Table II. Recovery Studies

herbicide	concn, ppm	% recovered from whole grain wheat	whole wheat flour	whole wheat cereal
LC				
benzoylprop ethyl	5.0	91	91	98
	1.0	82	97	83
	0.5	92	86	83
	0.1	78	65	75
bromoxynil octanoate	5.0	92	81	95
	1.0	97	106	108
	0.5	82	98	111
	0.1	75	83	78
GC[a]				
benzoylprop ethyl	0.1	78, 88	82, 83	90, 91
bromoxynil octanoate	0.1	59, 59	87, 89	83, 71

[a] GC was carried out on the OV-210/SE-30 column.

not alter the detectability of the two herbicides.

Table II lists some recoveries through the extraction procedure with analysis by both LC and GC. The extraction method produced comparable recoveries for both compounds in refined flour and the two types of bread. Although extensive recovery studies were not performed, the data suggests that the method has good potential for routine screening of these two compounds.

The described extraction procedure has been shown to be useful for the determination of benzoylprop ethyl and bromoxynil octanoate in various types of wheat samples by both LC and GC at levels as low as 0.1 ppm. The GC method proved to be superior to LC with a potential of detecting the herbicides in the low part per billion range. However, GC is not suitable for the direct determination of other wild oat herbicides such as asulam or barban; thus, it does not have the potential of LC for screening all five of these compounds without chemical derivatization. The use of the GC analysis as a confirmation of LC results is dramatically illustrated in Figures 2–4. The small peaks of bromoxynil octanoate and benzoylprop ethyl in the LC chromatograms appear as large well-defined peaks when the same extracts are subjected to GC analysis.

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Some Antifungal Components of Diseased Blue Ribbon Iris Bulbs

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Methanolic extracts of tunic-free *Penicillium*-infected Blue Ribbon iris bulbs from 30 °C storage possessed antifungal properties when bioassayed with *Penicillium corymbiferum* and *Fusarium oxysporum* from iris, while comparable disease-free bulbs possessed none. Thin-layer chromatographic (TLC) fractions of the diseased bulb extract, after treatment with diazomethane, were examined by gas–liquid chromatography (GLC) and by gas chromatography–mass spectroscopy (GC–MS). Identified in the esterified active fraction were methyl benzoate, methyl salicylate, methyl cinnamate, coumarin, methyl caprate, and other compounds. Details of extraction, purification, and identification are reported.

It has been recognized that plants are able to synthesize a variety of antifungal substances. Some are present in plants in a nontoxic form until metabolized by the invading organism; others are produced in response to injury or to invasion by microorganisms and may occur at low levels in plant tissues or be completely absent in a healthy plant (Deverall, 1972; Kuc, 1972a,b; Ingham, 1972). It was with this in mind that diseased bulbs were selected from a badly infected set of *Penicillium*-susceptible Blue Ribbon iris bulbs stored at 30 °C and subsequently frozen. Methanolic extracts prepared from these bulbs were biologically active against the bioassay fungi, but it was not determined specifically whether the activity arose from the host or pathogen or from interaction of the two. Methanolic extracts repeatedly prepared from healthy bulbs without tunic produced no biological response except fungal growth enhancement. Thus, the active material was subjected to further examination by TLC, GLC, and GC–MS to determine the cause of this antifungal activity. This paper reports the results of that study.

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EXPERIMENTAL SECTION

Preparation of the Sample. *Penicillium*-infected Blue Ribbon iris bulbs from 30 °C growth-retarding storage were selected after freezing and removal of the tunic which was retained for a separate study. The bulbs were passed through a Toledo food chopper (Model 4120) into a polyethylene bag and mixed while frozen. An 0.69-kg amount of the chopped and still frozen sample was weighed

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into four 950-mL capacity jars (200 g/jar). The content of each jar was homogenized with 200 mL (or a proportional part) of redistilled methanol and transferred to a 4-L jar by using another 200 mL each of methanol per 100 g. The content of the 4-L jar was stirred by magnetic mixing overnight, and the liquid was separated by centrifugation (500g) and decantation through a plug of glass wool. The overnight extraction was repeated twice. The combined extract was reduced under vacuum at 35 °C to a methanol-free syrup. The methanol-free residue (~50 mL) was transferred with water (final volume 200 mL) to a 1-L separatory funnel equipped with a Teflon stopcock and extracted with 2 volumes of recently redistilled ethyl acetate. The extraction was repeated twice. The combined extract was taken to an ethyl acetate free state under vacuum at 35 °C. The residual syrup was taken up in methanol and then transferred to a 30 mL screw-capped test tube with a methanol wash. This was reduced to near dryness under vacuum. Ten milliliters of ether was added to the residue and thoroughly mixed in. This suspension was centrifuged, and the ether phase was decanted through a glass fiber filter under vacuum. This extraction was repeated twice. The extracts were combined, and the ether was removed. (The ether-insoluble material was inactive.) The combined ether-free extract was made to 10 mL in methanol. This solution was active against *Penicillium* and *Fusarium*.

A 0.70-kg amount of undiseased Blue Ribbon iris bulbs was treated in an analogous manner except that the methanol-free residue, after addition of 50 mL of water, was extracted directly with ether (3 × 75 mL) and reduced to 8 mL in volume for the bioassay.

Thin-Layer Chromatography (TLC). About 0.4–0.6 mL of the above 10 mL was applied to a 20 × 20 cm TLC silica gel G (SGG) (E. Merck) plate spread through a gate allowing 0.5-mm thickness. This was developed in a chloroform–methyl ethyl ketone–ethyl acetate–formic acid, water saturated system (70:20:10:3), dried, and scraped in 10 horizontal 1.5-cm strips between R_f values 0.0 and 1.0. Each strip was extracted with methanol 3 times. The process was repeated for the entire 10 mL, and the extracts of corresponding scrapings were combined, evaporated, and designated as TLC sections $\sum$1–$\sum$10, in the order of increasing R_f values. These subfractions were made to 5 mL in volume.

$\sum$2–$\sum$3 contained most of the anti-*Penicillium* activity (Table I). These are still under study. $\sum$4–$\sum$6 contained most of the anti-*Fusarium* activity with some anti-*Penicillium* activity. $\sum$1 and $\sum$7–$\sum$10 contained no activity. $\sum$5 was selected as typical of the anti-*Fusarium* activity of $\sum$4–$\sum$6 and was further fractionated by TLC.

A 170-μL amount of the $\sum$5 was placed on a 0.25 × 20 × 20 mm polyamide 11 column (J. T. Baker Co. no. 2901) containing 20% microcrystalline cellulose (JTB no. 1529), developed in the same solvent system as the silica gel G, and scraped in eight strips according to the lines of major fluorescence activated by transmitted UV 365-nm light. The active area was from R_f 0.4 to R_f 0.65. Most of the activity was from R_f 0.5 to R_f 0.65 (designated $\sum$5:6). After extraction in the same manner as the SGG strips, the extract was brought to the original applied liquid volume of 170 μL in methanol.

Gas Chromatography. Thirty microliters of $\sum$5 or $\sum$5:6 was placed in a 4-cm^3 vial. Freshly made diazomethane (Fales and Jaouni, 1973) in ether was added to excess. The mixture was allowed to stand at room temperature for 15 min with occasional mixing. The ether and excess reagent were evaporated with air and minimal heat. The residue was taken up in methanol to 200-μL volume.

GLC Instrument: Varian 2740 with 2 m × 2.1 mm i.d. nickel tubing packed with Supelco 10% SP2100 (or 10% SP2340) on 100/120 mesh Chromosorb WAW (or 100/120 mesh Supelcoport); injector, 260 °C; oven, 3 min at 170 °C, 170–260 °C at 6 °C/min (or 3 min at 130 °C, 130–260 °C at 6 °C/min), and hold; flame ionization detector, 280 °C; N_2 flow, 30 cm^3/min; sample size, 1 μL; attenuation, 64 × 10^{-11} AFS.

GC–MS Instrument: *Finnigan 4023.* 70 eV; SP2100 capillary, wall-coated open tubing, 30 m × 0.25 mm i.d.; 50 °C isothermal for 2 min, 50–260 °C at 10 °C/min; He flow, 1.0 cm^3/min; precolumn splitter ratio, 1:30; at 1.7 kV; sample size, 1 μL of diazomethane-treated (Me) $\sum$5:6.

Hewlett-Packard 5992. 70 eV; 2 m × 2.1 mm i.d. Ni column; 10% SP2100 on 100/120 mesh Supelcoport; injection port, 278 °C; 3 min at 170 °C isothermal, 170–260 °C at 6 °C/min, and hold for 15 min; N_2 flow rate, 30 mL/min; electron multiplier, 2400; sample size, 0.5 μL of Me $\sum$5.

Bioassay. Cultures of *Penicillium corymbiferum* West. and *Fusarium oxysporum*, f. sp. gladioli (Mass.) S & H, were propagated in 125–250-mL flasks containing 12 g of whole oats sterilized on two successive days for 30 min at 1.05 kg/cm^2 pressure. The inoculated oats were incubated at 20 °C to a stage where growth covered about one-half the exposed oats. Sterile water (40 mL) was added and mixed in. A 2-mL portion of the suspension was removed and added to 100 mL of Difco potato dextrose agar at 40 °C and subsequently mixed. About 15 mL of this mixture was used per each 100-mm diameter petri dish. Spore concentration was not determined. Methanolic solutions of 1–2 μL were applied directly with a microliter syringe or a calibrted capillary tubing to obtain the data in Table II. Diseased bulb extracts or TLC sections thereof were applied first to $^1/_4$-in. diameter paper disks (20 μL) and then placed on the spore-containing agar.

Table I. Bioassay of Diseased Bulb Extract after Thin-Layer Chromatography (TLC)

extract (20 μL/disk)	R_f	*P. corymbiferum*	*F. oxysporum*
TLC section[a]			
1	0.0–0.1	0	0
2	0.1–0.2	⊕, 7[b]	0
3	0.2–0.3	⊕, 5	0
4	0.3–0.4	+sl	⊕, 1
5	0.4–0.5	+sl	⊕, 2
6	0.5–0.6	+sl	⊕, 3
7	0.6–0.7	0	0
8	0.7–0.8	0	0
9	0.8–0.9	0	0
10	0.9–1.0	0	0
whole diseased extract		⊕, 1	⊕, 3
whole undiseased extract		0	0

[a] Solutions of TLC section extracts were brought to the volume of the applied whole sample before assay. [b] Symbols: (0) no effect, bioassay negative; (⊕, x) clear band around bioassay disk, x mm wide, distinctly antifungal; (+sl) slight positive.

RESULTS

Methanolic extracts and TLC sections 2–6 (referred to also as $\sum$2–$\sum$6) derived from the extracts of *Penicillium*-infected Blue Ribbon iris bulbs were active in the bioassay against *P. corymbiferum* and *F. oxysporum*. This is shown in Table I. Sections 2 and 3 were set aside for later study. Sections 4–6 were similar. Section 5 was selected as typical of sections 4–6 and studied in further detail.

The following compounds were identified in section $\sum 5$ or $\sum 5{:}6$ after esterification of the extract with diazomethane.

GC–MS with Hewlett-Packard 5992. Methyl benzoate: retention time 1.1 min; MS *m/e* 136 (M^+, 35%), 105 ($M^+ - CH_3O$, 100%), 77 ($M^+ - C_2H_3O_2$, 83%), 51 (42%), 50 (26%).

Methyl salicylate: retention time 1.6 min; MS *m/e* 152 (M^+, 32%), 121 ($M^+ - CH_3O$, 25%), 120 ($M^+ - CH_4O$, 79%), 93 ($M^+ - C_2H_3O_2$, 20%), 92 (C_6H_4O, 100%), 65 (C_5H_5, 42%), 64 (27%), 63 (29%), 53 (18%), 39 (C_3H_3, 34%).

Methyl cinnamate: retention time 3.1 min; MS *m/e* 162 (M^+, 30%), 161 (22%), 131 ($M^+ - CH_3O$, 73%), 103 ($M^+ - C_2H_3O_2$, 98%), 102 (28%), 77 ($M^+ - C_4H_5O_2$, 100%), 76 (22%), 75 (18%), 74 (19%), 63 (16%), 51 (59%), 50 (33%).

Coumarin: retention time 3.9 min; MS *m/e* 146 (M^+, 24%), 118 ($M^+ - CO$, 100%), 90 ($M^+ - C_7H_6$, 58%), 89 ($M^+ - C_7H_5$, 51%), 64 (20%), 63 (57%), 62 (30%), 51 (19%), 50 (16%), 39 (C_3H_3, 26%).

Methyl stearate: retention time 14.4 min; MS *m/e* 298 (M^+, 12%), 267 ($M^+ - CH_3O$, 3%), 255 ($M^+ - C_2H_3O$, 5%), 199 ($M^+ - C_7H_{15}$, 8%) 143 [$-(CH_2)_6C{=}O(OCH_3)$, 23%], 101 [$-(CH_2)_3C{=}O(OCH_3)$, 9%], 87 [$-(CH_2)_2C{=}O(OCH_3)$, 58%], 74 [$CH_2{=}COH(OCH_3)$, 91%], 43 (C_3H_7, 100%).

Methyl linoleate: retention time 13.9 min; MS *m/e* 294 (M^+, 4%), 262 ($M^+ - 32$, 2%), 110 ($M^+ - C_8H_{14}$, 17%), 109 (C_8H_{13}, 17%), 96 (C_7H_{12}, 29%), 95 (C_7H_{11}, 41%), 93 (19%), 91 (17%), 83 (20%), 82 (34%), 81 (C_6H_9, 68%), 80 (24%), 79 (57%), 77 (19%), 74 [$CH_2{=}COH(OCH_3)$, 20%], 69 (33%), 68 (33%), 67 (C_5H_9, 98%), 59 (32%), 55 (C_4H_7, 94%), 54 (32%), 53 (20%), 43 (C_3H_7, 46%), 41 (C_3H_5, 100%), 39 (21%). The spectrum matched that known for methyl linoleate. The peak resolved on polar SP2340 as 30% methyl oleate and 70% methyl linoleate by comparison of retention times and areas.

GC–MS with Finnigan 4023. Propanedioic acid dimethyl ester: retention time 210 s, occurred on the GC chromatogram ahead of methyl benzoate; MS (M^+ not detected) *m/e* 101 ($M^+ - CH_3O$, 89%), 74 ($M^+ - C_3H_6O_2$, 41%), 69 (13%), 59 ($M^+ - CH_2CO_2CH_3$, 100%), 57 ($M^+ - CH_2CO_2CH_3 - 2H$), 30%), 45 (11%), 43 (11%), 42 ($M^+ - CH_3 - CO_2CH_3$, 38%). This matched the known spectrum of the title compound.

Trimethyl phosphate: retention time 200 s, occurred after propanedioic acid dimethyl ester and before methyl benzoate; MS *m/e* 140 (M^+, 13%), 110 ($M^+ - C_2H_6$, 100%), 109 ($M^+ - CH_3O$, 35%), 95 (28%), 93 (3%), 80 (35%), 79 (45%), 65 (6%), 47 (14%), 45 (2%). This was presumed to be an artifact.

Dimethyl pentyl phosphate: retention time 490 s, occurred immediately before methyl salicylate; MS (M^+ not observed) *m/e* 128 (5%), 127 ($M^+ - C_5H_{11}$, 100%), 110 (6%), 109 ($M^+ - C_5H_{11} - H_2O$, 40%), 96 (57%), 95 (7%), 79 (7%). This was presumed to be an artifact.

Saturated fatty acid methyl ester: retention time 649 s; MS, decreasing intensity of alkyl groups from *m/e* 43 (C_4H_4, 47%), 57 (C_4H_9, 10%), and 71 (C_5H_{11}, 4%) through *m/e* 85 (C_6H_{13}, 0.5%), base *m/e* 74 [$CH_2{=}C(OH)OCH_3$], prominent *m/e* 87 [$CH_2CH_2C{=}O(OCH_3)$, 46%], *m/e* 59 (CO_2CH_3, 13%), 129 [$(CH_2)_5CO_2CH_3$, 1%], 143 [$(CH_2)_6C{=}O(OCH_3)$, 7%]. This was identified as a C_{10} saturated fatty acid methyl ester, methyl caprate, by retention time comparison with the known ester.

Other saturated fatty acid methyl esters were found at retention times of 828, 986, and 1129 s. All three showed mass spectral characteristics of the above described ester. Molecular peaks were not obtained during this run. These

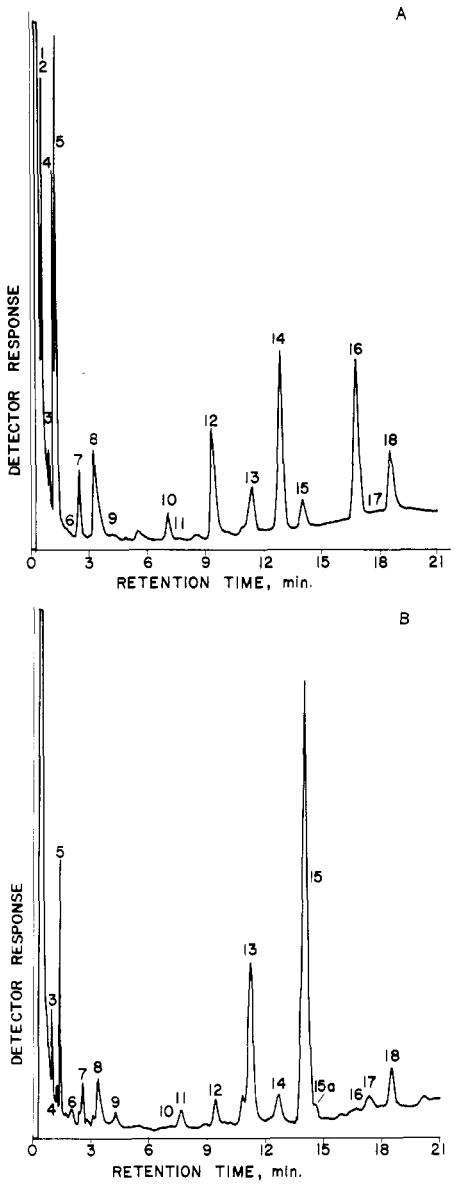

Figure 1. Gas chromatograms of extracts. (A) Diazomethane-treated $\sum 5{:}6$, 0.15 μL (of 5-mL total extract). (B) Diazomethane-treated $\sum 5$, 0.15 μL (of 5-mL total). (1) Propanedioic acid dimethyl ester, (2) trimethyl phosphate, (3) methyl benzoate, (4) dimethyl pentyl phosphate, (5) methyl salicylate, (6) methyl caprate, (7) methyl cinnamate, (8) coumarin, (9) methyl laurate, (10) unidentified, (11) methyl myristate, (12) unidentified, (13) methyl palmitate, (14) unidentified, (15) mixture of methyl esters of oleic (30%) and linoleic (70%) acids, (15a, in part B) methyl stearate, (16) unidentified, (17) methyl arachidate (identified by retention time only), and (18) unidentified. Conditions were as given under Experimental Section for GLC (Varian 2740, SP2100). The unidentified peaks generally occurred in other fractions of the extract that were biologically inactive.

esters were identified as lauric, myristic, and palmitic acid methyl esters by comparison of the GC retention times with known acid esters. A subsequent run of diazomethane-treated $\sum 5$ gave molecular peaks at *m/e* 242 (4%) and 270 (3%) corresponding to myristic and palmitic acid methyl esters.

DISCUSSION

Substances present and identified in the biologically active fractions $\sum 5$ and $\sum 5{:}6$ from diseased iris bulbs were propanedioic acid, phosphoric acid, benzoic acid, salicylic acid, cinnamic acid, coumarin, and the fatty acids capric, lauric, myristic, palmitic, stearic, oleic, and linoleic (Figure

Table II. Bioassay of Commercial Acids and Other Compounds against *P. corymbiferum* and *F. oxysporum*

methanolic soln of (direct application to agar)	response[a] 1 μL (20 μg) P	1 μL (20 μg) F	2 μL (40 μg) P	2 μL (40 μg) F
cinnamic acid	+, 5	⊕, 15	⊕, 7	⊕, 7
coumarin	0	0	+sl	0
benzoic acid	+, 5	⊕, 9	⊕, 7	⊕, 7
salicyclic acid	+, 5	⊕, 5	+, 4	⊕, 2
phosphoric acid	0	0		
methanol	0	0	0	0
isocaproic acid	+, 5	+		
caproic acid	+, 5	+sl		
heptanoic acid	⊕, 6	+, [10]		
caprylic acid	⊕, 7	+, [10]		
nonanoic acid	+, 6	+		
capric acid	⊕, 10	⊕, 8		
lauric acid	0	0		
myristic acid	0	0		

[a] (+) Inhibition; (⊕) strong inhibition; bracketed values indicate an indistinct borderline; (0) no effect; (sl) slight. Numerals indicate ring diameters of inhibition, measured in millimeter 24 h after direct application of methanolic solution. P = *P. corymbiferum*; F = *F. oxysporum*.

1). Of the substances present (in $\sum 5$ or $\sum 5{:}6$) and also fungicidal against *Penicillium* and/or *Fusarium* were, in the order of decreasing apparent effectiveness, capric acid (estimated concentration 0.24 mg/kg), cinnamic acid (11 mg/kg), salicylic acid (77 mg/kg), benzoic acid (7 mg/kg), and coumarin (26 mg/kg).

A bioassay was conducted with acids and coumarin obtained from commercial sources. Results are shown in Table II. Six carbon to nine carbon aliphatic acids are included because their presence is suspected by the characteristically rancid odor of the extract after the material was concentrated.

Capric acid (at 20 μg) had the strongest inhibitory effect on *Penicillium*, maintaining a clear area 10 and 4 mm in diameter after the first and the fourth day after application of 1 μL of 20 μg/μL methanolic solution. The effect of capric acid on *Fusarium* was moderate: an 8-mm diameter not completely clear area and a 6-mm diameter incompletely clear inhibition area on the first and fourth day. Capric acid in diseased bulb was estimated (in $\sum 4$, $\sum 5$, and $\sum 6$) at 0.24 mg/kg compared with the 0.3 mg/kg recovered by Ando and Tsukamoto (1974) from healthy bulbs.

The capric acid peak increased threefold after an HCl hydrolysis of $\sum 5$ (followed by evaporation and treatment with diazomethane), indicating that some of this acid was combined in a nonchromatographable form, but there is a possibility that combination may have taken place during storage after extraction from the diseased plant material.

Cinnamic acid displayed the strongest inhibition on *Fusarium*, maintaining a 15-mm clear area on the first day after application and a 10-mm diameter completely clear area on the fourth day. Coumarin, the lactone, had no effect at the 20-μg level.

All of the identified substances have previously been found in plants. Capric acid has recently been implicated as a summer dormancy factor in the Wedgwood iris bulb (Ando and Tsukamoto, 1974). Cinnamic acid is the well-known first step in the enzymatic deamination and conversion of phenylalanine to the other phenylpropanoids and to lignin (Koukol and Conn, 1961). Its hydroxylated and methylated forms such as coumaric, caffeic, ferulic, and sinapic acids, along with the benzoic acids, occur almost universally in hydrolyzed plant material. Free cinnamic acid has been reported in plants, but this is of less common occurrence than the combined form (Ribereau-Gayon, 1972). Salicylic acid apparently is also of less common occurrence, but in any case, all the phenolic acids occur naturally in combination, usually in the form of esters (Harborne, 1973; Ribereau-Gayon, 1972). The occurrence of these acids in diseased iris is in the form of the free acid. This is indicated by the volatility of the acid compounds after a mild diazomethane treatment with no prior hydrolysis. The reasons for the occurrence of these free antifungal acids are open to speculation. That they may constitute part of an antifungal mechanism in the bulb is one possibility. Admittedly, there are serious gaps in our understanding of the roles of the different types of phenolics (Friend, 1979).

Coumarin in plants, according to Brown (1979), is an artifact of isolation; the precursor, *cis*-2′-glucosyloxycinnamic acid, upon cell disruption, is acted upon by a glucosidase, liberating the unstable *cis*-2′-hydroxycinnamic acid which immediately lactonizes to coumarin.

Trimethyl phosphate and dimethyl pentyl phosphate are presumed to be artifacts from plasticware (Biemann, 1962) along with phthalates which were also detected by the characteristic *m/e* 149 peak in the mass spectrum.

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