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BIBENZYLS AND PHENANTHRENOIDS OF SOME SPECIES OF ORCHIDACEAE

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Key Word Index—Orchidaceae; bibenzyls; batatasin-III; 9,10-dihydrophenanthropyrans; flavidin; coelogin; imbricatin; flaccidin; pyrones; coeloginin.

Abstract—In a survey of 26 species from nine genera of the Orchidaceae, batatasin-III was found to be the most common constituent in the subtribes *Coelogyninae, Dendrobiinae, Bulbophyllinae* and *Bletiinae* and absent in other subtribes *Laeliinae* and *Sarcanthinae*. Coelogin, coeloginin and flavidin along with batatasin-III were found only in *Coelogyninae*. The morphological heterogenetic character of the Orchidaceae is revealed from the chemical constituents isolated.

INTRODUCTION

Orchids constitute the largest family of the flowering plants (Orchidaceae of Monocotyledons) containing *ca* 22 000 to 35 000 species belonging to 700 to 800 genera [1]. The present classification is arranged according to the system of Dressler [2].

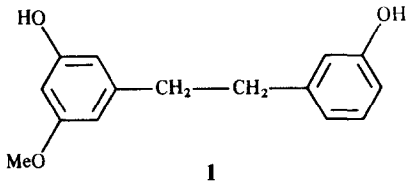
Earlier chemical investigations of the orchid family dealt with the alkaloid constituents and flower pigments in the species of ornamental value. A number of physiologically active alkaloids such as dendrobine and its structural analogues were isolated from the genus *Dendrobium* [3–6]. The species from *Coelogyne, Pholidota,* and *Otochilus* (subtribe *Coelogyninae*) yielded a number of 9,10-dihydro-5H phenanthro-(4,5*bcd*)-pyrans and pyrones [7–12]. The present paper deals with the chemical examination of 26 species of orchids mainly belonging to *Dendrobium* and *Coelogyne*. Two species each of *Bulbophyllum* and *Aerides* and one each of *Pholidota, Anthogonium, Arundina, Calanthe* and *Epidendrum* were also examined for their chemical constituents.

RESULTS AND DISCUSSION

The distribution of the 9,10-dihydrophenanthropyrans and pyrones and batatasin-III (**1**) identified from the 26 species is given in Table 1.

Batatasin-III (**1**), which was known to induce dormancy [13], was identified and isolated from the four subtribes namely *Coelogyninae, Dendrobiinae, Bulbophyllinae* and *Bletiinae* (except *Arundina bambusifolia*) and absent in the other subtribes *Laeliinae* and *Sarcanthinae*.

Coelogin (**3**), coeloginin (**4**) and flavidin (**2**) were found mainly in the subtribe *Coelogyninae* and absent in other subtribes. Flavidin (**2**) was found only in *Dendrobium pierardii* (*Dendrobiinae*) and *Bulbophyllum fuscopurpureum* (*Bulbophyllinae*) outside *Coelogyninae* in our study.



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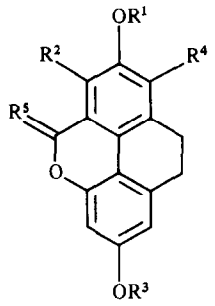

2 $R^1 = R^2 = R^3 = R^4 = H, R^5 = H_2$
3 $R^1 = Me, R^2 = OH, R^3 = H, R^4 = OMe, R^5 = H_2$
4 $R^1 = Me, R^2 = OH, R^3 = H, R^4 = OMe, R^5 = O$
5 $R^1 = R^3 = R^4 = H, R^2 = OMe, R^5 = H_2$
6 $R^1 = Me, R^2 = OH, R^3 = R^4 = H, R^5 = H_2$

Imbricatin (**5**) and flaccidin (**6**) were found in some species of the three subtribes *Coelogyninae, Dendrobiinae* and *Bulbophyllinae* and absent in other subtribes. The distribution of these compounds in the species might be useful in chemotaxonomic classification.

The morphologically heterogenous nature of the *Orchidaceae* having both advanced and primitive characters in a single species [14] was reflected in the heterogenous distribution of the six compounds. A single family pattern could not be easily distinguished. The subtribes *Coelogyninae, Dendrobiinae* and *Bulbophyllinae* were closely related, not only in morphological characters, but

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Table 1. Distribution of 9,10-dihydrophenanthrene derivatives

No. Taxa (Wt of dried plant)	**1**	**2**	**3**	**4**	**5**	**6**
1. *Dendrobium densiflorum* (450 g)	+† (15 mg)	—	—	—	—	—
2. *D. chrysanthum* (420 g)	+† (16 mg)	—	—	—	—	—
3. *D. graminifolium** (255 g)	+ (8 mg)	—	—	—	—	—
4. *D. lituiflorum** (225 g)	+ (9 mg)	—	—	—	—	—
5. *D. terminale** (90 g)	+ (3.5 mg)	—			—	—
6. *D. amoenum* (650 g)	+† (25 mg)	—	—	—	+† (68 mg)	+† (20.2 mg)
7. *D. nobile* (70 g)	+† (2.5 mg)	—	—	—	—	—
8. *D. herbaceum** (310 g)	+ (7.2 mg)	—	—	—	+ (10.5 mg)	—
9. *D. pierardii* (70 g)	+† (3.3 mg)	+† (5 mg)	—	—	—	—
10. *D. spathaceum** (145 g)	+ (2 mg)	—	—	—	—	—
11. *Bulbophyllum fuscopurpureum** (150 g)	+ (8.1 mg)	+ (4.5 mg)	—	—	+ (7.5 mg)	—
12. *B. guttulatum** (124 g)	+ (2.3 mg)	—	—	—	—	+ (13 mg)
13. *Coelogyne corymbosa* (325 g)	+† (7.3 mg)	—	+† (13 mg)	—	—	—
14. *C. odorotissima** (145 g)	+ (6.2 mg)	—	—	—	—	—
15. *C. elata* (750 g)	+† (17.2 mg)	+† (42.5 mg)	—	—	—	—
16. *C. flaccida* (165 g)	+† (2.2 mg)	—	—	—	+ (3.2 mg)	+ (2.3 mg)
17. *C. barbata** (145 g)	+ (43 mg)	+ (4 mg)	+ (4.3 mg)	—	—	—
18. *C. ochracea* (2000 g)	+† (22 mg)	+† (7 mg)	+ (28 mg)	+ (17.2 mg)	—	—
19. *C. nitida** (1110 g)	+ (19.2 mg)	+ (18 mg)	+ (20 mg)	—	+ (7.2 mg)	+ (4.2 mg)
20. *Pholidota imbricata* (90 g)	+† (9 mg)	+† (6.5 mg)	—	—	+ (14.5 mg)	—
21. *Anthogonium gracile** (110 g)	+ (4.5 mg)	—	—	—	—	—
22. *Arundina bambusifolia** (65 g)	—	—	—	—	—	—
23. *Epidendrum radicans** (55 g)	—	—	—	—	—	—
24. *Calanthe masuca** (70 g)	+ (2 mg)	—	—	—	—	—
25. *Aerides crispum** (45 g)	—	—	—	—	—	—
26. *A. cylindricum** (90 g)	—	—	—	—	—	—

1: Batatasin-III; **2**: flavidin **3**: coelogin **4**: coeloginin **5**: imbricatin **6**: flaccidin.

* First chemical examination.

† First report in the plant.

Table 2 Plant materials

Species	Locality	Date of Collection	Collector & herbarium No.
Sub family: Epidendroideae			
Epidendroid orchids			
Tribe: Dendrobieae			
Subtribe: Dendrobiinae			
1. *Dendrobium densiflorum* wall.	Gangtok Sikkim	22–10–1985	6†
2. *D. chrysanthum* Wall.	Mangan Sikkim	23–10–1985	7†
3. *D. graminifolium* Wt.	Naduvattam Ooty	25–2–1986	16*
4. *D. lituiflorum* Ldl.	Ooty	25–2–1986	17*
5. *D. terminale* Par and Rchb. F.	Ooty	25–2–1986	18*
6. *D. amoenum* Wall.	Gangtok Sikkim	26–4–1986	42†
7. *D. nobile* Ldl.	Gangtok Sikkim	26–4–1986	43†
8. *D. herbaceum* Ldl.	Naduvattam Ooty	27–4–1986	46*
9. *D. pierardii* Roxb.	Saramsa Sikkim	23–5–1987	81*
10. *D. spathaceum* Ldl.	Mangan Sikkim	25–5–1987	83*
Subtribe: Bulbophyllinae			
11. *Bulbophyllum fuscopurpureum* Wt.	Ooty	26–2–1986	22*
12. *B. quttulatum* Hook, F.	Ooty	26–2–1986	23*
Tribe: Coelogyneae			
Subtribe: Coelogyninae			
13. *Coelogyne corymbosa* Ldl.	Naduvattam Ooty	26–2–1986	24*
14. *C. odorotissima* Ldl.	Naduvattam Ooty	26–2–1986	25*
15. *C. flaccida* Ldl.	Naduvattam Ooty	26–2–1986	26*
16. *C. elata* Ldl.	Gangtok Sikkim.	27–4–1986	44†
17. *C. barbata* Griff.	Saramsa Sikkim.	27–4–1986	45†
18. *C. ochracea* Ldl.	Gangtok Sikkim.	24–5–1987	82*
19. *C. nitida* Ldl.	Mangan Sikkim.	25–5–1987	84*
20. *Pholidota imbricata* Ldl.	Saramsa Sikkim.	27–4–1986	46†
Tribe: Epidendreae			
Subtribe: Laeliinae			
21. *Epidendrum radicans* Pavon ex Ldl.	Ooty	26–2–1986	27*
Tribe: Arethuseae			
Subtribe: Bletiinae			
22. *Anthogonium gracile* Ldl.	Saramsa Sikkim	23–10–1985	8†
23. *Arundina bambusifolia* Ldl.	Saramsa Sikkim	23–10–1985	9†
24. *Calanthe masuca* Ldl.	Ooty	25–2–1986	19*
Vandoid orchids			
Tribe: Vandeae			
Subtribe: Sarcanthinae			
25. *Aerides crispum* Ldl.	Ooty	25–2–1986	20*
26. *A. cylindricum* Ldl.	Ooty	25–2–1986	21*

* Collected by P. Veerraju.
† Collected by P. R. Mohana Rao.

also in chemical characters as revealed by the presence of batatasin-III (1) as a common chemical constituent in all species examined in our laboratory. Phenanthrene derivatives were found only in *Dendrobium amoenum*, *D. herbaceum* and *D. pierardii* among *Dendrobiinae* species. *Coelogyninae* and *Bulbophyllinae* exhibited advanced characters as shown by the presence of advanced phenanthrene derivatives. Batatasin-III (1) or its derivatives were considered as biosynthetic precursors to phenanthrenes [15]. The difference between the *Epidendroid* and *Vandoid* orchids was also indicated by the presence of batatasin-III (1) and phenanthrene derivatives in the former and absence in the latter. The combination of 9,10-dihydrophenanthropyrans and pyrones in specific species and the common occurence of batatasin-III (1) in *Coelogyninae*, *Dendrobiinae* and *Bulbophyllinae* appears to be a remarkable distinguishing character in *Orchidaceae*. The presence and co-occurrence of phenanthropyrans and pyrones was not reported in any other family of the plant kingdom.

Out of 26 species, 16 species were examined for the first time for their chemical constituents. The remaining eight species showed the presence of some more phenanthrene derivatives which has not been previously reported (Table 1).

EXPERIMENTAL

Mps: uncorr. Silica gel (100–200 mesh) was used for CC and silica gel-G for TLC. ^{1}H NMR spectra were recorded at 100 and 90 MHz; ^{13}C NMR spectra at 67.89 MHz.

Plant materials. The plant materials were collected from various places of Sikkim (Eastern Himalayas) and Ooty (South India) shown in Table 2. Voucher specimens have been deposited in the Botany Department of Nagarjuna University.

Isolation and identification. The plant materials were allowed to dry in shade after which the materials were powdered. The powdered materials (50–2000 g) were extracted with *n*-hexane, Me_2CO, EtOH, and EtOH–HOAc (9:1). The above compounds were isolated from the Me_2CO extracts of various plants using chromatographic techniques. They were independently identified with the help of spectral data and chemical degradative methods and direct comparison with authentic samples.

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