assumed to be exclusively the *dl*-pair of **5a** and **5b** [R = H].

Callosumidin is thus a novel example of a *dl*-pair of two highly stable conformational enantiomers which are unable to flip to the diastereomeric forms owing to severe steric interaction. Compound **2g** may be assumed to be formed through the intermediacy of the oxonium species **a** followed by nucleophilic attack by ethanol from the less-hindered axial side. The oxonium species, **a**, in turn, is assumed to have generated by hydroperoxylation at the oxymethylene carbon of **2a** followed by conversion of the resultant hydroperoxy derivative into the corresponding lactol and, finally, by elimination of the lactol hydroxyl group.

EXPERIMENTAL

Mps: uncorr. Silica gel (100–200 mesh) was used for CC and silica gel G for TLC. UV were measured in 95% aldehyde-free EtOH and IR in KBr discs. ^{1}H and ^{13}C NMR were measured at 300 and 75 MHz, respectively, in $CDCl_3$ and Me_2CO-d_6, using TMS as int. standard. Chemical shifts are expressed in δ (ppm). MS were recorded with a direct inlet system at 70 eV. All analyt. samples were routinely dried over P_2O_5 for 24 hr *in vacuo* and were tested for purity by TLC and MS. Na_2SO_4 was used for drying organic solvents and the petrol used had bP 60–80°.

Isolation of callosumin (**1d**), *callosuminin* (**4a**) *and callosumidin* (**2g**) *as its diacetate* (**2h**). Air-dried, powdered whole plants (3 kg) were soaked in MeOH (10 l) for 3 weeks. The MeOH extract was then drained, concd under red. pres. to *ca* 100 ml, diluted with H_2O (500 ml) and the liberated solids exhaustively extracted with Et_2O. The Et_2O extract was fractionated into acidic and non-acidic frs with 2 M aq. NaOH. The aq. alkaline soln was acidified in the cold with conc. HCl and the liberated solids extracted with Et_2O, washed with H_2O, dried and the solvent removed. The Et_2O extract left after removal of the acidic constituents was also washed with H_2O, dried and the solvent removed. The residue was chromatographed. Early frs of the petrol–EtOAc (50:1) eluate afforded a semi-

solid mass containing a mixt. of **1d** and **4a** in a ratio of *ca* 10:1. Repeated chromatography of this mixt. finally gave pure **1d** (0.2 g) and **4a** (0.02 g), both as semi-solid mass. Later frs of the same eluate also gave a mixt. of **1d** and **4a** in a ratio of *ca* 1:9. The above mixt. on further chromatography also gave pure **1d** (0.02 g) and **4a** (0.18 g). **1d** (Found: C, 71.76; H, 6.59. $C_{18}H_{20}O_4$ requires: C, 72.00; H, 6.67%); **4a** (Found: C, 72.34; H, 5.98. $C_{18}H_{18}O_4$ requires: C, 72.48; H, 6.04%)]. **1d**: IR ν_{max} cm^{-1}: 1600, 1590, 1560, 1510, 1450, 870, 820, 800 (aromatic nucleus). MS *m/z* (rel. int.) [significant peaks]: 300 $[M]^+$ (100), 285 (30), 270 (20), 242 (25). **4a**: IR ν_{max} cm^{-1}: 1615, 1520, 1490, 1440, 870, 850, 830 (aromatic nucleus). MS *m/z* (rel. int.) [significant peaks]: 298 $[M]^+$ (100), 283 (32), 268 (22), 240 (26). The petrol–EtOAc (30:1) eluate gave **2f** (0.2 g) recrystallized from the same solvent mixt. mp 101°.

The residue containing the acidic constituents was similarly chromatographed. The petrol–EtOAc (20:1) eluate afforded a gummy solid which on rechromatography gave pure **3b** (0.02 g), recrystallized from petrol–EtOAc, mp 86°. Early frs of the petrol–EtOAc (10:1) eluate yielded pure **2c** (0.04 g), recrystallized from the same solvent mixt., mp 200°. Later frs of the same eluate afforded a solid containing 4-hydroxy-3,5-dimethoxybenzoic acid, **1a**, **1b**, **1c**, **2a**, **2d**, **2e** and **3a**. Repeated chromatography of the above solid finally gave pure **1a** (0.02 g), recrystallized from petrol–EtOAc, mp 168°; **1b** (0.03 g) as a glassy solid; **2a** (0.05 g), recrystallized from petrol–EtOAc, mp 145°; **2e** (0.03 g), recrystallized from the same solvent mixt. mp 270°; 4-hydroxy-3,5-dimethoxybenzoic acid (0.015 g), amorphous; **1c** (0.05 g), recrystallized from petrol–EtOAc, mp 205°; **2d** (0.02 g) and **3a** (0.025 g), both as amorphous powder.

Further elution of the column with petrol–EtOAc (8:1) afforded a gummy solid which contained mostly **2g** mixed with a number of other minor phenolic compounds. Repeated chromatography of this solid failed to give pure **2g**. The crude mixt. was then acetylated with Ac_2O–pyridine in the usual manner and the crude acetylated mixt. chromatographed. The petrol–EtOAc (15:1) eluate gave pure **2h** (0.05 g) as an amorphous powder. (Found: C, 66.20; H, 5.49. $C_{22}H_{22}O_7$ requires: C, 66.33; H, 5.53%). IR ν_{max} cm^{-1}: 1760 and 1230 (OAc), 1625, 1605, 1485, 830, 770, 725 (aromatic nucleus). MS *m/z* (rel. int.) [significant peaks]: 398 $[M]^+$ (5), 356 (7), 353 (4), 314 (18), 269 (75), 254 (49), 253 (18), 239 (12), 225 (28), 209 (7), 197 (8), 181 (9), 168 (10), 152 (19), 139 (31), 115 (26), 43 (100).

Hydrolysis of **2h** *to* **2g**. Compound **2h** (0.02 g) was treated with 1 M aq. ethanolic NaOH (15 ml) and the mixt. heated under reflux for 2 hr. The solvent was removed under red. pres. and the residue treated with H_2O (10 ml) and extracted with Et_2O. The aq. alkaline soln left after extraction with Et_2O was acidified with conc. HCl in the cold and the liberated solids extracted with Et_2O, washed with H_2O, dried and the solvent removed. The residue was chromatographed. The petrol–EtOAc (8:1) eluate gave pure **2g** as an amorphous solid.

Conversion of **1b** *and* **1c** *into* **1d**. To solns of **1b** (0.02 g) and **1c** (0.02 g) in MeOH (20 ml) was added separately an excess of CH_2N_2 in Et_2O (20 ml) and the reaction mixts kept overnight in an ice-bath. Solvents were then removed under red. pres. to give a semi-solid mass in each case. The residues were separately chromatographed. The petrol–EtOAc (50:1) eluate in each case gave pure **1d** (0.018 g).

Conversion of **1d** *to* **4a** by *DDQ oxidization*. To a soln of **1d** (0.03 g) in dry C_6H_6 (20 ml) was added 0.035 *g* DDQ and the mixt. heated under reflux for 16 hr. The solvent was removed under red. pres. to give a solid which was extracted with Et_2O, washed ×3 with 2 M aq. NaOH and then with H_2O, dried and the solvent removed. The residue was chromatographed. The petrol–EtOAc (50:1) eluate gave **4a** (0.025 g) as a semi-solid mass.

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