

Dinitroanilines

Herbicide / plant growth regulator

Background Information

Dinitroanilines were first discovered during evaluation of dyes and their intermediates in the early 1960s. They are often referred to as the “yellow” compounds as they are typically bright yellow in colour due to the presence of two nitro (NO₂) groups on the phenyl ring in the 2 and 6 positions (Figure 1).

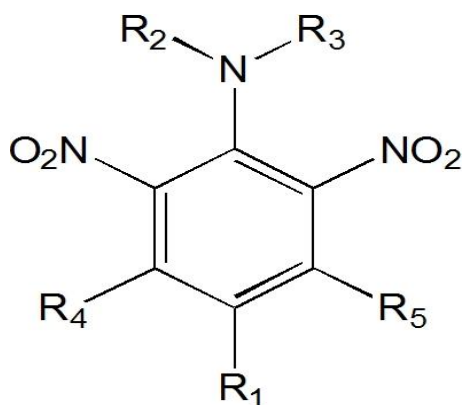


Figure 1. Basic dinitroaniline chemical structure

Flumetralin, first registered for use with the US EPA in 1983, is a local-systemic plant growth regulator (trade-names: Prime[®] [Syngenta], Flupro [Chemtura], and Drexalin Plus [Drexel Chemical Co.]) and is often used alone or in conjunction with maleic hydrazide to control tobacco suckers post-topping. Where used, flumetralin is applied only once per growing season and is typically applied between 3-7 days after the tobacco plant has been topped.

The herbicide butralin is also used as a local-systemic plant growth regulator on tobacco and was first registered in the U.S. in 1976. As with flumetralin it can be used alone or with maleic hydrazide (as tank-mix or sequential combination).

Pendimethalin is an herbicide that also possesses suckercide properties but is not used as extensively as either flumetralin or butralin. Pendimethalin is registered in certain countries as a herbicide and in others as a plant-growth regulator (PGR).

The remaining dinitroanilines (benfluralin and trifluralin) are all selective herbicides for pre-emergence control of annual grasses and broadleaf weeds in a wide range of crops but are not used intensively.

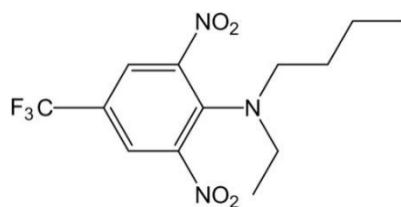
When applied as herbicides, dinitroanilines are absorbed by the plant root systems but are not metabolized¹. They are usually non-ionic compounds, have low water solubilities, vary in volatility and are relatively immobile in soil systems².

Because dinitroanilines are lipophilic and are not very soluble in water, they do not pose an environmental threat to surface or ground water. They are volatile and evaporate quite readily. They are also susceptible to photodegradation. In tobacco, flumetralin metabolizes rapidly and extensively leading to reduction or complete removal.

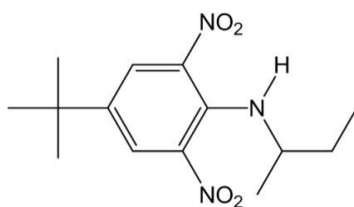
Dinitroaniline herbicides inhibit root development by interrupting mitosis^{1,3}. With a few exceptions they do not control established weeds.

The CORESTA Guide No.1 sets the Guidance Residue Levels (GRLs) for benfluralin, butralin, flumetralin, pendimethalin and trifluralin⁴.

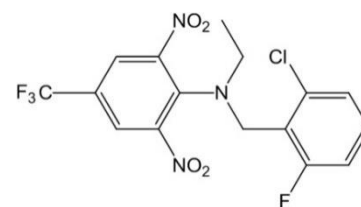
Properties ⁵



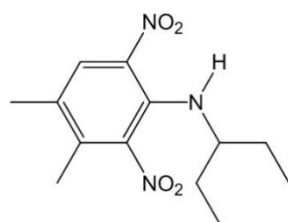
Benfluralin
1861-40-1



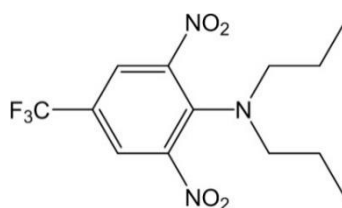
Butralin
33629-47-9



Flumetralin
62924-70-3



Pendimethalin
40487-42-1



Trifluralin
1582-09-8

Properties (continued)⁵

Compound	Molecular Weight	Formula	Melting Point (°C)	Boiling Point (°C)	Solubility (at 20-25 °C)	Stability
Benfluralin	335.3	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	66.4	369-370	Water 0.064 mg/L; acetone and ethyl acetate, both > 250 g/L; methanol 41 g/L	Decomposed by UV light; stable at pH 5-9 (30 days; 26°C)
Butralin	295.3	C ₁₄ H ₂₁ N ₃ O ₄	60	381.3 (calculated)	Water 0.3 mg/L; methanol 68.3 g/L; acetone, dichloromethane and ethyl acetate, all > 700 g/L	Decomposes at 253 °C; hydrolytically stable; DT ₅₀ >1 y; photolysis in water DT ₅₀ 13.6 d (pH 7, 25 °C)
Flumetralin	421.7	C ₁₆ H ₁₂ ClF ₄ N ₃ O ₄	104.6	460	Water 0.07 mg/L; acetone 560 g/L; toluene 400 g/L; ethanol 18 g/L; n-hexane 14 g/L	Decomposes exothermically above 250 °C; hydrolytically stable between pH 5 and pH 9
Pendimethalin	281.3	C ₁₃ H ₁₉ N ₃ O ₄	56	330	Water 0.26-0.33 mg/L; acetone, dichloromethane and toluene, all > 1000 g/L; hexane 49 g/L; methanol > 250 g/L	Slowly decomposed by light; DT ₅₀ in water <21 d
Trifluralin	335.3	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	47.2	369 (calculated)	Water 0.184-0.221 mg/L; acetone, acetonitrile, ethyl acetate and toluene, all > 1000 g/L; hexane 50-67 g/L; methanol 33-40 g/L	Stable at 52 °C; stable to hydrolysis at pH 3, 6 and 9 (52 °C); decomposed by UV irradiation

Sample Preparation (extraction and clean-up)

Selective extraction of dinitroanilines would be ideal but is very expensive. The tobacco sample should be homogenous and sieved through proper screen size (1 mm recommended). A simple extraction technique is to add an organic solvent with the correct polarity at room temperature. The sample should be blended, homogenized, soaked to ensure high extraction efficiency. Sediment and organic solvent are separated from each other by centrifugation or filtration.

Solid phase extraction (SPE), liquid-liquid extraction, pressurized liquid extraction or dispersive SPE (QuEChERS) are frequently used clean-up techniques, to remove unwanted co-extracts. Large extraction volumes can be reduced to milliliters by evaporation of the organic solvent, e.g. under vacuum or under a stream of nitrogen. Nowadays, dinitroanilines are frequently analyzed together with other classes of pesticides in multi-residue methods, covering > 100 pesticides in tobacco¹¹⁻¹⁴.

Analysis (chromatography and quantitation)

Gas and liquid chromatographic procedures are used to analyze dinitroanilines⁶⁻¹³. GC-ECD and GC-MS are routinely used, nowadays also GC-MS/MS¹¹⁻¹⁴. LC-MS/MS can be used to analyze many dinitroanilines. Electrospray-tandem mass spectrometry operating in selected reaction monitoring (SRM) mode is the most common configuration.

The disadvantage of LC-MS/MS is that the tobacco matrix is rather complex which requires improved sample clean-up, matrix-matched standards, standard addition or the use of isotopically labeled surrogate standards, which can be expensive.



References

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