($s \times 2$, C-13, C-23), 147.84, 147.64 ($d \times 2$, C-9, C-19), 127.74, 127.63 ($s \times 2$, C-10, C-20), 124.17, 124.05 ($d \times 2$, C-15, C-25), 116.45, 116.37 and 115.39, 114.77 ($d \times 4$, C-14, C-24 and C-8, C-18), 111.84, 111.78 ($d \times 2$, C-11, C-21), 75.74, 71.21, 69.85 ($d \times 2$, dd, C-2, C-3, C-4, C-5), 56.34, 56.23 ($q \times 2$, C-16, C-26). FABMS m/z: 561 $[M-H]^-$, 385 $[M-C_{10}H_9O_3]^-$, 209 $[M-C_{20}H_{17}O_6]^-$.

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p-HYDROXYACETOPHENONE DERIVATIVES OF THE MONOTYPIC GENUS *PLATYPODANTHERA*

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Key Word Index—*Platypodanthera melissaefolia*; Compositae; *p*-hydroxyacetophenone derivatives; tremetone derivatives.

Abstract—The aerial parts of *Platypodanthera melissaefolia* afforded several known *p*-hydroxyacetophenone derivatives and two new ones. Furthermore, coumarins and a guaianolide were isolated. The chemotaxonomic relevance of these findings is discussed.

The monotypic genus *Platypodanthera* (Compositae, tribe Eupatorieae) is placed in the subtribe Gyptidinae [1]. The only species *P. melissaefolia* (DC) K. et R. was originally described as *Ageratum melissaefolium* DC and later transferred to *Trichogonia* by Mattfeld. However, the morphology clearly differs from both genera [2]. We now have studied the chemistry of this species. In addition to the coumarins herniarin and ayapin the *p*-hydroxyacetophenone derivative **1** [3] and the derived vinyl compounds **2** [4] and **3** [4] were isolated. Furthermore, the tremetone derivative **5** [5] and the guaianolide **7** [6] were present. Two further compounds (**4** and **6**) were closely related to **3** and **5** respectively.

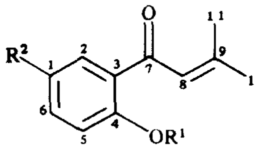
The structure of **4** followed from its ^{1}H NMR spectrum which was in part similar to that of **3**. However, the signals of the vinylic protons were replaced by a singlet at δ9.91, clearly indicating an aldehyde proton. Furthermore, the signals of the aromatic protons were shifted down field while the coupling remained unchanged. Accordingly, we were dealing with the aldehyde **4** most likely formed by oxidative degradation of **3**.

The structure of **6** also could be deduced from the ^{1}H NMR spectrum which was similar to that of 3α-hydroxy-11-acetoxytoxol [7]. However, some signals were clearly different. Especially, the pair of broadened doublets at δ4.18 and 4.34 (H-11) required a more rigid structure. Therefore, in agreement with the molecular formula, the corresponding cyclic anhydro derivative was present. The observed coupling of H-2 required a *cis*-ring closure if the value was compared with those of *cis*- and *trans*-substituted toxol derivatives [3, 4]. We have named compound **6**, platypodantherone.

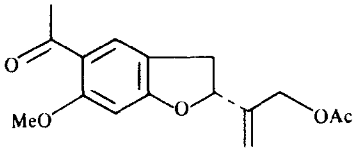
The chemistry of *Platypodanthera* is in part related to that of some *Trichogonia* species, where vinyl derivatives like **2** and **3** and other *p*-hydroxyacetophenone derived compounds are present [4, 9]. From one species also guaianolides are reported [9]. Derivatives of *p*-hydroxyacetophenone are also isolated from representatives of *Bahianthus* [10], *Stylotrichium* [11] and *Campuloclinium* [unpublished], all placed in the subtribe Gyptidinae. However, these compounds are relatively widespread in many genera of the Compositae. The isolation of **2**–**4** and **7** indicated closest relationship of *Platypondanthera* to *Trichogonia* and not to *Ageratina*.

EXPERIMENTAL

The air-dried aerial parts (80 g, collected in February 1987 in Peru, voucher RMK 8597, deposited in the US National Herbarium Washington) was extracted and worked-up as reported previously [12]. The extract was first separated by CC into five fractions (petrol with increasing amounts of Et_2O). The first



	1	2	3	4
R¹	Me	H	Me	Me
R²	COMe	CH═CH₂	CH═CH₂	CHO



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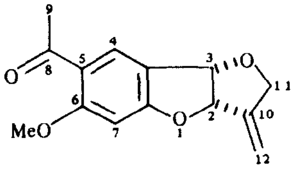

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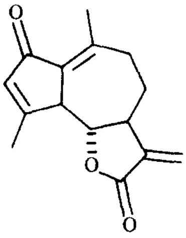

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fraction gave 100 mg **2** and the second 80 mg **3**. Fraction 3 was separated by HPLC (always MeOH–H_2O, 3:2, RP-8, *ca* 100 bar) affording 60 mg ayapin and 20 mg herniarin. Fraction 4 gave by HPLC 40 mg ayapin, 30 mg herniarin, 10 mg **6** (R_t 13.2 min), 35 mg **4** (R_t 16.3 min), 40 mg **1** (R_t 20.0 min) and 50 mg **5** (R_t 22.5 min). The last CC fraction gave by HPLC 30 mg **7**. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

3-Senecioyl anisaldehyde (**4**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2720, 1690 (CHO), 1665, 1610 (PhCOC=C); MS *m/z* (rel. int.): 218.094 $[M]^+$ (48) (calc. for $C_{13}H_{14}O_3$: 218.094), 203 $[M-Me]^+$ (100), 189 $[M-CHO]^+$ (61), 163 $[M-C_4H_7]^+$ (92), 83 $[C_4H_7CO]^+$ (98), 55 $[83-CO]^+$ (84); ^{1}H NMR ($CDCl_3$, 400 MHz): 8.05 (*d*, H-2), 7.07 (*d*, H-5), 7.97 (*dd*, H-6), 6.67 (*br s*, H-8), 1.99 (*br s*, H-10), 2.25 (*br s*, H-11), 9.91 (*s*, CHO) 3.98 (*s*, OMe) (J [Hz]: 2,6 = 2; 5,6 = 8.5).

Platypodantherone (**6**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1615 (PhCO); MS *m/z* (rel. int.): 246.089 $[M]^+$ (51) (calcd for $C_{14}H_{14}O_4$: 246.089), 231 $[M-Me]^+$ (100), 176 $[231-C_4H_7]^+$ (31), 161 $[176-Me]^+$ (12), 133 $[161-CO]^+$ (21); ^{1}H NMR ($CDCl_3$, 400 MHz): 5.45 (*br d*, H-2), 5.69 (*d*, H-3), 7.93 (*s*, H-4), 6.42 (*s*, H-7), 2.56 (*s*, H-9), 4.18 (*br d*, H-11), 4.34 (*br d*, H-11′), 5.54 (*br s*, H-12), 5.35 (*br s*, H-12′), 3.89 (*s*, OMe).

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