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(−)-CRYPTOCARYALACTONE AND (−)-DEACETYLCRYPTOCARYALACTONE—GERMINATION INHIBITORS FROM *CRYPTOCARYA MOSCHATA* SEEDS

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Abstract—(−)-Cryptocaryalactone (6-[2-acetoxy-4-phenyl-3-butenyl]-5,6-dihydro-2-pyranone) and (−)-deacetylcryptocaryalactone (6-[2-hydroxy-4-phenyl-3-butenyl]-5,6-dihydro-2-pyranone) isolated from *Cryptocarya moschata* seeds are natural germination inhibitors Applied at 0 004 M, the second compound completely arrested germination of velvetleaf (*Abutilon theophrasti*) and decreased the germination rate of soybeans, but did not appear to affect corn The first compound was not as effective, 0 004 M reduced velvetleaf germination 50%

INTRODUCTION

Substituted 2-pyranones are important natural products with diverse biological activities [1] Reported germination inhibitors include parasorbic acid [2] and psilotin [3] In the course of our effort to find compounds with weed control potential [4], extracts of *Cryptocarya moschata* Nees and Mort showed good activity against velvetleaf (*Abutilon theophrasti* Medic), a troublesome competitor of corn and soybeans Isolation and characterization of the active principles proved them to be (−)-cryptocaryalactone (**1**) and its deacetyl analog (**2**) (+)-Cryptocaryalactone was isolated from *C bourdillonii* [5] and 6-(2-phenylethenyl)-5,6-dihydro-2-pyranone from *C caloneura* [6], but this is the first report of levorotatory cryptocaryalactone, of its deacetyl analog, and of their antigermination activity

RESULTS AND DISCUSSION

Compound **1** gave mass and NMR spectra identical to those of (+)-cryptocaryalactone [5] These spectra were also exhibited by the acetyl derivative of compound **2** Both were levorotatory, the magnitude of rotation for **1** (−20°) is about the same as that for (+)-cryptocaryalactone (+16°) [5]

The respective antigermination activities of the two are given in Table 1 Compound **2** was decidedly more active against velvetleaf, so further experiments to determine its toxicity against the crop plants of corn and soybeans were performed Corn was relatively unaffected at a concentration virtually lethal to velvetleaf (0 004 M) but soybean germination was about 75% as great as controls These compounds are not as toxic as benzyl isothiocyanate [4] but have an effect similar to that of psilotin on turnips [3]

The activity of psilotin could be reversed by the addition of gibberellic acid (GA_3) to the medium [3] Our experiments (Table 1) showed that GA_3 had no effect on the activity of compound **2** applied to velvetleaf

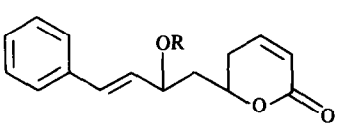
Table 1 Effect of cryptocaryalactones **1** and **2** on germination

Compound and concentration (M)	% Germination relative to controls		
	Velvetleaf	Soybeans	Corn
1 0 004	55*	—	—
1 0 001	94	—	—
2 0 004	6*	79*	83
2 0 002	59*	92	100
2 0 001	59*	105	90
2 0 0008	85		
2 0 004 + 0 0003 GA_3† simultaneous treatment	15*		
2 0 004 + 0 0003 GA_3 delayed treatment			
(1) before GA_3	8*		
(2) after GA_3	10*		

*Significantly different from controls at 95% level or better as determined by the Chi-square one-tailed test
†Gibberellic acid

EXPERIMENTAL

The *C moschata* seeds were collected in Uruguay and were identified by botanists at the Beltsville Agricultural Research Center, Beltsville, MD Seeds (150 g) were separated into kernel



R
1 Ac
2 H

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the U S Department of Agriculture over other firms or similar products not mentioned

(50 g) and hull (100 g) fractions Each fraction was then finely ground and extracted in a Soxhlet with hexane (8 hr) and Me_2CO (16 hr) The two extracts of the hulls were combined, slurried onto a dry silica column, and eluted sequentially with 300 ml portions of EtOAc–hexane (1 9), EtOAc–hexane (1 1), EtOAc–hexane–EtOH (25 25 1) and EtOAc–hexane–EtOH (5 5 1) HPLC of the fractions on Partisil 10/50 PAC (Whatman) with EtOAc–hexane–EtOH (66 33 5) gave highly enriched portions of **1** and **2** These were purified by reversed-phase HPLC on a Zorbax C-8 (Dupont) column eluted with Me_2CO–H_2O (1 1) Bioassays were used as a guide to active materials throughout the isolation procedure

The hexane extract of seed kernels produced crystals after most of the hexane had been removed These crystals were recovered and washed × 3 with cold hexane TLC on silica plates [0 25 mm, Brinkman, C_6H_6–EtOH (9 1)] showed them to be virtually pure **1** The remainder of this extract and the Me_2CO extract were taken through the chromatographic steps given above for the hull extracts Total yields from all processes were **1**, 137 mg and **2**, 286 mg Optical rotations were measured in $CHCl_3$ **1**, $[\alpha]_D^{27}$ $-20°$ (*c* 1 0), **2**, $[\alpha]_D^{27}$ $-94°$ (*c* 2 2)

Compound **2** was allowed to stand overnight in Ac_2O–pyridine (1 2) and the product (**1**) was recovered by ether/H_2O extraction

Mass and NMR spectroscopic equipment and techniques and details of the bioassay procedure are described in previous work [4, 7] Concentrations are given in Table 1 To test whether or not the activity could be negated or reversed by gibberellic acid, GA_3 and compound **2** were applied together (simultaneous treatment, Table 1), or GA_3 was added 2 days after the original treatment with **2** and another 2 days were allowed to elapse before germination was evaluated (delayed treatment)

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