Dionysia are so far very uniform and do not as yet give any indication of correlations with phylogeny in the genus.

In the previous paper on the flavonoids of the Primulaceae,[4] the provisional identification of the rare farina constituent, primetin (5,8-dihydroxyflavone) in *P. chionantha* was mentioned. This identification has now been fully confirmed (see Experimental) by means of direct comparison with natural material from *P. modesta*[5] and with a synthetic sample.[6]

EXPERIMENTAL

Plant material. Plant material was provided by Professor P. Wendelbo or Mr. J. C. Archibald (as indicated in Table 1) and identified by them. It was supplied as fresh material, except for *D. microphylla*, which was dried leaves and flowers, collected by P. W. in Afghanistan from plants growing at Maimana, Darrah Abdullah near Belcheragh. Voucher specimens are held by Professor Wendelbo.

Flavonoid identifications. Flavonoids were identified in leaf, flower or farina by methods outlined earlier.[4] Hirsutin was identified in flowers of *D. microphylla* by direct chromatographic and spectral comparison with an authentic sample from *P. capitata* flowers.[4] It was further identified by acid hydrolysis to give hirsutidin. Due to shortage of material it could only be identified in flowers of the other three *Dionysia* species by chromatographic comparison and by its colour properties.

Primetin (5,8-dihydroxyflavone) was identified in the farina of *P. chionantha* (cf. Ref. 4) by direct comparison with both a natural specimen supplied by Professor Hattori and a synthetic specimen supplied by Professor W. Baker. Material from all three sources had the following properties: λ_{max} in EtOH 282, 366, in EtOH–$AlCl_3$, 296, 360, and in EtOH–NaOEt, 290, 350 nm; R_f 0·76 on SiO_2 in 10% HOAc in $CHCl_3$, 0·68 on SiO_2 in 45% EtOAc in C_6H_6, 0·91 on paper in *n*-BuOH–HOAc–H_2O (4:1:5) and 0·24 in 15% HOAc; yellow in visible light, dull brown in u.v. light, immediate blue with Folin Ciocalteu reagent. Primetin differed in R_f, colour and/or spectral maxima from a number of other simple flavones examined at the same time, including 5-, 6-, and 7-monohydroxyflavone, 5,6-, 7,8- and 3,4′-dihydroxyflavone and 5-hydroxy-8-methoxyflavone.

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PROTEACEAE

METHYL (*p*-HYDROXYBENZOYL) ACETATE AND AN ALKALOID, BELLENDINE, FROM *BELLENDENA MONTANA*

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Abstract—The previously unreported methyl (*p*-hydroxybenzoyl) acetate, and the first alkaloids from the Proteaceae, have been isolated from the flowers of *Bellendena montana*. The major alkaloidal constituent, bellendine, was obtained crystalline and characterized spectroscopically.

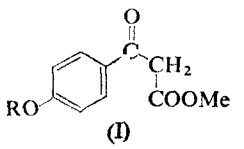
INTRODUCTION

THE MONOTYPIC *Bellendena montana*, an endemic Tasmanian proteaceous shrub abundant on mountain plateaux,[1] first attracted our attention in a survey of the local flora for the presence of alkaloids. The flowers of this plant gave a relatively strong Mayer's test for alkaloids and in view of the complete lack of reports of alkaloids in the Proteaceae,*[,3,4] detailed phytochemical work was initiated. We now wish to report the preliminary results of this work.

RESULTS AND DISCUSSION

Extraction of the fresh flowering heads with Prollius solution[4] and subsequent fractionation by standard methods, gave a crude basic fraction which contained both non-alkaloidal and alkaloidal material.

From the non-alkaloidal material a colourless, crystalline compound, m.p. 83–84°, was isolated. The high-resolution mass spectrum of this compound indicated the molecular formula $C_{10}H_{10}O_4$, a base peak from loss of $C_3H_5O_2$, and other prominent peaks due to loss of $C_3H_4O_2$ and CH_3O. The i.r. spectrum showed two of the oxygens to be in an ester group (ν_{max} 1740 cm^{-1}), and the other two in hydroxy and carbonyl groups (3300 and 1670 cm^{-1}). A *para*-disubstituted benzene ring was suggested by absorption bands at 1600, 1570, 1507, 1430 and 825 cm^{-1}. The latter deduction was supported by the aromatic proton absorptions (τ 2·62, q, 4H, J 9 Hz) in the NMR spectrum which also showed that the compound was a methyl ester (τ 6·28, s, 3H), and suggested a β-keto ester structure for it, with an unsubstituted α-methylene group (τ 6·02, s, 2H). An exchangeable proton singlet at τ 8·4 was assigned to a phenolic hydroxyl group. The u.v. spectrum in water showed absorption maxima at 209 and 272 nm (ϵ_{max} 8878 and 10,940) and on addition of alkali, the latter band shifted to 328 nm. A bathochromic shift of this order suggested a *p*-hydroxyphenone chromophore on the basis of Scott's Rules,[5] the calculated values being 271 nm and 324 nm respectively. The structure which is uniquely consistent with the above data is methyl (*p*-hydroxybenzoyl) acetate (I, R=H). While (I, R=H) has not been recorded previously, it has been suggested[6] as a precursor in the biosynthesis of coumarins and chromones. Methylation of (I, R=H) gave the known[7] methyl ether (I, R=CH_3).



(I)

TLC analysis (silica gel, $CHCl_3$–10% methanol) of the alkaloidal material from the original basic fraction indicated the presence of at least three alkaloids of R_f 0·62, 0·48

* Four other proteaceous plants were reported to give positive tests, but no alkaloids have been isolated.[2,3]

[1] W. M. CURTIS, *Student's Flora of Tasmania*, Part 3, p. 600, Tasmanian Government Printer, Hobart (1967).
[2] L. J. WEBB, Bulletin Nos. 241 and 268 (CSIRO Melbourne, 1949 & 1952), p. 40 and p. 70.
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[5] A. I. SCOTT, *Interpretation of the Ultraviolet Spectra of Natural Products*, p. 109, Pergamon Press, Oxford (1964).
[6] T. A. GEISSMAN, in *Biogenesis of Natural Compounds*, (edited by P. BERNFELD) 2nd edn., p. 790, Pergamon Press, Oxford (1967).
[7] *Beilsteins Handbuch der Organischen Chemie*, Suppl. I, Vol. X, p. 462. Verlag von Julius Springer, Berlin (1932).

and 0·46. The major alkaloid (R_f 0·48) which we have named bellendine, was isolated as colourless needles, m.p. 162–163°, in 0·0013 per cent yield (fr. wt.), while the other two alkaloids were obtained as oils. A high-resolution mass spectrum of bellendine revealed the formula $C_{12}H_{15}NO_2$, and indicated the ready loss of an ethyl group (base peak). The characteristic features of the NMR spectrum included an *N*-methyl group at τ 7·68, and a methyl group (τ 8·11, s, 3H, *J* 1·2 Hz) with allylic coupling to a single proton (τ 2·42, q, *J* 1·2 Hz). Protonation of the nitrogen in trifluoroacetic acid resulted in a downfield shift of the methyl resonance of 0·97 τ, and a splitting of the signal into a doublet (*J* 7·8 Hz) which was confirmed by spin decoupling. Both the i.r. and u.v spectra pointed to the presence of a conjugated carbonyl group possibly containing a β-substituent with +M characteristics (ν_{max} 1650 cm^{-1}; λ_{max} (EtOH) 257, 212 nm; ϵ_{max} 10,680, 10,290). No complete structural assignment for bellendine could be made on the basis of these data, and further work on the structural elucidation of this and other constituents of the plant is proceeding.

EXPERIMENTAL

M.ps are uncorrected. NMR spectral data (100 Mc/s) refer to solutions in $CDCl_3$; chemical shifts are quoted as values relative to tetramethylsilane.

Source of Plant Material

The flowers of *B. montana* were collected in January from the Hartz Mountain area of Southern Tasmania.

Extraction and Isolation Procedure

Fresh flowers together with their stalks (7 kg) were extracted with Prollius solution (MeOH–$CHCl_3$–0·88 NH_4OH 30:10:2) (4 × 6 l.) until the extract gave only a weak Mayer's test. The plant material was allowed to dry in the shade and the dried, ground material (1 kg) then re-extracted with Prollius solution. The combined Prollius extract was concentrated by evaporation of the solvents *in vacuo*, and $CHCl_3$ (300 ml) added to the residue. The $CHCl_3$ solution was then exhaustively extracted with 1N H_2SO_4, the acidic extract basified (0·88 NH_4 OH) and extracted successively with benzene and $CHCl_3$. Evaporation of the dried ($MgSO_4$) extracts *in vacuo* and combination of the residues afforded a crude basic fraction (9 g) which was adsorbed in silica gel (200 g; 200 mesh) from a warm benzene solution. The eluate was passed through two other silica gel columns (100 g and 60 g) and then collected automatically in 10 ml fractions (104 l. × 10 ml). Elution with benzene, benzene–$CHCl_3$ (5, 10, 15, 20, 25–99% $CHCl_3$), $CHCl_3$, and $CHCl_3$–MeOH (2, 2½, 3, 3½ 5, 10 and 15% MeOH) afforded the following:

(a) Crude *Methyl* (p-*hydroxybenzoyl*)*acetate* (I, R=H) (1·7 g, 0·024%) purified by crystallization from benzene–petroleum ether; m.p. 83–84°. Methyl ether (I, R=CH_3), m.p. 24° (lit.[8] 26–27°) NMR, 2·62τ 4H, q, aromatic protons), 7·4τ (3H, s, aromatic methoxyl), 6·35τ (3H, s, methyl ester) and 6·22τ (2H, s, methylene protons).

(b) Alkaloid A_1, (13 mg, 0·002%) as an oil, after purification by preparative TLC (silica gel; $CHCl_3$–10% MeOH).

(c) Bellendine (65 mg) after recrystallization from ether–petroleum ether, m.p. 162–163°; $[\alpha]_D^{20}$ + 168·5° (c, = 0·64, $CHCl_3$); pK_a 7·3. A further quantity of bellendine (28 mg) was obtained as colourless needles, m.p. 162°, after separation from alkaloid A_2 (18 mg; 0·003%) by preparative TLC and sublimation (85°/1·5 × 10^{-4} mm).

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