Phytochemistry, Vol. 30, No. 1, pp. 321–324, 1991
Printed in Great Britain.

0031-9422/91 $3.00+0.00

TWO BIBENZYL DERIVATIVES FROM THE ORCHID *CIRRHOPETALUM ANDERSONII*

P. L. MAJUMDER* and MAUSUMI BASAK

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

(*Received in revised form* 27 *February* 1990)

Key Word Index—*Cirrhopetalum andersonii*; Orchidaceae; cirrhopetalidin; cirrhopetalinin; bibenzyl derivatives.

Abstract—Cirrhopetalidin and cirrhopetalinin, two new bibenzyl derivatives, and 3,3′-dihydroxy-5-methoxybibenzyl (batatasin-III) were isolated from the orchid *Cirrhopetalum andersonii*. The structures of the new bibenzyls were established as 2′,3-dihydroxy-3′-methoxy-4,5-methylenedioxybibenzyl and 3,3′-dihydroxy-4,5-methylenedioxybibenzyl, mainly from spectral evidence.

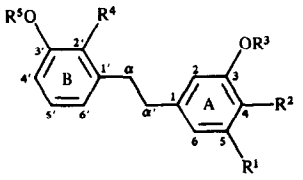
INTRODUCTION

We reported earlier the isolation of 7-hydroxy-4-methoxy-2,3-methylenedioxyphenanthrene (cirrhopetalin) from the orchid *Cirrhopetalum andersonii* [1]. Further chemical investigation of this orchid has now resulted in the isolation of two new bibenzyl derivatives, cirrhopetalidin and cirrhopetalinin, besides the known bibenzyl batatasin-III (**1h**) [2]. The structures of cirrhopetalidin and cirrhopetalinin were established as **1a** and **1f** respectively.

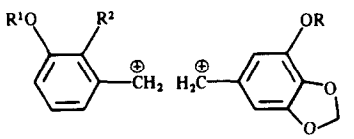
RESULTS AND DISCUSSION

Both cirrhopetalidin (**1a**), $C_{16}H_{16}O_5$ ($[M]^+$ *m/z* at 288), mp 137°, and cirrhopetalinin (**1f**), $C_{15}H_{14}O_4$ ($[M]^+$ *m/z* at 258), mp 130°, showed typical benzenoid UV absorptions [**1a**: λ_{max} 214 and 273 nm (log ε 4.42 and 3.43); **1f**: λ_{max} 247 and 275 nm (log ε 3.32 and 3.47)] similar to those of bibenzyl derivatives [3–5]. The phenolic nature of both the compounds was indicated by colour reactions, alkali-induced bathochromic shifts of their UV maxima and their characteristic IR bands [**1a**: ν_{max} 3400 cm^{-1}; **1f**: ν_{max} 3280 cm^{-1}]. The presence of two phenolic hydroxyl groups in both the compounds was confirmed by the formation of their respective diacetyl derivatives with acetic anhydride and pyridine [cirrhopetalidin diacetate (**1b**), $C_{20}H_{20}O_7$ ($[M]^+$ *m/z* at 372); cirrhopetalinin diacetate (**1g**), $C_{19}H_{18}O_6$ ($[M]^+$ *m/z* at 342)]. Treatment of **1a** with diazomethane gave the monomethyl ether **1c**, $C_{17}H_{18}O_5$ ($[M]^+$ *m/z* at 302), mp 60°, which on treatment with acetic anhydride and pyridine formed the corresponding acetate **1d**, $C_{19}H_{20}O_6$ ($[M]^+$ *m/z* at 344). Cirrhopetalidin dimethyl ether (**1e**), $C_{18}H_{20}O_5$ ($[M]^+$ *m/z* at 316), mp 56°, was, however, obtained by heating **1a** under reflux with MeI in dry acetone in the presence of dry K_2CO_3 for 24 hr.

The ^1H NMR spectra of **1a** and **f** showed signals for two phenolic hydroxyl groups [**1a**: δ4.85 and 5.73 (each 1H, *s*); **1f**: δ4.80 (2H, *s*); each signal disappeared on deuterium exchange], a methylenedioxy group [**1a**: δ5.91 (2H, *s*); **1f**: δ5.83 (2H, *s*)] and four benzylic protons [**1a**: δ2.83 (4H, *m*); **1f**: δ2.76 (4H, *s*)] typical of the bibenzyl derivatives [3–5]. The ^1H NMR spectrum of **1a** also showed signals for an aromatic methoxyl group (δ3.83, 3H, *s*) and five aromatic protons (δ6.36–6.76), while that of **1f** exhibited additional signals for six aromatic protons (δ6.20–6.72). Two of the five aromatic protons of **1a** appeared as a pair of doublets at δ6.36 ($J = 1.4$ Hz) and 6.38 ($J = 1.4$ Hz) indicating that they are *meta* to each other. The above signals of **1a** are shifted downfield by 0.19 and 0.04 ppm respectively in the spectrum of its diacetate (**1b**) suggesting that while the proton of **1a** corresponding to the signal at δ6.36 is *ortho* to a phenolic



1a R^1,R^2 = —OCH_2O—, R^3 = H, R^4 = OH, R^5 = Me
1b R^1,R^2 = —OCH_2O—, R^3 = Ac, R^4 = OAc, R^5 = Me
1c R^1,R^2 = —OCH_2O—, R^3 = R^5 = Me, R^4 = OH
1d R^1,R^2 = —OCH_2O—, R^3 = R^5 = Me, R^4 = OAc
1e R^1,R^2 = —OCH_2O—, R^3 = R^5 = Me, R^4 = OMe
1f R^1,R^2 = —OCH_2O—, R^3 = R^4 = R^5 = H
1g R^1,R^2 = —OCH_2O—, R^3 = R^5 = Ac, R^4 = H
1h R^1 = OMe, R^2 = R^3 = R^4 = R^5 = H
1i R^1 = OMe, R^2 = R^4 = H, R^3 = R^5 = Ac



a *m/z* 137 (R^1 = Me, R^2 = OH) **d** *m/z* 151 (R = H)
b *m/z* 151 (R^1 = Me, R^2 = OMe) **e** *m/z* 165 (R = Me)
c *m/z* 107 (R^1 = R^2 = H)

hydroxyl group, that representing the signal at δ6.38 is possibly *para* to a hydroxyl function. Similarly two of the six aromatic protons of **1f** resonated as a pair of ill-resolved *meta*-coupled doublets at δ6.20 and 6.24, which were shifted to δ6.49 and 6.36, each appearing as a clear doublet with $J = 1.2$ Hz, in the ^{1}H NMR spectrum of its diacetate (**1g**) indicating that the protons corresponding to the above signals of **1f** have an identical structural environment to those corresponding to the signals at δ6.36 and 6.38 of its congener **1a**. The above signals of **1a** and **f** may then be assigned to H-2 and H-6 respectively of a 3-hydroxy-4,5-methylenedioxybenzyl moiety present in both the compounds. This is also supported by the striking resemblance of the chemical shifts and the splitting patterns of the above protons of **1a** and **f** with those of the corresponding protons of the methyl ether derivatives of a few bibenzyls containing identical benzylic moiety reported earlier by Asakawa *et al.* [6]. While the second benzylic moiety of **1a** should contain its remaining three aromatic protons, the lone methoxyl group and the other hydroxyl function, that of **1f** must bear its remaining four aromatic protons and the second hydroxyl group. In the ^{1}H NMR spectrum of **1b**, the remaining three aromatic protons of **1a** resonating at δ6.39–6.76 as an ill-resolved complex multiplet, appeared as three distinct signals at δ6.76 (1H, *d*, $J = 7.9$ Hz), 7.10 (1H, apparent triplet, due to coupling with two adajcent *ortho* protons) and 6.83 (1H, *d*, $J = 8.1$ Hz), which may be assigned to the three consecutive aromatic protons at C-4′, C-5′ and C-6′ respectively of **1b** with the acetoxy group at C-2′ and the methoxy function at C-3′. The signals for the corresponding three aromatic protons of cirrhopetalidin monomethyl ether (**1c**) at δ6.47–6.77 (3H, *m*), likewise, appeared in the spectrum of its acetate (**1d**) at δ6.75 (1H, *br d*, $J = 7.8$ Hz), 7.10 (1H, apparent triplet) and 6.83 (1H, *br d*, $J = 8.1$ Hz), which may, accordingly, be assigned to H-4′, H-5′ and H-6′ respectively of **1d**. These observations thus suggest the presence of a 2-hydroxy-3-methoxybenzylic moiety in both **1a** and **c**. This, in turn, also implies that it is the hydroxyl group at C-2′ of **1a** which does not undergo methylation with diazomethane, presumably due to the steric effect of the two *ortho* substituents (OMe at C-3′ and the benzylic side chain at C-1′). The complex multiplet at δ6.60–6.72 in the ^{1}H NMR spectrum of **1f** representing its remaining four aromatic protons is partially resolved in the spectrum of its diacetate (**1g**) and appeared at δ7.04 (1H, apparent triplet), 6.83–6.86 (2H, *m*) and 6.95 (1H, ill-resolved *d*, $J = 7.8$ Hz). The chemical shifts and the splitting patterns of these protons of **1g** are almost identical with those of the ring-B aromatic protons of batatasin-III diacetate (**1i**) [2] and are also comparable with those of the aromatic protons of the 3-methoxybenzyl residue of a number of bibenzyl derivatives [6, 7]. The above observations thus clearly establish the presence of the same 3-hydroxybenzyl moiety in both **1f** and batatasin-III (**1h**) [2].

The distribution of the oxygen substituents between the two benzene rings of both **1a** and **f** was also ascertained by the mass spectral fragmentations of the compounds and those of **1c** and **e**. Thus, the mass spectra of both **1a** and **f** showed an intense peak at *m/z* 151 (due to the ion-fragment **d**). In the mass spectra of both **1c** and **e**, the above peak was shifted to *m/z* 165 (ion-fragment **e**) indicating that the phenolic hydroxyl group which underwent methylation with diazomethane was the one associated with the ring-A of **1a**. But while the mass spectra of both **1a** and its monomethyl ether (**1c**) exhibited another fairly intense peak at *m/z* 137 (ion-fragment **a**), that of **1f** showed a second peak at *m/z* 107 (ion-fragment **c**). In the mass spectrum of cirrhopetalidin dimethyl ether (**1e**), the peak at *m/z* 137 of **1a** was shifted to *m/z* 151 (ion-fragment **b**).

Structures **1a** and **f** were finally confirmed by the ^{13}C NMR spectral data of **1a–e** and **g** (Table 1). The degree of protonation of the carbon atoms of each compound was determined by DEPT experiments and the assignments of the carbon chemical shifts for each compound were made by comparison with the δ_C values of structurally related compounds [3–5] taking into consideration the known additive parameters of the functional groups. The presence of a methylenedioxy group in each of the above compounds was indicated by the appearance of a methylene carbon signal at *ca* δ_C 101 in the spectrum of each of these compounds. The virtual identity of the δ_C values of the ring-A carbon atoms of **1b** and **g**, which corresponded to those calculated for a 3-acetoxy-4,5-methylenedioxybenzyl moiety, indicated the presence of the above structural unit in both the compounds. Replacement of the acetoxy group of this moiety by hydroxyl function as in **1a**, and by methoxyl group as in **1c–e** resulted in the appropriate shifts of the δ_C values of the *ortho* (C-2 and C-4) and the *para* (C-6) carbon atoms. The δ_C values of the ring-B carbon atoms of **1a** and **c** are also in good agreement with those calculated for a 2-hydroxy-3-methoxybenzyl moiety. The assignments of the above δ_C values of **1a** and **c** were confirmed by the appropriate shifts of the C-1′, C-3′ and C-5′ resonances in **1b** and **d** (due to replacement of hydroxyl at C-2′ by acetoxy function) and in **1e** (due to methylation of the C-2′ hydroxyl group). In the light of the general observation that the carbon atom of an aromatic methoxyl group having at least one *ortho* hydrogen atom resonates at the normal position (*ca* δ_C 55–56) [3–5, 8–11], while that of such a group flanked between two *ortho* substituents are shifted downfield to *ca* δ_C 60–62 [3–5, 12–15], the appearance of the methoxyl carbon signals of **1a–d** at the normal position (δ_C 55–56) indicated the methoxyl group in each of these compounds to be at C-3′ (having an *ortho* hydrogen atom at C-4′) rather than at C-2′ with hydroxyl or acetoxyl group at C-3′. The most convincing proof in support of the placement of a methoxyl group at C-2′ in **1a** was provided by the appearance of one of the methoxy carbons of **1e** at δ_C 60.28, while those of its other two methoxyl groups showing normal resonances at δ_C 55.48 and 56.30. The downfield methoxy carbon signal of **1e** thus corresponds to a methoxyl group at C-2′, which was generated by methylation of a hydroxyl group at the same position in **1a**. The δ_C values of C-α, C-α′, C-1′, C-2′, C-3′, C-4′, C-5′ and C-6′ of **1g** are essentially the same as those of the corresponding carbon atoms of batatasin-III diacetate (**1i**) confirming the structural identity of this part of their molecules. It may be noted that while both the benzylic methylene carbon atoms of **1g** and **i** appeared at the normal positions (*ca* δ_C 36–37), the signal for one of such carbon atoms of each of **1a–e** were shifted upfield by *ca* 5 ppm (the other benzylic methylene carbon atoms of these compounds resonated at the normal positions). The upfield benzylic methylene carbon signals of the above compounds correspond to their C-α, and the observed upfield shifts of the above carbon atoms may be attributed to the steric effects of the substituents at C-2′, which find analogy with similar upfield shifts of C-10 of

Table 1. ^{13}C NMR spectral data of **1a–e, g** and **i**

C	Chemical shifts (δ values)*						
	1a	**1b**	**1c**	**1d**	**1e**	**1g**	**1i**
1	137.16[a]	136.66[b]	136.80	135.94[d]	136.57[f]	137.03	143.68[g]
2	108.47	115.17	107.39	107.40	107.67	115.34	113.73
3	138.72[a]	132.74	143.33[c]	143.15	143.18	132.85	151.45
4	131.9	135.85[b]	133.02	134.43[e]	133.10	135.62	105.17
5	148.50	149.16	148.46	148.53	148.56	149.22	160.24
6	102.15	106.60	102.38	102.09	102.29	106.55	111.76
1′	127.35	134.38[b]	127.25	133.14[c]	135.11[f]	142.97	142.98[g]
2′	143.42	137.99[b]	143.16[c]	137.92[d]	147.04	121.34	121.35
3′	146.23	151.02	146.16	150.93	152.54	150.68	150.65
4′	110.51	110.07	108.37	109.88	110.30	119.04	119.06
5′	119.14	126.18	119.05	125.99	121.77	129.11	129.14
6′	122.23	121.50	122.19	121.49	123.46	125.77	125.81
α	32.04	32.01	32.07	32.18	32.08	37.37	37.33
α′	35.70	35.75	35.90	36.04	36.88	36.99	36.99
$-OCH_2O-$	101.10	101.64	100.94	100.95	100.82	101.61	—
OMe	55.9	55.82	56.25	56.21	60.28	—	55.23
			55.77	55.63	56.30		
					55.48		
OAc		168.84		168.67		167.88	169.32
		168.03		20.28		169.21	20.95
		20.43				20.92	
						20.37	

* The δ values are in ppm downfield from TMS: $\delta_{(TMS)} = \delta_{(CDCl_3)} + 76.9$ ppm.
[a–g] Values are interchangeable.

coelogin and coeloginin diacetate [15] caused by methoxyl substituent at C-1 and that of C-9 of confusarin diacetate and confusridin by methoxyl group at C-8 [14].

EXPERIMENTAL

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

Isolation of cirrhopetaldin (**1a**), *cirrhopetalinin* (**1f**) *and batatasin-III* (**1h**). Air-dried powdered whole plant of *Cirrhopetalum andersonii* (2 kg) was kept soaked in MeOH (7 l) for 3 weeks. The MeOH extract was then drained out, concd under red. pres. to *ca* 100 ml, diluted with H_2O (500 ml) and extracted with Et_2O. The ether extract was fractionated into acidic and nonacidic fractions with 2 M aq. NaOH soln. The aq. alkaline soln was acidified with conc. HCl in the cold and the liberated solid was extracted with Et_2O, washed with H_2O, dried and the solvent removed. The residue was chromatographed. The petrol–EtOAc (20:1) eluate gave cirrhopetalin (0.12 g), crystallized from petrol–EtOAc, mp 142°. The petrol–EtOAc (15:1) eluate gave **1a** (0.2g), crystallized from petrol–EtOAc mixt., mp 137°. (Found: C, 66.55; H, 5.61. $C_{16}H_{16}O_5$ requires: C, 66.60; H, 5.55%), UV (EtOH–0.1 M NaOH); λ_{max} 224 and 290 nm (log ε 4.44 and 3.59); IR ν_{max} cm^{-1}: 3400 (OH), 1628, 1590, 850, 830, 809, 780, 740 and 730 (aromatic nucleus); MS *m/z* (rel. int.): 288 ($[M]^+$, 64), 152 (43), 151 (100), 137 (64), 122 (20), 121 (18), 94 (17), 77 (19), 65 (24) and 53 (44). Acetate (**1b**) semisolid (Found: C, 64.38; H, 5.41. $C_{20}H_{20}O_7$ requires: C, 64.50; H, 5.30%). UV λ_{max} nm: 212, 264, 280 and 321 (log ε 4.42, 3.40, 3.35 and 2.51); IR ν_{max} cm^{-1}: 1280 and 1770 (OAc), 1635, 1610, 1590, 890, 840, 820, 790 and 750 (aromatic nucleus); ^1H NMR: δ2.29 and 2.34 (each 3H, *s*; 2 × OAc), 2.69 (4H, complex multiplet; H_2-α and H_2-α′), 3.81 (3H, *s*; ArOMe), 6.37 (2H, *s*; $-OCH_2O-$), 6.42 (1H, *br s*; H-2), 6.55 (1H, *br s*; H-6), 6.76 (1H, *br d*, J = 7.8 Hz; H-4′), 6.83 (1H, *br d*, J = 8.1 Hz; H-6′) and 7.10 (1H, apparent triplet; H-5′). Dimethylether **1c** crystallized from petrol–EtOAc, mp 60° (Found: C, 67.47; H, 6.11. $C_{17}H_{18}O_5$ requires: C, 67.54; H, 5.96%). IR ν_{max} cm^{-1}: 3400 (OH), 1630, 1510, 890, 830, 815, 800 and 775 (aromatic nucleus). ^1H NMR: δ2.89 (4H, *br m*, H_2-α and H_2-α′), 3.80 (6H, *s*, 2 × ArOMe), 5.71 (1H, *s*, ArOH), 5.94 (2H, *s*, $-OCH_2O-$), 6.30 (1H, *br s*, H-2), 6.39 (1H, *br s*, H-6), 6.47–6.77 (3H, *m*, H-4′, H-5′ and H-6′); MS *m/z* (rel. int.): 302 ($[M]^+$, 15), 165 (100), 137 (85), 122 (46), 120 (60), 94 (42), 92 (59), 79 (50), 77 (80) and 64 (46). Dimethyl ether acetate (**1d**) semisolid (Found: C, 66.20; H, 5.87. $C_{19}H_{20}O_6$ requires: C, 66.27; H, 5.81%). IR ν_{max} cm^{-1}: 1750 and 1220 (OAc), 1630, 1510, 845, 830, 825, 810 and 780 (aromatic nucleus). ^1H NMR: δ2.35 (3H, *s*, OAc), 2.77 (4H, *s*, H_2-α and H_2-α′), 3.81 and 3.84 (each 3H, *s*, 2 × ArOMe), 5.91 (2H, *s*, $-OCH_2O-$), 6.29 (1H, *br s*, H-2), 6.38 (1H, *br s*, H-6), 6.75 (1H, *br d*, J = 7.8 Hz; H-4′), 6.83 (1H, *br d*, J = 8.1 Hz; H-6′) and 7.10 (1H, apparent triplet; H-5′). Trimethyl ether (**1e**), crystals from petrol–EtOAc (30:1), mp 56°. (Found: C, 68.23; H, 6.40. $C_{18}H_{20}O_5$ requires: C, 68.35; H, 6.32%). IR - ν_{max} cm^{-1}: 1630, 1500, 840, 825, 810 and 785 (aromatic nucleus); MS *m/z* (rel. int.): 316 ($[M]^+$, 61), 165 (100), 151 (26), 136 (26) and 91 (23).

Elution of the main column with petrol–EtOAc (10:1) gave a mixt. of **1f** and **1h**. Repeated chromatography of the mixt. gave in the early fractions of the petrol–EtOAc (12:1) eluate **1h** (0.08 g) as a semisolid mass. The UV, IR, ^{1}H and ^{13}C NMR and mass spectral data of the compound and its diacetate compared excellently with those reported for batatasin-III and its diacetate respectively establishing their identity, although direct comparison could not be made due to non-availability of authentic samples. The ^{13}C NMR spectral data of the diacetate **1i** is reported here for the first time.

The later fractions of the above chromatography afforded pure **1f** (0.07 g), crystallized from petrol–EtOAc, mp 130°. (Found: C, 69.65, H, 5.50. $C_{15}H_{14}O_4$ requires: C, 69.70; H, 5.42%). UV (EtOH–0.1 M NaOH): λ_{max} 253 and 291 nm (log ε 3.54 and 3.61); IR ν_{max} cm^{-1}: 3280 (OH), 1600, 1520, 860, 840, 820 and 780 (aromatic nucleus); MS m/z (rel int.): 258 ([M]$^+$, 8), 152 (21), 151 (100), 121 (4), 107 (4), 77 (12), 65 (13) and 53 (37). Acetate (**1g**) semisolid (Found: C, 66.67; H, 5.14. $C_{19}H_{18}O_6$ requires: C, 66.60; H, 5.20%). UV λ_{max} nm: 246 and 279 (log ε 3.50 and 3.54); IR ν_{max} cm^{-1}: 1275 and 1758 (OAc), 1602, 1582, 880, 856, 835, 806 and 788 (aromatic nucleus); ^{1}H NMR: δ 2.22 (6H, *s*, 2 × OAc), 2.78 (4H, *m*, H_2-α and H_2-α'), 5.89 (2H, *s*, $-OCH_2O-$), 6.36 (1H, *br s*, H-6), 6.49 (1H, *d*, J = 1.2 Hz; H-2), 6.83–6.86 (2H, *m*, H-2′ and H-4′), 6.95 (1H, *m*, H-6′) and 7.21 (1H, apparent triplet; H-5′).

Acknowledgements—We thank Dr J. M. Wilson (University of Manchester, U.K.) for the MS and Prof. W. Kraus (University of Hohenheim Stuttgart, F.R.G.) for the ^{13}C NMR spectrum of **1a**. The work was supported by CSIR, New Delhi, India.

REFERENCES

1. Majumder, P. L. and Basak, M. (1990) *Phytochemistry* **29**, 1002.
2. Sachdev, K. and Kulshreshtha, D. (1986) *Phytochemistry* **25**, 499.
3. Majumder, P. L. and Joardar, M. (1984) *Indian J. Chem.* **23B**, 1040.
4. Majumder, P. L. and Sen, R. C. (1987) *Phytochemistry* **26**, 2121.
5. Majumder, P. L. and Chatterjee, S. (1989) *Phytochemistry* **28**, 1986.
6. Asakawa, Y., Takikawa, K. and Tori, M. (1987) *Phytochemistry* **26**, 1023
7. Asakawa, Y., Matsuda, R. and Cheminat, A. (1987) *Phytochemistry* **26**, 1117.
8. Majumder, P. L., Laha, S. and Datta, N. (1982) *Phytochemistry* **21**, 478.
9. Majumder, P. L. and Banerjee, S. (1988) *Tetrahedron* **44**, 7303.
10. Majumder, P. L. and Sen, R. C. (1987) *Indian J. Chem.* **26B**, 18.
11. Majumder, P. L. and Lahiri, S. (1990) *Phytochemistry* **29**, 621.
12. Majumder, P. L. and Joarder, M. (1985) *Indian J. Chem.* **24B**, 1192.
13. Bhandari, S. R., Kapadi, A. H., Majumder, P. L., Joardar, M. and Shoolery, J. N. (1985) *Phytochemistry* **24**, 801.
14. Majumder, P. L. and Kar, A. (1987) *Phytochemistry* **26**, 1127.
15. Majumder, P. L., Bandyopadhyay, D. and Joarder, S. (1982) *J. Chem. Soc. Perkin Trans I* 1131.