Pergamon

0031-9422(95)00942-2

Phytochemistry, Vol. 39, No. 3, pp. 649–653, 1995

0031-9422/95 $9.50 + 0.00

STILBENOIDS FROM THE ORCHIDS *AGROSTOPHYLLUM CALLOSUM* AND *COELOGYNE FLACCIDA*

P. L. MAJUMDER,* S. BANERJEE, D. C. MAITI and S. SEN

Department of Chemistry, University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta 700 009, India

(*Received* 21 *September* 1994)

Key Word Index—*Agrostophyllum callosum*; *Coelogyne flaccida*; Orchidaceae; callosin; 9,10-dihydrophenanthrene; callosinin; 9,10-dihydrophenanthropyran derivative.

Abstract—Callosin and callosinin, two new stilbenoids, were isolated from the orchid *Agrostophyllum callosum*, which also afforded, 4-hydroxy-3,5-dimethoxybenzoic acid, orchinol, 6-methoxycoelonin, imbricatin, flaccidin, oxoflaccidin, iso-oxoflaccidin, flaccidinin and agrostophyllin of previously known structures. Callosin was also isolated from another orchid, *Coelogyne flaccida*. The structures of callosin and callosinin were established as 2,6-dihyroxy-4,7-dimethoxy-9,10-dihydrophenanthrene and 2,6,7-trimethoxy-9,10-dihydro-5*H*-phenanthro [4,5-bcd]pyran-5-one, respectively, from spectral and chemical evidence. For ease of comparison of the spectral data the phenanthrene numbering system is used in this paper.

INTRODUCTION

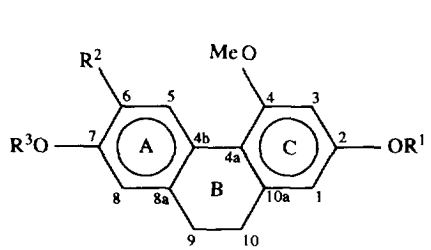
We reported earlier the isolation of a fairly large number of stilbenoids of diverse structural types [1–7], several triterpenoids [8] and steroids of biogenetic importance [9] from a series of Indian orchids. Our continued search for phytochemicals from the same source has resulted in the isolation of two further new stilbenoids, designated callosin and callosinin, from the orchid *Agrostophyllum callosum* which also afforded 4-hydroxy-3,5-dimethoxybenzoic acid, orchinol (**1a**) [10, 11], 6-methoxy coelonin (**1b**) [12], imbricatin (**2a**) [13], flaccidin (**2b**) [14], oxoflaccidin (**2c**) [15], iso-oxoflaccidin (**2d**) [4], flaccidinin (**2e**) [15] and agrostophyllin (**2f**) [16] of previously known structures. Callosin was also isolated from the orchid *Coelogyne flaccida* [4, 14, 15]. The structures of callosin and callosinin were established as **1c** and **2g**, respectively, from the spectral and chemical evidence.

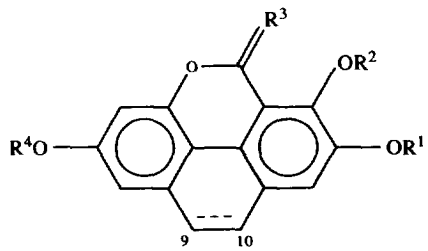
RESULTS AND DISCUSSION

Both callosin (**1c**), $C_{16}H_{16}O_4$ ($[M]^+$ *m/z* 272), and callosinin (**2g**), $C_{18}H_{18}O_4$ ($[M]^+$ *m/z* 298), showed UV absorptions [**1c**: λ_{max}^{EtOH} 222, 273, 277 and 303 nm (log ε 4.23, 4.08, 4.05 and 4.02); **2g**: λ_{max}^{EtOH} 220, 284 and 304 nm (log ε 4.55, 4.20 and 4.18)] that are typical of 9,10-dihydrophenanthrene derivatives [5, 17]. The phenolic nature of **1c** was indicated by its characteristic colour reactions [$FeCl_3$: violet; phosphomolybdic acid: deep blue), alkali-induced bathochromic shift of its UV maxima [λ_{max} (EtOH–0.1 M NaOH) 230, 273, 288 and 313 nm (log ε 4.14, 4.05, 4.04 and 4.02)] and also by its IR spectrum showing a band at 3400 cm^{-1}. The presence of two phenolic hydroxyl groups in **1c** was confirmed by the formation of a diacetyl derivative **1d**, $C_{20}H_{20}O_6$ ($[M]^+$ *m/z* 356), with Ac_2O and pyridine. Callosinin (**2g**), on the other hand, is devoid of any phenolic hydroxyl function.

The ^1H NMR spectrum of **1c** showed signals for two phenolic hydroxyl functions [δ5.36 and 5.27 (each 1H, *s*; disappeared on deuterium exchange)], two aromatic methoxyl groups [δ3.79 and 3.83 (each 3H, *s*)], four aromatic protons [δ7.81 (1H, *s*), 6.64 (1H, *s*), 6.33 and 6.27 (each 1H, *d*, *J* = 2 Hz)] and a four-proton singlet at δ2.62 which is typical of the H_2-9 and H_2-10 of a 9,10-dihydrophenanthrene derivative [5, 17], indicating that **1c** also possesses a 9,10-dihydrophenanthrene moiety bearing two aromatic methoxyl and two phenolic hydroxyl groups. The aromatic proton signal at δ7.81 is again similar to that of H-4 or H-5 of a 9,10-dihydrophenanthrene derivative [4, 17, 18]. If this signal is assigned to H-5 of **1c**, H-4 must contain one of the oxygen substituents. Again the appearance of the signal at δ7.81 as a sharp singlet implies that each of H-6 and H-7 of **1c** must contain one of the remaining oxygen functions. Consequently, the singlet at δ6.64 corresponded to H-8 of **1c**. The remaining two aromatic proton signals at δ6.33 and 6.27 (each *d*, *J* = 2 Hz), corresponding to two *meta*-coupled protons, may then be attributed to H-1 and H-3 of **1c**, separated by its remaining oxygen function at C-2. The relative positions of the hydroxyl and methoxyl functions in **1c** were indicated by the chemical shifts of the aromatic protons of the diacetyl derivative, **1d** of callosin (**1c**). In the light of the earlier observation [19], that H-5

*Author to whom correspondence should be addressed.





	R^1	R^2	R^3
1a	Me	H	H
1b	H	OMe	H
1c	H	OH	Me
1d	Ac	OAc	Me
1e	Ac	OMe	Ac
1f	H	H	H
1g	Ac	H	Ac
1h	Me	OMe	Me
1i	Me	OH	Me

	R^1	R^2	R^3	R^4
2a	H	Me	H_2, 9, 10-dihydro-	H
2b	Me	H	H_2, 9, 10-dihydro-	H
2c	Me	H	O, 9, 10-dihydro-	H
2d	H	Me	O, 9, 10-dihydro-	H
2e	H	Me	O, 9, 10-dehydro-	H
2f	H	Me	H_2, 9, 10-dehydro-	Me
2g	Me	Me	H_2, 9, 10-dihydro-	Me
2h	Ac	Me	H_2, 9, 10-dihydro-	Ac

of a 4-hydroxy-9,10-dihydrophenanthrene is shifted upfield by *ca* 0.2 ppm in the ^{1}H NMR spectrum of its 4-*O*-acetyl derivative, the observed downfield shift of H-5 of **1c** by 0.10 ppm in the spectrum of **1d** indicated the substituent at C-4 of **1c** to be a methoxyl group rather than a hydroxyl function. The placement of a hydroxyl group at C-2 of **1c** is again affirmed by the low-field shifts of its H-1 and H-3 signal by 0.22 and 0.26 ppm, respectively, in the ^{1}H NMR spectrum of **1d**. The remaining hydroxyl and methoxyl group of **1c** must, therefore, be placed at C-6 and C-7, respectively. The above argument was supported by the striking similarities of the chemical shifts of the aromatic protons and the splitting patterns of their corresponding signals of **1c** and 6-methoxylcoelonin (**1b**) and their respective diacetates, **1d** and **1e**. This would suggest that if 6-methoxycoelonin is 2,7-dihydroxy-4,6-dimethoxy-9,10-dihydrophenanthrene (**1b**), callosin must be represented by the isomeric 2,6-dihydroxy-4,7-dimethoxy-9,10-dihydrophenanthrene, **1c**, although the marginally low-field shifts of H-5 and H-8 of **1e** by 0.10 and 0.11 ppm, respectively, in the ^{1}H NMR spectrum of **1d** failed to provide unambiguous evidence in support of the placement of a hydroxyl group at C-6 and a methoxyl function at C-7 in **1c**.

The most convincing evidence in support of the assigned structure of **1c** was provided by the ^{13}C NMR spectral data of the compound and its diacetyl derivative **1d** (Table 1). The degree of protonation of the carbon atoms of **1c** and **1d** were determined by DEPT experiments and the assignments of the carbon chemical shifts were made by comparison with the δ_c values of structurally similar compounds, *viz.* 6-methoxycoelonin (**1b**) [12], coelonin (**1f**) [6, 17] and coelonin diacetate (**1g**) [6, 17]. Thus, the δ_c values of C-1, C-2, C-3, C-4, C-4a, C-9, C-10 and C-10a of **1c** are strikingly similar to those of the corresponding carbon atoms of **1b** and **1f** indicating an identical structure of their B- and C-rings. This was corroborated by the practically identical δ_c values of the above carbon atoms of **1d** and **1g**. Furthermore, the appearance of C-9 and C-10 of **1c** and **1d** at the normal region (*ca* 29–31 ppm) ruled out the placement of any substituent at either C-1 or C-8 of these compounds. Any substituent at these carbon atoms would have caused a high-field shift of *ca* 6 ppm of C-9 and C-10 [20]. Again, interchange of the acetoxy and methoxy groups of **1d** between C-4 and C-2, as in lusianthridin diacetate [19], would have caused a low-field shift of C-3 of **1d** by *ca* 3 ppm. The observed low-field shifts of C-5 and C-8a and high-field shifts of, C-4b and C-8 of **1c**, compared to the corresponding carbon atoms of **1b**, lent further support in favour of the placement of the hydroxyl group at C-6 and methoxyl group at C-7 in the compound, as against a methoxyl group at C-6 and a hydroxyl group at C-7, as in **1b**. This was confirmed by the fact that while C-4b and C-8 of **1d** showed only marginal downfield shifts of 1.1 and 1.4 ppm, respectively, compared to the corresponding carbon atoms of **1c**, C-5 and C-8a of **1c** were shifted downfield by 8.4 and 7.1 ppm, respectively, in the spectrum of **1d**. The structure of **1c** was finally confirmed by the formation of the same dimethylether derivative **1h**, $C_{18}H_{20}O_4$ ($[M]^+$ *m/z* 300), on treatment of both **1c** and **1b** with CH_2N_2. In the above reaction, **1c** also afforded a monomethyl ether derivative, **1i**, $C_{17}H_{18}O_4$ ($[M]^+$ *m/z* 286), as a minor product.

The ^{1}H NMR spectrum of **2g** showed signals for three aromatic methoxyl groups [δ3.82, 3.83 and 3.87 (each 3H, *s*)], a four-proton singlet at δ2.89 and a two-proton singlet at δ5.23, which are typical of the 9- and 10-methylene, and the oxymethylene protons, respectively, of 9,10-dihydrophenanthropyran derivatives [13, 14, 20], indicating that **2g** also possesses an identical skeletal structure bearing three aromatic methoxyl functions. The

Table 1. ^{13}C NMR spectral data of compounds **1c**, **1d**, **1b**, **1f**, **1g**, **2g** and **2h**

C	1c*	1d†	1b*	1f*	1g†	2g†	2h†
1	107.3	113.5	108.5	108.0	113.5	111.8	121.5
2	154.9	149.7[a]	157.4	155.8[a]	149.9[a]	145.1[a]	142.2
3	99.1	104.2	99.4	99.1	104.0	143.3[a]	145.2
4	158.0	157.3	158.7	158.5	157.6	121.6[b]	122.2
4a	114.6	120.7	115.3	116.1	120.7	121,2[b]	124.5
4b	124.0	125.1	131.7	125.5	129.9	112.4	116.3
5	114.5	122.9	113.4	129.6	129.4	153.3	152.9
6	145.7	137.6[b]	146.1	114.7[b]	120.3[b]	100.0	107.8
7	143.3	149.4[a]	145.3	157.1[a]	149.0[a]	151.4	150.6
8	110.1	111.5	114.9	113.3[b]	118.9[b]	107.5	114.1
8a	129.9	137.0	125.6	141.0[c]	141.1[c]	135.3	135.6
9	29.6[a]	30.2[c]	31.6[a]	30.5[d]	30.1[d]	28.1[c]	27.1[a]
10	29.5[a]	29.5[c]	30.1[a]	31.1[d]	29.5[d]	27.6[c]	26.4[a]
10a	141.2	140.3	141.4	139.7[c]	139.8[c]	128.1	128.9
OMe	55.5	55.8	55.6	55.5	55.7	60.8	61.0
	56.0	55.9	55.9	—	—	(OMe at C-3) 55.3 & 56.1 (OMe at C-2 and C-7)	
OCOMe	—	169.1, 169.2	—	—	169.5, 169.6	—	168.9, 168.2
		20.5 21.0	—	—	21.2		20.6
Ar-OCH_2-Ar		—	—	—		63.8	63.1

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

spectrum of **2g** also exhibited signals for three aromatic protons [δ6.38 and 6.39 (each 1H, ill-resolved *meta*-coupled *d*) and 6.69 (1H, *s*)]. The chemical shifts of these protons and the splitting patterns of their signals are strikingly similar to those of H-6, H-8 and H-1, respectively, of imbricatin (**2a**). The above ^{1}H NMR spectral data of **2g** thus strongly suggested it to be the dimethyl-ether derivative of imbricatin.

The above assumption was also supported by a comparative study of the ^{13}C NMR spectral data of **2g** and imbricatin diacetate (**2h**). Thus, while the δ_c values of C-9, C-10, C-4, C-5, C-8a, C-10a and the oxymethylene carbon of both **2g** and **2h** are almost identical, those of C-1, C-3, C-4a, C-4b, C-6 and C-8 of **2g** are shifted to high-field by 9.7, 1.9, 3.3, 3.9, 7.8 and 6.7 ppm, respectively, compared to the corresponding carbon atoms of **2h** (Table 1). Such high-field shifts of these carbon atoms of **2g** are intelligible only in terms of replacement of the two acetoxy functions at C-2 and C-7 of **2a** by two methoxyl groups at the same positions in **2g**. This also conforms with the methoxyl carbon resonances of the two compounds. The carbon atom of the lone methoxyl group of **2a** and that of one of the three methoxyl functions appearing at relatively low-field positions (*ca* δ_c 60–62) [**2a**: δ_c 61.0; **2g**: δ_c 60.8] correspond to the methoxyl group at C-3 flanked by two *ortho* substituents at C-2 and C-4, while the two additional methoxyl groups in **2g** exhibiting normal carbon resonances at δ_c 55.3 and 56.1 must, therefore, be placed at C-2 and C-7 having *ortho*-hydrogen atom(s). The structure of callosinin is thus established as 2,3,7-trimethoxy-9,10-dihydrophenanthropyran (**2g**). Final confirmation of the structure of **2g** was provided by its formation on methylation of both imbricatin (**2a**) and flaccidin (**2b**) with CH_2N_2.

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 acetone-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 analytical samples were routinely dried over P_2O_5 for 24 hr *in vacuo* and were tested for purity by TLC and MS. Dry Na_2SO_4 was used for drying organic solvents and the petrol used had bp 60–80°.

Isolation of callosin (**1c**), *callosinin* (**2g**), *4-hydroxy-3,5-dimethoxybenzoic acid*, **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **1a** *and* **1b** from A. callosum. 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 2M aq. NaOH soln. 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 residue was chromatographed. The petrol–EtOAc (20:1) eluate afforded a gummy solid

which on rechromatography gave pure **2f** (0.02 g), recrystallized from petrol–EtOAc, mp 86°. The early frs of the petrol–EtOAc (10:1) eluate yielded pure **2b** (0.04 g), recrystallized from petrol–EtOAc, mp 200°. The later frs of the same eluate afforded a solid containing 4-hydroxy-3,5-dimethoxybenzoic acid, **1a**, **1b**, **1c**, **2a** and **2d**. 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°; **2d** (0.03 g), recrystallized from the same solvent mixt. mp 270°; 4-hydroxy-3,5-dimethoxybenzoic acid (0.015 g), amorphous and **1c** (0.05 g), recrystallized from petrol–EtOAc, mp 205°. For **1c**, (Found: C, 70.53; H, 5.81. $C_{16}H_{16}O_4$ requires: C, 70.59, H, 5.88%). IR ν_{max} cm^{-1}: 3400 (OH), 1595, 1500, 1450, 870, 815, 800 (aromatic nucleus). MS *m/z* (rel. int.): 272 $[M]^+$ (100), 257 (70), 243 (16), 242 (8), 229 (15), 214 (10), 197 (12), 169 (6) and 43 (22). Compound **1c** was acetylated with Ac_2O and pyridine in the usual manner to give **1d**, recrystallized from petrol–EtOAc, mp 170°. For **1d**, (Found: C, 67.35; H, 5.57. $C_{20}H_{20}O_6$ requires: C, 67.41; H, 5.62%). UV λ_{max} nm: 216, 278, 295 and 304 (log ε 4.45, 4.17, 4.19 and 4.14). IR ν_{max} cm^{-1}: 1270 and 1755 (OAc), 1610, 895, 832, 810, 750 (aromatic nucleus). MS *m/z* (rel. int.): 356$[M]^+$ (30), 314 (40), 272 (100), 257 (43), 243 (4), 229 (10), 213 (5), 197 (5), 169 (6), 152 (4), 139 (5), 128 (6), 77 (3), 43 (45). ^1H NMR: δ7.91 (1H, *s*, H-5), 6.75 (1H, *s*, H-8), 6.55 (1H, *d*, J = 2 Hz, H-1), 6.53 (1H, *d*, J = 2 Hz, H-3), 3.83 and 3.78 (each 3H, *s*, 2 × OMe), 2.70 (4H, *s*, H_2-9 and H_2-10), 2.27 and 2.24 (each 3H, *s*, 2 × OAc).

Further elution of the main column with petrol–EtOAc (15:1) gave a mixt. of **2c** and **2e**, which on repeated chromatography finally afforded pure **2c** (0.02 g) and **2e** (0.025 g), both as amorphous powders.

Chromatography of the non-acidic fr. afforded in the petrol–EtOAc (30:1) eluate, **2g** (0.2 g), recrystallized from petrol–EtOAc, mp 101°. (Found: C, 72.42; H, 5.99. $C_{18}H_{18}O_4$ requires: C, 72.48; H, 6.04%) IR ν_{max} cm^{-1}: 1620, 1485, 870, 850, 755 (aromatic). MS *m/z* (rel. int.): 298 $[M]^+$ (100), 283, (40), 268 (22), 253 (5), 181 (7), 165 (10), 153 (5), 149 (13), 139 (10), 134 (9).

Isolation of collosin (**1c**) *from* C. flaccida. Air-dried, powdered whole plants (5 kg) were soaked in a MeOH (15 l) for 3 weeks. The MeOH extract was drained, concd under red. pres. to 100 ml, diluted with H_2O (500 ml) and extracted with Et_2O. The Et_2O extract was fractionated into acidic and neutral frs with 2M aq. NaOH soln. 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 residue was then chromatographed. The early frs of the petrol–EtOAc (7:1) eluate on evapn, gave a yellow solid which was triturated with $CHCl_3$, whereupon part of the solid went into soln. Evapn of the $CHCl_3$ soln gave a solid which was chromatographed. The later frs of the petrol–EtOAc (10:1) eluate gave pure **1c** (0.25 g).

Conversion of 6*-methoxycoelonin* (**1b**) *and callosin* (**1c**) *to* **1h**. 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–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 (30:1) eluate in the chromatography of the reaction products of both **1c** and **1b** gave **1h** as a semi-solid mass (0.018 g from **1b** and 0.015 g from **1c**). The later frs of the same eluate in the chromatography of the reaction products of **1c** gave **1i** (0.003 g), also as a semi-solid mass. **1h**: ^1H NMR: δ2.62 (4H, *br si*, H_2-9 and H_2-10), 3.77, 3.81, 3.82 and 3.88 (each 3H, *s*, 4 × ArOMe), 6.36 (1H, *d*, J = 3 Hz, H-3), 6.37 (1H, *d*, J = 3Hz, H-1), 6.67 (1H, *s*, H-8), 7.84 (1H, *s*, H-5). **1i**: ^1H NMR: δ2.62 (4H, *br s*, H_2-9 and H_2-10), 3.77, 3.80, 3.81 (each 3H, *s*, 3 × ArOMe), 5.36 (1H, *s*, disappeared on deuterium exchange, ArOH), 6.34 (1H, *d*, J = 2.7 Hz, H-3), 6.38 (1H, *d*, J = 2.7 Hz, H-1), 6.64 (1H, *s*, H-8), 7.82 (1H, *s*, H-5).

Conversion of **2a** *and* **2b** *to* **2g**. To solns of **2a** (0.02 g) and **2b** (0.02 g) in MeOH (20 ml) was added separately an excess of CH_2N_2–Et_2O (20 ml) and the reaction mixts were kept overnight in an ice-bath. Removal of solvents from both the mixts afforded the same compound, identical to **2g**.

Acknowledgements—We thank Dr J. M. Wilson (University of Manchester, U.K.) for the MS. This work was supported by CSIR and DST, New Delhi, India.

REFERENCES

1. Majumder, P. L. and Ghosal, S. (1994) *Phytochemistry* **33**, 205.
2. Majumder, P. L. and Pal, S. (1993) *Phytochemistry* **32**, 1561.
3. Majumder, P. L. and Sen, R. C. (1991) *Phytochemistry* **30**, 2432.
4. Majumder, P. L. and Maiti, D. C. (1991) *Phytochemistry* **30**, 971.
5. Majumder, P. L. and Basak, M. (1991) *Phytochemistry* **30**, 3429.
6. Majumder, P. L. and Banerjee, S. (1988) *Tetrahedron* **44**, 7303.
7. Majumder, P. L. and Lahiri, S. (1990) *Tetrahedron* **46**, 3621.
8. Majumder, P. L. and Ghosal, S. (1991) *J. Indian Chem. Soc.* **68**, 88.
9. Majumder, P. L. and Pal, S. (1990) *Phytochemistry* **29**, 2717.
10. Gäumann, E. and Kern, H. (1959) *Phytopathol. Z.* **36**, 1.
11. Hardegger, E., Biland, H. R. and Carrodi, H. (1963) *Helv. Chim. Acta* **46**, 1354.
12. Juneja, R. K., Sharma, S. C. and Tandon, J. S. (1987) *Phytochemistry* **26**, 1123.
13. Majumder, P. L. and Sarkar, A. K. (1982) *Indian J. Chem.* **21B**, 829.
14. Majumder, P. L. and Maiti, D. C. (1988) *Phytochemistry* **27**, 899.

15. Majumder, P. L. and Maiti, D. C. (1989) *Phytochemistry* **28**, 887.
16. Majumder, P. L. and Sabzabadi, E. (1988) *Phytochemistry* **27**, 1899.
17. Majumder, P. L., Laha, S. and Dutta, N. (1982) *Phytochemistry* **21**, 478.
18. Letcher, R. M. and Nhamo, L. R. M. (1971) *J. Chem. Soc(C)*, 3070.
19. Majumder, P. L. and Lahiri, S. (1990) *Phytochemistry* **29**, 621.
20. Majumder, P. L., Bandyopadhyay, D. and Joardar, S. (1982) *J. Chem. Soc. Perkin Trans. I*, 1131.