Pestic. Sci. 1995, **44**, 137–144

Synthesis and Herbicidal Activity of Substituted Tetrahydronaphthalenes: I

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(Received 19 May 1994; revised version received 1 September 1994; accepted 3 January 1995)

Abstract: This paper reports the synthesis and the biological activity of substituted 6-alkyl-1,2,3,4-tetrahydro-1,1-dimethylnaphthalenes in which the substituents at the 5- and/or 7-position are varied with a multitide of functional groups. These compounds exhibited pre-emergent herbicidal activity which was a function of the electron-withdrawing ability and the size of the groups substituted at the 5- and/or 7-position. Nitro and/or nitrile groups at these positions tended to optimize activity.

Key words: tetrahydronaphthalene, tetralin.

1 INTRODUCTION

As part of a systematic search for herbicidal compounds, a series of substituted 6-alkyl-1,2,3,4-tetrahydro-1,1-dimethylnaphthalenes were prepared.[1] The synthesis program was initiated after methyl 5,6,7,8-tetrahydro-2,5,5-trimethyl-1-naphthalenecarboxylate (obtained from Dr S. P. Tanis, Michigan State University, E. Lanseng, MI 48824) demonstrated significant pre-emergent activity on economically important monocotyledonous weeds.[2] The primary focus of this program was to optimize herbicidal activity through preparation of additional analogs.

This paper reports the synthesis and biological activity of substituted 6-alkyl-1,2,3,4-tetrahydro-1,1-dimethylnaphthalenes (6-alkyl-1,1-dimethyltetralins). The biological activity of these compounds has been optimized by varying the substituents R_5 and R_7 in structure **1** (Fig. 1). The herbicidal unit activity is determined by the nature of the substituents R_5 and R_7, depending on the electron-withdrawing capability and size of the groups.

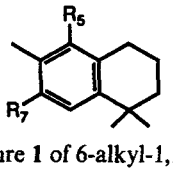

Fig. 1. General structure **1** of 6-alkyl-1,1-dimethyltetralin.

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2 EXPERIMENTAL

2.1 General

The compounds prepared, together with their physical properties, are shown in Tables 1–5. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{19}F) were recorded using Bruker WM-360 and Varian XL-400 NMR spectrometers. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA. Sample purity was determined by gas liquid chromatography (GLC) analysis on a Varian 3400 gas chromatograph utilizing a $\frac{1}{8}$" i.d × 6' (3·2 mm × 1·83 m) stainless steel column packed with 10% Supelco SP-2100 (methyl silicone) on 80/100 Supelcoport. Normally, a temperature program from 150°C to 300°C at 15°C min^{-1} was employed. Column chromatography was performed on a Waters preparative liquid chromatography (LC) Model 500 using silica gel columns. Most reported yields are unoptimized as synthetic emphasis was placed on purity of products rather than quantity.

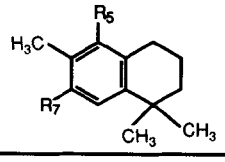
2.2 Synthesis

Detailed reaction schemes for the synthesis and derivatization of the tetralins are described in Ref. 1.

The synthesis of the tetralin derivatives has been accomplished following the procedures described below.

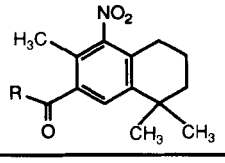
Pestic. Sci. 0031-613X/95/$09.00

TABLE 1
Tetralins of Structure **2**



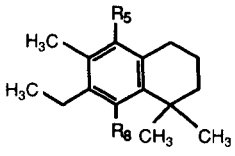
Entry	R_5	R_7	*m.p.* (°C)	*Yield* (%)
2a	H	H	Oil	95
2b	NO_2	H	Oil	30
2c	H	NO_2	Oil	70
2d	NO_2	NO_2	101–102	80
2e	NO_2	CN	131–132	88
2f	NH_2	H	Oil	99
2g	H	NH_2	Oil	75
2h	NH_2	NH_2	Oil	77
2i	H	$COCH_3$	60–61	99
2j	H	CO_2H	187–188	95
2k	H	CO_2CH_3	Oil	100
2l	H	SO_2Cl	84–85	82
2m	NO_2	$COCH_3$	84–85	76
2n	NO_2	CO_2H	230–231	94
2o	NO_2	NH_2	172–173	90
2p	H	$NHCOCF_3$	137–138	95
2q	H	$NHCOCH_3$	170–171	93
2r	$NHCOCF_3$	H	120–121	27
2s	$NHCOCF_3$	NO_2	144–145	99
2t	$NHCOCF_3$	$NHCOCF_3$	239–240	45

TABLE 2
Tetralins of Structure **3**



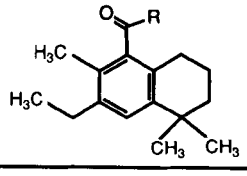
Entry	*R*	*m.p.* (°C)	*Yield* (%)
3a	OCH_3	70–71	82
3b	OC_2H_5	66–67	67
3c	OC_4H_9	Oil	66
3d	NH_2	190–191	81
3e	$NHCH_3$	118–119	79
3f	$N(CH_3)_2$	109–110	66

TABLE 3
Tetralins of Structure **4**



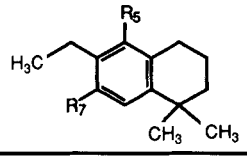
Entry	R_5	R_8	*m.p.* (°C)	*Yield* (%)
4a	H	H	Oil	86
4b	NO_2	NO_2	131–133	21

TABLE 4
Tetralins of Structure **5**



Entry	*R*	*m.p.* (°C)	*Yield* (%)
5a	H	Oil	27
5b	CH_3	Oil	79
5c	CH_2Br	67–68	93
5d	CBr_3	Oil	83
5e	C_2H_5	Oil	88
5f	C_3C_7	Oil	88
5g	C_4H_9	Oil	78

TABLE 5
Tetralins of Structure **6**



Entry	R_5	R_7	*m.p.* (°C)	*Yield* (%)
6a	H	H	Oil	83
6b	H	$COCH_3$	Oil	52
6c	H	CO_2H	159–160	95
6d	H	CO_2CH_3	Oil	70
6e	NO_2	NO_2	89–90	32
6f	NO_2	CN	133–134	90
6g	NO_2	$COCH_3$	112–113	57
6h	NO_2	CO_2H	234–235	77
6i	NO_2	$CONH_2$	215–216	100

*2.2.1 Procedure A: cyclization of β-ionone (methyl 2-(2,6,6-trimethyl-1-cyclohexenyl)ethylidene ketone) and 1-methyl-β-ionone (ethyl 2-(2,6,6-trimethyl-1-cyclohexenyl)ethylidene ketone) (Table 1, **2a**; Table 5, **6a**)*
β-ionone or 1-methyl-β-ionone (0·098 mol) and iodine (~1·0 g) were stirred neat and slowly heated to 110°C or 140°C. When the temperature of the solution reached approximately 100°C, the evolution of steam occurred. At 110°C or 140°C the reaction was vigorous initially, but gradually subsided and proceeded to completion as determined by gas chromatography (GC). The solution was diluted with hexane and washed with water and brine, and the solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (100% hexane). Yields were 80–95%.

*2.2.2 Procedure B: general procedure for the nitration of the tetralin ring (**2d**, **2m**, **2s**, **4b**, **6e**, **6g**)*
At −5°C, tetralin (0·0098 mol) dissolved in 96% sulfuric acid (25 ml), was treated with 70% nitric acid

(0·88 g, 0·0098 mol) as a solution in 96% sulfuric acid (19·6 ml). The solution was closely monitored to maintain 0°C during addition and was stirred mechanically for 1–5 h after complete addition. The solution was poured over ice/water (200 g) which was then extracted with methylene chloride. The methylene chloride layer was washed with water, sodium hydrogen carbonate and brine, and the solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 80–95%.

*2.2.3 Procedure C: general procedure for the reduction of aromatic nitro groups (**2f–h**)*

The nitrated tetralin (0·010 mol) and 10% palladium on carbon (0·30 g) were added to ethanol (250 ml) and the mixture was hydrogenated on a Parr Hydrogenator at room temperature to 40°C, with the pressure maintained at 50 psi until hydrogen uptake was completed. The mixture was filtered through Celite and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 21–99%.

*2.2.4 Procedure D: general procedure for the preparation of acetamides (**2p–r**, **2t**)*

The aniline (0·010 mol) and triethylamine (0·011 mol) were stirred in anhydrous dichloromethane (20 ml). Trifluoroacetic anhydride or acetic anhydride (0·011 mol) in dichloromethane (10 ml) was added dropwise. After stirring at room temperature for 1–16 h, the solvent was removed and the residue was stirred with diethyl ether and water. The ether solution was washed with water and brine, dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 27–95%.

*2.2.5 Procedure E: general procedure for the Friedel–Craft acylation (**2i**, **5a–b**, **5e–g**, **6b**)*

A solution of the tetrahydronaphthalene (0·010 mol) dissolved in 1,2-dichloroethane (10 ml) was added dropwise to a cold (0°C) solution of anhydrous aluminum chloride (0·013 mol) and acid chloride (0·011 mol) in 1,2-dichloroethane (50 ml). The solution was maintained at 0°C during addition and was stirred for 15 minutes to several hours after complete addition. The solution was poured over ice/water (500 g) which was then extracted with diethyl ether. The ether layer was washed with water and brine, and the solution was dried over magnesium sulfate, filtered and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 27–99%.

*2.2.6 Procedure F: general procedure for the haloform reaction with methyl ketones (**2j**, **2n**, **5c–d**, **6e**, **6h**)*

At 0°C, 2.5 M sodium hydroxide (52 ml, 0·13 mol) was treated dropwise with bromine (5·3 g, 0·033 mol). The solution was closely monitored during addition to maintain the temperature below 5°C. Upon complete addition, the solution was diluted with cold 1,4-dioxane (30 ml), and this pre-made solution of sodium hypobromite was added dropwise to a solution of the methyl ketone (0·010 mol) and water (30 ml) in 1,4-dioxane (100 ml) at 0°C. Upon complete addition, the solution was stirred at room temperature for 1–14 h. Anhydrous sodium sulfite (3·0 g) in water (15 ml) was added to destroy the remaining sodium hypobromide. The solution was poured over ice/hydrochloric acid (200 g) and subsequently extracted with diethyl ether. The ether layer was washed with water and brine, and the solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 70–100%

*2.2.7 Procedure G: general procedure for the preparation of carboxylate esters and amides (**2k**, **3a–f**, **6d**, **6i**)*

Oxalyl chloride (0·050 mol) and one drop of dimethyl formamide were added to the acid (0·010 mol) dissolved in dichloromethane (50 ml). After the solution had been stirred at room temperature for 15 minutes to several hours, the solvent was removed to give the acid chloride. The acid chloride (0·010 mol) was dissolved in dichloromethane (20 ml) and this was added to a solution of the alcohol or amine (0·011 mol) and triethylamine (2 ml) in dichloromethane (20 ml). After the solution had been stirred at room temperature for 15 minutes to several hours, the solvent was removed and the residue was mixed with diethyl ether and water. The mixture was washed with water, 3% aqueous hydrochloric acid, water, saturated sodium hydrogen carbonate, water and brine. The solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 66–100%.

*2.2.8 Procedure H: general procedure for the preparation of the nitrile from the amide (**2e**, **6f**)*

At 0°C, the solution of carboxamide (0·010 mol) and triethylamine (0·022 mol) dissolved in dichloromethane (50 ml) was treated with trichloroacetyl chloride (0·011 mol). After complete addition, the solution was stirred at room temperature for 30 min, the dichloromethane layer was washed with water, and brine, and the solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (ethyl acetate–hexane) or crystallization. Yields were 88–90%.

2.2.9 Procedure I: preparation of 5,6,7,8-tetrahydro-3,8,8-trimethyl-2-naphthalenesulfonyl chloride (2l)
Compound **2a** (1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene) (2·0 g, 0·011 mol) was added dropwise to chlorosulfonic acid (3·8 ml, 0·057 mol), and the solution was stirred neat at room temperature for 2 h. The solution was poured over ice/water (100 g), extracted with diethyl ether, and the ether layer was washed with water and brine. The solution was dried over magnesium sulfate, filtered, and the solvent was removed to give a mixture of two products. Fraction one of column chromatography (10% ethyl acetate–hexane) gave 2·4 g (82%) of a white solid of **2l**, m.p. 84·5–85°C; [^{1}H] NMR (deuterochloroform) ppm: 1·29(s,6H), 1·58(m,2H), 1·71(m,2H), 2·66(s,3H), 2·78(t,2H), 7·05(s,1H), 7·96(s,1H).

2.2.10 Procedure J: preparation of 7-ethyl-1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene (4a)
Compound **2i** (methyl 5,6,7,8-tetrahydro-3,8,8-trimethyl-2-naphthyl ketone) (7·3 g, 0·034 mol), 37% hydrochloric acid (20 ml) water (40 ml), and 10% palladium on carbon (1·0 g) were added to ethanol (120 ml) and the mixture was hydrogenated on a Parr Hydrogenator at room temperature with the pressure maintained at 50 psi until hydrogen uptake was complete. The mixture was filtered through Celite, and the solvent was removed to give the crude product. The product was purified by column chromatography (100% hexane) to give 5·9 g (86%) of a clear oil of **4a**; [^{1}H] NMR (deuterochloroform) ppm: 1·19(t,3H), 1·54(s,6H), 1·66(m, 2H), 1·79(m,2H), 2·25(s,3H), 2·59(q,2H), 2·71(t,2H), 6·84(s,1H), 7·11(s,1H).

2.2.11 Procedure K: preparation of 1,2,3,4-tetrahydro-1,1,6-trimethyl-7-nitronaphthalene (2c).
At −5°C, **2a** (1,2,3,4-tetrahydro-1,1,6-trimethyl-naphthalene); (5·0 g, 0·029 mol) dissolved in glacial acetic acid (13·1 ml, 0·24 mol) and acetic anhydride (10·8 ml, 0·114 mol), was treated with 70% nitric acid (6·5 g, 0·072 mol) in glacial acetic acid (13·1 ml, 0·24 mol) and acetic anhydride (10·8 ml, 0·114 mol). The solution was maintained at 0°C and stirred for 15 min at room temperature after complete addition. The solution was poured over ice/water (200 g) and subsequently extracted with methylene chloride. The methylene chloride layer was washed with water, sodium hydrogen carbonate and brine, and the solution was dried over magnesium sulfate, filtered, and the solvent was removed to give a mixture of two products. Fraction two of column chromatography (100% hexane) gave (70%) of a yellow oil of **2c**; [^{1}H] NMR (deuterochloroform) ppm: 1·28(s,6H), 1·66(m,2H), 1·79(m,2H), 2·51(s,3H), 2·76(t,2H), 6·97(s,1H), 7·96(s,1H).

2.2.12 Procedure L: preparation of 5,6,7,8-tetrahydro-3,8,8-trimethyl-4-nitro-2-naphthylamine (2o)
Compound **2c** (1,2,3,4-tetrahydro-1,1,6-trimethyl-5,7-dinitronaphthalene) (24·2 g, 0·092 mol) and Adam's Catalyst (PtO_2) (0·50 g) were added to ethanol (350 ml), and the mixture was hydrogenated on a Parr Hydrogenator at room temperature with the pressure maintained below 40 psi until hydrogen uptake was complete. The mixture was filtered through Celite and the solvent was removed to give the crude product. The product was purified by recrystallization from hexane to give 19·44 g (90%) of a yellow solid of **2o**, m.p. 172–172·5°C; [^{1}H] NMR (deuterochloroform) ppm: 1·23(s, 6H), 1·58(m,2H), 1·71(m,2H), 1·99(s,3H), 1·50(t,2H), 3·63(bs,2H), 6·73(s,1H).

2.2.13 Procedure M: preparation of 1,2,3,4-tetrahydro-1,1,6-trimethyl-5-nitronaphthalene (2b)
At 5°C, **2o** (5,6,7,8-tetrahydro-3,8,8-trimethyl-4-nitro-2-naphthylamine) (2·0 g, 0·0085 mol) dissolved in 35% sulfuric acid (20 ml) was treated dropwise with aqueous sodium nitrite (10 ml, 0·65 g, 0·0094 mol) solution. The solution was maintained below 5°C and stirred an additional 15 min at 5°C upon complete addition. This cold solution was subsequently added dropwise to ethanol (30 ml) and Cu-bronze (0·20 g) at reflux. Upon complete addition, the solution was stirred at reflux for 1 h, cooled, and extracted with dichloromethane. The dichloromethane layer was washed with water and brine. The solution was dried over magnesium sulfate, filtered, and the solvent was removed to give the crude product. The product was purified by column chromatography (10% ethyl acetate–hexane) to give 1·94 g (83%) of a clear oil of **2b**; [^{1}H] NMR (deuterochloroform) ppm: 1·19(s,6H), 1·63(m,2H), 1·78(m,2H), 2·22(s,3H), 2·63(t,2H), 7·05(d,1H,J = 6·7 Hz), 7·33(d,1H,J = 6·7 Hz).

2.3 Determination of herbicidal activity

2.3.1 Primary pre-emergence herbicidal screen
A Dupo silt loam soil containing less than 2% organic matter was placed in an aluminum pan and compacted with furrows to a depth of approximately $\frac{1}{2}$ in. (1·27 cm) from the top of the pan. Seeds of yellow nutsedge, annual bluegrass, seedling johnsongrass, downy brome, barnyardgrass, annual morningglory, cocklebur, velvetleaf, Indian mustard, and wild buckwheat were placed in the furrows prior to chemical treatment. A known amount of the test compound was dissolved in acetone to provide a 10 g litre^{-1} solution, and a dilution was made from this stock solution to provide a rate of 11·2 kg ha^{-1}. The solution was subsequently sprayed over the entire pan with the seeds exposed in the furrows. The seeds were subsequently covered with a layer of soil to fill the pan completely, and the pans were placed in a greenhouse maintained at day/night temperatures of 30/21°C. All pans were watered by subirrigation, and the species were rated visually against an untreated control at approximately 14 days after application. The rating scale ranged from 0 to 100% with 0%

representing no injury and 100% complete death of the plant, and the data were presented as averages over the monocotyledons of annual bluegrass (*Poa annua* L.), seedling johnsongrass (*Sorghum halepense* (L.) Pers.), downy brome (*Bromus tectorum* L.), and barnyardgrass (*Echinochloa crus-galli* (L.) Beauv.) and dicotyledons annual morningglory (*Ipomea* spp.), cocklebur (*Xanthium stumarium* L.), velvetleaf (*Abutilon theophrasti* Medic.), Indian mustard (*Brassica juncea* (L.) Coss.), and wild buckwheat (*Polygonum convolvulus* L.). The monocotyledon average also included the yellow nutsedge (*Cyperus esculentus* L.) component. Compounds with sufficient herbicidal activity were selected for evaluation in the secondary screen, while all others were eliminated from further testing.

2.3.2 Secondary pre-plant incorporated herbicidal screen

All pans used for the herbicide screen were prepared as described above. In one pan, seeds of corn (*Zea mays* L.), rice (*Oryza sativa* L). soybeans (*Glycine max* (L.) Merr.), cotton (*Gossypium hirsutum* L.), large crabgrass (*Digitaria sanguinalis* (L.) Scop.), seedling johnsongrass, barnyardgrass, velvetleaf, annual morningglory, and cocklebur, which make up the warm-season spectrum, were placed in the furrows. In a second pan, the cool-season spectrum consisting of wheat (*Triticum aestivum* L.), oilseed rape (*Brassica napus* L.), wild oat (*Avena fatua* L.), downy brome, blackgrass (*Alopecurus myosuroides* Huds.), green foxtail (*Setaria viridis* (L.) Beauv.), cleavers (*Galium oparine* L.), wild buckwheat, common chickweed (*Stellaria media* (L.) Vill.), and Russian thistle (*Salsola kali* L.) were seeded in the furrows. From the 10 g litre^{-1} stock solution prepared above, aliquots were taken to make dilutions which correspond to rates ranging from 0·07 to 11·2 kg ha^{-1}. All chemical treatments were made by mixing the appropriate solution with the layer of soil needed to cover the seeds in the pans. The pans containing the warm season species were placed in a greenhouse maintained at day/night temperatures of 30/21°C, and the pan containing the cool season species were maintained at day/night temperatures of 24/16°C. The pans were initially overhead irrigated with approximately 0·5 cm of water and all subsequent moisture was supplied through sub-irrigation. At approximately 14 days after treatment, all species were rated visually as described earlier. All data for the weeds from the secondary screen were converted to average GR_{80} values (the amount of herbicide, in kg ha^{-1}, causing an average of 80% injury over a given subset of weeds). This GR_{80} value was determined by extrapolation between two adjacent rates in the titration where the higher rate had an average of greater than 80% injury and the lower rate had an average of less than 80% injury. If the average of 80% injury occurred at the actual applied rate, then that value was selected for the GR_{80}. The variability of the data in these tests was determined to be a factor of ± 2 in the rate titration.

3 RESULTS AND DISCUSSION

All chemicals with herbicidal activity caused symptoms of mitotic inhibition, which included severe root pruning, stunting, and lack of emergence.[3] These symptoms were similar to those produced by the dinitroaniline class of herbicides which suggests that the tetralins may be inhibitors of tubulin formation.[4]

Table 6 is a list of tetralin analogs in which the 5- and/or 7-position is substituted with electron-withdrawing groups or hydrogen. All compounds were substantially less active than pendimethalin*, *N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine. It appears from the data that electron-withdrawing groups are needed for biological activity and that small, compact electron-withdrawing groups (NO_2, CN, $COCH_3$) at the 5- and/or 7-position may be necessary for optimal herbicidal activity. Also, compound **2e** containing a nitrile substituent at the 7-position caused less root pruning than pendimethalin where weed control was observed.

Table 7 is a list of tetralin analogs in which an electron-donating group is substituted at the 5- and/or 7-position. The data indicate that an electron-donating group at the 5- and/or 7-position generally inactivates the molecule.

Table 8 shows the herbicidal activity of the various 7-ester/amide-1,1,6-trimethyl-5-nitrotetralins. As the esters increase in size, the herbicidal activity tends to decrease, as the methyl ester, **3a**, had superior activity over the other esters. The amides demonstrated no herbicidal activity.

Table 9 shows the herbicidal activity of the unsubstituted and disubstituted 7-ethyl-1,1,6-trimethyltetralin. It is interesting to note that the 5,8-dinitrotetralin, **4b**, was inactive.

Table 10 shows the herbicidal activity of the various 5-keto-7-ethyl-1,1,6-trimethyltetralins. When the length of the ketone increases from methyl to butyl the activity decreases, with the methyl ketone, **5b**, demonstrating the highest activity.

Table 11 shows the herbicidal activities of the 6-ethyltetralin analogs (**6**). These compounds demonstrated a structure–activity relationship similar to the 6-methyltetralin analogs. Compounds **6e** and **6f** substituted with small, compact electron-withdrawing substituents (CN, NO_2) exhibited the highest herbicidal activity.

In summary, the greatest overall herbicide activities were obtained when R_5, R_7 were substituted with $-NO_2$ and/or $-CN$ groups. Substitution at these posi-

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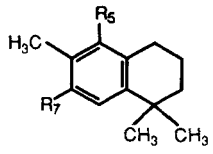
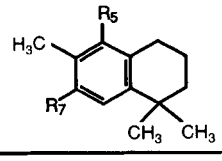
TABLE 6
Soil-Applied Herbicidal Activity of Compounds of General Structure **2**, Possessing Electron-Withdrawing Groups



			Primary (screen) (*Mean phytotoxicity %*)		*Secondary screen, GR_{80} (kg ha^{-1})*			
					Warm season		*Cool season*	
Entry	R_5	R_7	*MC*	*DC*	*MC*[a]	*DC*[a]	*MC*[a]	*DC*[b]
2a	H	H	0	0	—	—	—	—
2e	H	SO_2Cl	0	0	—	—	—	—
2j	H	CO_2H	6	0	—	—	—	—
2i	H	$COCH_3$	6	0	—	—	—	—
2k	H	CO_2CH_3	54	0	4·7	>11·2	>5·6	>5·6
2m	NO_2	$COCH_3$	74	42	1·1	>11·2	4·1	8·8
2n	NO_2	CO_2H	4	8	—	—	—	—
2b	NO_2	H	68	24	>5·6	>5·6	4·9	>5·6
2c	H	NO_2	74	24	3·0	>5·6	4·8	>5·6
2d	NO_2	NO_2	64	0	1·1	>11·2	1·1	11·2
2e	NO_2	CN	72	12	0·94	>5·6	0·99	>5·6
Pendimethalin	—	—	—	—	0·04	1·0	0·78	0·55

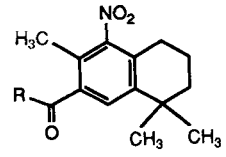
[a] Average of monocot yledonous (MC) or dicot yledonous (DC) weeds, only.
[b] Average of dicot yledonous weeds plus oilseed rape.

TABLE 7
Soil-Applied Herbicidal Activity of Compounds of General Structure **2**, Possessing an Electron-Donating Group



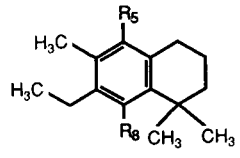
			Primary screen phytotoxicity (%)	
Entry	R_5	R_7	*MC*	*DC*
2g	H	NH_2	0	0
2p	H	$NHCOCF_3$	0	0
2q	H	$NHCOCH_3$	0	0
2o	NO_2	NH_2	0	0
2f	NH_2	H	0	0
2h	NH_2	NH_2	4	0
2t	$NHCOCF_3$	$NHCOCF_3$	0	0
2r	$NHCOCF_3$	H	0	0
2s	$NHCOCF_3$	NO_2	0	0

TABLE 8
Soil-Applied Herbicidal Activity of Compounds of General Structure **3**



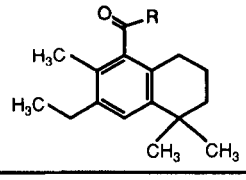
		Primary screen Mean phytotoxicity (%)		*Secondary screen, GR_{80} (kg ha^{-1})*			
				Warm season		*Cool season*	
Entry	*R*	*MC*	*DC*	*MC*	*DC*	*MC*	*DC*
3a	OCH_3	58	4	4·8	>5·6	>5·6	>5·6
3b	OC_2H_5	10	0	>11·2	>11·2	>11·2	>11·2
3c	OC_4H_9	0	0	—	—	—	—
3d	NH_2	2	0	—	—	—	—
3e	$NHCH_3$	0	2	—	—	—	—
3f	$N(CH_3)_2$	14	0	—	—	—	—

TABLE 9
Soil Applied Herbicidal Activity of Compounds of General Structure **4**



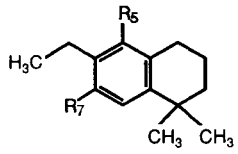
			Primary screen Mean phytotoxicity (%)	
Entry	R_5	R_8	*MC*	*DC*
4a	H	H	18	0
4b	NO_2	NO_2	0	0

TABLE 10
Soil-Applied Herbicidal Activity of Compounds of General Structure **5**



		Primary screen Mean phytotoxicity (%)		*Secondary screen GR_{80} (kg ha^{-1})*			
				Warm season		*Cool season*	
Entry	*R*	*MC*	*DC*	*MC*	*DC*	*MC*	*DC*
5a	H	0	0	—	—	—	—
5b	CH_3	78	34	2·1	>11·2	1·9	9·4
5c	CH_2Br	0	0	—	—	—	—
5d	CBr_3	16	0	—	—	—	—
5e	C_2H_5	34	14	9·1	>11·2	>11·2	>11·2
5f	C_3H_7	12	0	>11·2	>11·2	>11·2	>11·2
5g	C_4H_9	12	0	—	—	—	—

TABLE 11
Soil-Applied Herbicidal Activity of Compounds of General Structure **6**



			Primary screen Mean phytotoxicity (%)		*Secondary screen, GR_{80} (kg ha^{-1})*			
					Warm season		*Cool season*	
Entry	R_5	R_7	*MC*	*DC*	*MC*	*DC*	*MC*	*DC*
6a	H	H	12	0	—	—	—	—
6b	H	$COCH_3$	50	14	>5·6	>5·6	>5·6	>5·6
6c	H	CO_2H	0	0	—	—	—	—
6d	H	CO_2CH_3	70	12	4·6	>5·6	5·3	>5·6
6e	NO_2	NO_2	54	10	0·85	>5·6	1·1	>5·6
6f	NO_2	CN	28	0	0·93	>11·2	3·9	>11·2
6g	NO_2	COMe	56	10	1·8	>5·6	5·6	>5·6
6h	NO_2	CO_2H	0	4	—	—	—	—
6i	NO_2	$CONH_2$	0	0	—	—	—	—
Pendimethalin	—	—	—	—	0·04	1·0	0·078	0·55

tions with —H, $-NH_2$, —C(O)R, —C(O)OR, or —C(O)NR′R″ tended to decrease activity or inactivate the tetralin altogether. Methyl substitution at R_6 tended to be more active than ethyl. Also, placing a $-NO_2$ group at R_8 inactivated the molecule.

The most active herbicidal compounds (**2d**, **2e**) had R_5, R_7 = $-NO_2$ and/or —CN, R_6 = $-CH_3$ and R_8 = —H.

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