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STUDIES IN FUNGITOXICITY. IV.*—Fungitoxicity of Certain Ethylenic Compounds

By J. D. EDWARDS and M. PIANKA

Several benzylidene and related compounds have been tested for fungitoxicity to certain economically important fungi. They were found to be generally less active than β-nitrostyrenes. Certain electron-attracting groups attached to the ethylenic bond conferred activity, but cyano groups did not.

Introduction

In Part III[1] were described the results of tests of a number of β-nitrostyrenes p-R·C_6H_4·CH:CR′·NO_2 and related compounds for toxicity against the spores of *Venturia inaequalis* (Cooke) Wint. ; *Botrytis cinerea* Pers. ; and *Fusarium bulbigenum*, Cooke & Massee, var. *lycopersici* (Brushi) Wollenw. It was considered of interest to prepare and test compounds in which both groups R′ and NO_2 were replaced by electronegative groups, such as COOEt, COR″, CN, and in which the ring substituent was a chlorine atom or a nitro group in different positions.

Roblin & Hechenbleikner[2] observed the insecticidal activity of benzylidene and furfurylidene malonates and McGowan and co-workers[3] noted the fungistatic activity of ethylenic compounds in which one group—COOR, COR, COOH or CHO—was attached to the ethylenic bond.

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* Part III : preceding paper

Experimental

All but the four compounds (nos. 2, 8, 17 and 24) are known and were prepared by methods described in the literature.

Diethyl 4-chlorobenzylidenemalonate (Compound no. 2)

Diethyl malonate (8 g.), *p*-chlorobenzaldehyde (7·02 g.) and piperidine (0·2 g.) were heated on a steam-bath for 6 h. The mixture was then kept at room temperature for 3 days. The water formed was removed from the reaction mixture by distillation with chloroform, and the residue was distilled, to yield a colourless oil (7·7 g.), b.p. 122–124°/0·01 mm. (Found : Cl, 12·2. $C_{14}H_{15}ClO_4$ requires Cl, 12·6%).

4-Chlorobenzylideneacetylacetone (Compound no. 8)

A mixture of acetylacetone (3·55 g.), *p*-chlorobenzaldehyde (5·0 g.) and piperidine (0·02 c.c.) was kept at room temperature for 24 h. 3N-Sulphuric acid (10 c.c.) was added and the mixture extracted with ether. The ether extract was washed twice with water and dried (sodium sulphate) and the ether evaporated. The oily residue solidified after several days and was recrystallised from petroleum, b.p. 60–80° (charcoal). White crystals were obtained, m.p. 73–75·5° (Found: Cl, 15·5. $C_{12}H_{11}ClO_2$ requires Cl, 15·9%).

4-Chlorobenzylidene-dehydracetic acid (Compound no. 17)

p-Chlorobenzaldehyde (5 g.), dehydracetic acid (6 g.), piperidine (0·7 c.c.) and chloroform (50 c.c.) were heated under reflux for 6 h. The flask was then equipped with a Dean & Stark trap to remove the water formed in the reaction and the mixture refluxed for a further 7½ h. The solvent was distilled off *in vacuo*, leaving a solid that on recrystallisation from methanol and then from ethanol yielded yellow needles, m.p. 162–163° (Found : Cl, 12·5. $C_{15}H_{11}ClO_4$ requires Cl, 12·2%).

Diethyl 3,7-dimethyl-5-(3-nitrophenyl)-4,6-dioxanona-2,7-dien-1,9-dioate (Compound no. 24)

m-Nitrobenzaldehyde (4·6 g.), ethyl acetoacetate (3·9 g.) piperidine (3 drops) and ethanol (0·5 c.c.) were kept at −5° to −9° for 5 days, then at room temperature for another 5 days. The crystalline solid that separated was filtered off and recrystallised twice from ethanol. White crystals (3·1 g.) were obtained, m.p. 152–154° (Found : N, 3·3. $C_{19}H_{23}NO_8$ requires N, 3·5%).

Fungitoxicity tests

All the tests were carried out by the Montgomery–Moore[4] slide germination technique, and the values of LD_{95} were determined against *Venturia*, *Botrytis*, *Fusarium* and *Cercospora melonis*, Cooke, as described in Part I.[5]

Results and discussion

Table I shows the results of fungitoxicity tests on 24 ethylenic compounds. The weaker electron-attracting properties of the ethoxycarbonyl and methylcarbonyl groups may be responsible for the activity of compounds nos. 1–9 being lower than that of the β-nitrostyrenes.[1] The specificity of position (*meta*) required for the activity of diethyl nitrobenzylidenemalonate is surprising (Compounds nos. 3 and 4). Other ethylenic compounds derived from *m*-nitrobenzaldehyde (nos. 6, 7, 9, 21, 22) have, however, little or no activity.

Though cyano groups generally contribute to activity against *Venturia*, condensation products of ring-substituted benzaldehydes and ethyl cyanoacetate (Compounds nos. 10–12) or malononitrile (Compounds nos. 13–15) were unexpectedly inactive.

Condensation products of benzaldehyde and of ring-substituted benzaldehydes with dehydracetic acid (nos. 16, 17), with 1-phenyl-3-methyl-5-pyrazolone (no. 22), with fluorene (nos. 18, 19) or with 2,7-dibromofluorene (nos. 20–21) proved to be inactive. Compounds of the acetal type, in which the ethylenic bond was not in conjugation with the aromatic ring (nos. 23, 24), were also inactive.

Table I

Results of fungitoxicity tests with benzylidene compounds

No. of compound	Name of compound	M.p.	Reference	*Venturia*	*Botrytis*	*Fusarium*	*Cerospora*
				LD_{95} values, p.p.m.			
	Diethyl malonate						
1	Benzylidene-	b.p. 138°/0·6 mm.	6	120	>100	200	>100
2	4-Chlorobenzylidene-	b.p. 122–124°/0·01 mm.		80	>1000	>100	>100
3	4-Nitrobenzylidene-	93°	7	>1000	>1000	>1000	>1000
4	3-Nitrobenzylidene-	75°	8	25	>1000	80	>1000
	Ethyl acetoacetate						
5	4-Chlorobenzylidene-	85–87°	18	130	540	180	100
6	3-Nitrobenzylidene-	110°	9	200	>1000	80	>100
	Ethyl benzoylacetate						
7	3-Nitrobenzylidene-	106–107°	8	100	>1000	>1000	>1000
	Acetylacetone						
8	4-Chlorobenzylidene-	73–75°		130	540	170	100
9	3-Nitrobenzylidene-	101–102°	10	180	>1000	440	180
	Ethyl cyanoacetate						
10	4-Chlorobenzylidene-	93°	11	>1000	>1000	>1000	>1000
11	4-Nitrobenzylidene-	169–170°	12	>1000	>1000	>1000	>1000
12	3-Nitrobenzylidene-	130–133°	13	>1000	>1000	>1000	>1000
	Malononitrile						
13	4-Chlorobenzylidene-	162–163°	14	400	>1000	200	1000
14	4-Nitrobenzylidene-	161–162°	15	>100	>1000	1000	>100
15	3-Nitrobenzylidene-	103-104°	16	1000	>1000	>1000	>1000
	Dehydracetic acid						
16	Benzylidene-	130–131°	17	>1000	>1000	>1000	>1000
17	4-Chlorobenzylidene	162–163°		>1000	>1000	>1000	>1000
	Fluorene						
18	4-Chlorobenzylidene-	148–149°	19	>1000	>1000	>1000	>1000
19	3-Nitrobenzylidene-	111–112°	20	>1000	>1000	>1000	>1000
	2,7-*Dibromofluorene*						
20	4-Chlorobenzylidene-	215–216°	19	>1000	>1000	>1000	>1000
21	3-Nitrobenzylidene-	155–156°	19	>1000	>1000	>1000	>1000
	1-*Phenyl*-3-*methyl*-5-*pyrazolone*						
22	3-Nitrobenzylidene-	157–158°	21	>1000	>1000	>1000	>1000
	Miscellaneous compounds						
23	Diethyl 3,7-dimethyl-5-(4-chlorophenyl)-4,6-dioxanona-2,7-dien-1,9-dioate	156°	18	>1000	>1000	>1000	>1000
24	Diethyl 3,7-dimethyl-5-(3-nitrophenyl)-4,6-dioxanona-2,7-dien-1,9-dioate	152–154°		>1000	>1000	>1000	>1000

Conclusions

From the very limited results available the following very tentative conclusions may perhaps be drawn on the relationship between fungitoxicity to the parasitic fungi : *Venturia, Botrytis, Fusarium* and *Cercospora,* and chemical structure of certain benzylidene compounds:

(*a*) ethylenic compounds in which ethoxycarbonyl and methylcarbonyl groups are attached to the ethylenic bond are less active than those with a nitro group ;[1, 3]

(*b*) ethylenic compounds in which the electronegative CN is attached to the ethylenic bond are inactive ;

(*c*) benzylidene compounds in which the double bond carries a carbonyl heterocyclic group or a fluorene group are inactive.

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CITRUS ESSENTIAL OILS. III.*—Evaluation of Sicilian Natural Lemon Oils

By C. A. SLATER

An examination of the infra-red spectra of the oxygenated fractions of Sicilian natural lemon oils has made possible a new method of evaluation which agrees very closely with the results obtained by classical methods of analysis and organoleptic testing. In addition, methods are suggested for the detection of adulteration of natural lemon oils.

Introduction

The first paper in this series[1] described a method for the evaluation of natural and terpeneless lemon oils by physical methods. Since then many more samples of Sicilian natural lemon oil have been examined, and certain weaknesses in the previous method have been found. Reappraisal of the results has given better criteria and a physical method is now described for the evaluation of natural lemon oils, which shows a very high degree of agreement with results obtained by classical methods.

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