Pergamon

S0031-9422(96)00022-2

Phytochemistry, Vol. 42, No. 4, pp. 1157–1161, 1996

0031-9422/96 $15.00 + 0.00

FOUR STILBENOIDS FROM THE ORCHID *AGROSTOPHYLLUM KHASIYANUM*

P. L. MAJUMDER, S. LAHIRI and N. MUKHOTI

Department of Chemistry, University College of Science, 92 Acharya Prafulla Chandra Road, Calcutta 700009, India

(*Received* 29 *August* 1995)

Key Word Index—*Agrostophyllum khasiyanum*; Orchidaceae; stilbenoids; agrostophyllone; agrostophylloxin; agrostophylloxidin; agrostophyllidin.

Abstract—The orchid *Agrostophyllum khasiyanum*, which earlier yielded agrostophyllin (7-hydroxy-2,6-dimethoxy-5*H*-phenanthro[4,5-*bcd*]pyran), on further chemical investigation has now yielded four more new stilbenoids, besides imbricatin (2,7-dihydroxy-6-methoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran), flaccidinin (2,6-dihydroxy-7-methoxy-5*H*-phenanthro[4,5-*bcd*]pyran-5-one), isoflaccidinin (2,7-dihydroxy-6-methoxy-5*H*-phenanthro[4,5-*bcd*]pyran-5-one) and moscatilin (4,4′-dihydroxy-3,3′,5-trimethoxybibenzyl) of previously known structures. The structures of the new stilbenoids, designated agrostophyllone, agrostophylloxin, agrostophylloxidin and agrostophyllidin, were established as 7-hydroxy-2,6-dimethoxy-5*H*-phenanthro[4,5-*bcd*]pyran-5-one, 2,6,7-trimethoxy-5*H*-phenanthro[4,5-*bcd*]pyran-5-one, 7-hydroxy-2,5,6-trimethoxy-5*H*-phenanthro[4,5-*bcd*]pyran and 7-hydroxy-2,6-dimethoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran, respectively, from spectral and chemical evidence.

INTRODUCTION

In previous papers we have reported on the isolation of a wide variety of stilbenoids [1–10], several triterpenoids [11], steroids of biogenetic importance [12], lignans [13], flavonoids [14, 15] and simple aromatic compounds [16] from members of the Indian Orchidaceae. The orchid *Agrostophyllum khasiyanum* afforded the phenanthropyan derivative agrostophyllin (**1a**) [17]. Further chemical investigation of this orchid has now resulted in the isolation of four more new stilbenoids, besides the known compounds imbricatin (**2a**) [18], flaccidinin (**1c**) [19], isoflaccidinin (**1e**) [8] and moscatilin (**3**) [20]. The new stilbenoids, designated agrostophyllone, agrostophylloxin, agrostophylloxidin and agrostophyllidin, were shown to have the structures **1g**, **1i**, **1j** and **2c**, respectively, from detailed spectral and chemical evidence. Although in naming the above compounds in the abstract the systematic numbering system has been adopted, for ease of comparison of spectral results the phenanthrene numbering system for these compounds is used in this paper.

RESULTS AND DISCUSSION

Both agrostophyllone (**1g**), $C_{17}H_{12}O_5$ ($[M]^+$, m/z = 296), and agrostophylloxin (**1i**), $C_{18}H_{14}O_5$ ($[M]^+$, m/z = 310) showed UV absorptions [**1g**: λ_{max}^{EtOH} 219, 249 (sh), 257 and 284 (sh) nm (log ε 3.82, 4.14, 4.20 and 3.60); **1i**: λ_{max}^{EtOH} 219.5, 248 (sh), 257.5 and 283 (sh) nm (log ε 3.84, 4.15, 4.22 and 3.61)], which were strikingly similar to those of phenanthropyrone derivatives like flaccidinin (**1c**) [19] and isoflaccidinin (**1e**) [8]. The UV spectra of agrostophylloxidin (**1j**), $C_{18}H_{16}O_5$ ($[M]^+$, m/z = 312) and agrostophyllidin (**2c**), $C_{17}H_{16}O_4$ ($[M]^+$, m/z = 284), on the other hand, were different from those of **1g** and **1i** [**1j**: λ_{max}^{EtOH} 228, 263 and 297 (sh) nm (log ε 4.51, 4.72 and 3.53); **2c**: λ_{max}^{EtOH} 218, 286 and 306 nm (log ε 4.66, 4.21 and 4.18)] and exhibited a close resemblance to those of phenanthropyrans [17] and their 9,10-dihydro-derivatives [18], respectively. While **1i** contains no phenolic hydroxyl function, the presence of such a group in each of **1g**, **1j** and **2c** was confirmed by the formation of the respective monoacetyl derivatives **1h**, $C_{19}H_{14}O_6$ ($[M]^+$, m/z = 338), **1k**, $C_{20}H_{18}O_6$ ($[M]^+$, m/z = 354) and **2d**, $C_{19}H_{18}O_5$ ($[M]^+$, m/z = 326). The IR spectra of **1h**, **1k** and **2d** showed the usual bands for a phenolic acetate function and those of **1h** and **1i** also exhibited additional bands for a δ-lactone function [**1h**: ν_{max} 1240 and 1765 (OAc) and 1735 (δ-lactone) cm^{-1}; **1i**: ν_{max} 1728 (δ-lactone) cm^{-1}; **1k**: ν_{max} 1260 and 1760 (OAc) cm^{-1}; **2d**: ν_{max} 1220 and 1760 (OAc) cm^{-1}].

The ^1H NMR spectrum of **1g** showed signals for two aromatic methoxyl groups (δ 3.87 and 3.94, each 3H, *s*), a phenolic hydroxyl function (δ 8.79, 1H, *s*; disappeared on deuterium exchange) and five aromatic protons. The signal for two of these aromatic protons at δ 7.71 (*s*) is typical of that for H-9 and H-10 of a

phenanthropyrone derivative [8, 19]. Two of the remaining three aromatic protons appeared as a pair of doublets at δ 7.23 ($J = 2.4$ Hz) and 6.98 ($J = 2.4$ Hz), corresponding to two *meta*-coupled protons which were assigned to H-6 and H-8, respectively, thus placing the methoxyl group at C-7 as in **1a**. The remaining aromatic proton signal of **1g** appearing at δ 7.77 (*s*) must then correspond to H-1 with substituents at C-2, C-3 and C-4. The lowfield shift of the above proton compared to that of the corresponding proton of **1a** favoured the placement of the lactone carbonyl group at C-4. The placement of the lone hydroxyl group at C-2 was corroborated by the observed lowfield shift of its H-1 resonance (δ 7.77) by 0.19 ppm in the ^{1}H NMR spectrum of its acetyl derivative (**1h**). The two aromatic methoxyl groups of **1g** must therefore be located at C-3 and C-7 as in **1a**. The foregoing spectral data for **1g** and **1h** thus imply that **1g** is the corresponding pyrone derivative of **1a**.

The ^{1}H NMR spectrum of **1i** differed essentially from that of **1g** by having an additional signal for one more aromatic methoxyl group [δ 3.91, 4.01 and 4.05 (each 3H, *s*)]. The chemical shifts and the splitting patterns of the five aromatic protons of **1i** [δ 7.06 and 7.12 (each 1H, *d*, $J = 2.2$ Hz), 7.64 (2H, *s*) and 7.69 (1H, *s*)] thus clearly indicated that **1i** was the *O*-methyl ether derivative of **1g.** The above assumption was finally confirmed by the conversion of **1g** into **1i** with diazomethane.

Further evidence in support of the assigned structures of **1g** and **1i** was provided by the ^{13}C NMR spectral data of **1h** and **1i** itself (Table 1). The degree of protonation of the carbon atoms of each compound in Table 1 was determined by both APT and DEPT experiments, and the assignments of the carbon chemical shifts were made by comparison with the δ_c values of structurally similar compounds. Thus, the δ_c values of **1h** and **1i** when compared with those of **1d** [19] and **1b** [17], after taking into consideration the additive parameters of the different functional groups, are in excellent agreement with their proposed structures. The placement of one of the aromatic methoxyl groups at C-3 and the absence of an *ortho*-hydrogen at C-2 and C-4 in both **1h** and **1i** was confirmed by the lowfield methoxyl carbon signals at δ_c 62.9 (in **1h**) and 62.0 (in **1i**).

The structures of **1g** and **1i** were finally confirmed by the conversion of agrostophyllin acetate (**1b**) into **1h** by refluxing the former with DDQ in dry benzene for 16 hr. In this reaction, two more compounds were also obtained in extremely poor yield. They could not be characterized due to the lack of material.

Compound **1j** was isolated as its acetyl derivative (**1k**). The ^{1}H NMR spectrum of the latter differed essentially from that of **1b** by the replacement of the signal at δ 5.65 for the oxymethylene protons of **1b** by signals at δ 3.60 (3H, *s*) and 6.51 (1H, *s*), which were attributed to the methoxyl and methine protons, respect-

Table 1. ^{13}C NMR spectral data for compounds **1b**, **1d**, **1h**, **1i** and **1k**

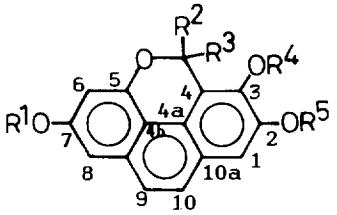
C	1h*	1i*	1d*	1k*	1b*
1	127.4	115.3	115.0†	121.5	119.3
2	143.6	151.1	150.2	142.2	142.1
3	144.1	152.7	151.6	145.8	145.1
4	108.8	109.3	113.0	119.0	120.0
4a	121.9	123.0	126.9	123.0	122.4
4b	125.1	125.5	128.1	115.0	111.4
5	151.5	152.8	151.9	150.9	152.9
6	102.0	101.8	107.5	102.2	101.1
7	160.3	159.5	149.8	158.8	159.6
8	104.8	104.4	114.7†	103.0	101.5
8a	132.3	131.4	136.0	132.8	131.6
9	126.4†	125.9†	126.9‡	126.1	125.6†
10	126.3†	126.4†	126.5‡	126.1	125.4†
10a	125.1	124.3	130.6	124.6	124.2
$-OCH_2-Ar$	—	—	—	—	63.7
$-\overset{O}{\overset{\|}{C}}-Ar$	158.2	158.1	157.2	—	—
OMe	55.9 (OMe at C-7) 62.9 (OMe at C-3)	55.8, 56.2 (OMe at C-2 and C-7), 62.0 (OMe at C-3)	56.6	55.6 (OMe at C-7 and MeO-CH<) 62.12 (OMe at C-3)	55.0 (OMe at C-7) 61.0 (OMe at C-3)
-OCH(OMe)	—	—	—	95.9	—
Ar-OAc	169.3 20.7	—	169.2 169.0 21.2, 20.9	168.6 20.3	168.5 20.3

*Spectra were determined in $CDCl_3$ and chemical shifts measured with $\delta_{(TMS)} = \delta_{(CDCl_3)} + 76.9$ ppm.

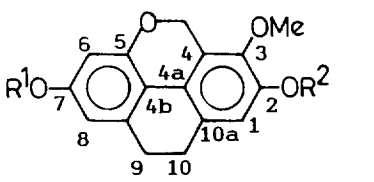
†,‡Values are interchangeable within the same column.

ively, of the moiety Ar–O–CH(OCH_3)–Ar. This would suggest that **1k** differed from **1b** by the replacement of one of the oxymethylene protons of the latter by a methoxyl group. This was supported by the ^{13}C NMR spectrum of **1k**, which again differed essentially from that of **1b** by the replacement of the oxymethylene carbon signal at δ_C 63.7 of the latter by the signals at δ_C 95.9 and 55.6 (two methoxyl carbons, one of which was attributed to the methoxyl group at C-7) for the methine and methoxyl carbons, respectively, of a lactol methyl ether moeity. Compound **1j** is thus a derivative of **1a** with an additional methoxyl group at the oxymethylene carbon and contains a chiral centre at the same position. A Dreiding model of **1j** showed that the additional methoxyl group may be either axial, as in **4a** or its mirror image, or equatorial, as in **4b** or its mirror image. Since **1j** is optically inactive, it may be the *dl*-pair of **4a** and its mirror image or **4b** and its mirror image. In **4a** or its mirror image, the methoxyl group at the oxymethylene carbon is far away from the aromatic methoxyl group at C-3, while in **4b** these two methoxyl groups are in close proximity to each other, creating a severe steric interaction which would prevent the otherwise expected facile flipping of **4a** to **4b** or the mirror image of the former to the mirror image of the latter. On the basis of this steric consideration, **1j** was assumed to be a *dl*-pair of the conformer **4a** and its mirror image.

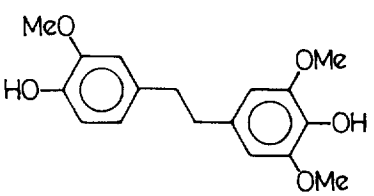
Compound **2c** was also isolated as its acetyl derivative (**2d**). The ^1H NMR spectrum of **2d** showed, besides the signals for a phenolic acetate methyl [δ 2.28 (3H, *s*)], two aromatic methoxyl groups [δ 3.90 and 3.94 (each 3H, *s*)] and three aromatic protons [δ 6.58 (2H, *br.* signal) and 6.76 (1H, *s*)], a two-proton singlet at δ 5.27 and a four-proton singlet at δ 2.88, which are typical of the oxymethylene protons and H_2-9 and H_2-10, respectively, of 9,10-dihydrophenanthropyran derivative [18, 21]. The chemical shifts and the splitting patterns of the three aromatic protons of **2d** exhibited striking similarities with the corresponding aromatic protons of imbricatin diacetate (**2b**) [18] and particularly with those of H-1, H-6 and



1a: $R^1=R^4=Me, R^2,R^3=H_2, R^5=H$
1b: $R^1=R^4=Me, R^2,R^3=H_2, R^5=Ac$
1c: $R^1=R^4=H, R^2,R^3=O, R^5=Me$
1d: $R^1=R^4=Ac, R^2,R^3=O, R^5=Me$
1e: $R^1=R^5=H, R^2,R^3=O, R^4=Me$
1f: $R^1=R^5=Ac, R^2,R^3=O, R^4=Me$
1g: $R^1=R^4=Me, R^2,R^3=O, R^5=H$
1h: $R^1=R^4=Me, R^2,R^3=O, R^5=Ac$
1i: $R^1=R^4=R^5=Me, R^2,R^3=O$
1j: $R^1=R^4=Me, R^2=OMe(ax), R^3=R^5=H$
1k: $R^1=R^4=Me, R^2=OMe(ax), R^3=H, R^5=Ac$



2a: $R^1=R^2=H$
2b: $R^1=R^2=Ac$
2c: $R^1=Me, R^2=H$
2d: $R^1=Me, R^2=Ac$



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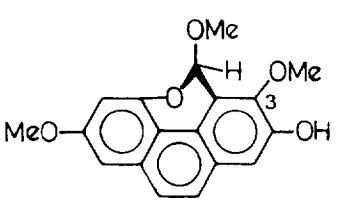
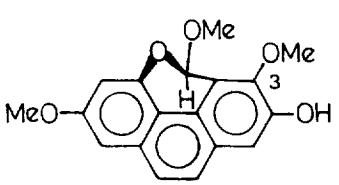


4a



4b

H-8 of isoflavidinin acetate [21], a 9,10-dihydrophenanthropyran derivative, bearing an acetoxy function at C-2 and methoxyl group at C-7. Mild acid hydrolysis of **2d** produced the parent phenolic agrostophyllidin (**2c**), which showed the expected upfield shift of its H-1 (δ 6.43) confirming the placement of its lone hydroxyl group at C-2 and the two aromatic methoxyl groups at C-3 and C-7. Compound **2c** is thus the 9,10-dihydro-derivative of its congener, **1a**.

Compounds **1g**, **1i**, **1j** and **2c** are thus four new additions to the growing list of stilbenoids isolated from Orchidaceae plants which have already been shown to elaborate such compounds preponderantly.

EXPERIMENTAL

Mps: uncorr.; CC; Silica gel (100–200 mesh); MPLC: silica gel (230–400 mesh); TLC: silica gel G; UV: 95% aldehyde-free EtOH; IR: KBr discs; ^{1}H and ^{13}C NMR: 300 and 250, and 75 and 62.5 MHz, respectively, in $CDCl_3$ and Me_2CO-d_6 using TMS as int. standard. Chemical shifts are expressed in δ (ppm). MS: direct-inlet system, 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 agrostophyllone (**1g**), *agrostophylloxin* (**1i**), *agrostophylloxidin* (**1j**), *agrostophyllidin* (**2c**), *agrostophyllin* (**1a**), *imbricatin* (**2a**), *flaccidinin* (**1c**), *isoflaccidinin* (**1e**) *and moscatilin* (**3**) *from* A. khasiyanum. Air-dried, powdered whole plants (5 kg) were soaked in MeOH (15 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 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 residue was subjected to CC. The petrol–EtOAc (20:1) eluate gave a semi-solid mass containing **1a**, **1g**, **1j** and **2c**. The above mixt. was then subjected to MPLC using petrol–EtOAc (2:1) as the solvent. The early frs in the above MPLC gave a mixt. of **1a** and **2c**, and the later frs afforded a solid containing **1g** and **1j**. The mixt. of **1a** and **2c** and that of **1g** and **1j** could not be sepd even on repeated CC. Both the residues were separately acetylated with Ac_2O and pyridine in the usual manner and the two acetylated mixts were separately subjected to CC. The early frs of the petrol–EtOAc (50:1) eluate in the CC of acetylated mixt. of **1a** and **2c** afforded pure **2d** (0.015 g) as a semi-solid mass and the later frs of the same eluate gave pure **1b** (0.1 g), crystallized from petrol–EtOAc mixture, mp 125°. **2d** (Found: C, 69.89; H, 5.49. $C_{19}H_{18}O_5$ requires: C, 69.94; H, 5.52%). IR ν_{max} cm^{-1}: 1220, 1760 (OAc), 1610, 1590, 834, 820, 722 (aromatic nucleus); EIMS *m/z* (rel. int.): 326 $[M]^+$ (51), 284 (100), 269 (30).

A soln of **2d** (0.01 g) in 5 ml 2 M methanolic HCl was refluxed for 2 hr. The MeOH was removed under red. pres. and the residue was extracted with Et_2O, washed with H_2O, dried and the solvent removed. The residue was subjected to CC. The petrol–EtOAc (30:1) eluate gave pure **2c** (0.008 g) as an amorphous powder. (Found: C, 71.76; H, 5.57. $C_{17}H_{16}O_4$ requires: C, 71.83; H, 5.63%). UV λ_{max} nm: 218, 286, 306 (log ε 4.66, 4.21, 4.18); ^{1}H NMR: δ 2.76 (4H, *s*; H_2-9, H_2-10), 4.0, 4.1 (each 3H, *s*; 2 × ArOMe), 5.31 (2H, *s*; Ar–OCH_2–Ar), 5.81 (1H, *s*; disappeared on ^{2}H exchange; ArOH), 6.36, 6.38 (each 1H, *d*, J = 1.8 Hz; H-6, H-8), 6.43 (1H, *s*; H-1): EIMS *m/z* (rel. int.): 284 $[M]^+$ (100), 269 (25).

The acetylated mixt. of **1g** and **1j** on repeated CC gave in the early frs of petrol–EtOAc (50:1) pure **1k** (0.03 g), crystallized from petrol–EtOAc, mp 196°, and pure **1h** (0.04 g) in the later frs, crystallized also from the same solvent mixt., mp 220°. **1k** (Found: C, 67.76; H, 4.99. $C_{20}H_{18}O_6$ requires: C, 67.80; H, 5.08%). IR ν_{max} cm^{-1}: 1260, 1760 (OAc), 1630, 1600, 1470, 840, 720 (aromatic nucleus); ^{1}H NMR: δ 2.34 (3H, *s*; OAc), 3.60 (3H, *s*; Ar–OCH(OMe)–Ar), 3.90, 3.94 (each 3H, *s*; 2 × ArOMe), 6.51 (1H, *s*; Ar–O–CH(OMe)–Ar), 6.85 (1H, *d*, J = 2.1 Hz; H-6), 6.90 (1H, *d*, J = 2.1 Hz, H-8), 7.53 (1H, *s*; H-1), 7.56 (2H, ABq, J = 8.4 Hz; H-9, H-10). EIMS *m/z* (rel. int.): 354 $[M]^+$ (40), 312 (52), 281 (100); CIMS *m/z* (rel. int.): 355 $[M+1]^+$ (4). Mild alkaline hydrolysis of **1k** with 0.5 M ethanolic NaOH, followed by usual workup, afforded **1j** as an amorphous powder. **1h** (Found: C, 67.42; H, 4.10. $C_{19}H_{14}O_6$ requires: C, 67.46; H, 4.14%). IR ν_{max} cm^{-1}: 1240 and 1765 (OAc), 1735 (δ-lactone), 1635, 1465, 850, 720 (aromatic nucleus); ^{1}H NMR: δ 2.45 (3H, *s*; OAc), 3.99, 4.0 (each 3H, *s*; 2 × ArOMe), 7.15, 7.21 (each 1H, *d*, J = 1.8 Hz; H-6, H-8), 7.76 (2H, ABq, J = 9 Hz; H-9, H-10), 7.96 (1H, *s*; H-1); EIMS *m/z* (rel. int.): 338 $[M]^+$ (25), 296 (60), 278 (29), 250 (30), 43 (100); CIMS *m/z* (rel. int.): 339 $[M+1]^+$ (100). Mild acid-catalysed hydrolysis of **1h** with 2 M methanolic HCl, followed by usual workup, gave **1g** as a semi-solid mass.

The petrol–EtOAc (10:1) eluate from the main chromatographic column of the acidic fr. gave **2a** (0.05 g), crystallized from petrol–EtOAc, mp 145°. Washing the column with petrol–EtOAc (7:1) afforded **3** (0.08 g), crystallized from the same solvent mixt., mp 84°. Further elution of the above column with petrol–EtOAc (5:1) gave, in the early frs, **1c** (0.05 g), crystallized from petrol–EtOAc, mp 325° (d). The later frs of the same eluate afforded **1e** (0.04 g), crystallized from the same solvent mixt., mp 300° (d).

The Et_2O extract left after removal of the acidic constituents was washed with H_2O, dried and the solvent removed. The residue was subjected to CC. The petrol–EtOAc (30:1) eluate gave **1i** (0.06 g), crystallized from petrol–EtOAc, mp 226°. (Found: C, 69.54; H, 4.45. $C_{18}H_{14}O_5$ requires: C, 69.68; H, 4.52%). IR ν_{max} cm^{-1}: 1728 (δ-lactone), 1630, 1610,

892, 810, 768 (aromatic nucleus); ^{1}H NMR: δ 3.91, 4.01, 4.05 (each 3H, *s*; 3 × ArOMe), 7.06, 7.12 (each 1H, *d*, $J = 2.2$ Hz; H-8, H-6), 7.64 (2H, *s*; H-9, H-10), 7.69 (1H, *s*; H-1); EIMS *m/z* (rel. int.): 310 $[M]^+$ (100), 295 (18), 281 (65), 267 (16), 168 (20).

Conversion of agrostophyllin acetate (**1b**) *to agrostophyllone acetate* (**1h**) *and of* **1i** *into* **1g**. A soln of **1b** (0.04 g) and DDQ (0.04 g) in dry C_6H_6 (10 ml) was heated under reflux for 16 hr. C_6H_6 was removed under red. pres. and the residue was extracted with Et_2O. The Et_2O extract was washed with 2 M NaOH and then with H_2O, dried and the solvent removed. The residue was subjected to CC. The petrol–EtOAc (50:1) eluate gave **1h** (0.02 g). Further elution of the column with petrol–EtOAc (10:1) afforded traces of two other uncharacterized compounds.

To a soln of **1g** (0.01 g) in MeOH (10 ml) was added excess of CH_2N_2 in Et_2O in the cold and the mixt. kept overnight. The solvent was then removed under red. pres. and the residue was subjected to CC. The petrol–EtOAc (30:1) eluate gave **1i** (0.008 g).

Acknowledgements—We thank Prof. W. Kraus (University of Hohenheim, Stuttgart, Germany) for some of the ^{1}H and ^{13}C NMR spectra, and Dr J. M. Wilson (University of Manchester, U.K.) for the mass spectra. The work was supported by the CSIR, UGC and DST, New Delhi, India.

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