J Plant Growth Regul (1984) 3:75–84

Journal of
Plant
Growth
Regulation

Schiff's Bases and Derived Secondary Amines as Plant Growth Inhibitors

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Received September 29, 1983; accepted January 26, 1984

Abstract. Seventy-two Schiff's bases, 44 corresponding secondary amines, and 12 N-acetylated compounds were tested on their growth activity. Eighty-one compounds were active as growth inhibitors in at least one of three bioassays.

Lunularic acid, a bibenzyl derivative, is a naturally occurring growth inhibitor in liverworts (Valio and Schwabe 1970). By reason of the structural similarity of bibenzyls with Schiff's bases and the corresponding secondary amines, we have synthesized numerous Schiff's bases, the corresponding secondary amines, and the acetylated compounds and report subsequently on their plant growth activities (Scheme 1). The results of this publication are put down in three patents (Huneck et al. 1976, Grimmecke et al. 1976a, Grimmecke et al. 1976b).

Materials and Methods

All Schiff's bases were prepared by condensation of aromatic aldehydes with aromatic primary amines and characterized by their elemental analysis and their IR spectra. Reduction of the Schiff's bases with Raney-Ni or lithiumaluminiumhydride yielded the corresponding secondary amines; N-acetylation was done with acetic anhydride in pyridine. Addition of nitromethane to N-(benzylidene)aniline gave the amine *113* and reduction of *113* gave the amine

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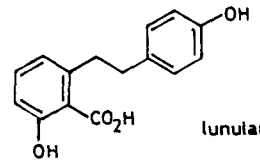
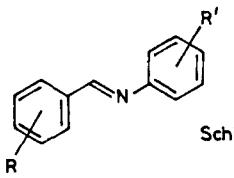
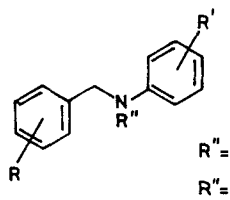


lunularic acid



Schiff's base



R''= H: secondary amine

R''= Ac: acetylated secondary amine

Scheme 1.

114. The imidazole *69* was made from benzaldehyde and o-phenylenediamine and subsequent dehydrogenation with oxygen. Addition of trichloroacetic acid to *1* and *47* yielded the corresponding trichloroacetates *71* and *72* (Scheme 2).

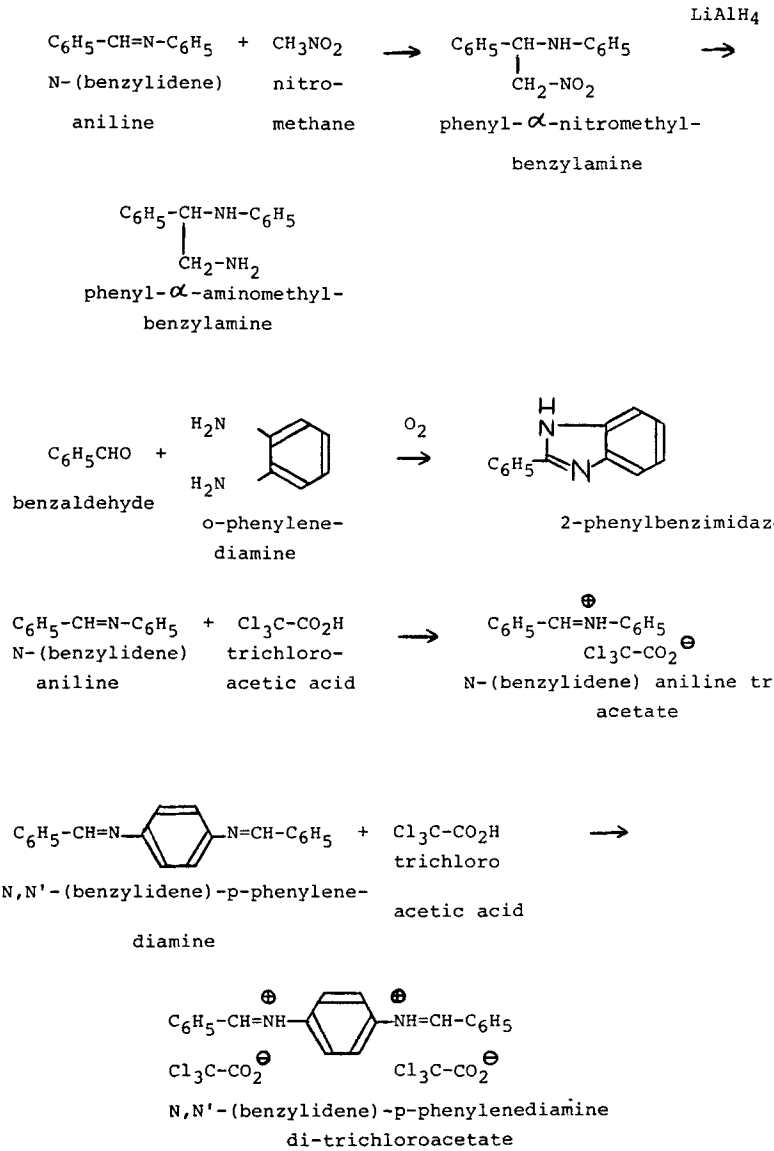
Schiff's Bases

Equimolar amounts of aldehyde and amine are dissolved in the necessary amount of ethanol and heated under reflux for 5 min; excess solvent is removed by distillation, and the solid base filtered and recrystallized from ethanol.

2-Phenyl-benzimidazole (*69*)
The Schiff's base *45* (1 g) is heated with hydrochloric acid (1 N, 5 drops) in ethanol (20 ml) under reflux for 30 min, the solvent removed, and the residue recrystallized from ethanol-water.

N-(Benzylidene)aniline trichloroacetate (*71*) and N,N'-(dibenzylidene)-p-phenylenediamine di-trichloroacetate (*72*)
The corresponding Schiff's base (4 mmol) is heated with trichloroacetic acid (4 mmol, 0.654 g per C = N − group) in toluene (50 ml) to 100°C for 30 min and the solid adduct recrystallized from toluene.

α-Nitromethyl-benzyl-phenylamine (*113*)



Scheme 2.

A mixture of N-(benzylidene)aniline (10 mmol, 1.8 g) and nitromethane (1.2 ml) in ethanol (10 ml) is heated under reflux for 10 h, the solvent removed, and the residue recrystallized from ethanol.

α-Trichloromethyl-benzyl-phenylamine (*115*) and di-α-trichloromethyl-benzyl-p-phenylenediamine (*116*)
The corresponding Schiff's base (4 mmol) is heated with trichloroacetic acid

(4.8 mmol per C = N − group) in toluene (100 ml) for 2 h under reflux, the solvent removed, and the residue recrystallized from toluene.

Secondary Amines

Method A. The Schiff's base (1–2 g) is dissolved in ethanol (50–100 ml) and hydrogenated with Raney-Ni (1 g) under normal pressure at room temperature.

Method B. The Schiff's base (4 mmol) is dissolved in diethyl ether or tetrahydrofurane (50 ml) and heated with lithiumaluminiumhydride (60 mg) under reflux for 30 min. Excess of hydride is destroyed with water and the secondary amine isolated in the usual way.

Bioassays

For the bioassays, seedlings of wheat (cultivar "Remo"), rye (cultivar "Petka"), and barley (cultivar "Elgina") were used; standard of comparison was ethrel (Dathe et al. 1978). The seeds were germinated on wet filter paper in darkness at 25°C. After coleoptile emergence, the seedlings were put into the 10^{-3} M test solution; the length of the primary leaf was measured 5 days later. The response was considered as inhibitory (indicated by + or ++ in Tables 1 and 2) if, at the least, the inhibition of 10^{-3} M ethrel was reached.

From the bioassays the following relationships can be derived:

1. Schiff's bases with aniline as one component are inactive in the used tests, for example, *1–5*.
2. Schiff's bases with benzaldehyde as one component are partially active in at least one bioassay, for example, *6, 28, 40, 43, 48, 51–55*.
3. Schiff's bases with 2-, 3-, 4-monochloro- or 2.3- and 2.5-dichloroaniline as amine are specifically active on rye, for example, *28–31, 35–37, 39, 40–42*.
4. Schiff's bases derived from 2- and 4-aminophenol are active in most cases, for examples, *51–64, 66, 67*.
5. The growth inhibition property is not limited to the C = N double bond, because numerous secondary amines are also active, for instance *73, 76, 80, 81, 83–84, 86, 87, 90, 93–100, 102–105, 107–109, 111, 113–115, 124–128*.
6. Exchange of a carboxyl group to a chloro atom in the N-phenyl part leads either to an active compound or increases the existing activity, for example, *6 → 28, 14 → 19, 21 → 40, 15 → 30, 22→ 41, 23 → 42*.
7. Exchange of a carboxyl group to a hydroxyl group in the N-phenyl part leads again to active compounds, for example, *6 → 51, 7 → 52, 8 → 53, 9 → 54, 21 → 55, 22 → 56, 23 → 57, 24 → 58*.
8. Exchange of the hydroxyl group to a chloro atom in the benzylidene part does not influence the activity, for example, *17 → 20, 24 → 27, 36 → 37, 58 → 62*.
9. Introduction of the nitromethyl group into the amine *73* leads from an inactive to a very active compound (*113*).

Table 1. Schiff's bases and their growth inhibitory activities.

No.	Compound*	Melting (or boiling) point (°C)	Plant growth inhibition in tests wheat	rye	barley
1	N-(benzylidene)aniline	53–54	–	–	–
2	N-(2-hydroxybenzylidene)aniline	51–52	–	–	–
3	N-(4-hydroxybenzylidene)aniline	195–196	–	–	–
4	N-(3.4-dihydroxybenzylidene)aniline	174–176	–	–	–
5	N-(3-methoxy-4-hydroxybenzylidene)aniline	156–158	–	–	–
6	2-carboxy-N-(benzylidene)aniline	129–130	–	+	–
7	2-carboxy-N-(2-hydroxybenzylidene)aniline	200–204	–	–	–
8	2-carboxy-N-(3-hydroxybenzylidene)aniline	182–184	–	–	–
9	2-carboxy-N-(4-hydroxybenzylidene)aniline	236–238	–	–	–
10	2-carboxy-N-(3.4-dihydroxybenzylidene)aniline	226–228 (dec)	–	–	–
11	2-carboxy-N-(3-methoxy-4-hydroxybenzylidene)aniline			–	–
	yellow modification	176–177	–	–	–
	red modification	172–173	–	–	–
12	2-carboxy-N-(3-nitrobenzylidene)aniline	206–209	–	–	–
13	2-carboxy-N-(4-nitrobenzylidene)aniline	164–165	–	–	–
14	3-carboxy-N-(benzylidene)aniline	129–134	–	–	–
15	3-carboxy-N-(2-hydroxybenzylidene)aniline	186–190	–	+	–
16**	3-carboxy-N-(3-hydroxybenzylidene)aniline	174–176	–	+	–
17	3-carboxy-N-(4-hydroxybenzylidene)aniline	238–240 (dec)	–	–	+
18**	3-carboxy-N-(3.4-dihydroxybenzylidene)aniline	210 (dec)	–	–	–
19	3-carboxy-N-(3-methoxy-4-hydroxybenzylidene)aniline	180–182	–	+	–
20**	3-carboxy-N-(4-chlorobenzylidene)aniline	177–180	–	–	+
21	4-carboxy-N-(benzylidene)aniline yellow modification	192–195	–	–	–
	red modification	195–198	–	–	–
22	4-carboxy-N-(2-hydroxybenzylidene)aniline	269–270	–	–	–
23**	4-carboxy-N-(3-hydroxybenzylidene)aniline	236–238	–	–	–
24	4-carboxy-N-(4-hydroxybenzylidene)aniline	257–258 (dec)	–	+	–
25	4-carboxy-N-(2.4-dihydroxybenzylidene)aniline	250 (dec)	–	–	–

Table 1. Continued

No.	Compound*	Melting (or boiling) point (°C)	Plant growth inhibition in tests wheat	rye	barley
26	4-carboxy-N-(3-methoxy-4-hydroxybenzylidene)aniline yellow modification	213–214	–	+	–
27**	4-carboxy-N-(4-chlorobenzylidene)aniline	268–270	–	+	–
28	2-chloro-N-(benzylidene)aniline	54–58	–	+	–
29	3-chloro-N-(benzylidene)aniline	oil, 338–340	–	+	–
30	3-chloro-N-(2-hydroxybenzylidene)aniline	95–96	–	+ +	–
31**	3-chloro-N-(3-hydroxybenzylidene)aniline	116–117	–	+	–
32	3-chloro-N-(4-hydroxybenzylidene)aniline	177–179	–	–	–
33**	3-chloro-4-methyl-N-(3-hydroxybenzylidene)aniline	124–126	–	–	–
34**	3-chloro-4-methyl-N-(4-hydroxybenzylidene)aniline	195–197	–	–	–
35**	2,3-dichloro-N-(3-hydroxybenzylidene)aniline	100–102	–	+	–
36**	2,3-dichloro-N-(4-hydroxybenzylidene)aniline	182–184	–	+	–
37**	2,3-dichloro-N-(4-chlorobenzylidene)aniline	215–217	–	+	–
38**	2,5-dichloro-N-(3-hydroxybenzylidene)aniline	85–88	–	–	–
39**	2,5-dichloro-N-(4-hydroxybenzylidene)aniline	113–115	–	+	–
40	4-chloro-N-(benzylidene)aniline	60–61	–	+ +	–
41	4-chloro-N-(2-hydroxybenzylidene)aniline	101–102	–	+ +	–
42**	4-chloro-N-(3-hydroxybenzylidene)aniline	135–137	–	+ +	–
43	3-nitro-N-(benzylidene)aniline	68–70	–	+	–
44	4-nitro-N-(benzylidene)aniline	113–116	–	–	–
45	2-amino-N-(benzylidene)aniline	58–60	–	+	–
46**	4-amino-N-(benzylidene)aniline	133–136	–	+	–
47	N,N′-(benzylidene)-p-phenylenediamine	139–140	+	+	–

Table 1. Continued

No.	Compound*	Melting (or boiling) point (°C)	Plant growth inhibition in tests wheat	rye	barley
48	N,N′-(benzylidene)-o-phenylenediamine	109–111	–	+	+
49**	N,N′-(3-ethoxy-4-hydroxybenzylidene)-p-phenylenediamine	177–180	–	+	+
50**	N-(3-hydroxybenzylidene)-2-naphthylamine	131–132	–	+	–
51	2-hydroxy-N-(benzylidene)aniline	89–90	–	+	+
52	2-hydroxy-N-(2-hydroxybenzylidene)aniline	184–186	–	+	+
53**	2-hydroxy-N-(3-hydroxybenzylidene)aniline	121–122	–	+	+
54**	2-hydroxy-N-(4-hydroxybenzylidene)aniline	130–133	–	+	+
55	4-hydroxy-N-(benzylidene)aniline	184–185	–	+	+
56	4-hydroxy-N-(2-hydroxybenzylidene)aniline	137–138	+	+	+
57**	4-hydroxy-N-(3-hydroxybenzylidene)aniline	197–198	+	+	+
58	4-hydroxy-N-(4-hydroxybenzylidene)aniline	212–215	+	+	+
59	4-hydroxy-N-(4-methoxybenzylidene)aniline	192–194	–	+	–
60**	4-hydroxy-N-(2-hydroxy-3-methoxybenzylidene)aniline	155–156	–	–	+
61**	4-hydroxy-N-(2.3-dimethoxybenzylidene)aniline	101–103	–	+	–
62**	4-hydroxy-N-(4-chlorobenzylidene)aniline	182–183	+	+	+
63	4-hydroxy-N-(3-nitrobenzylidene)aniline	161–162	–	+	+
64	4-hydroxy-N-(4-nitrobenzylidene)aniline	170–171	–	+	–
65	4-hydroxy-N-(2-hydroxynaphthylidene)aniline	225–227	–	–	–
66	4-hydroxy-N-(2-furfurylidene)aniline	192–196	–	+	–
67**	4-hydroxy-N-(2-thenylidene)aniline	206–207	–	+	–
68	4-hydroxy-N-(cinnamylidene)aniline	208–210 (dec)	–	+	–
69	2-phenylbenzimidazole	280–281	–	+	+
70**	N-acetyl-2-phenylbenzimidazole	267–272	+	+	+
71**	N-(benzylidene)aniline trichloroacetate	158 (dec)	–	+	+ +
72**	N,N′-(benzylidene)p-phenylenediamine di-trichloroacetate	123–128	–	–	+

* Most compounds are described in the Beilstein *Handbook of Organic Chemistry*.

** New compound.

Table 2. Secondary amines, their acetamides, and their growth inhibitory activities.

No.	Compound*	Melting point (°C)	Plant growth inhibition in tests wheat	rye	barley
73	N-phenyl-benzylamine	37–39	–	–	+
74	N-phenyl-2-hydroxybenzylamine	112–114	–	–	–
75	N-phenyl-4-hydroxybenzylideneamine hydrochloride	154–156	–	–	–
76**	N-phenyl-3-methoxy-4-hydroxybenzylamine hydrochloride	146–148	–	+	–
77	N-(2-carboxyphenyl)-benzylamine	175–177	–	–	–
78**	N-(2-carboxyphenyl)2-hydroxybenzylamine	130–132	–	–	–
79**	N-(2-carboxyphenyl)3-hydroxybenzylamine	144–146	–	–	–
80**	N-(2-carboxyphenyl)4-hydroxybenzylamine	138–140	–	+	+
81**	N-(2-carboxyphenyl)3-methoxy-4-hydroxybenzylamine	179–182	–	+	+
82	N-(3-carboxyphenyl)benzylamine	110–111	–	–	–
83**	N-(3-carboxyphenyl)2-hydroxybenzylamine	145–146	–	+	–
84**	N-(3-carboxyphenyl)3-hydroxybenzylamine	125–126	+	–	+
85**	N-(3-carboxyphenyl)4-hydroxybenzylamine hydrochloride	163–166	–	–	–
86**	N-(3-carboxyphenyl)3-methoxy-4-hydroxybenzylamine	168–171	–	+	–
87**	N-(3-carboxyphenyl)4-chlorobenzylamine	124–127	+	+	+
88**	N-(3-hydroxymethylphenyl)4-chlorobenzylamine hydrochloride	136–138	–	–	–
89	N-(4-carboxyphenyl)benzylamine	165–168	–	–	–
90**	N-(4-carboxyphenyl)2-hydroxybenzylamine	203–204	–	+	–
91**	N-(4-carboxyphenyl)3-methoxybenzylamine	198–200	–	–	–
92**	N-(4-carboxyphenyl)4-hydroxybenzylamine	190–192	–	–	–
93**	N-(4-carboxyphenyl)3-methoxy-4-hydroxybenzylamine	173–175	–	+	–
94**	N-(4-carboxyphenyl)4-chlorobenzylamine	211–213	–	+	–
95**	N-(4-hydroxymethylphenyl)4-chlorobenzylamine hydrochloride	159–161	–	+	–
96	N-(2-chlorophenyl)benzylamine hydrochloride	88–91	–	+ +	+
97**	N-(3-chlorophenyl)benzylamine hydrochloride	107–110	–	+	+
98	N-(4-chlorophenyl)benzylamine	45–47	–	+	–
99*	N-(2.3-dichlorophenyl)4-chlorobenzylamine	45–48	–	+	–

Table 2. Continued

No.	Compound*	Melting point (°C)	Plant growth inhibition in tests wheat	rye	barley
100	N,N'-dibenzyl-o-phenylenediamine	132–133	–	+	–
101	N-(3-aminophenyl)benzylamine di-hydrochloride	196	–	–	–
102	N-(4-aminophenyl)benzylamine	102–103	–	+ +	–
103	N,N'-dibenzyl-p-phenylenediamine	96–97	–	+	+
104*	N-(2-naphthyl)3-hydroxybenzylamine hydrochloride	182–183	–	+	+
105*	N-(2-hydroxyphenyl)benzylamine hydrochloride	160–165	–	–	+
106	N-(2-hydroxyphenyl)2-hydroxybenzylamine hydrochloride	185–188	–	–	–
107	N-(4-hydroxyphenyl)benzylamine	89–90	–	+ +	–
108	N-(4-hydroxyphenyl)2-hydroxybenzylamine	122–123	–	+	–
109*	N-(4-hydroxyphenyl)3-hydroxybenzylamine	153–156	–	+	+
110*	N-(4-hydroxyphenyl)4-hydroxybenzylamine	170–174	–	–	–
111	N-(4-hydroxyphenyl)4-methoxybenzylamine	102–103	–	+	+
112*	N-(4-hydroxyphenyl)4-chlorobenzylamine hydrochloride	186–191	–	–	–
113	phenyl-α-nitromethyl-benzylamine	85–86	–	+ +	+
114*	phenyl-α-aminomethyl-benzylamine di-hydrochloride	264 (dec)	+	–	–
115	phenyl-α-trichloromethyl-benzylamine	80–82	–	–	–
116*	N,N'-di-α-trichloromethyl-benzyl-p-phenylenediamine	134–135	–	–	–
117*	N-acetyl-(phenyl)3-methoxy-4-acetoxybenzylamine	105–107	–	–	–
118*	N-acetyl-(2-carboxyphenyl)4-acetoxybenzylamine	176–179	–	–	–
119*	N-acetyl-(2-carboxyphenyl)3-methoxy-4-acetoxybenzylamine	120–123	–	–	–
120*	N-acetyl-(3-carboxyphenyl)2-acetoxybenzylamine	126–128	–	–	–
121*	N-acetyl-(3-carboxyphenyl)3-acetoxybenzylamine	195–199	–	–	–
122*	N-acetyl-(3-carboxyphenyl)3-methoxy-4-acetoxybenzylamine	249–251	–	–	–
123*	N-acetyl-(4-carboxyphenyl)2-acetoxybenzylamine	80–83	–	–	–
124*	N-acetyl-(4-carboxyphenyl)3-methoxy-4-acetoxybenzylamine	183–185	–	+	–
125*	N-acetyl-(4-chlorophenyl)benzylamine	89–91	–	+	–
126	N-acetyl-(4-acetaminophenyl)benzylamine	116–117	–	+	+
127*	N,N'-di-acetyl-di-benzyl-p-phenylenediamine	118–119	–	+	+
128*	N-acetyl-(4-acetoxyphenyl)benzylamine	169–171	+	+	+

* Most compounds are described in the Beilstein *Handbook of Organic Chemistry*.
** New compound.

Acknowledgments. We thank Prof. Dr. G. Sembdner and Dipl. Biol. C. Schulze, Institute of Plant Biochemistry, Halle/Saale, for the bioassays.

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