G along with further quantities of substances D and F.

TABLE 1—SUBSTANCES ISOLATED FROM *B. grandiflora*

Sl. No.	Compounds	Molecular formula	m.p. °C	Yield† percentage
1.	Substance A (*n*-Hentriacontane)	$C_{31}H_{64}$	64	0.141
2.	Substance B (*n*-Triacontane)	$C_{30}H_{62}$	66	0.026
3.	Substance C (Palmitic acid)	$C_{16}H_{32}O_2$	61	0.013
4.	Substance D (β-sitosterol)	$C_{29}H_{50}O$	135	0.050
5.	Substance E (Linoleic acid)	$C_{18}H_{32}O_2$	202(BP)*	0.032
6.	Substance F (Ursolic acid)	$C_{30}H_{48}O_3$	283	0.108
7.	Substance G (β-sitosterol-β-D-glucopyranoside)	$C_{35}H_{60}O_6$	301(d)	0.031

† Based on the weight of dry plant material
* Yellowish viscous liquid

Characterisation of the substances A-G was based on physical data (uv, ir, nmr and mass spectra) and formation of acetyl and methyl ester derivatives, wherever possible.

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Occurrence of 2,7-Dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene in *Coelogyne ovalis*, A High Altitude Himalayan Orchid : Application of C-13 NMR Spectroscopy in Structure Elucidation

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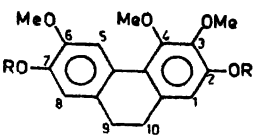
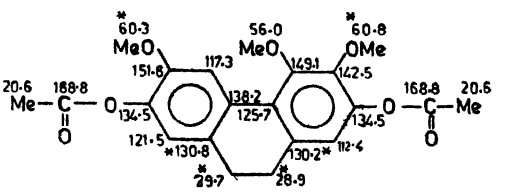
THE isolation of physiologically active alkaloids like dendrobine and a number of its structural analogues from the orchid *Dendrobium nobile*[1,2] prompted us to undertake systematic chemical investigation of a series of high altitude Himalayan orchids. In this communication we report the characterisation of the title compound (1a) isolated from one of these orchids, *Coelogyne ovalis*.

Air-dried powdered whole plant of *C. ovalis* (1 kg) was exhaustively extracted with chloroform in a soxhlet apparatus. The concentrated chloroform extract was chromatographed over silica gel. The petrol-ethylacetate (5 : 1) eluate afforded a crude phenolic mass which was taken in ether and extracted with 1*N* NaOH solution. The aqueous alkaline solution was acidified with HCl in the cold and the liberated solid was extracted with ether, dried and the solvent removed. The residue on repeated chromatography over silica gel gave a pure compound, $C_{17}H_{18}O_5$ ($M^{\cdot+}$302), m.p. 109°, crystallised from petrol-benzene mixture. With Ac_2O and pyridine it formed a diacetyl derivative, $C_{21}H_{22}O_7$ ($M^{\cdot+}$ 386), m.p. 107°. The physical constants and the spectral data (uv, ir, pmr and mass) of the coelogyne-phenol and its diacetate compare excellently with those reported[3] for 1a isolated from the heart-wood of *Combretum psidioides* and its diacetyl derivative (1b) respectively. Since a direct comparison was not possible due to non-availability of authentic samples of 1a and 1b, further evidence was sought to confirm the structure



1a : R=H, 1b : R=Ac

of the coelogyne-phenol. The compound was heated in a sealed tube filled with nitrogen, with D_2O/KOBu^t for 70 hr. The ^{1}H-nmr spectrum of the product was identical with that of the parent compound except that the integrated areas of the aromatic proton signals at δ 6.55 (H-1) and 6.70 (H-8) were reduced to about 65% and 50% respectively, contrary to complete disappearance of these signals as reported[3] earlier for 1a. The MS of the reaction mixture showed molecular ions at m/e 302 and 304. This observation is in conformity with the structure 1a for coelogyne-phenol.



1b

Further confirmation of the structure of the compound was made by ^{13}C-nmr spectral analysis of its diacetyl derivative. The carbon shifts and the degree of protonation of the carbons were determined by the proton-noise decoupled (NDC) and the single frequency off-resonance (SFORD) spectra, respectively of 1b. Excepting C–3, C–4 and C–5, the carbon shifts (the carbon shifts were measured using the relationship $^{\delta}$TMS = $^{\delta}$CDCl$_3$ + 76.9 ppm

and those having close values as marked with asterisk are interchangeable) of 1b as portrayed in its structure are in good agreement with the values calculated by using the known additivity parameters of the functional groups on the reported carbon shifts of the 9,10-dihydrophenanthrene[4]. The observed downfield shift of C−3 and C−4 by ~9 ppm is characteristic[5] of adjacent aromatic carbons bearing oxygen functions. The downfield shift of C−5 by ~9 ppm may be attributed to the proximity of the C−4 methoxyl group. This constitutes the first report of the application of ^{13}C-nmr spectroscopy in the structure elucidation of the naturally occurring 9, 10-dihydrophenanthrene derivative and the diagnostic features that are revealed may be used for future structural studies of this group of natural products.

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O-(N-α-Pyrrolideneimino)Benzene Sulphonic Acid as an Analytical Reagent for Estimation of V(V)

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A number of organic reagents[1,2] have been suggested for gravimetric estimation of vanadium(V). The present work is undertaken with the aim to introduce a new reagent, *o*-(N-α-Pyrrolideneimino)-benzene sulphonic acid (H_2PB), for gravimetric estimation of vanadium(V). The vanadium(V)-complex is insoluble in water and can form the basis of a quantitative separation procedure. H_2PB, prepared by the method already reported[3,4], (m.p. 172°) gives a rose red precipitate with V(V) in the *p*H range 3.2-4.0.

Experimental

1% ethanolic solution of H_2PB was used as the reagent. VO_2NO_3 was standardised gravimetrically[5]. All chemicals used were of A.R. grade.

Determination of vanadium(V): An aliquot of the vanadium solution [25 to 55 mg of V(V)] was diluted to about 125 ml with distilled water, *p*H was adjusted between 3.2-4.0 with $HClO_4$ and NH_4OH and heated at 40°-50°. The reagent solution was added gradually with stirring till precipitation completed. It was heated on a water-bath for ½ hr and allowed to stand for 2-3 hrs when a granular precipitate formed. It was filtered through a weighed sintered-glass crucible (porosity 4), washed successively with warm water and 10% alcohol until free from the reagent. The complex was dried to a constant weight at 100-110° in a vacuum desiccator, cooled and weighed as $[VO_2(C_{11}H_8N_2SO_3)(H_2O)]$. The operation was repeated several times using different quantities of V(V) solutions and results obtained are summarized in Table 1.

Table 1—Determination of Vanadium

Wt. of complex (mg)	Vanadium (mg)		Error %
	Calcd.	Found	
181.6	26.53	26.45	−0.30
241.0	35.21	35.14	−0.19
279.4	40.82	40.92	+0.24
306.5	44.78	44.69	−0.20
340.7	49.78	49.89	+0.22

The complex was soluble in concentrated mineral acids, alkalies, dioxan and DMF.

The thermogravimetric analysis of the precipitate indicated a weight lose at 120°-180° corresponding to a water molecule. On further heating a gradual loss in weight due to slow decomposition of the complex was observed. On heating between 380-440°, a sudden loss in weight was recorded and V_2O_5 obtained as the end product.

Effect of foreign ions: In order to assess possible analytical applications of the reagent effect of some ions which often accompanied vanadium was studied.

The interference due to salts of foreign ions was removed in most of the cases by working at controlled *p*H. In V(V) determination in the *p*H range 3.2-4.0, anions like CH_3COO^-, Cl^-, Br^-, I^-, NO_3^- and SO_4^{2-}-did not interfere.

For 0.1 mg of V(V) solution, the tolerence limit was 25 mg for Be(II), Mn(II), Co(II), Cr(II), Cd(II), Zn(II); 10-15 mg for U(VI), Zr(IV), Th(IV) and Sc(III) and 5 mg for Pt(IV). The Fe(III), Ni(II)