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TO: J. Miller/E. Wilson  
Product Manager #23  
Registration Division (H7505C)

FROM: Emil Regelman, Supervisory Chemist  
Chemistry Review Section #2  
Environmental Fate and Ground Water Branch

THRU: Hank Jacoby, Chief  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

Attached, please find the EFGWB review of ...

Reg./File #: 524-UGN

Chemical Name: 2-(Difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-  
3,5-pyridinedicarbothoic acid, S.S-dimethyl ester

Type Product: Herbicide

Common Name: Dithiopyr

Company Name: Monsanto Agricultural Company

Purpose: Addendum to the dithiopyr registration standard (review of  
field volatility study (163-3).

Date Received: 10 October 1990

Date Completed: 14 Jan. 1991

Action Code: \_\_\_\_\_

EFGWB #(s): 91-0022

Total Reviewing Time: 1.0 day

Deferrals to: Ecological Effects Branch, EFED

Science Integration and Policy Staff, EFED

Non-Dietary Exposure Branch, HED

Dietary Exposure Branch, HED

Toxicology Branch

1. CHEMICAL:

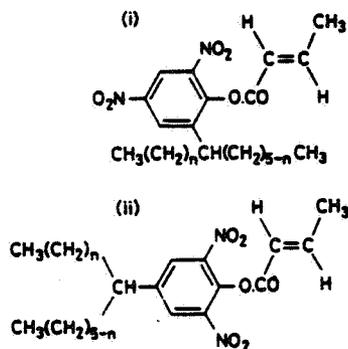
Chemical name: 2-(Difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)  
3,5-pyridinedicarbothoic acid, S,S-dimethyl ester

CAS no.: 97866-45-8

Common name: Dithiopyr

Trade name: Mon 15100

Chemical structure:



Formulation: 1 and 3 lb/gal EC, 4 lb/gal Mcap, and 0.5% G

Physical/Chemical properties of PURE GRADE active ingredient:

Physical characteristics: Brown solid with musty odor

Molecular formula:  $C_{15}H_{16}F_5NO_2S_2$

Molecular weight: 401.4

Melting point: 65 - 67°C

Vapor Pressure:  $4 \times 10^{-6}$  mm Hg at 25°C

Solubility: 1.4 ppm in water at 25°C

Octanol/water partition coefficient: 56250

2. TEST MATERIAL:

See DER attached.

3. STUDY/ACTION TYPE:

Addendum to the dithiopyr registration standard (review of field volatility study (163-3).

4. STUDY IDENTIFICATION:

Fleschar, E.M., Mueth, M.G., and Gustafson, D.I. VOLATILIZATION OF DITHIOPYR RESIDUES FOLLOWING APPLICATION TO TURFGRASS. Sponsored and Submitted by Monsanto Agricultural Company, St. Louis, MO under Laboratory Project No. MSL-9686, R.D. No. 1012; Completed May 1990; Received by EPA 31 August 1990, MRID No. 41615601.

5. REVIEWED BY:

Gail Maske  
Chemist, Review section #2  
OPP/EFED/EFGWB

Signature: 

Date: 

6. APPROVED BY:

Emil Regelman  
Supervisory Chemist  
Review section #2  
OPP/EFED/EFGWB

Signature: 

Date: FEB 26 1991

7. CONCLUSIONS:

The registrant is submitting a field volatility study as part of a request by RD in 1989 for further data to better characterize potential exposure and the state of dithiopyr in the environment. This request was part of verbal conversations EEB had with RD over concerns of persistence of dithiopyr. This data was requested to be submitted prior to making a decision on conditional registration.

Studies submitted to support registration of dithiopyr indicated that there was a significant difference between laboratory and field studies. Drastically shorter soil half-lives were observed with dithiopyr under field conditions. This difference appeared to be attributed to volatility, photochemical lability, and enhanced microbial degradation.

The field volatility study was conducted with dithiopyr as an EC formulation at three geographically different sites with diverse climates. Immediately after application, the reported data indicated there is about 5% of the applied dithiopyr in the air, about 25% in the upper inch of turf, about 50% in the lower two inches of turf, and about 20% on the soil surface. At 30 days posttreatment, it was reported an average of about 45% had volatilized in the air, about 10% had remained in the turf or clippings, about 5% had metabolized in the soil, and about 40% had remained

in the soil as dithiopyr. Meteorological conditions appeared to be a factor in the dissipation of dithiopyr. The registrant using models, stated that under conditions of high temperatures and strong winds it is conceivable that as much as 50% (the study reported 12 to 38%) of the applied dithiopyr can be lost to volatilization by day 30 posttreatment. The field volatility study indicates that the lower rate of dithiopyr metabolized reported in the field studies than in laboratory studies (approximately 15 to 30% difference) is most likely due to a greater volatilization rate under field conditions.

The field volatility study is not acceptable to fulfill the Subdivision N Data Requirement for the following reason:

The soil and turf grass data was not furnished which is required to confirm the application rate and rate of volatilization. However, the registrant did indicate this data was available.

The registrant must satisfactorily address this deficiency to fulfill the field volatility data requirement. If the registrant does not address this deficiency, the data requirement will be considered a data gap for use patterns which require this data.

The field volatility study is not a requirement for registration of dithiopyr for the intend uses and sites of application at present. However, the fulfillment of this data requirement may be easier at this time than in the future when the registrant and Agency is less familiar with the study and the registrant is applying for registration of new uses which require this data.

8. RECOMMENDATIONS:

- a. The field volatility study is not acceptable to fulfill the Subdivision N Data Requirement. If the registrant does not address this deficiency, the data requirement will be considered a data gap for use patterns which require this data.
- b. The environmental fate data are adequate to support the proposed conditional registration of dithiopyr for terrestrial nonfood and domestic outdoor uses.
- c. The current status of environmental fate data requirements<sup>1</sup> to support the registration of Dithiopyr for use to control annual grasses and broadleaf weeds in ornamental turf (terrestrial nonfood and domestic outdoor uses) is as follows:

<u>Environmental Fate Data Requirement</u>	<u>Status of Data Requirement</u>	<u>MRID No.</u>
Degradation Studies-Lab		
161-1 Hydrolysis	Fulfilled (AR;09/06/88)	40638627
161-2 Photodegradation in water	Fulfilled (AR;09/06/88)	40638628
161-3 Photodegradation on soil	Required postregistration (Science Chapter)	
Metabolism Studies-Lab		
162-1 Aerobic (Soil)	Fulfilled (AR;09/06/88) (WGM;04/05/90)	40638629 41001517
162-3 Anaerobic (aquatic)	Required postregistration (Science Chapter)	
Mobility Studies		
163-1 Leaching, Adsorption/ Desorption	Fulfilled (AR;09/06/88) (WGM;04/05/90)	40638630 41135601
Dissipation Studies-Field		
164-1 Terrestrial	Partially (WGM;04/05/90) (Science Chapter)	41001519
164-2 Aquatic/sediment	Required postregistration <sup>1</sup>	
Accumulation Studies		
165-4 In fish	Fulfilled (WGM;04/05/90)	41001518

<sup>1</sup> Based on a reevaluation of the environmental fate of dithiopyr, EFGWB-Surface Water Section has determined that a pond water degradation study as required in the science chapter is not needed at this time.

9. BACKGROUND:

Dithiopyr, a pyridine compound, is a herbicide proposed for use as a pre-emergent and postemergent to control annual grasses and broadleaf weeds in ornamental turf (terrestrial nonfood and domestic outdoor uses). Single active ingredient formulations include 1 to 3 lb/gal EC, 4 lb/gal Mcap, and 0.5% G. The proposed maximum application rate for dithiopyr is 1 lb ai/A.

Dithiopyr, codename MON 7200, is referred to by Monsanto as a "rice/turf herbicide". In spite of this reference, Monsanto does not intend to register dithiopyr for use on rice or other food crops in the United States. In fact, rice grown in the United States is entirely direct-seeded (i.e. is not transplanted), and application of dithiopyr severely injures direct-seeded rice.

#### **ENVIRONMENTAL FATE BACKGROUND:**

Dithiopyr was stable at pH 5 and pH 7 and only about 2% of it degraded at pH 9 when added to sterile buffered solutions for 30 days. These results indicate that hydrolysis is unlikely to play a major role in degradation of dithiopyr.

Dithiopyr degraded with a half-life of 17.6 days when exposed to light in an sterile aqueous buffered solution. The addition of sensitizers did not change the rate of photodegradation in water of dithiopyr. These results indicate that dithiopyr will degrade in the environment under aqueous conditions when exposed to light. However, a half-life of >10 months was demonstrated when dithiopyr was applied to soil and exposed to light.

In soil metabolism studies under aerobic laboratory condition, dithiopyr demonstrated a relatively long half-life (523 to 2300 days) depending on soil type. Volatile material, identified as dithiopyr residues, was found to constitute 7.5 to 26% of the total applied material in these studies. Three metabolites (mono-acid-1, monoacid-11, and diacid) were identified. Each of the degradation products constituted <6% of the applied radiolabelled material.

Adsorption/desorption studies were conducted separately with dithiopyr and the three soil metabolites. These studies demonstrated that dithiopyr was extensively adsorbed to soil while the three metabolites were mobile in soil.

Terrestrial dissipation of dithiopyr and its three acid metabolites were studied at fourteen test sites established throughout the continental United States. These sites were chosen representing states with the highest annual turfgrass maintenance costs as an indicator of potentially high use areas for dithiopyr and geographically distributed to encompass a complete mixture of climates, soil textures, and irrigation methods. The average overall soil half-life of dithiopyr formulation as an EC was found to be 17 days with a range of 3 to 49 days. The three soil metabolites were formed and dissipated almost completely within 365 days. The major route of dissipation from the terrestrial studies appeared to be volatilization, since dithiopyr disappeared rapidly and only about 10 to 15% of the applied material was detected as metabolites.

Based on a need to obtain further data on the degradation and metabolism of dithiopyr, the following environmental fate studies were required postregistration in the science chapter:

- 161-3 Photodegradation on soil - additional data,
- 162-3 Anaerobic aquatic metabolism,
- 164-1 Terrestrial field dissipation on bare soil, and,

Further data is being submitted by the registrant to address EEB's and RD's concerns, as well.

10. DISCUSSION:

See attached DER.

Based on the volatilization of dithiopyr, there may appear to be some concern regarding the potential for dithiopyr vapors to translocate and cause injury to non-target vegetation. However, the following facts appear to make a concern for injury of non-target vegetation from vapor translocate baseless:

1. The mode of action of dithiopyr is antitubulin which is similar but not the same as that of the general class of herbicides called dinitroanilines. However, the resulting mitotic inhibition is basically the same as for dinitroanilines. Herbicides having this mode of action have been on the market for nearly 30 years and have not caused offsite vegetation injury due to vapor movement.
2. Of all species tested, crabgrass is clearly the most sensitive to dithiopyr action. It is the only species known to be controlled by dithiopyr as a plant, and then only as a seedling. In fact, crabgrass (and barnyardgrass) control are the major source of dithiopyr use.
3. Dithiopyr has been applied to a number of test field plots with control plots bordering and has not shown biological action outside the treated plot, either by surface water movement or by vapor movement. The line between treated and non-treated areas were reported to be very clear. Therefore, if the most sensitive species known is not affected when only a few inches outside the treated plot, the more resistant species of offsite vegetation should not show detectable biological activity.
4. If adjacent non-target vegetation were to show symptoms, the first symptom of mitotic inhibition is growth retardation or stunting. Following stunting, leaf tissue often appears darker green, a symptom not all that undesirable. If growth were to remain arrested, it would take up to 4 to 5 weeks for natural leaf aging to occur in grasses. For broadleaf weeds, trees, and shrubs, no symptoms would be apparent to fully grown plants since the foliage lasts the entire season. Thus, symptoms are most likely to occur in the spring when vegetation is in the process of initiating new foliage. Intentional applications on landscape ornamentals at the rate recommended for crabgrass control were reported to show no detectable symptoms.

11: COMPLETION OF ONE-LINER:

See attached one-liner.

12: CBI APPENDIX:

N/A

## **DITHIOPYR ADDENDUM**

### **TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES**

December 10, 1990

**FINIAL REPORT**

Contract No. 68D90058

Submitted to:  
Environmental Protection Agency  
Arlington, VA 22202

Submitted by:  
Dynamac Corporation  
The Dynamac Building  
11140 Rockville Pike  
Rockville, MD 20852

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Dithiopyr

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## INTRODUCTION

Dithiopyr is an herbicide proposed for use to control annual grasses and broadleaf weeds in ornamental turf (terrestrial nonfood and domestic outdoor uses). Single active ingredient formulations include 1 and 3 lb/gal EC, 4 lb/gal Mcap, and 0.5% G. The proposed maximum application rate for dithiopyr is 1 lb ai/A.



3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

soil and turf grass data were not provided; therefore, the application rate was not confirmed and the concentration of dithiopyr in the air could not be related to the concentration of dithiopyr remaining on the soil and turf grass surfaces.

4. In order for this study to be considered acceptable, the registrant should submit analytical data for the soil and turf grass surfaces to confirm the application rate and the rate of volatilization.

#### METHODOLOGY:

Test plots (60 x 60 feet) were established in existing turf grass at three locations in two states to reflect different geographical regions. Dithiopyr (Dimension, 1 lb/gal EC, Monsanto) was applied at 1 lb ai/A on 4-inch-high tall fescue turf (sandy clay loam soil: 56% sand, 16% silt, 28% clay, 2.4% organic matter, pH 5.7, and CEC 5.6 meq/100 g) located west of Atlanta, Georgia (southernmost location), on March 14, 1989; on 2-inch-high blue grass turf (silt loam soil: 22% sand, 54% silt, 24% clay, 3.4% organic matter, pH 6.6, and CEC 10.3 meq/100 g) located north of Columbus, Ohio (central location) on April 4, 1989; and on 2.5-inch-high blue grass turf (clay loam soil: 22% sand, 42% silt, 36% clay, 2.2% organic matter, pH 7.8, and CEC 12.4 meq/100 g) located southwest of Cleveland, Ohio (northernmost location) on April 24, 1989. Prior to application of dithiopyr, the plots were mowed, and weather stations were erected either in the center or adjacent to the plots. Soil and air temperature, wind speed and direction, relative humidity, rainfall, and pan evaporation were measured and recorded on a datalogger. Plot maintenance consisted of mowing the turf (clippings left in place) after the 7- and 14-day air samples were collected and, for the remainder of the experiment, mowing as needed except that the turf was not mowed within 5 days before obtaining the 30-day air samples.

Volatilization of dithiopyr from the turf grasses was evaluated using air-sampling pumps to pull air from over the plots through silica gel absorption tubes, which were then solvent-extracted and analyzed. Air was sampled at 1-, 2-, and 6-foot heights in the center and at the downwind edge of the plots (position of the latter varied depending on the wind direction at each sampling period) on the day prior to application and at 0, 0.125, 1, 2, 3, 7, 14, and 30 days posttreatment. At each designated sampling interval, the pumps were run at a calibrated flow rate for 2 hours to expose the sampling tubes to 240 L of air. Sampling generally occurred during the warmest part of the day. The number of tubes connected in series varied from one to three and was based on the anticipated concentration of volatilized dithiopyr and the possibility of overloading the sampling tubes (Table 1). To guard against pump failure at the center-plot sampling station, a second pump and

associated sampling tubes were used at the Columbus and Cleveland locations. After each 2-hour sampling period, the tubes were capped, placed within a vial, and boxed for shipping to the analytical laboratory on dry or blue (artificial) ice. Analytical recovery and storage stability were evaluated by field spiking the absorption tubes with 2, 20, and 200 ug of dithiopyr and drawing 240 L of air through the tubes. These fortified tubes were shipped to the laboratory under the same conditions as the sample tubes.

The silica gel absorption tubes were removed from frozen storage, and the entire contents (gel packing, cotton, and wire) were placed in a French square bottle. After the addition of 50 mL of acetonitrile and 5 minutes of agitation on a shaker, a 25-mL aliquot was removed and placed in a separatory funnel with 1 mL of 3 M sodium chloride solution and 7 mL of isooctane. After shaking for 5 minutes, the mixture was allowed to stand for 15 minutes. The aqueous layer was discarded, and the isooctane was transferred to a 10-mL centrifuge tube where it was brought to a final volume of 10 mL with additional isooctane and analyzed for dithiopyr by GC with Ni<sup>63</sup> detection. Recovery of dithiopyr from laboratory fortifications of the silica tubes averaged 88.1%; recoveries from field fortifications from the three sites averaged 69.7%. Since there was no significant statistical difference between recoveries from the three field sites, all field samples were corrected for 69.7% recovery. The lower limit of method validation was determined to be <0.06 ug/m<sup>3</sup>. For computational purposes, residue values below this were treated as zero.

#### DATA SUMMARY:

Dithiopyr (Dimension, 1 lb/gal EC), applied to turf grass plots at 1 lb ai/A near Atlanta, Georgia (tall fescue on sandy clay loam soil), Columbus, Ohio (blue grass turf on silt loam soil), and Cleveland, Ohio (blue grass turf on clay loam soil), volatilized with maximum air concentrations (1-foot sampling level immediately posttreatment) of 7.82, 2.60, and 5.13 ug/m<sup>3</sup> at the Atlanta, Columbus, and Cleveland locations, respectively (Tables 1, 2, and 3). The air concentrations of dithiopyr decreased to  $\leq 0.5$  of the initial concentration by 1 day at the Atlanta location and by 2 days at the Columbus and Cleveland locations (Tables 1-3 and Figures 1-3).

Based on modeling, the volatilization data for dithiopyr from 60-foot square plots [assuming volatilization occurred only downwind and vertically and during daylight hours (Figure 4)], the cumulative loss during 30 days was 38.2, 19.5, and 12.5% of the applied at the Atlanta, Columbus, and Cleveland locations, respectively (Table 4).

Air temperatures during the 30-day study period varied from approximately 38 to 68 F, 30 to 64 F, and 39 to 70 F at the Atlanta, Columbus, and Cleveland locations, respectively; precipitation varied from a trace amount to approximately 1.5, 1.1, and 1.6 inches at the

respective locations; and wind speeds varied from approximately 1.2 to 5.3, 1.9 to 10, and 1.5 to 7.6 mph at the respective locations (Appendix G). Temperatures recorded during the 2-hour air sampling periods over the first 7 days posttreatment varied from 13.2 to 16.9 C, 4.8 to 13.0 C, and 9.9 to 12.5 C at the Atlanta, Columbus, and Cleveland locations, respectively (Tables K-I, K-II, and K-III).

COMMENTS:

1. No data on the concentration of dithiopyr in the soil and on the surfaces of the turf grass were provided; therefore, the application rate was not confirmed and the concentration of dithiopyr in the air could not be directly related to the concentration of nonvolatilized dithiopyr. Comments made by the study author in the original document suggest that soil and turf samples were collected and analyzed, but were not submitted to EFGWB. In order for this study to fulfill the field volatility data requirement, the soil and turf data should be submitted to EFGWB for review.
2. As noted in the "Notes to Reviewers of MSL-9686" statement, this study was not required by the Pesticide Assessment Guidelines, but rather was requested by Anne Lindsay, Director of the Registration Division.
3. The vapor pressure of dithiopyr and relative humidity data were not provided, as required in the Guidelines. However, the study authors reported that relative humidity and pan evaporation data were measured and recorded at each location. Either or both of these parameters could have been useful in interpreting the widely different volatility values obtained for the three locations (Table 4).
4. The soil described as a silty clay loam for the Atlanta location is a sandy clay loam by the USDA Soil Textural Classification System and is reported as such in this review.
5. The study author discussed the effects of rainfall, temperature, and wind speed on the volatility of dithiopyr. The highest calculated, cumulative volatilization of dithiopyr occurred at the Atlanta location (Table 4), which was exposed to the highest temperatures (Table K-I). Conversely, the lowest cumulative volatilization of dithiopyr occurred at the Cleveland location, which was exposed to the lowest temperatures (Table K-III). The study author reported that the Columbus location (which was intermediate in volatilization of dithiopyr, temperature, and geographical location) was subjected to heavy rains the week preceding application of dithiopyr and to cloudy, wet, and cold conditions for 2 weeks posttreatment.

The data submitted in this study appear to support the study authors' hypothesis that the greater volatility of dithiopyr at the Atlanta location was, in part, related to the higher temperatures at this

location. However, the statement that air temperatures were 65-80 F on the day of application is in conflict with the values given on the field data sheets and Table K-I for 0 and 0.25 days (actually 0.125 days) posttreatment. These data indicate a temperature range of 61-64 F. The difference between a high of 64 and a high of 80 F could be significant with respect to volatilization.

6. Air concentrations were expressed as  $\text{ug}/\text{m}^3$ , but volatility was not expressed as  $\text{ug}/\text{ha}/\text{day}$ ; rather, it was expressed as percent of applied that was volatilized (Table 4). However, the data presented in Table K-I, K-II, and K-III can be readily converted to  $\text{ug}/\text{ha}/\text{day}$ .
7. Although the Guidelines state, in part, that the test substance should be applied to the soil, they also state that it should be applied to sites typical of those to which the product would be applied. Because dithiopyr is being developed as a turf herbicide, the study authors selected turf grass areas for their plots.

**Dithiopyr Science Review**

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Pages 17 through 42 are not included in this copy.

The material not included contains the following type of information:

\_\_\_\_\_ Identity of product inert ingredients.

\_\_\_\_\_ Identity of product inert impurities.

\_\_\_\_\_ Description of the product manufacturing process.

\_\_\_\_\_ Description of product quality control procedures.

\_\_\_\_\_ Identity of the source of product ingredients.

\_\_\_\_\_ Sales or other commercial/financial information.

\_\_\_\_\_ A draft product label.

\_\_\_\_\_ The product confidential statement of formula.

\_\_\_\_\_ Information about a pending registration action

X FIFRA registration data.

\_\_\_\_\_ The document is a duplicate of page(s) \_\_\_\_\_

\_\_\_\_\_ The document is not responsive to the request.

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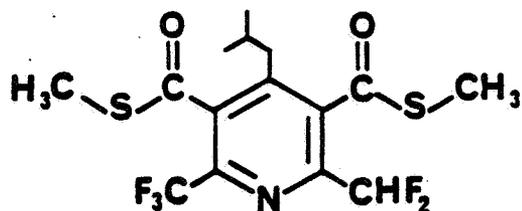
The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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APPENDIX

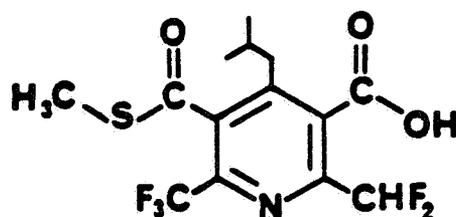
DITHIOPYR AND ITS DEGRADATES



3,5-Pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-, S,S-dimethyl ester

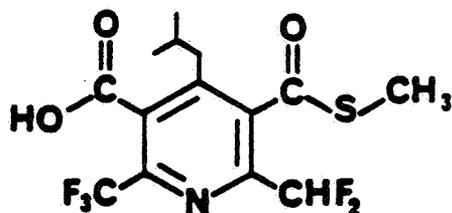
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Dithiopyr (MON 15151, MON 7200, MON 15100)



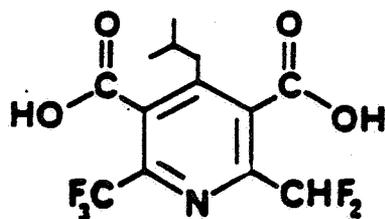
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(Normal acid; II)



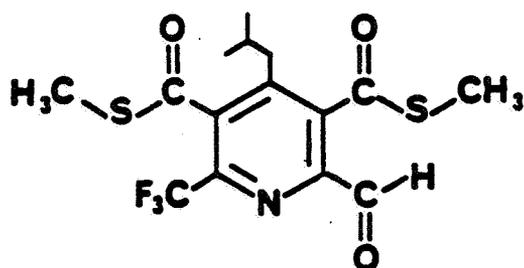
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(Reverse acid; III)



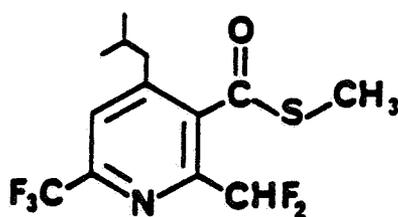
2-(Difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylic acid

(Diacid; IV)



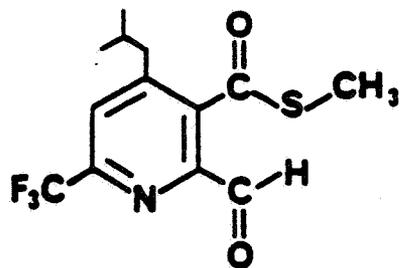
3,5-bis(Methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine

(V)



3-(Methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethylpyridine

(VI)



3-(Methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethylpyridine

(VII)