



Dicamba, 2,4-D, 2,4,5-T

Auxin Herbicides

Background Information

Dicamba, 2,4-D, and 2,4,5-T are selective pre- and post-emergent acid herbicides. Primarily effective for the control of woody plants and broadleaf weeds, they have been widely used throughout the world in areas such as pastures, forests, along railways, fencerows, roadways, and residential lawns. In a process that is not completely understood, these herbicides act systemically to mimic synthetic auxin hormones by increasing the plant's production of ethylene, resulting in abnormal cellular growth. This process continues at the growth points of the plant, resulting in leaf deformation, eventual tissue necrosis, and death¹.

The chlorophenoxyacetic acid herbicides 2,4-D and 2,4,5-T were developed in the 1940's^{2,3} and were the two primary ingredients of Agent Orange⁴. These compounds have been made available in a variety of salt and ester forms with the dimethylamine and 2-ethylhexyl ester forms of 2,4-D accounting for over 90 % of the total 2,4-D used⁵. While 2,4-D remains one of the most widely used herbicides⁶, 2,4,5-T has been largely phased out or replaced.

Agent Orange was a defoliant used in the late 1960's by the U.S. military during the Vietnam War⁴. Serious illnesses ranging from the skin disease chloracne to a variety of cancers and birth defects have been attributed to the use of Agent Orange. However, it was discovered that the majority of health effects from its use were caused by the existence of the chemical contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and not from the herbicides themselves. TCDD is formed as a side product when the reaction temperature is not properly maintained during synthesis of 2,4,5-T. As a result of the usage of TCDD laced Agent Orange, large areas of the Vietnam countryside, particularly in Laos and Cambodia and former U.S. military bases, such as Da Nang, are still heavily contaminated with dioxin.

Dicamba, a benzoic acid herbicide, was developed in the early 1960's and is widely used in the acid and dimethylamine salt forms⁷. Dicamba and 2,4-D are also sold in various premix formulations combined with a wide range of other herbicide products⁸.

The versatility of dicamba and 2,4-D allows for tailored applications by virtue of their various chemical forms. Some ester forms have a higher volatility than the salt and acid forms and are therefore better able to penetrate stubbles and protected areas⁹. However, as a result of their volatility they also pose a risk for non-target plants. Development of longer chain ester forms with lower volatility increases their effectiveness in warmer environments.

Because they are absorbed through the plant's foliage, the esters are considered more potent than the salt forms. This quick absorption makes them useful in pre planting "burn down" applications. Salt forms are more readily absorbed through the root systems and are better suited for pre-emergence applications, such as winter broadleaf weed control on golf courses¹⁰.

Degradation of dicamba, 2,4-D, and 2,4,5-T is primarily attributed to microbial action with some microorganisms capable of using 2,4-D as their sole source of carbon. The half-lives range widely in soil and water, depending on the temperature, pH, and oxygen content, with higher microbial action resulting in a shorter half-life. Salts and esters are generally converted to the anionic form with degradation occurring more quickly in higher pH environments¹¹.

Shorter half-lives help to minimize ecological impacts. Toxicities, expressed as LD50s for Dicamba and 2,4-D in Mallard ducks are 2009 mg/kg and 1000 mg/kg, respectively. Toxicity levels are species-specific and vary also according to the chemical form. However, the tendency of the esters to be more toxic to fish is likely due to higher absorption through the gills^{11,12,13}.

Dicamba and 2,4-D are of much interest as residues may result from misuse of products or simply accidental 'drift' from treated adjacent crops onto off-target highly sensitive tobacco fields^{14,15,16}. Accidental 'drift' is especially likely when temperature inversion occurs. Temperature inversions occur when the warm air close to the ground is replaced by cooler air (typically in the late afternoon). This could affect Dicamba in such a manner to cause it to stay just above the ground's surface and then any breeze could cause it to 'drift' to unwanted areas or fields causing those areas to be positive for Dicamba even though it was never applied in that area¹⁷.

With the introduction of genetically engineered (GE) herbicide resistant crops, such as GE corn, cotton, and soybeans, the increased use of 2,4-D and Dicamba presents an even higher potential for drift damage to tobacco and other broadleaf crops. Increased training, along with certification programs for applicators, as well as highly specific application instructions for the use of these herbicides are intended to minimize the number of drift events^{14,15}.

The CORESTA Guide No.1 sets the Guidance Residue Levels (GRLs) for Dicamba, 2,4-D and 2,4,5-T¹⁸.

Properties 12,13,19,20,21,22,23,24

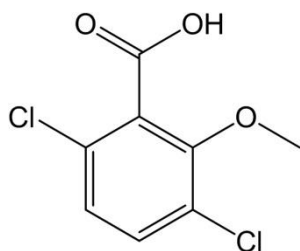
Dicamba


Figure 1. Dicamba structure

IUPAC name: 3,6-Dichloro-2-methoxybenzoic acid

Formula: C₈H₆Cl₂O₃
Mass: 221.04

CAS RN 1918-00-9

Form: White crystalline solid¹²
Solubility: Water (6500 mg/L @ 25 °C)
Ethanol (922 g/L)

Stability: Reacts with organic and inorganic bases to form salts. May react with strong oxidizing agents¹²
pKa: 1.97

Melting Point: 114 – 116 °C

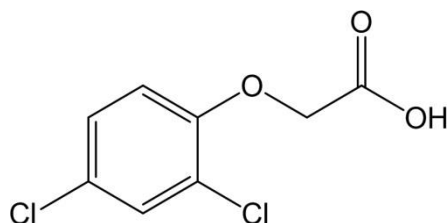
Production: Dicamba is produced by chlorination of o-methylsalicylic acid²²
2,4-D


Figure 2. 2,4-D structure

IUPAC name: (2,4-Dichlorophenoxy)acetic acid

Formula: C₈H₆Cl₂O₃
Mass: 221.04

CAS RN 94-75-7

Form: Yellow to white powder

Solubility: Water (900 mg/L @ 25 °C)

Stability: Reacts with organic and inorganic bases to form salts. Reacts with strong oxidizing agents²⁴
pKa: 2.64

Melting Point: 138 °C

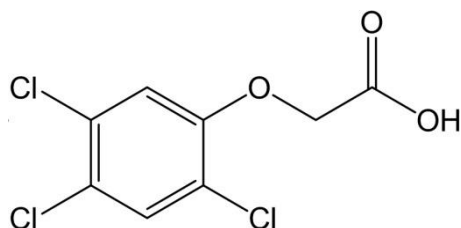
Production: 2,4-D is produced from 2,4-dichlorophenol and monochloroacetic acid in alkaline conditions²⁰
2,4,5-T


Figure 3. 2,4,5-T structure

IUPAC name: (2,4,5-Trichlorophenoxy)acetic acid

Formula: C₈H₅Cl₃O₃
Mass: 255.49

CAS RN 93-76-5

Form: White to yellow crystalline solid

Solubility: Water (238 mg/L @ 30 °C)

Stability: Reacts with organic and inorganic bases to form salts. Reacts with strong oxidizing agents²⁴.

pKa: 2.88

Melting Point: 153 °C

Production: 2,4,5-T is produced from 2,4,5-trichlorophenol²⁰

Salts of dicamba, 2,4-D, and 2,4,5-T are produced through reaction with the appropriate metal or amine base. Esters may be obtained through reaction of the chlorinated phenol starting material with the selected ester of monochloroacetic acid.

Sample Extraction

Following application, the rate of absorption of auxin herbicides depends on the formulation type and the plant species. Esters will generally penetrate waxy leaf surfaces better and are more quickly rainproof than amine salts. Once incorporated into the plant, ester and salt forms will generally both convert to the acid form and may translocate to the growth points within the plant. This potential movement within the plant makes collection of a representative sample for residue analysis imperative²⁵.

Extraction of dicamba, 2,4-D, and 2,4,5-T from plant material should take into consideration the potential presence of the various acid, salt, and ester forms of these herbicides. Generally, a hydrolysis step within the method is recommended in order to ensure a comprehensive extraction. Validation of the methodology should include an evaluation of the accuracy of the extraction procedure using representative forms of esters and salts, as well as the acids.

Modes of Analysis

The analysis of dicamba, 2,4-D, and 2,4,5-T is amenable to the use of a multi-residue method approach. Historical gas chromatographic (GC) methods require methylation of the acids prior to instrumental analysis. Derivatization may be accomplished with the use of reagents such as diazomethane or tetrabutylammonium hydroxide and methyl iodide²⁶. Detection and measurement of the analytes are typically made by halogen specific detectors such as an electron capture detector (ECD) or electro-conductivity detector. Alternatively, the use of GC with selected ion monitoring mass spectrometry is suitable.

The advent of liquid chromatography coupled with tandem mass spectrometry has allowed for direct analysis of the herbicide acid forms without derivatization.

The chromatograms shown below (Figure 5) were collected using LC-MS/MS with negative polarity electro-spray ionization and a 0.1 % acetic acid water and methanol gradient elution from a C18 analytical column.

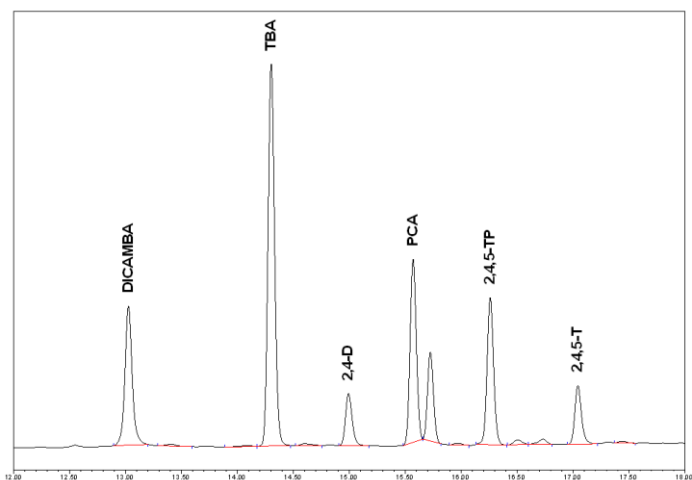


Figure 4. Gas chromatogram (electron capture detection) of a standard containing dicamba (0.14 mg/mL), 2,4-D (0.15 mg/mL), and 2,4,5-T (0.04 mg/mL), all derivatized to the methyl ester forms. Also included are two additional analytes (tribromoanisole [TBA], pentachloroanisole [PCA]) and an internal standard, 2,4,5-TP.

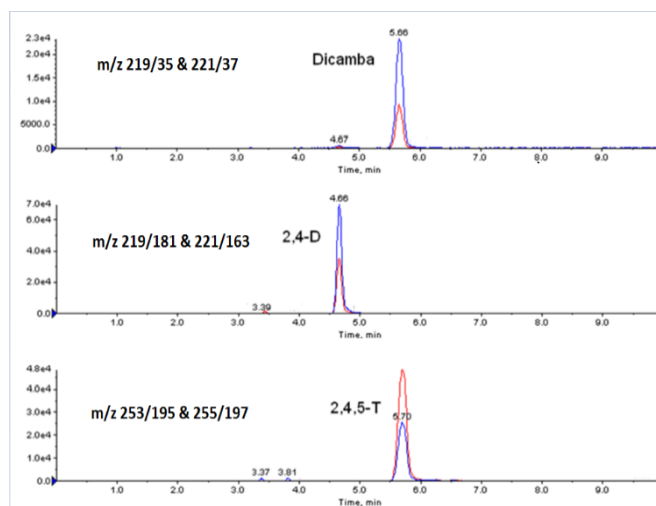


Figure 5. Extracted total ion liquid chromatograms (LC-MS/MS) of a matrix-matched standard containing dicamba (0.2 mg/mL), 2,4-D (0.05 mg/mL), and 2,4,5-T (0.05 mg/mL).



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