Phytochemistry, 1979, Vol. 18, p. 1409. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0801-1409 $02.00/0

CINNAMIC ACID ESTERS IN *ANTHOCEROS* SPECIES

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(*Received* 2 *November* 1978)

Key Word Index—*Anthoceros laevis*; *Phaeoceros laevis*; *Anthoceros punctatus*; Anthocerotaceae; methyl *p*-coumarate; methyl caffeate; cinnamates.

In a general survey for growth regulators in lower plants, *Anthoceros laevis* L. (= *Phaeoceros laevis* L.) and *A. punctatus* L. (Anthocerotaceae) were examined. It was readily found that lunularic acid, abscisic acid and lunularin were all absent from these plants, but fluorescent compounds were detected under UV light when the chromatograms were fumed with ammonia.

From the phenolic extract of *A. laevis*, a strong green fluorescence was eluted with MeOH. The small amount isolated restricted the structural information to that obtained from UV spectral and chromatographic studies. The UV spectrum in MeOH showed bathochromic shifts after NaOAc and H_3BO_3 addition, suggesting an ester [1] and an *o*-dihydroxyl group, respectively. The eluted compound co-chromatographed with methyl caffeate in 9 solvents and in toluene–acetic acid–water (4:1:5, upper phase); its R_f 0.09 was different from that of ethyl caffeate (R_f 0.29). To our knowledge, the isolation of methyl caffeate from a plant source is reported for the first time [2–4].

The neutral fraction chromatograms of both species showed bright purple fluorescent bands. Their eluates upon saponification afforded *p*-coumaric acid. They also exhibited UV spectra in MeOH, alone and in the presence of KOH, $AlCl_3$, $AlCl_3$ + HCl, NaOAc and H_3BO_3 [5, 6] superimposable on those of synthetic methyl *p*-coumarate, co-chromatographed with an authentic sample in ten solvents, and their MS showed peaks at *m/e* 178 (M^+, $C_{10}H_{10}O_3$), 147 ($M^+ - OMe$) and 119 ($M^+ - CO_2Me$). This cinnamic derivative is of narrow occurrence in the plant kingdom and has been reported in *Grevillea robusta* (Proteaceae) [7], *Boenninghausenia albiflora* (Rutaceae) [8], *Cuscuta lehmanniana* (Convolvulaceae) [9], *Chromolaena leptocephala* [10] and *Printzia laxa* (Compositae) [11], but only once in lower plants (*Lentinus lepideus*) [3].

That these methyl esters are artifacts is unlikely, since even traces of the corresponding acids were not detected and several other alkyl cinnamates were also present and they are under investigation. On the other hand, esters of caffeic acid and related cinnamic acids have been reported in liverworts [12].

EXPERIMENTAL

A. laevis (7.1 g, dry wt) and *A. punctatus* (15 g, dry wt), collected in Muñigo (Asturias) in July, 1977, were homogenized with MeOH and allowed to stand overnight in the dark. After filtration, the extraction was repeated for 3 (*A. laevis*) or 6 (*A. punctatus*) consecutive 24 hr periods. The filtrates were combined, concd *in vacuo* and the residues taken up in Et_2O. The ether soln was separated into neutral and phenolic fractions by extraction with 5% $NaHCO_3$ (× 4). The aq. extracts were acidified, back-extracted with Et_2O (× 4) and the Et_2O fractions were dried. The phenolic extract of *A. laevis* was successively chromatographed on Si gel HF 254 in C_6H_6–EtOAc–HOAc (50:5:2) (R_f 0.0), Whatman 3 mm paper in 10% HOAc (R_f 0.39–0.64) and *n*-BuOH–EtOH–H_2O (4:1:2.2), and the fluorescent band at R_f 0.74–0.94 was eluted and analysed by UV spectroscopy and chromatography. The neutral fractions of both *Anthoceros* species were chromatographed in 10% HOAc, then in *iso*-PrOH–NH_3–H_2O (10:1:1) and the bands showing fluorescence at R_f 0.73–0.85 were eluted and analysed as above.

Acknowledgements—We thank Dr. R. M. Simó (Botany Department, University of Oviedo) for providing authenticated plant material and Dr. R. D. H. Murray (Chemistry Department, Glasgow University) for the mass spectrum.

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NOTE ADDED IN PROOF

Methyl caffeate has recently been isolated from the Compositae *Gochnatia rusbyana* ((1979) *Phytochemistry* **18**, 95), and previously from *Tanacetum odessanum*, *Vernonia novebarecensis*, and *Bedfordia salicina* ((1978) *Phytochemistry* **17**, 319, 475, 1173, respectively) by Bohlmann *et al.*