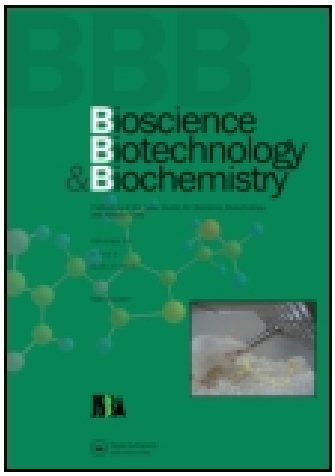

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Synthesis and Antifungal Activity of Cinnamic Acid Esters

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Note

Synthesis and Antifungal Activity of Cinnamic Acid Esters

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Cinnamic, *p*-coumaric and ferulic acids were isolated from pineapple stems (*Ananas comosus* var. Cayenne). Twenty-four kinds of esters were prepared from these acids, alcohols and the components of *Alpinia*. Isopropyl 4-hydroxycinnamate (11) and butyl 4-hydroxycinnamate (12) were found to have almost the same effectiveness in antifungal activity against *Pythium* sp. at 10 ppm as that of the commercial fungicide iprobenfos (Kitazin P).

Key words: pineapple (*Ananas comosus* var. Cayenne); isopropyl 4-hydroxycinnamate; butyl 4-hydroxycinnamate; antifungal activity; *Pythium* sp.; cinnamic acid

Our research on Okinawan plants has isolated cinnamic, *p*-coumaric, and ferulic acids from pineapple stems. Ferulic and *p*-coumaric acids limit the biodegradation of plant fiber, and *in vitro* studies indicate that a concentration of these phenolic acids above 1 mM inhibits the growth of many species of ruminal bacteria.[1] Further research has shown that these phenolic acids are esterified into arabinoxylans within the plant cell wall, and the digestibility of the plant cell wall has been related to the amount of phenolic acids released by an alkali treatment.[2] A feruloyl arabinobiose has been isolated from both spinach and sugar beet cells,[3] and the antimicrobial activity of various cinnamic acids with substitution in the benzene ring has been reported by Ramanan.[4] Many alkyl hydroxycinnamates have been reported to have antimicrobial activity against yeast,[5] *Aspergillus niger* and *Penicillium* sp.[6]

In our previous papers,[7-9] we have reported the antifungal activity of compounds which were prepared from *Alpinia speciosa* K. Schum. In the present study, we tested the antifungal activity of 24 esters prepared from these phenolic acids and alcohols which are components of *Alpinia*.

The agar dilution method for the antimicrobial activity test has been described in our previous paper.[8] We found citronellol, thymol, eugenol, and isothymol to have very strong antimicrobial activity. All of the compounds were prepared by the standard method,[10] compounds **1**–**7** being prepared from cinnamic acid, **8**–**16** from *p*-coumaric acid, and **17**–**24** from ferulic acid. The Table shows refractive indexes, IR and NMR spectral data, and the antifungal activity of cinnamic acid esters. *p*-Coumaric acid (**26**) showed much less activity than ferulic acid (**27**) did, and when ferulic acid (**27**) was combined with propanol, compound **19** became much weaker in activity. However, when *p*-coumaric acid (**26**) was combined with propanol, compound **10** became almost 10 times stronger in activity against *Pythium* sp. In a comparison of these three acids (**25**, **26**, and **27**), cinnamic acid (**25**) showed the strongest activity against both *Pythium* sp. and *Corticium rolfsii*. Since compounds **10**, **11**, and **25** showed the highest activity, we tested them at 10 ppm to further compare them with iprobenfos. Isopropyl 4-hydroxycinnamate (**11**) and butyl 4-hydroxycinnamate (**12**) were found to have almost the same effectiveness at 10 ppm against *Pythium* sp. as that of the commercial fungicide iprobenfos.

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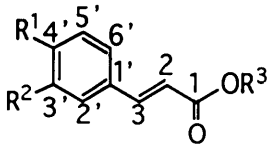
Table Refractive Indexes, IR and NMR Spectral Data, and Antifungal Activity of Cinnamic Acid Esters



Compound[a]	R^1	R^2	R^3OH	Yield (%)	n_D (°C) or mp	IR[b] ν_{max}^{neat} cm^{-1}		^{1}H-NMR[c] $\delta_{TMS}^{CDCl_3}$ ppm		^{13}C-NMR $\delta_{TMS}^{CDCl_3}$ ppm			Growth inhibition (%)			
													Pythium sp.		*Corticium rolfsii*	
						ν_{O-H}	$\nu_{C=O}$	H-2	H-3	C-1	C-2	C-3	10 (ppm)	100 (ppm)	10 (ppm)	100 (ppm)
1	H	H	Methanol					7.69 (d)	6.43 (d)	167.2	144.7	117.6		66		53
2	H	H	Citronellol	7		—	1712 (vs)	7.79 (d)	6.46 (d)	171.8	146.8	117.5		0		0
3	H	H	Thymol	15			1733 (vs)	7.73 (d)	6.45 (d)	165.2	147.3	116.6		54		45
4	H	H	Eugenol	13		—	1735 (vs)	7.68 (d)	6.43 (d)	167.0	146.4	117.1		28		22
5	H	H	Phenethyl alcohol	4		—	1712 (vs)	7.68 (d)	6.43 (d)	166.8	144.8	118.1		28		22
6	H	H	1-Heptanol	29			1716 (vs)	7.68 (d)	6.44 (d)	167.0	144.5	118.3		42		10
7	H	H	1-Octyl alcohol	17		—	1716 (vs)	7.68 (d)	6.44 (d)	166.9	144.4	118.1		56		13
8	OH	H	Methanol	17	125.2–127.5 C	3371 (br.)	1678 (vs)	7.64 (d)	6.29 (d)	168.8	145.4	114.6	0	54		41
9	OH	H	Ethanol	23	1.5992 (22.0)	3369 (br.)	1684 (vs)	7.64 (d)	6.29 (d)	168.4	145.2	114.9	29	87	8	45
10	OH	H	1-Propanol	16	1.5891 (22.9)	3369 (br.)	1684 (vs)	7.64 (d)	6.30 (d)	168.4	145.1	115.0	31	91	9	70
11	OH	H	Isopropanol	13	1.5848 (24.6)	3346 (br.)	1680 (vs)	7.62 (d)	6.27 (d)	167.9	144.9	115.5	41	98	10	84
12	OH	H	1-Butanol	21	1.5842 (23.5)	3369 (br.)	1687 (vs)	7.64 (d)	6.30 (d)	168.5	145.2	114.9	35	71	29	81
13	OH	H	Phenol	15	1.5671 (25.1)	3379 (br.)	1705 (vs)	7.80 (d)	6.42 (d)	166.9	147.2	115.3	16	80		53
14	OH	H	Citronellol	5		3406 (br.)	1711 (vs)	7.63 (d)	6.29 (d)		144.6	115.2		63		55
15	OH	H	Isothymol	10	1.5339 (22.5)	3381 (br.)	1705 (vs)	7.83 (d)	6.51 (d)	166.1	147.1	113.6		36		38
16	OH	H	Thymol	7		3369 (br.)	1703 (vs)	7.85 (d)	6.49 (d)	166.2	147.3	113.3		33		31
17	OH	OCH_3	Methanol	18	1.5947 (23.5)	3410 (br.)	1695 (vs)	7.62 (d)	6.29 (d)	167.7	145.0	114.7		0		37
18	OH	OCH_3	Ethanol	29	1.5837 (25.0)	3406 (br.)	1701 (vs)	7.61 (d)	6.29 (d)	167.3	144.7	114.7		50		43
19	OH	OCH_3	1-Propanol	20	1.5458 (25.5)	3413 (br.)	1732 (vs)	7.62 (d)	6.30 (d)	167.5	144.7	114.8		9		26
20	OH	OCH_3	Isopropanol	42	1.5709 (25.5)	3406 (br.)	1697 (vs)	7.60 (d)	6.28 (d)	166.8	144.4	114.7		18		38
21	OH	OCH_3	1-Butanol	22	1.5574 (23.0)	3413 (br.)	1705 (vs)	7.61 (d)	6.29 (d)	167.5	144.7	114.8		0		0
22	OH	OCH_3	Isothymol	17	1.5703 (21.0)	3406 (br.)	1720 (vs)	7.83 (d)	6.51 (d)	165.2	147.5	113.9		49		37
23	OH	OCH_3	Thymol	11	1.5864 (23.5)	3411 (br.)	1718 (vs)	7.81 (d)	6.50 (d)	166.0	147.1	114.0		9		58
24	OH	OCH_3	Eugenol	28	1.5972 (18.5)	3415 (br.)	1724 (bs)	7.78 (d)	6.51 (d)	165.6	146.7	114.1		31		38
25	H	H											12	97	24	100
26	OH	H												10		46
27	OH	OCH_3												48		54
Iprobenfos													42	89	69	100

[a] **25**, cinnamic acid; **26**, *p*-coumaric acid (4-hydroxycinnamic acid); **27**, ferulic acid (4-hydroxy-3-methoxycinnamic acid).
[b] vs, very strong; br., broad.
[c] d, doublet.