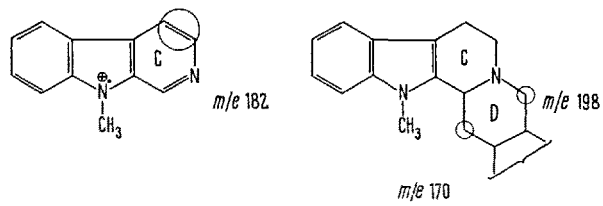
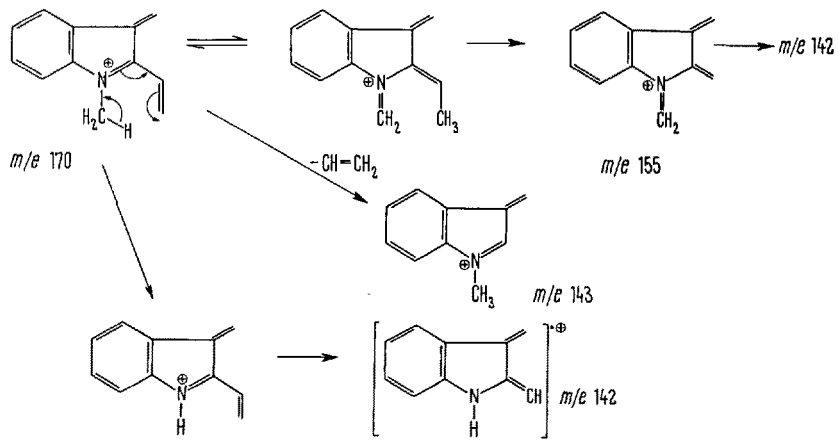
Ensuite le pic *m/e* 170 correspond à une des deux fragmentations.



Le fragment *m/e* 170 donne les fragments 156, 155 et autres par des clivages ou/et des transferts.
L'absence *m/e* 156 du fragment *m/e* 182 signifie que l'autre substitution du noyau C que tel que proposée n'est pas possible.

Spectre de masse de la Cannagunine (**1**)

m/e	I%		m/e	I%	
324	2.4		184	22.7	
323	22.4		183	40.2	
322	100.0	$M^{\oplus}$	170	82.5	
321	64.4		169	22.1	
307	8.1		161	17.4	$M^{2\oplus}$
306	12.4		156	31.7	
292	5.7		155	30.5	
288	7.4		144	11.8	
278	7.3		143	7.8	
252	11.2		142	10.8	
198	62.4		54	22.0	



La fragmentation du noyau D – surtout les pics *m/e* 170 et 198 – soutient également notre proposition de la substitution de ce noyau.

Quatre fragments provenant de l'ionisation du noyau E sont des pics à *m/e* 278, 252, 292; le fragment *m/e* 278 correspond à une rupture du cycle E avec une perte du CO_2 ($M^{\oplus}$–44), une perte de 70 (CO_2 et CH = CH) – *m/e* 252 – confirme la structure CH=CH-CO_2 du noyau E. Le fragment 292 ($M^{\oplus}$–30) correspond à une perte de CH_2O caractéristique pour les lactones[7]. Le fragment intense *m/e* 54 (CH=CH-C≡$^{\oplus}$O) confirme également la structure du noyau E.

L'hydrolyse basique du produit **1** donne un alcool-acide (SM $M^{\oplus}$340). Le spectre de RMN de ce dernier démontre 2 protons en α d'hydroxyle (4.5 ppm). L'acétylation d'hydroxyle (pyridine, anhydride acétique, 40°) déplace de ces protons environ 0.55 ppm (5.05 ppm) ce qui finalement confirme la presence du groupement OH primaire.

La déshydrogenation catalytique du produit **1** (C, Pd, 280°) donne principalement deux produits. Le premier a été identifié comme étant éthyl-3 (méthyl-4'éthyl-3'pentyl)-2 indole par le spectre de RMN[8] et par la comparaison avec le produit synthetisé[8]. L'autre produit possède également le noyau d'éthyl-3 indole substitué par la β-méthyl γ-éthyl pyridine.

Les deux dernières réactions prouvent finalement la structure de la Cannagunine[9].

Summary. A new alkaloid $C_{20}H_{22}O_2N_2$ (cannagunine) obtained from canadian Vaccinium Oxycoccus is shown to have structure **1**. The structure of this compound was supported by NMR-, SM-, IR- and UV-spectra.

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[9] Ce travail a été supporté par le Conseil National de Recherche du Canada.

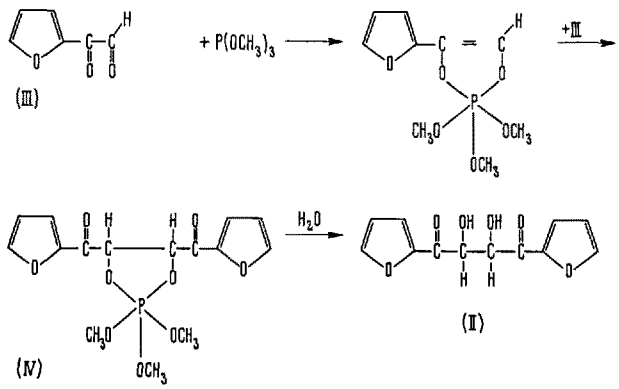
New Furanoid Metabolites from *Rhizoctonia solani*

We report the isolation and identification of two furanoid metabolites from a Union Carbide isolate of *Rhizoctonia solani* Kühn, a plant pathogen with a variety of plants as hosts. The major product isolated was 2-furyl-hydroxymethyl ketone (I) and the other has been identified as 1,2-*bis*-(2-furoyl)-1,2-dihydroxyethane (II). The latter, isolated in very small amounts, is a novel compound, for which we propose the trivial name Rhizosolaniol. The fungus was grown on a cornmeal-sand culture medium for a period of 18 to 30 days. The darkened cornmeal together with the mycelia was sterilized, homogenized with distilled water in a Waring blender and filtered. The metabolites were isolated from the concentrated aqueous extract (pH 5.7) according to the method of Sherwood

and LINDBERG[1]. The ether extract on concentration yielded a brown semi-crystalline material. Recrystallization from chloroform-ether after decolorizing with activated charcoal, gave colorless needles, m.p. 83–84° (Lit 81–82°)[2], (oxime 132–134°)[3], λ_{max}^{EtOH} 269 nm (log ε 4.20). The infrared and nuclear magnetic resonance spectral data are consistent with the structure of (I).

Extraction of the concentrated aqueous extract with organic solvents such as chloroform, ethyl ether or ethylacetate also yielded (I) in varying amounts. Up to 2% has been isolated based on the weight of cornmeal. Since (I) is quite soluble in water the amount formed is probably even greater.

Although the formation of small quantities of (I) together with the isomeric 5-hydroxymethylfurfural, by the acid-catalyzed dehydration of sugars is well known[4–7], we did not detect either (I) or (II) in the sterile medium subjected to the same work up procedure. To our knowledge this is the first example wherein (I) has been isolated as a natural product from any source.



The crude isolate inhibited the growth of rye seeds when placed on moist filter paper, but pure (I) was completely inactive. Thin layer chromatography (TLC) (on 1 mm thick silica gel plates developed with benzene-dioxane-acetic acid-45:8:4) of crude (I) or the mother liquor after crystallizing out most of (I), indicated the presence of 4 to 5 minor components. One of these (Rf 0.64) corresponding to the spot immediately below (I) (Rf 0.73), has been isolated as colorless crystals, m.p. 138–140° and identified as 1,2-*bis*-(2-furoyl)-1,2-dihydroxyethane (II). The IR-spectrum (in $CHCl_3$) exhibited peaks at 3490 (OH, hydrogen bonded), 1685 (conjugated C=O), 1573 (C=C) and other strong peaks at 1,400, 1,300, 1,100, 990, 900 and 595 cm^{-1}; UV-absorption (in EtOH) at 272 nm (log ε 4.40). The NMR-spectrum (in $CDCl_3$) displayed a doublet at τ 6.15, J = 7.0 Hz (secondary OH); a doublet at τ 4.55, J = 7.0 Hz (-CH-O) which collapses into a singlet on addition of D_2O, with the concomitant disappearance of the hydroxyl doublet at 6.15; a quartet centered at τ 3.12, J = 1.5–2.0 Hz; a doublet at τ 2.49 with some fine splitting J = 3.5–4.0 Hz and a partially resolved quartet at τ 2.25, $W_{H/2}$ = 3.5 Hz. The last 3 peaks are typical of 2-ketofurans. All the peaks are of equal intensities.

The molecular composition of compound (II), as determined by high resolution mass spectroscopy, corresponds to $C_{12}H_{10}O_6$ (measured 250.0483; calculated 250.0477), with the base peak at 95 and other major peaks at 155, 126, 124. The fragments at 155 and 95 are due to cleavage of the $\left(-C-\underset{O}{\overset{\|}{C}}-\underset{OH}{\overset{|}{C}}-\right)$ bond and the ion at 126 is due to symmetrical cleavage and abstraction of hydrogen.

The structure of (II) was confirmed by a total synthesis using the reaction discovered by RAMIREZ et al.[8]. Two equivalents of furyl glyoxal (III)[9] were slowly added to trimethyl phosphite and the reaction mixture allowed to stand at room temperature under nitrogen for 4 days. Hydrolysis of the crude oxyphosphorane (IV) followed by chromatographic purification led to the isolation of (II) from among other hydrolytic by-products.

The synthetic product was identical in every respect to the isolated metabolite. The stereochemistry of natural and synthetic (II) remains to be determined.

From cursory tests for inhibition of seed germination, synthetic (II) has exhibited moderate activity at concentrations of 50 to 100 ppm. This activity however, is not great enough to account for the phytotoxity of the crude extract.

The other minor components in the crude extract were elusive to isolation, and none of these correspond to *o*-nitrophenol (by TLC). SHERWOOD and LINDBERG suggested a glucoside of *o*-nitrophenol to be the phytotoxic metabolite isolated from a Union Carbide strain, when grown on cornmeal, but the same was not detected when the fungus was grown in glucose-nitrate medium.

From a potato-sucrose culture of another isolate of *R. solani*, AOKI et al.[10] isolated β-furoic acid as the only furanoid metabolite, in addition to a number of phenolic and carboxylic acids. Of these, the compound reported to be phytotoxic was m-hydroxyphenyl acetic acid. However, the (TLC) Rf values of this acid and those of phenylacetic acid and *para*-hydroxyphenyl acetic acid did not correspond to the Rf values of any of the minor components in our crude extract[11].

Zusammenfassung. Zwei neue, furanoide Metaboliten wurden aus einer Kultur von *Rhizoctonia solani* isoliert und als 2-Furyl-hydroxymethyl-Keton und 1,2-*bis*-(2-Furoyl)-1,2-Dihydroxyaethan identifiziert und durch Totalsynthese bestätigt.

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[11] We wish to acknowledge the important contributions of Dr. D. H. PARKER, and to thank Dr. R. M. MANYIK for useful discussions and Mr. M. R. SAMPLES for technical assistance.
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