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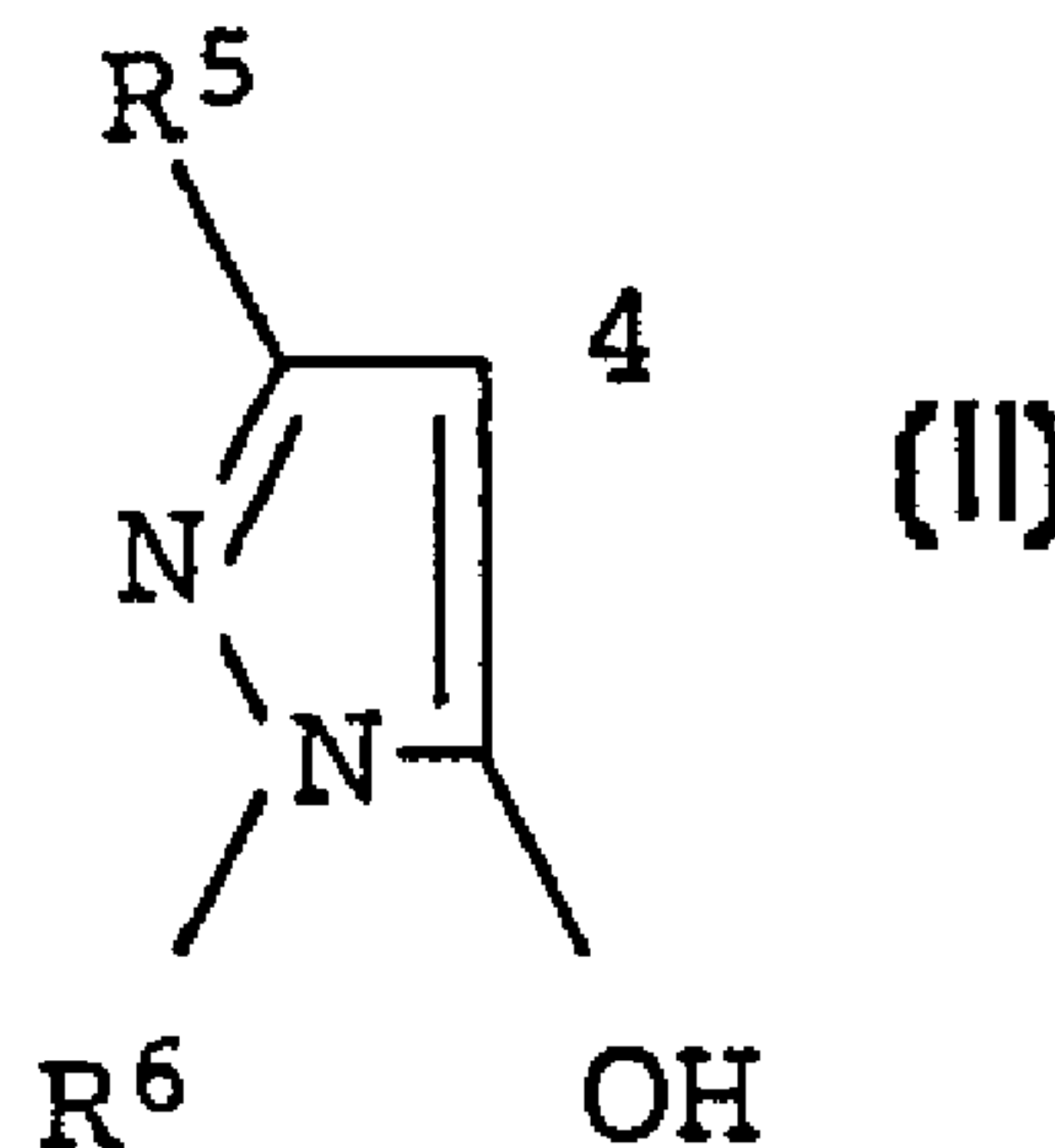
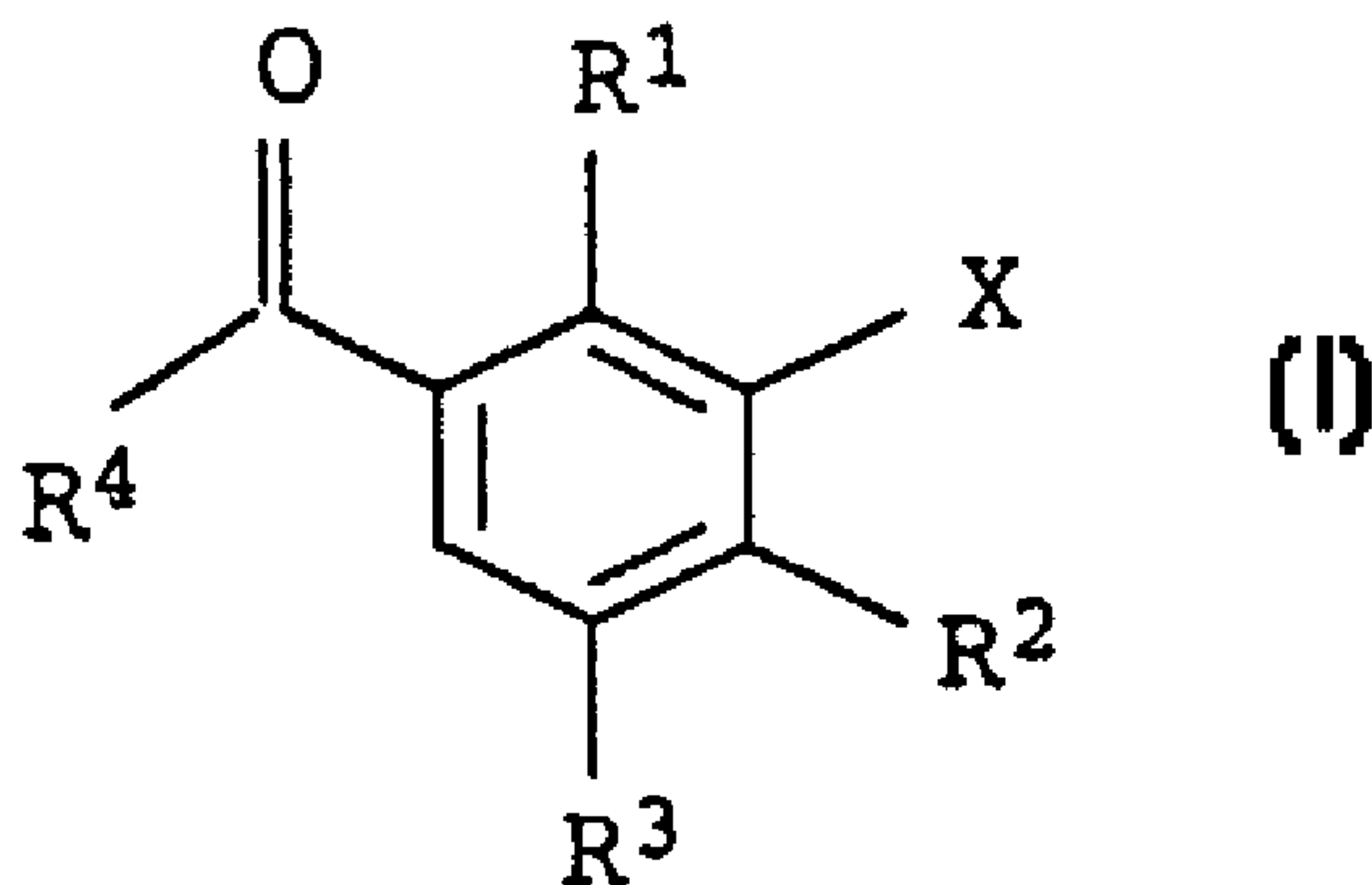
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(72) Inventeurs/Inventors:
BRATZ, MATTHIAS, DE;
BERGHAUS, RAINER, DE;
OTTEN, MARTINA, DE;
SIEVERNICH, BERND, DE;
KIBLER, ELMAR, DE;
VANTIEGHEM, HERVE, DE

(73) Propriétaire/Owner:
BASF AKTIENGESELLSCHAFT, DE

(74) Agent: ROBIC

(54) Titre : MELANGE HERBICIDE CONTENANT UN DERIVE DE BENZOYLE A SUBSTITUTION 3-HETEROCYCLYLE
(54) Title: HERBICIDAL MIXTURE CONTAINING A 3-HETEROCYCLYL-SUBSTITUTED BENZOYL DERIVATIVE AND
AN ADJUVANT



(57) Abrégé/Abstract:

The invention relates to a herbicidal mixture containing a) a herbicidally effective amount of a 3-heterocyclyl-substituted benzoyl derivative of formula (I) in which the variables have the following meanings: R¹, R² represent hydrogen, halogen, C₁-C₆ alkyl, C₁-C₆ alkylthio, C₁-C₆ alkyl sulfinyl, C₁-C₆ alkyl sulfonyl, C₁-C₆ alkyl halide, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy; R³ represents hydrogen, halogen, C₁-C₆ alkyl; X represents a heterocycle selected from the group of isoxazolyl, 4,5-dihydroisoxazolyl and thiazolyl, whereby the heterocycle can be optionally substituted once or multiple times with halogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ alkyl halide, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio; R⁴ represents a pyrazole which is linked in position 4 and which is of formula (II), whereby R⁵ represents hydrogen or C₁-C₆ alkyl, R⁶ represents C₁-C₆ alkyl, or the environmental friendly salts thereof. The inventive herbicidal mixture also consists of b) an adjuvant containing i) a C₁-C₅-alkyl-C₅-C₂₂ alkanoate, ii) a C₁₀-C₂₀ carboxylic acid, iii) a partial phosphoric ester or a partial sulfuric acid ester of a monohydroxy functional polyalkylether and iv) optionally one alkyl polyoxyalkylene polyether in a synergistically effective quantity.



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(21) Internationales Aktenzeichen: PCT/EP00/01641 (22) Internationales Anmeldedatum: 28. Februar 2000 (28.02.00) (30) Prioritätsdaten: 199 09 833.6 5. März 1999 (05.03.99) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): BRATZ, Matthias [DE/DE]; Sachsenweg 10, D-67117 Limburgerhof (DE). BERGHAUS, Rainer [DE/DE]; Rotkehlchenweg 25, D-67346 Speyer (DE). OTTEN, Martina [DE/DE]; Gunterstr. 28, D-67069 Ludwigshafen (DE). SIEVERNICH, Bernd [DE/DE]; Brahmstrasse 8, D-67459 Böhl-Iggelheim (DE). KIBLER, Elmar [DE/DE]; Im Wachtelschlag 13, D-67454 Hassloch (DE). VANTIEGHEM, Herve [BE/DE]; Zollhausstrasse 5, D-76297 Stutensee (DE). (74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; D-67056 Ludwigshafen (DE). (81) Bestimmungsstaaten: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO Patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>		
(54) Title: HERBICIDAL MIXTURE CONTAINING A 3-HETEROCYCLYL-SUBSTITUTED BENZOYL DERIVATIVE AND AN ADJUVANT (54) Bezeichnung: HERBIZIDE MISCHUNG, ENTHALTEND EIN 3-HETEROCYCLYL-SUBSTITUIERTES BENZOYLDERIVAT UND EIN ADJUVANT (57) Abstract The invention relates to a herbicidal mixture containing a) a herbicidally effective amount of a 3-heterocyclyl-substituted benzoyl derivative of formula (I) in which the variables have the following meanings: R¹, R² represent hydrogen, halogen, C₁-C₆ alkyl, C₁-C₆ alkylthio, C₁-C₆ alkyl sulfinyl, C₁-C₆ alkyl sulfonyl, C₁-C₆ alkyl halide, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy; R³ represents hydrogen, halogen, C₁-C₆ alkyl; X represents a heterocycle selected from the group of isoxazolyl, 4,5-dihydroisoxazolyl and thiazolyl, whereby the heterocycle can be optionally substituted once or multiple times with halogen, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ alkyl halide, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio; R⁴ represents a pyrazole which is linked in position 4 and which is of formula (II), whereby R⁵ represents hydrogen or C₁-C₆ alkyl, R⁶ represents C₁-C₆ alkyl, or the environmental friendly salts thereof. The inventive herbicidal mixture also consists of b) an adjuvant containing i) a C₁-C₅-alkyl-C₅-C₂₂ alkanoate, ii) a C₁₀-C₂₀ carboxylic acid, iii) a partial phosphoric ester or a partial sulfuric acid ester of a monohydroxy functional polyalkylether and iv) optionally one alkyl polyoxyalkylene polyether in a synergetically effective quantity. (I) (II)		

HERBICIDAL MIXTURE CONTAINING A 3-HETEROCYCLYL-SUBSTITUTED
BENZOYL DERIVATIVE AND AN ADJUVANT

The present invention relates to a herbicidal mixture of a 3-heterocyclyl-substituted benzoyl derivative and an adjuvant, said mixture having synergistic action.

3-Heterocyclyl-substituted benzoyl derivatives are known and described, for example, in WO 96/26206, WO 97/41116, WO 97/41117 and WO 97/41118.

EP-B-0584 227 discloses herbicidal compositions comprising substituted cyclohexanediones and nitrogen fertilizers.

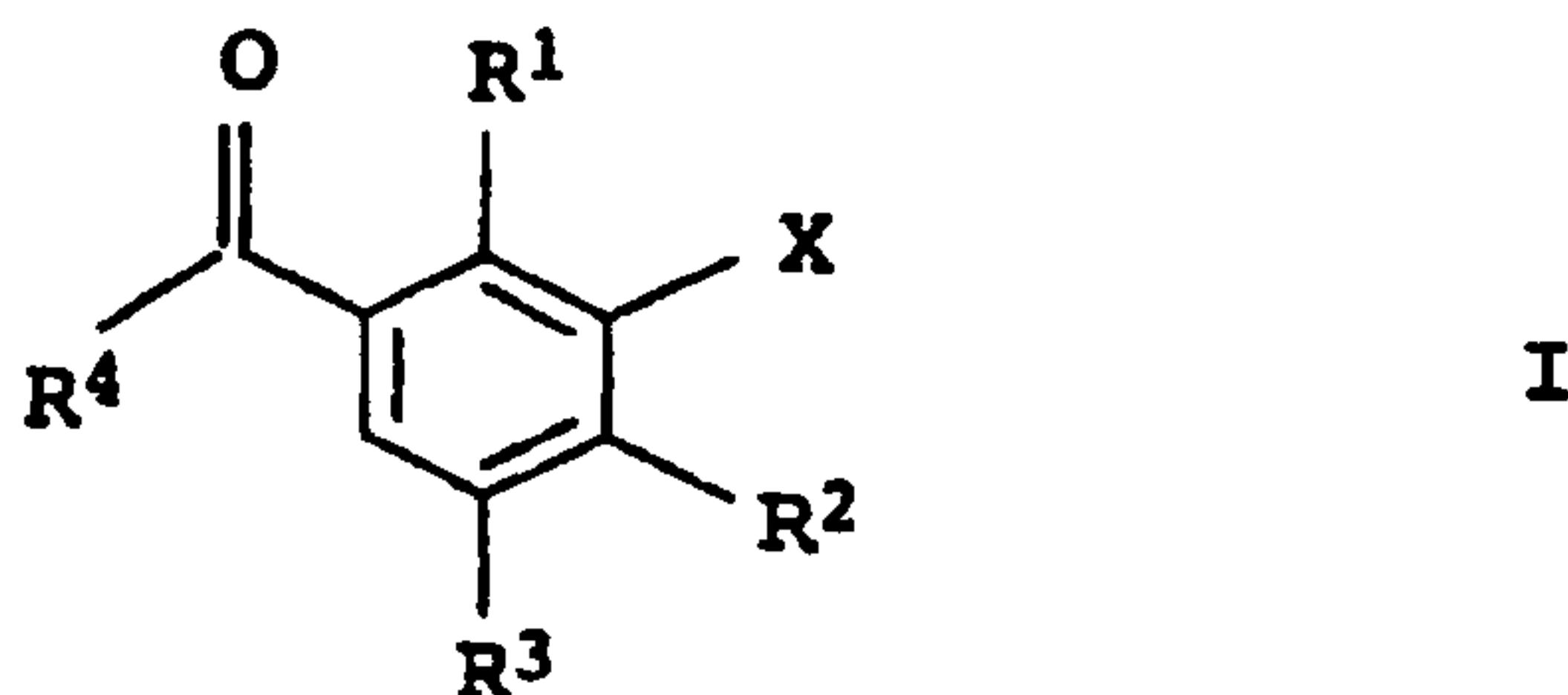
- 10 WO-99/63823 discloses herbicidal mixtures based on a 3-heterocyclyl-substituted benzoyl derivative, a nitrogen-containing fertilizer and an adjuvant.

It is an object of the present invention to provide a herbicidal mixture which comprises 3-heterocyclyl-substituted benzoyl derivatives and whose herbicidal activity is higher than the activity of the pure active compound.

This object was achieved by a herbicidal mixture, comprising

- a) a herbicidally effective amount of a 3-heterocyclyl-substituted benzoyl compound of the formula I

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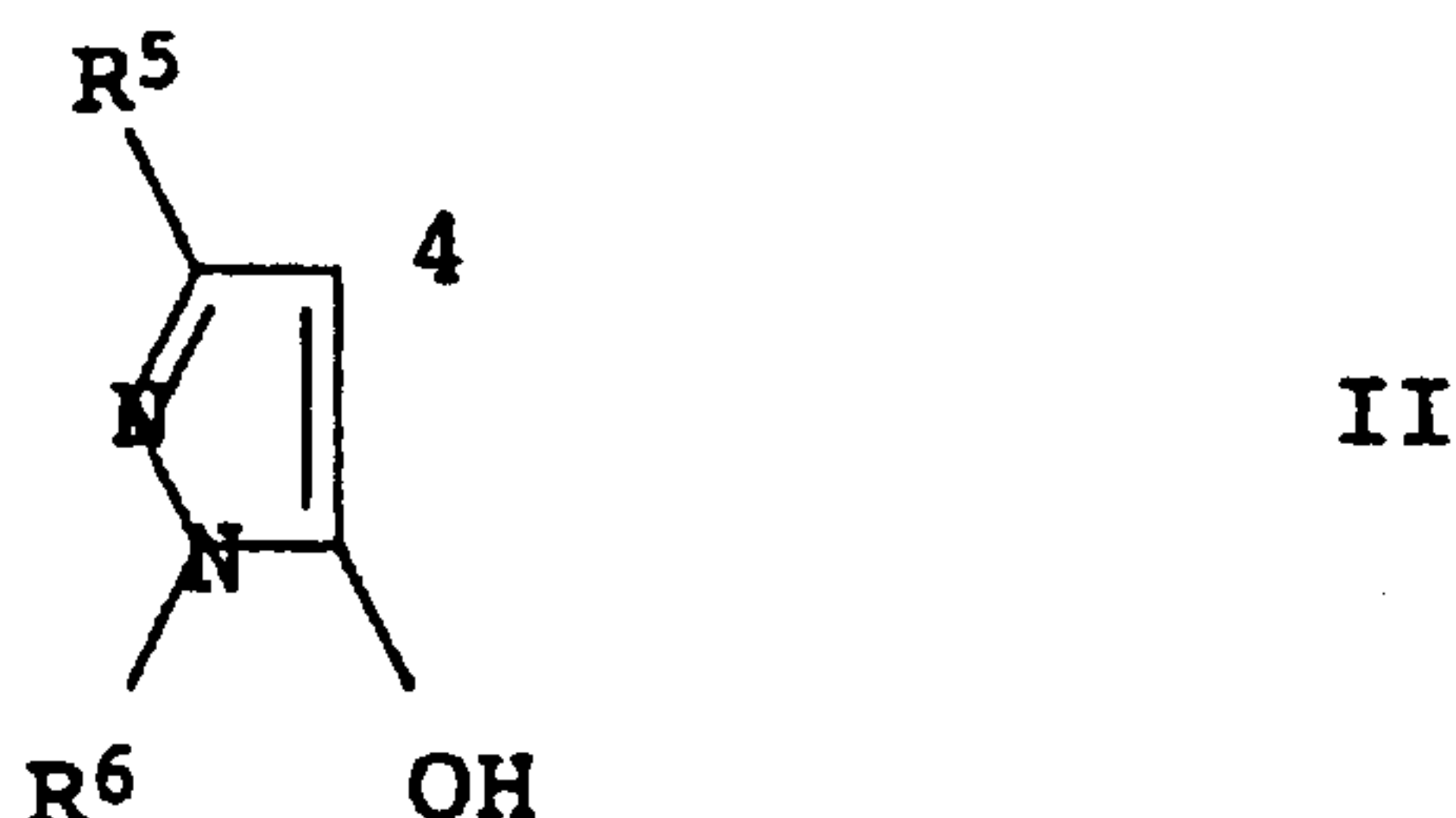


where:

- R¹ and R² each are hydrogen, halogen, C₁-C₆-alkyl, C₁-C₆-alkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-alkylsulfonyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy or C₁-C₆-haloalkoxy;
- R³ is hydrogen, halogen or C₁-C₆-alkyl;

X is a heterocycle from the group consisting of isoxazolyl, 4,5-dihydroisoxazolyl and thiazolyl, where the heterocycle may be unsubstituted or mono- or polysubstituted by halogen, C₁-C₆-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

R⁴ is a pyrazole of the formula II



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which is attached in the 4-position and where

R⁵ is hydrogen or C₁-C₆-alkyl,

R⁶ is C₁-C₆-alkyl,

or their environmentally compatible salts; and

b) an adjuvant comprising

i) a C₁-C₅-alkyl ester of a C₅-C₂₂-carboxylic acid, also called "C₁-C₅-alkyl",

ii) a C₁₀-C₂₀-carboxylic acid,

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iii) a partial phosphoric ester or a partial sulfuric ester of a monohydroxy-functional polyalkyl ether and

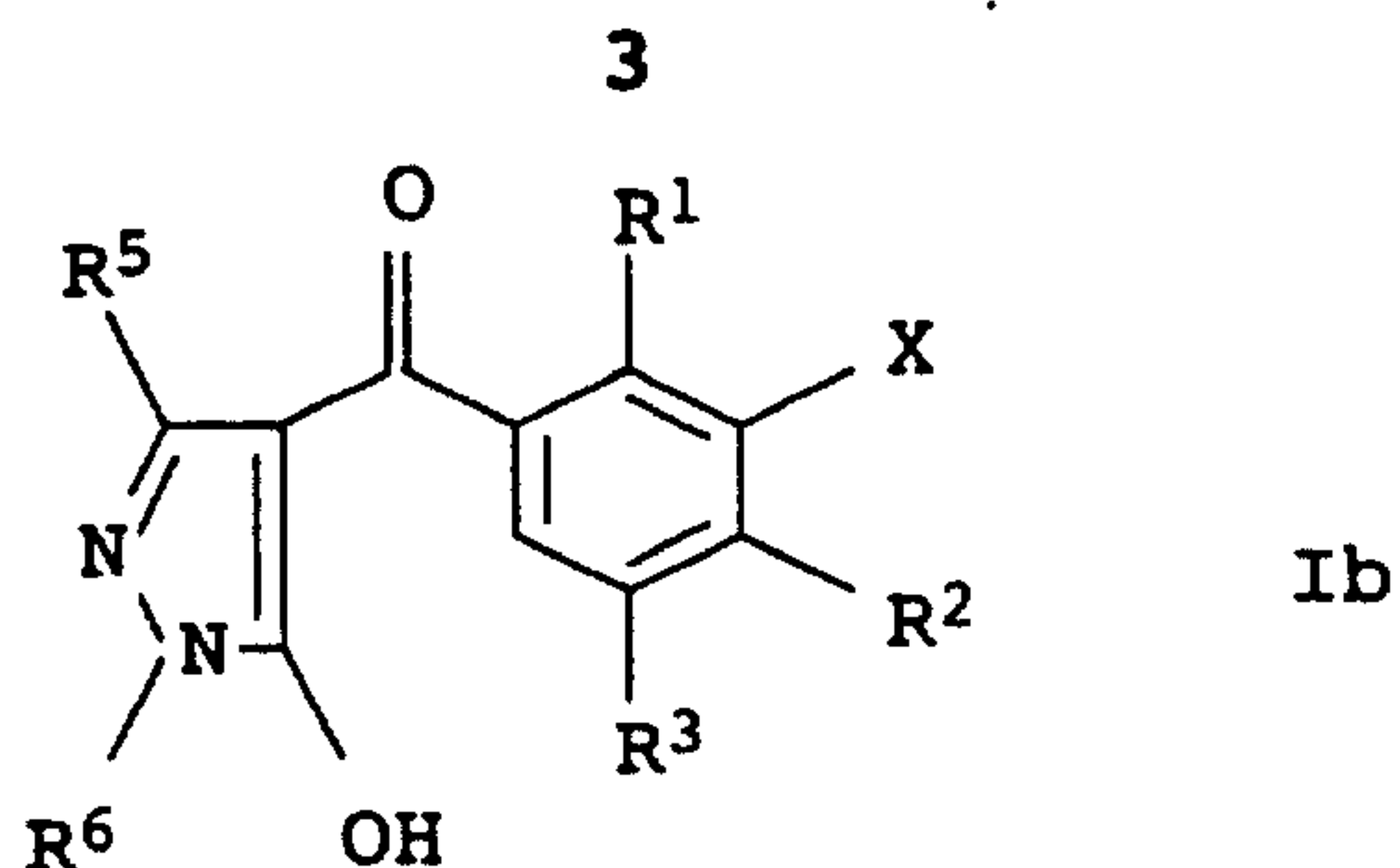
iv) optionally an alkyl polyoxyalkylene polyether

in a synergistically effective amount.

The herbicidal mixture according to the invention displays a synergistic effect and is selective for those crop plants which are also compatible with the individual compounds.

With respect to the synergistic herbicidal action, particular preference is given to 3-heterocycl-yl-substituted benzoyl compounds of the formula Ib in which

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- 10 R^1, R^2 are chlorine, methyl, ethyl, SCH_3 , SOCH_3 , SO_2CH_3 ;
- R^3 is hydrogen or methyl;
- R^5 is hydrogen, methyl, trifluoromethyl;
- 15 R^6 is methyl, ethyl, isopropyl;
- 20 X is a heterocycle from the group consisting of: isoxazolyl, 4,5-dihydroisoxazolyl and thiazolyl, where the heterocycle may be unsubstituted or mono- or polysubstituted by halogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_4\text{-alkoxy}$, $\text{C}_1\text{-C}_4\text{-haloalkyl}$, $\text{C}_1\text{-C}_4\text{-haloalkoxy}$, $\text{C}_1\text{-C}_4\text{-alkylthio}$,

or their environmentally compatible salts.

25 Preferred compounds of the formula Ib are compiled in the table below:

No.	R^1	R^2	R^3	R^5	R^6	X
30 1.	Cl	SO_2CH_3	H	CH_3	CH_3	2-thiazolyl
2.	Cl	SO_2CH_3	H	H	CH_3	2-thiazolyl
3.	Cl	SO_2CH_3	H	CH_3	CH_3	4,5-dihydroisoxazol-3-yl
4.	Cl	Cl	H	CH_3	CH_3	4,5-dihydroisoxazol-3-yl
5.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydroisoxazol-3-yl
35 6.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5-methylisoxazol-3-yl
7.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5,5-dimethylisoxazol-3-yl
8.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5-ethylisoxazol-3-yl
40 9.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5,5-diethylisoxazol-3-yl
10.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5-chloromethylisoxazol-3-yl
11.	Cl	SCH_3	H	H	CH_3	4,5-dihydroisoxazol-3-yl
12.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5-ethoxyisoxazol-3-yl
45 13.	Cl	SO_2CH_3	H	H	CH_3	4,5-dihydro-5-methoxyisoxazol-3-yl
14.	CH_3	SO_2CH_3	H	H	CH_3	4,5-dihydroisoxazol-3-yl

	No.	R ¹	R ²	R ³	R ⁵	R ⁶	X
5	15.	Cl	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-4,5-dimethyl-isoxazol-3-yl
	16.	Cl	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5-thioethyl-isoxazol-3-yl
	17.	Cl	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5-trifluoro-methylisoxazol-3-yl
	18.	SCH ₃	SCH ₃	H	H	CH ₃	4,5-dihydroisoxazol-3-yl
	19.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	2-thiazolyl
10	20.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydroisoxazol-3-yl
	21.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-methylisoxa-zol-3-yl
	22.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5,5-dimethyl-isoxazol-3-yl
	23.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-ethylisoxa-zol-3-yl
15	24.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5,5-diethyl-isoxazol-3-yl
	25.	Cl	SCH ₃	H	H	C ₂ H ₅	4,5-dihydroisoxazol-3-yl
	26.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-chloromethyl-isoxazol-3-yl
20	27.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-ethoxyisoxa-zol-3-yl
	28.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-4,5-dimethyl-isoxazol-3-yl
	29.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydroisoxazol-3-yl
25	30.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-thioethyl-isoxazol-3-yl
	31.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-trifluorome-thylisoxazol-3-yl
	32.	SCH ₃	SCH ₃	H	H	C ₂ H ₅	4,5-dihydroisoxazol-3-yl
	33.	Cl	SO ₂ CH ₃	H	H	i-C ₄ H ₉	4,5-dihydroisoxazol-3-yl
30	34.	Cl	SO ₂ CH ₃	H	H	CH ₃	3-methylisoxazol-5-yl
	35.	Cl	SO ₂ CH ₃	H	H	C ₂ H ₅	3-methylisoxazol-5-yl
	36.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	3-methylisoxazol-5-yl
	37.	CH ₃	SO ₂ CH ₃	H	CH ₃	CH ₃	4,5-dihydroisoxazol-3-yl
	38.	CH ₃	Cl	H	CH ₃	CH ₃	4,5-dihydroisoxazol-3-yl
35	39.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5-methylisoxa-zol-3-yl
	40.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5,5-dimethyl-isoxazol-3-yl
	41.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5-ethyl-isoxazol-3-yl
	42.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-5,5-ethyl-isoxazol-3-yl
40	43.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydroisoxazol-3-yl
	44.	CH ₃	SO ₂ CH ₃	H	H	CH ₃	4,5-dihydro-4,5-dimethyl-isoxazol-3-yl
	45.	CH ₃	Cl	H	H	C ₂ H ₅	4,5-dihydroisoxazol-3-yl
45	46.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-methylisoxa-zol-3-yl
	47.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5,5-dimethyl-isoxazol-3-yl

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No.	R ¹	R ²	R ³	R ⁵	R ⁶	X
48.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-5-ethyl-isoxazol-3-yl
49.	CH ₃	SO ₂ CH ₃	H	H	C ₂ H ₅	4,5-dihydro-4,5-dimethyl-isoxazol-3-yl
50.	CH ₃	SO ₂ CH ₃	H	H	i-C ₄ H ₉	4,5-dihydroisoxazol-3-yl

Very particular preference is given to the compounds

- 10 4-[2-chloro-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole,
 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole,
 4-[2-chloro-3-(3-methylisoxazol-5-yl)-4-methylsulfonylbenzoyl]-1-
 15 methyl-5-hydroxy-1H-pyrazole and/or their environmentally compatible salts.

Suitable environmentally compatible salts are, for example, salts of alkali metals, alkaline earth metals, ammonia or amines.

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Suitable adjuvants b) comprise a mixture of

- i) a C₁-C₅-alkyl C₅-C₂₂-alkanoate,
 25 ii) a C₁₀-C₂₀-carboxylic acid,
 iii) a partial phosphoric ester or a partial sulfuric ester of a monohydroxy-functional polyalkyl ether and
 30 iv) if appropriate an alkyl polyoxyalkylene polyether.

These adjuvants are described, for example, in US 4,834,908, EP 356 812 and EP 553 074.

- 35 Suitable C₁-C₅-alkyl C₅-C₂₂-alkanoates (i) are alkyl esters of a carboxylic acid, where the carboxylic acid contains 5-22 carbon atoms and the alkanol used for esterification contains 1-5 carbon atoms, such as, for example, methyl oleate, palmitate, myristate, linolenate, laurate, stearate, pelargonate, ethyl oleate,
 40 palmitate, myristate, linolenate, linoleate, laurate, stearate, pelargonate, n-propyl oleate, palmitate, myristate, linolenate, linoleate, laurate, stearate, pelargonate, isopropyl oleate, palmitate, myristate, linolenate, linoleate, laurate, stearate, pelargonate, n-butyl oleate, palmitate, myristate, linolenate,
 45 linoleate, laurate, stearate, pelargonate, isobutyl oleate, palmitate, myristate, linolenate, linoleate, laurate, stearate, pelargonate, n-pentyl oleate, palmitate, myristate, linolenate,

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linoleate, laurate, stearate, pelargonate. Preference is given to methyl oleate, methyl palmitate, ethyl oleate and mixtures thereof.

- 5 Suitable C₁₀-C₂₀-carboxylic acids (ii) include saturated and mono- and polyunsaturated carboxylic acids, such as, for example, oleic acid, palmitic acid, myristic acid, linoleic acid, linolenic acid, lauric acid and stearic acid. Preference is given to oleic acid.

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Suitable partial phosphoric esters and partial sulfuric esters of a monohydroxy-functional polyalkylene ether (iii) are those whose polyalkylene ether radicals can be prepared by oxalkylation of long-chain alcohols such as C₁₀-C₂₀-alkanols, preferably

- 15 C₁₀-C₁₆-alkanols, with alkylene oxides such as ethylene oxide, propylene oxide or butylene oxide. The alkylene oxides can be employed as a mixture, or else successively, for preparing block copolymers.

- 20 Preference is given to polyalkylene ethers having a C₁₀-C₁₆-alkyl chain with 10-15 mol of ethylene oxide units and 1-10, preferably 2-6, mol of propylene oxide units.

Preferred products are Klearfac™ AA 270 of BASF Corporation and

- 25 Lutensit® A-EP from BASF Aktiengesellschaft.

If appropriate, it is possible to use alkyl polyoxyalkylene polyethers concomitantly. Suitable alkyl polyoxyalkylene polyethers are those which can be prepared by oxalkylation of

- 30 C₁₀-C₂₅-alkanols with alkylene oxides such as ethylene oxide, propylene oxide or butylene oxide.

Preference is given to alkyl polyoxyalkylene polyethers having a C₁₀-C₂₅-alkyl chain, preferably C₁₂-C₂₀-alkyl chain, with an EO/PO

- 35 block copolymer, such as, for example,

Antarox® BO, Rhodia

Emulsogen® V 2436, Clariant

Plurafac® LF, BASF AG

- 40 Dehypon® LS, Henkel

Dehypon® LT, Henkel

Synperionic® LF, ICI Speciality Chemicals.

Particular preference is given to Plurafac® LF 700, BASF AG.

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The adjuvant b) comprises the components in the following concentrations:

5 to 90% of the C₁-C₅-alkyl C₅-C₂₂-alkanoate,

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2 to 40% of the C₁₀-C₂₀-carboxylic acid,

4 to 40% of the partial phosphoric ester or the partial sulfuric ester of a monohydroxy-functional polyalkyl ether and

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0 to 75% of the alkyl polyoxyalkylene polyether.

Preference is given to:

15 5 to 60% of the C₁-C₅-alkyl C₅-C₂₂-alkanoate,

2 to 40% of the C₁₀-C₂₀-carboxylic acid,

5 to 35% of the partial phosphoric ester or the partial sulfuric ester of a monohydroxy-functional polyalkyl ether and

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0 to 70% of the alkyl polyoxyalkylene polyether.

Particular preference is given to:

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5 to 40% of the C₁-C₅-alkyl C₅-C₂₂-alkanoate,

2 to 35% of the C₁₀-C₂₀-carboxylic acid,

30 5 to 30% of the partial phosphoric ester or the partial sulfuric ester of a monohydroxy-functional polyalkyl ether and

0 to 70% of the alkyl polyoxyalkylene polyether.

35 The herbicidal mixture according to the invention comprises the components a) and b) in the following amounts:

0.5 to 90% by weight of the 3-heterocyclyl-substituted benzoyl derivative a);

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10 to 99.5% by weight of the adjuvant b).

Preferred ratios are:

45 1 to 80% by weight of the 3-heterocyclyl-substituted benzoyl derivative a);

20 to 99% by weight of the adjuvant b).

Here, the components together are 100% by weight.

- 5 The individual components a) and b) of the herbicidal mixture according to the invention can be formulated and packaged together or individually.

The farmer employs the herbicidal mixture or its individual
10 components for use in the spray tank.

To this end, the herbicidal mixture is diluted with water, it being possible, if appropriate, to add other auxiliaries and additives. However, the farmer himself can also mix the
15 individual components a) and b) of the herbicidal mixture according to the invention in the spray tank and add, if appropriate, other auxiliaries and additives (tank mix method).

In the tank mix method, the components a) and b) are mixed in the
20 spray tank and diluted to the desired use concentration using water.

For better processability, it is possible to add further auxiliaries and additives. The following components have been
25 found to be useful auxiliaries and additives:

Solvents, antifoams, buffer substances, thickeners, spreading agents, compatibility-promoting agents.

30 Examples and brands of adjuvants and auxiliaries and additives are described in Farm Chemicals Handbook 1997; Meister Publishing 1997 p. C10 "adjuvant" or 1998 Weed Control Manual p. 86.

The mixture according to the invention is suitable as a
35 herbicide. The herbicidal mixture controls vegetation on non-crop areas very efficiently, especially at high rates of application. It acts against broad-leaved weeds and weed grasses in crops such as wheat, rice, maize, soya and cotton without causing any significant damage to the crop plants. This effect is mainly
40 observed at low rates of application.

Depending on the application method in question, the herbicidal mixture can additionally be employed in a further number of crop plants for eliminating undesirable plants. Examples of suitable
45 crops are the following:

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- Allium cepa, Ananas comosus, Arachis hypogaea, Asparagus officinalis, Beta vulgaris spec. altissima, Beta vulgaris spec. rapa, Brassica napus var. napus, Brassica napus var. napobrassica, Brassica rapa var. silvestris, Camellia sinensis,
- 5 Carthamus tinctorius, Carya illinoensis, Citrus limon, Citrus sinensis, Coffea arabica (Coffea canephora, Coffea liberica), Cucumis sativus, Cynodon dactylon, Daucus carota, Elaeis guineensis, Fragaria vesca, Glycine max, Gossypium hirsutum, (Gossypium arboreum, Gossypium herbaceum, Gossypium vitifolium),
- 10 Helianthus annuus, Hevea brasiliensis, Hordeum vulgare, Humulus lupulus, Ipomoea batatas, Juglans regia, Lens culinaris, Linum usitatissimum, Lycopersicon lycopersicum, Malus spec., Manihot esculenta, Medicago sativa, Musa spec., Nicotiana tabacum (N.rustica), Olea europaea, Oryza sativa, Phaseolus lunatus,
- 15 Phaseolus vulgaris, Picea abies, Pinus spec., Pisum sativum, Prunus avium, Prunus persica, Pyrus communis, Ribes sylvestre, Ricinus communis, Saccharum officinarum, Secale cereale, Solanum tuberosum, Sorghum bicolor (s. vulgare), Theobroma cacao, Trifolium pratense, Triticum aestivum, Triticum durum, Vicia
- 20 faba, Vitis vinifera and Zea mays.

In addition, the herbicidal mixture can also be used in crops which tolerate the action of herbicides owing to breeding, including genetic engineering methods.

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- The herbicidal mixture can be applied pre- or post-emergence. If the herbicidal mixture is less well tolerated by certain crop plants, application techniques may be used in which the herbicidal mixture is sprayed, with the aid of the spraying
- 30 equipment, in such a way that it comes into as little contact as possible, if any, with the leaves of the sensitive crop plants, while the herbicidal mixture reaches the leaves of undesirable plants growing underneath, or the bare soil surface (post-directed, lay-by).

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- The herbicidal mixture can be used, for example, in the form of ready-to-spray aqueous solutions, powders, suspensions, also highly-concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials
- 40 for broadcasting, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend on the intended aims; in any case, they should ensure the finest possible distribution of the herbicidal mixture according to the invention.

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Suitable inert additives are essentially: mineral oil fractions of medium to high boiling point, such as kerosene and diesel oil,

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furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example paraffin, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives, alcohols, 5 such as methanol, ethanol, propanol, butanol and cyclohexanol, ketones such as cyclohexanone, strongly polar solvents, for example amines such as N-methylpyrrolidone, and water.

Aqueous use forms can be prepared from emulsion concentrates, 10 suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the herbicidal mixture, either as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetting agent, tackifier, dispersant or emulsifier.

15 Alternatively, it is possible to prepare concentrates comprising active substance, wetting agent, tackifier, dispersant or emulsifier and, if desired, solvent or oil, which concentrates are suitable for dilution with water.

20 Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl sulfates, lauryl ether sulfates and 25 fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and also of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene, or of the naphthalenesulfonic acids with phenol and formaldehyde, 30 polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl or tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, 35 lauryl alcohol polyglycol ether acetate, sorbitol esters, lignin-sulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or grinding the herbicidal mixture together with a solid 40 carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the herbicidal mixture to solid carriers. Solid carriers are mineral earths, 45 such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground

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synthetic minerals, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders, or other solid carriers.

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The concentrations of the herbicidal mixture in the ready-to-use preparations can be varied within wide ranges. In general, the formulations comprise approximately from 0.001 to 98% by weight, preferably 0.01 to 95% by weight, of the herbicidal mixture.

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The mixture of the adjuvant b) can be formulated, for example, as shown in Table 2:

Table 2:

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Component/Mixture No.:	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
C-65 Methyl ester ¹⁾	37	30	10	35	5	37
20 Klearfac® AA 270 ²⁾	7	15	15	2	7.5	22
Lutensit® A-EP ⁴⁾				25		
Oleic acid	5	35		5		5
Plurafac® LF 700 ³⁾			75		37.5	
Silicone antifoam emulsion ⁵⁾				0.5		0.5
25 Solvesso® 150 ⁶⁾	51	20		34.5	50	35.5

1) 1:1 Mixtures of methyl oleate/methyl palmitate (Witco)

2) Phosphate of a fatty acid alcohol ethoxylate/propoxylate (BASF Corporation)

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3) Fatty acid alcohol ethoxylate/propoxylate (BASF AG)

4) Phosphate of a fatty acid alcohol ethoxylate/propoxylate (BASF AG)

35

5) Silicone SKE Wacker

6) Alkylated aromatic hydrocarbons (Exxon)

40

To widen the spectrum of action and to achieve synergistic effects, the herbicidal mixture may be mixed with a large number of representatives of other herbicidal or growth-regulating active compound groups and then applied concomitantly. Suitable co-components for mixtures are, for example, 1,2,4-thiadiazoles, 1,3,4-thiadiazoles, amides, aminophosphoric acid and its derivatives, aminotriazoles, anilides, (het)aryloxyalkanoic acids and their derivatives, benzoic acid and its derivatives,

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benzothiadiazinones, 2-aryl-1,3-cyclohexanediones, hetaryl aryl ketones, benzylisoxazolidinones, meta-CF₃-phenyl derivatives, carbamates, quinolinecarboxylic acid and its derivatives, dihydrobenzofurans, dihydrofuran-3-ones, dinitroanilines, 5 dinitrophenols, diphenyl ethers, dipyridyls, halocarboxylic acids and their derivatives, ureas, 3-phenyluracils, imidazoles, imidazolinones, N-phenyl-3,4,5,6-tetrahydrophthalimides, oxadiazoles, oxiranes, phenols, aryloxy- or heteroaryloxyphenoxypropionic esters, phenylacetic acid and its 10 derivatives, phenylpropionic acid and its derivatives, pyrazoles, phenylpyrazoles, pyridazines, pyridinecarboxylic acid and its derivatives, pyrimidyl ethers, sulfonylureas, triazines, triazinones, triazolinones, triazolcarboxamides and uracils.

15 It may furthermore be advantageous to apply the herbicidal mixture, alone or in combination with other herbicides, in the form of a mixture with other crop protection agents, for example with agents for controlling pests or phytopathogenic fungi or bacteria. Also of interest is the miscibility with mineral salt 20 solutions, which are employed for treating nutritional and trace element deficiencies.

Depending on the control target, the season, the target plants and the growth stage, the application rate of the herbicidal 25 mixture is from 0.01 to 1.0, preferably from 0.01 to 0.5, kg of active substance/ha, based on the pure components of the herbicidal mixture.

Use Example

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The herbicidal action of the compositions according to the invention could be demonstrated by greenhouse experiments:

The culture containers used were plastic pots containing loamy 35 sand with approximately 3.0% of humus as the substrate. The seeds of the test plants were sown separately for each species.

For the pre-emergence treatment, the herbicidal mixture, which had been suspended or emulsified in water, was applied directly 40 after sowing by means of finely distributing nozzles. The containers were irrigated gently to promote germination and growth and subsequently covered with transparent plastic hoods until the plants had rooted. This cover causes uniform germination of the test plants, unless this was adversely 45 affected by the herbicidal mixture.

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For the post-emergence treatment, the test plants were first grown to a height of 3 to 15 cm, depending on the plant habit, and then treated with the herbicidal mixture which had been suspended or emulsified in water. The test plants were for this purpose either sown directly and grown in the same containers, or they were first grown separately as seedlings and transplanted into the test containers a few days prior to treatment.

Depending on the species, the plants were kept at 10-25°C or 20-35°C. The test period extended over 2 to 4 weeks. During this time, the plants were tended, and their response to the individual treatments was evaluated.

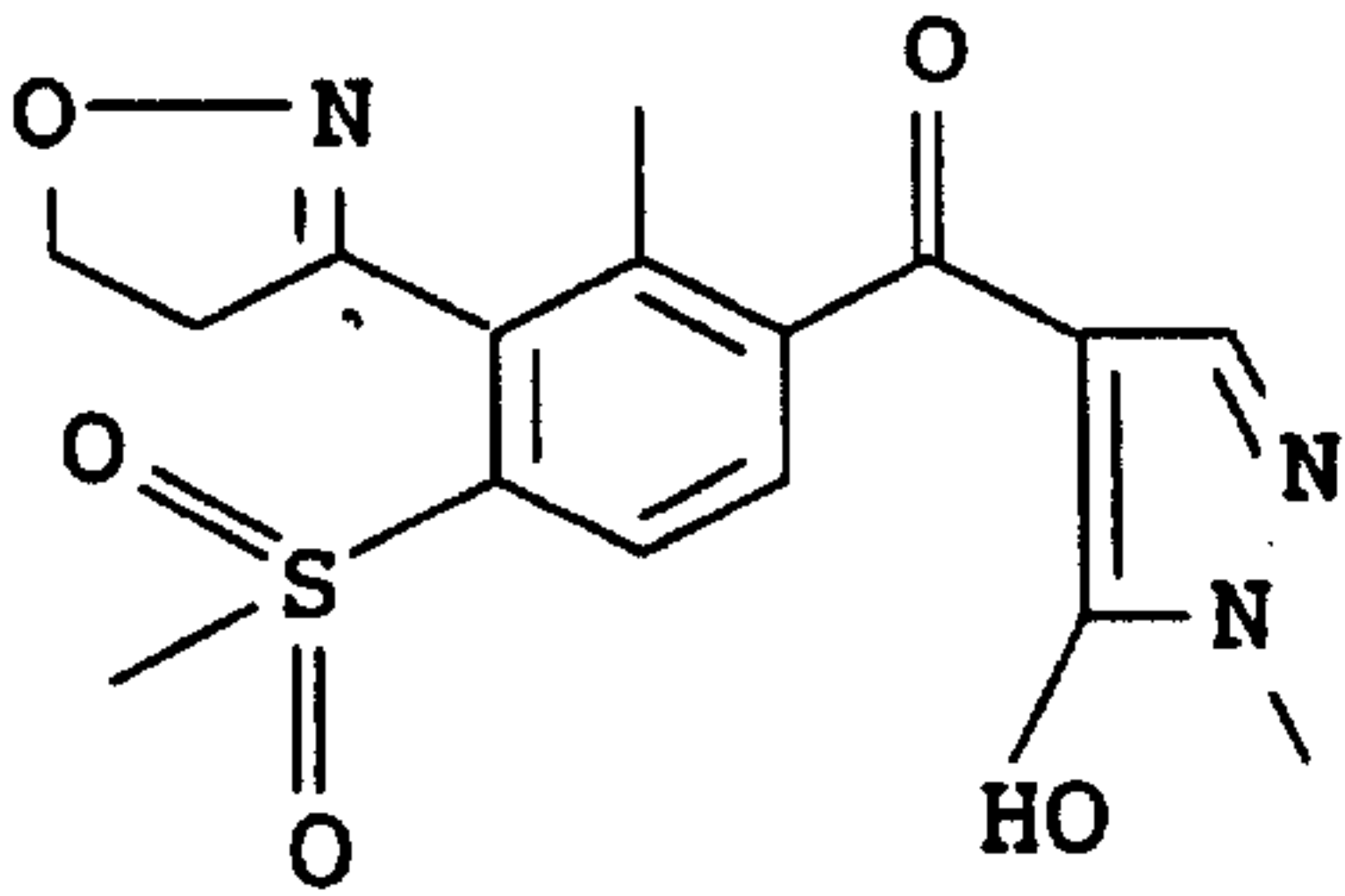
The evaluation was carried out using a scale from 0 to 100. 100 means no emergence of the plants, or complete destruction of at least the above-ground parts, and 0 means no damage, or normal course of growth.

The plants used for the greenhouse experiments were of the following species:

Abbreviation	Scientific name	Common name
ABUTH	Abutilon theophrasti	velvet leaf
25 SETVI	Setaria viridis	green foxtail
SETFA	Setaria faberi	giant foxtail

Example 1

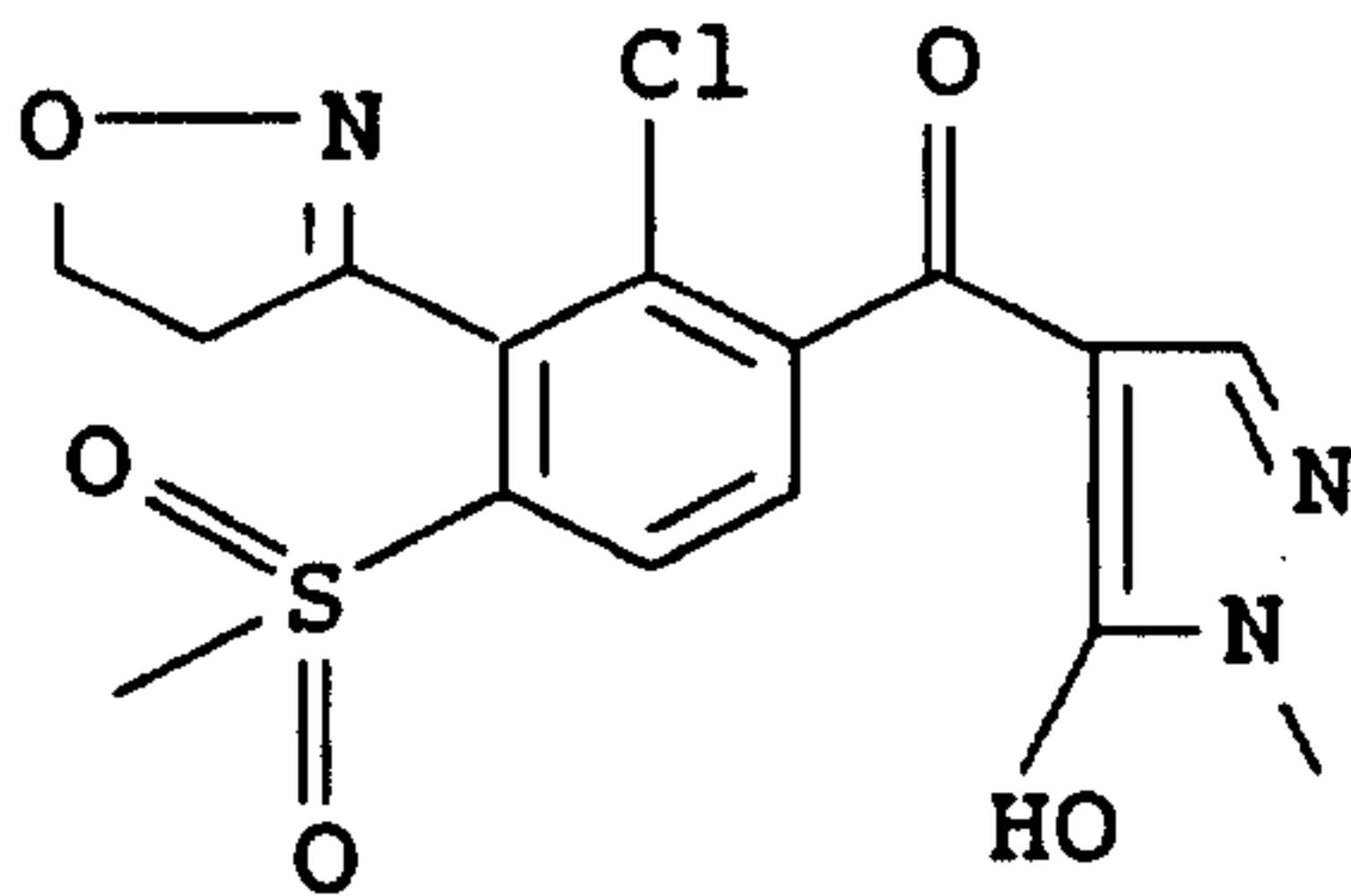
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Example 2

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Table 3

Post-emergent herbicidal activity in the greenhouse				
		Phytotoxicity		
5	Active compound	AWM kg of a.s./ha	SETFA	SETVI
	EX. 1	0.05	91.5	75
	EX. 1 +	0.05 +	95	95
10	No.6, Table 2	0.6		
	EX. 1 +	0.05 +	85	95
	AG 6202 +	0.5 +		
15	Ensol 28	5.0		

Table 4

Post-emergent herbicidal activity in the greenhouse					
		Phytotoxicity			
20	Active compound	AWM kg of a.s./ha	SETFA	SETVI	ABUTH
	EX. 2	0.05	57.5	80	92.5
	EX. 2 +	0.05 +	97.5	95	100
25	No.6, Table 2	0.6			
	EX. 2 +	0.05 +	82.5	77.5	96.5
	Lutensol ON 80 +	0.5 +			
30	Ensol 28	0.56			
	EX. 2 +	0.05 +	67.5	90	94
	AG 6202 +	0.5 +			
35	Ammonium sulfate	5.0			
	EX. 2 +	0.05 +	80	92.5	100
	Atplus +	0.5 +			
	Ensol 28	0.56			

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Legend for the adjuvants used:

Name		
AG® 6202	Akzo	alkyl glycoside APG
5 Lutensol® ON 80	BASF AG	alkyl ethoxylate
Lutensol® ON 110	BASF AG	alkyl ethoxylate
ENSOL® 28	BASF AG	ammonium nitrate/urea solution (28% total N)
Atplus	Unigema	83% paraffin oil + 17% nonionic emulsifier
10		

The data from Tables 3 and 4 show unambiguously the synergistic effect of the herbicidal two-component mixture according to the invention, compared to the respective three-component mixtures 15 and the pure active compound.

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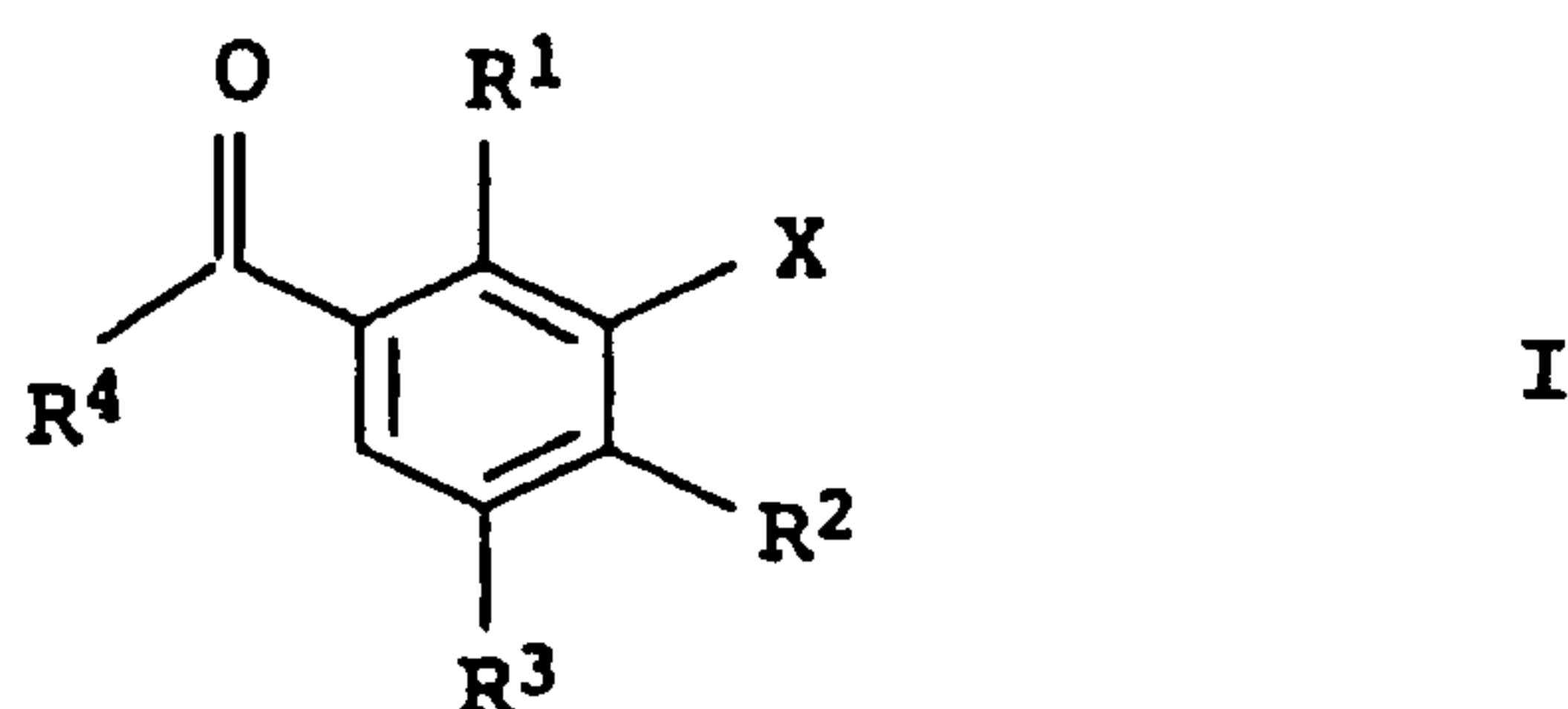
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WHAT IS CLAIMED IS:

1. A herbicidal mixture, comprising
 - a) a herbicidally effective amount of a 3-heterocyclyl-substituted benzoyl compound of the formula I



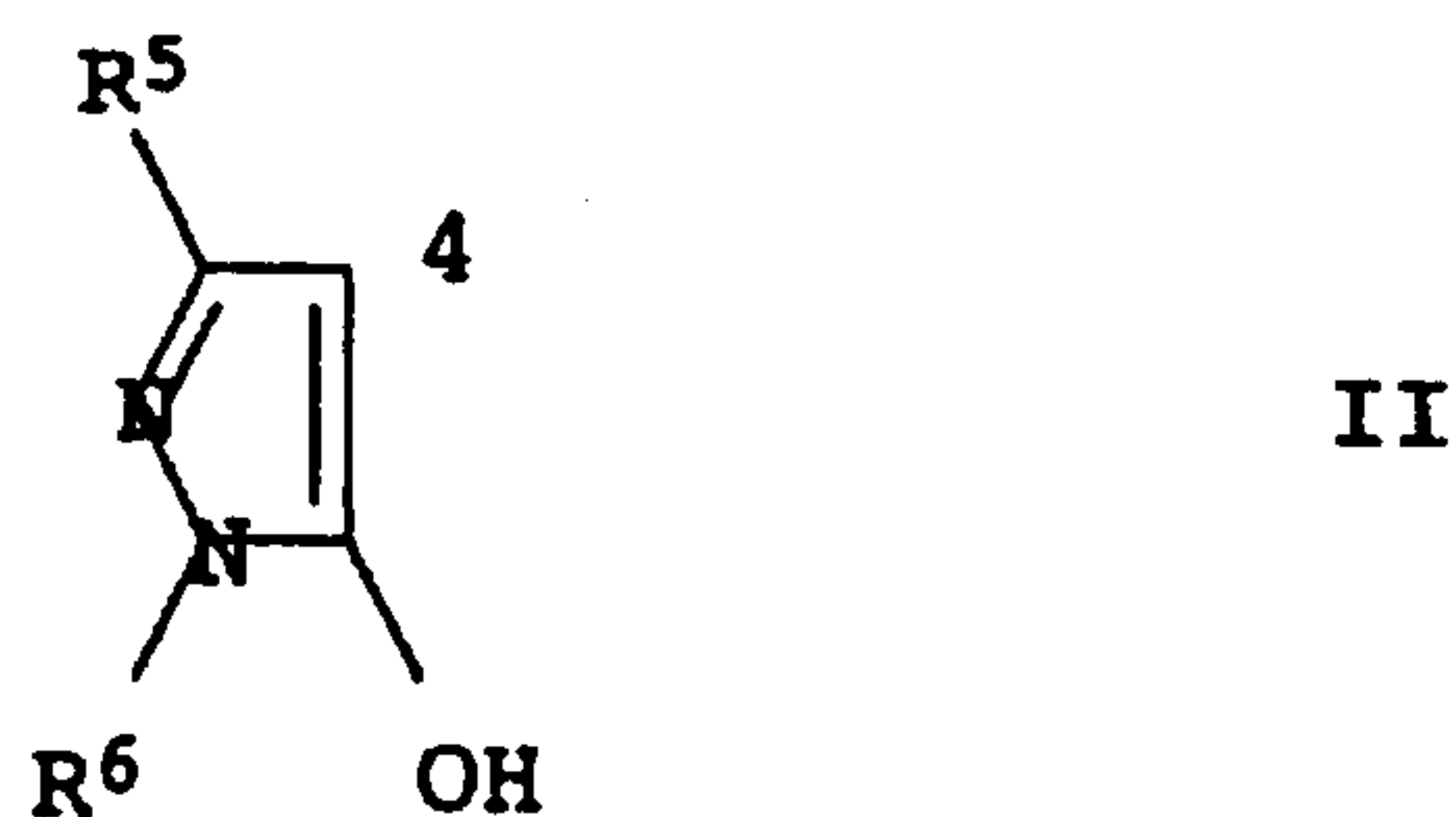
where:

R¹ and R² each are hydrogen, halogen, C₁-C₆-alkyl, C₁-C₆-alkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-alkylsulfonyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy or C₁-C₆-haloalkoxy;

10 R³ is hydrogen, halogen or C₁-C₆-alkyl;

X is a heterocycle from the group consisting of isoxazolyl, 4,5-dihydroisoxazolyl and thiazolyl, where the heterocycle may be unsubstituted or mono- or polysubstituted by halogen, C₁-C₆-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

R⁴ is a pyrazole of the formula II



which is attached in the 4-position and where

R⁵ is hydrogen or C₁-C₆-alkyl,

R⁶ is C₁-C₆-alkyl,

or their environmentally compatible salts; and

b) an adjuvant comprising

- i) a C₁-C₅-alkyl ester of a C₅-C₂₂-carboxylic acid;
- ii) a C₁₀-C₂₀-carboxylic acid,
- iii) a partial phosphoric ester or a partial sulfuric ester of a monohydroxy-functional polyalkyl ether and
- iv) optionally an alkyl polyoxyalkylene polyether

in a synergistically effective amount.

2. A herbicidal mixture as claimed in claim 1, comprising a 3-heterocyclyl-substituted benzoyl compound of the formula I as set forth in claim 1 where R₃ is hydrogen.
3. A herbicidal mixture as claimed in claim 1 or 2, comprising a 3-heterocyclyl-substituted benzoyl compound of the formula I as set forth in claim 1 where R¹ and R² are halogen, C₁-C₆-alkyl, C₁-C₆-alkylthio, C₁-C₆-alkylsulfinyl or C₁-C₆-alkylsulfonyl.
4. A herbicidal mixture as claimed in any one of claims 1 to 3, comprising a 3-heterocyclyl-substituted benzoyl compound of the formula I as set forth in claim 1 where X is isoxazolyl or 4,5-dihydroisoxazolyl which may be unsubstituted or substituted by C₁-C₆-alkyl.
5. A herbicidal mixture as claimed in any one of claims 1 to 4, comprising a 3-heterocyclyl-substituted benzoyl compound of the formula I as set forth in claim 1 where X is isoxazol-5-yl, 3-methylisoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydro-5-methylisoxazol-3-yl, 4,5-dihydro-5-ethylisoxazol-3-yl or 4,5-dihydro-4,5-dimethylisoxazol-3-yl.

6. A herbicidal mixture as claimed in claim 1, comprising 4-[2-chloro-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.
7. A herbicidal mixture as claimed in claim 1, comprising 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.
8. A herbicidal mixture as claimed in any one of claims 1 to 7, comprising
0.5 to 90% by weight of the 3-heterocyclyl-substituted benzoyl
compound a) and
10 10 to 99.5% by weight of the adjuvant b).
9. A process for preparing a herbicidal mixture as claimed in any one of claims 1 to 8, which comprises mixing the components a) and b) of the herbicidal mixture.
10. A method for controlling undesirable vegetation on plants or their habitat, which comprises allowing a synergistically effective amount of the components a) and b) of the herbicidal mixture as claimed in any one of claims 1 to 8 to act separately or jointly on the plants or their habitat.
11. A method for controlling undesirable vegetation, which comprises mixing
a synergistically effective amount of the components a) and b) of the
herbicidal mixture as claimed in any one of claims 1 to 8 and allowing it to
20 act on the undesirable vegetation or their habitat.

