

GRM: 96.09.S1 (Supplement to GRM 96.09)  
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SUPERSEDES: New

Supplemental Method for the Determination of Spinosad and Metabolites in Cereal Grains,  
Cucurbits, Legumes, Pears, Potatoes, Stone Fruits, Sweet Corn Forage, Grapes, and Grape  
Processed Commodities by HPLC with UV Detection

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A. Scope

Method GRM 96.09.S1 is a supplement to Method GRM 96.09, "Determination of Spinosad and Metabolites in Citrus Fruits and Orange Processed Commodities by High Performance Liquid Chromatography with Ultraviolet Detection" (1). The supplement provides recovery data for the method with 22 additional crop matrices, including cereal grains, cucurbits, legumes, pears, potatoes, stone fruits, sweet corn forage, grapes, grape juice, and grape wine. The method has been validated over the concentration range of 0.01-0.1 µg/g, and it has a validated limit of quantitation of 0.01 µg/g.

B. Principle

The reagents, equipment, and experimental procedures for the method supplement (GRM 96.09.S1) are the same as those described in Method GRM 96.09. Residues of spinosyns A, D, K, B, and *N*-demethyl spinosyn D are extracted from crop samples using 80% acetonitrile/20% water. For grape juice and wine, the extracting solvent is 40% acetonitrile/60% dichloromethane. An aliquot of the extract is purified by liquid-liquid partitioning prior to silica and cyclohexyl solid phase extraction (SPE). All five analytes are separated and determined simultaneously in the purified extracts by reversed-phase high performance liquid chromatography (HPLC) with ultraviolet (UV) detection at 250 nm.

## K. Results and Discussion

### 1. Method Validation

#### a. Recovery Levels and Precision

A method validation study was conducted to determine the recovery levels and the precision of the residue method for the five analytes in 22 different commodities. The results of the validation are summarized by sample type and fortification level in Tables I-VIII.

For all of the analytes and sample matrices, average recoveries ranged from 78% to 119% at 0.01 µg/g and from 78% to 123% at 0.1 µg/g. Most of the individual recovery values (345 out of 360) fell within the range of 70-120%. Recovery values of less than 70% or greater than 120% occurred with one or more samples of field corn (Table I), cantaloupe (Table III), snap beans (Table IV), peaches (Table V), pears and grapes (Table VI), and potatoes (Table VIII).

Most of the corresponding relative standard deviations (54 out of 60) were less than 20% (Tables I-VIII). Standard deviations of greater than 20% occurred with legumes (Table IV) and potatoes (Table VIII). The majority (5 out of 6) of the results for which the relative standard deviation was greater than 20% can be attributed to having only three data points, and it is likely that the relative standard deviation would decrease with additional data points.

Some method limitations were discovered during the validation study, such that a few sample matrices could not be adequately analyzed with the method. The limitations resulted from insufficient recovery of the analytes and/or insufficient purification of the sample extracts. The sample matrices that produced insufficient recovery and/or interferences on the chromatograms were alfalfa forage and hay, sweet corn stover, wheat hay and straw, and sorghum forage and fodder. It is recommended that these sample types be analyzed by LC-MS (2).

#### b. Calculated Limits of Detection and Quantitation

Following a published technique (3), the calculated limits of detection (LOD) and quantitation (LOQ) were obtained from the standard deviation of the results of fortified recovery samples at the validated LOQ, which was 0.01 µg/g. The LOD was calculated as 3X the standard deviation, and the LOQ was calculated as 10X the standard deviation (3).

For all five analytes, the calculated LOD ranged from 0.001 to 0.005 µg/g in the 22 sample matrices (Tables I-VIII). These calculated LOD values support the previously determined method LOD of 0.003-0.006 µg/g (1). Likewise, the calculated LOQ ranged from 0.004 to 0.018 µg/g for all five analytes in the 22 sample matrices (Tables I-VIII). These calculated values support the previously determined method LOQ of 0.01-0.02 µg/g (1).

## 2. Representative Chromatograms

Representative chromatograms demonstrating the determination of the analyte residues are illustrated in Figures 1-7. Additional chromatograms for several other sample matrices are included in the original method (1).

## 3. Confirmation of Residue Identity

The identity of spinosad and its metabolites in residue samples may be confirmed by HPLC-UV using the alternative chromatographic column and conditions provided for confirmation (1). If a more definitive confirmation of residue identity is desired, confirmation by LC-MS is recommended (2). The same final solutions that were injected for HPLC-UV determination may be injected into the LC-MS for confirmation.

## M. References

1. West, S. D. and Turner, L.G., "Determination of Spinosad and Metabolites in Citrus Fruits and Orange Processed Commodities by High Performance Liquid Chromatography with Ultraviolet Detection", GRM 96.09, 1997, unpublished method of Dow AgroSciences LLC (formerly DowElanco).
2. Schwedler, D. A.; Thomas, A. D.; Yeh, L. T., "Determination of Spinosad and Metabolites in Alfalfa Hay, Wheat Hay, Wheat Straw, Corn Stover, and Sorghum Fodder by Liquid Chromatography with Mass Selective Detection", GRM 97.06, 1998, unpublished method of Dow AgroSciences LLC.
3. Keith, L. H.; Crummett, W.; Deegan, J., Jr.; Libby, R. A.; Taylor, J. K.; Wentler, G., *Anal. Chem.*, **1983**, *55*, 2210-2218.

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Table I. Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Cereal Grains

Cereal Grain Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Field Corn	0.0	ND <sup>a</sup>	ND	ND	ND	ND	NA <sup>b</sup>	NA	NA	NA	NA	NA
Sweet Corn	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Sorghum	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Wheat	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Field Corn	0.01	0.0075	0.0066	0.0080	0.0071	0.0097	75	66	80	71	97	97
Field Corn	0.01	0.0091	0.0080	0.0088	0.0087	0.0112	91	80	88	87	112	112
Sweet Corn	0.01	0.0097	0.0089	0.0091	0.0086	0.0104	97	89	91	86	104	104
Sweet Corn	0.01	0.0079	0.0076	0.0117	0.0083	0.0103	79	76	117	83	103	103
Sorghum	0.01	0.0093	0.0076	0.0086	0.0079	0.0105	93	76	86	79	105	105
Sorghum	0.01	0.0076	0.0070	0.0088	0.0079	0.0097	76	70	88	79	97	97
Wheat	0.01	0.0086	0.0078	0.0093	0.0074	0.0109	86	78	93	74	109	109
Wheat	0.01	0.0086	0.0085	0.0085	0.0087	0.0105	86	85	85	87	105	105
$\bar{x}$ =		0.0085	0.0078	0.0091	0.0081	0.0104	85	78	91	81	104	104
$s$ =		0.0008	0.0007	0.0011	0.0006	0.0005	8	7	11	6	5	5
$(3s)^c$ =		0.002	0.002	0.003	0.002	0.002						
$(10s)^d$ =		0.008	0.007	0.011	0.006	0.005						
RSD =		9%	9%	12%	7%	5%						

Table I. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Cereal Grains

Cereal Grain Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Field Corn	0.1	0.084	0.076	0.088	0.081	0.099	84	76	88	81	99
Sweet Corn	0.1	0.093	0.084	0.097	0.090	0.109	93	84	97	90	109
Sorghum	0.1	0.082	0.078	0.087	0.082	0.084	82	78	87	82	84
Wheat	0.1	0.080	0.074	0.085	0.076	0.105	80	74	85	76	105
$\bar{x} =$		0.085	0.078	0.089	0.082	0.099	85	78	89	82	99
$s =$		0.006	0.004	0.005	0.006	0.011	6	4	5	6	11
RSD =		7%	5%	6%	7%	11%					

a ND = None detected at a detection limit of 0.003 µg/g.

b NA = Not applicable.

c Calculated limit of detection.

d Calculated limit of quantitation.

Table II. Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Sweet Corn Forage

Forage Crop Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Sweet Corn	0.0	ND <sup>a</sup>	ND	ND	ND	ND	NA <sup>b</sup>	NA	NA	NA	NA	NA
Sweet Corn	0.01	0.0098	0.0100	0.0092	0.0098	0.0091	98	100	92	98	91	91
Sweet Corn	0.01	0.0113	0.0113	0.0091	0.0102	0.0098	113	113	91	102	102	98
	$\bar{x}$ =	0.0106	0.0107	0.0092	0.0100	0.0095	106	107	92	100	100	95
	<i>s</i> =	NC <sup>c</sup>	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
	RSD =	NC	NC	NC	NC	NC						
Sweet Corn	0.1	0.093	0.094	0.093	0.094	0.090	93	94	93	94	94	90
	$\bar{x}$ =	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
	<i>s</i> =	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
	RSD =	NC	NC	NC	NC	NC						

<sup>a</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>b</sup> NA = Not applicable.

<sup>c</sup> NC = Not calculated due to an insufficient number of data points.

Table III. Summary of Recovery Data for Spinosyns A, D, K, B, and *N*-Demethyl Spinosyn D (Met-D) in Cucurbits

Cucurbit Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Cantaloupe <sup>a</sup>	0.0	ND <sup>b</sup>	ND	ND	ND	ND	NA <sup>c</sup>	NA	NA	NA	NA	NA
Cantaloupe <sup>d</sup>	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Cucumber	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Squash	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Cantaloupe <sup>a</sup>	0.01	0.0087	0.0084	0.0097	0.0101	0.0110	87	84	97	101	110	110
Cantaloupe <sup>a</sup>	0.01	0.0084	0.0091	0.0095	0.0103	0.0107	84	91	95	103	107	107
Cantaloupe <sup>d</sup>	0.01	0.0107	0.0107	0.0100	0.0104	0.0111	107	107	100	104	111	111
Cantaloupe <sup>d</sup>	0.01	0.0094	0.0084	0.0097	0.0097	0.0108	94	84	97	97	108	108
Cucumber	0.01	0.0096	0.0095	0.0103	0.0104	0.0113	96	95	103	104	113	113
Cucumber	0.01	0.0103	0.0104	0.0101	0.0104	0.0110	103	104	101	104	110	110
Squash	0.01	0.0086	0.0077	0.0085	0.0073	0.0093	86	77	85	73	93	93
Squash	0.01	0.0098	0.0081	0.0093	0.0085	0.0103	98	81	93	85	103	103
$\bar{x}$ =		0.0094	0.0090	0.0096	0.0096	0.0107	94	90	96	96	107	107
<i>s</i> =		0.0008	0.0011	0.0006	0.0011	0.0006	8	11	6	11	6	6
(3 <i>s</i> ) <sup>c</sup> =		0.002	0.003	0.002	0.003	0.002						
(10 <i>s</i> ) <sup>d</sup> =		0.008	0.011	0.006	0.011	0.006						
RSD =		9%	12%	7%	11%	6%						

Table III. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Cucurbits

Cucurbit Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Cantaloupe <sup>a</sup>	0.1	0.104	0.107	0.095	0.097	0.111	104	107	95	97	111
Cantaloupe <sup>d</sup>	0.1	0.112	0.115	0.112	0.118	0.121	112	115	112	118	121
Cucumber	0.1	0.097	0.099	0.099	0.102	0.110	97	99	99	102	110
Squash	0.1	0.100	0.092	0.102	0.094	0.114	100	92	102	94	114
$\bar{x}$ =		0.103	0.103	0.102	0.103	0.114	103	103	102	103	114
$s$ =		0.007	0.010	0.007	0.011	0.005	7	10	7	11	5
RSD =		7%	10%	7%	11%	4%					

<sup>a</sup> Edible cantaloupe fruit.  
<sup>b</sup> ND = None detected at a detection limit of 0.003 µg/g.  
<sup>c</sup> NA = Not applicable.  
<sup>d</sup> Whole cantaloupe.

Table IV. Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Legumes

Legume Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Snap Beans	0.0	ND <sup>a</sup>	ND	ND	ND	ND	NA <sup>b</sup>	NA	NA	NA	NA	NA
Snow Peas	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Soybeans	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Snap Beans	0.01	0.0075	0.0064	0.0070	0.0067	0.0094	75	64	70	67	94	94
Snap Beans	0.01	0.0074	0.0069	0.0087	0.0075	0.0100	74	69	87	75	100	100
Snow Peas	0.01	0.0109	0.0108	0.0101	0.0100	0.0119	109	108	101	100	119	119
Snow Peas	0.01	0.0105	0.0101	0.0096	0.0092	0.0109	105	101	96	92	109	109
Soybeans	0.01	0.0085	0.0072	0.0079	0.0077	0.0101	85	72	79	77	101	101
Soybeans	0.01	0.0091	0.0079	0.0084	0.0083	0.0103	91	79	84	83	103	103
	$\bar{x}$ =	0.0090	0.0082	0.0086	0.0082	0.0104	90	82	86	82	104	104
	<i>s</i> =	0.0015	0.0018	0.0011	0.0012	0.0009	15	18	11	12	9	9
	(3 <i>s</i> ) <sup>c</sup> =	0.005	0.005	0.003	0.004	0.003						
	(10 <i>s</i> ) <sup>d</sup> =	0.015	0.018	0.011	0.012	0.009						
	RSD =	17%	22%	13%	15%	9%						

Table IV. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Legumes

Legume Sample Type	µg/g Added	µg/g Found						Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K		
Snap Beans	0.1	0.071	0.064	0.076	0.066	0.094	71	64	76	66	94		
Snow Peas	0.1	0.114	0.107	0.101	0.097	0.119	114	107	101	97	119		
Soybeans	0.1	0.084	0.075	0.085	0.078	0.098	84	75	85	78	98		
	$\bar{x}$ =	0.090	0.082	0.087	0.080	0.104	90	82	87	80	104		
	$s$ =	0.022	0.022	0.013	0.016	0.013	22	22	13	16	13		
	RSD =	24%	27%	15%	20%	13%							

<sup>a</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>b</sup> NA = Not applicable.

Table V. Summary of Recovery Data for Spinosyns A, D, K, B, and *N*-Demethyl Spinosyn D (Met-D) in Stone Fruits

Stone Fruit Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Cherries <sup>a</sup>	0.0	ND <sup>b</sup>	ND	ND	ND	ND	NA <sup>c</sup>	NA	NA	NA	NA	NA
Cherries <sup>d</sup>	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Peaches	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Plums	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Prunes	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Cherries <sup>a</sup>	0.01	0.0107	0.0105	0.0098	0.0094	0.0099	107	105	98	94	99	99
Cherries <sup>a</sup>	0.01	0.0108	0.0105	0.0094	0.0091	0.0100	108	105	94	91	100	100
Cherries <sup>d</sup>	0.01	0.0104	0.0104	0.0091	0.0095	0.0106	104	104	91	95	106	106
Cherries <sup>d</sup>	0.01	0.0103	0.0101	0.0099	0.0091	0.0100	103	101	99	91	100	100
Peaches	0.01	0.0118	0.0119	0.0106	0.0102	0.0110	118	119	106	102	110	110
Peaches	0.01	0.0115	0.0116	0.0109	0.0105	0.0110	115	116	109	105	110	110
Plums	0.01	0.0090	0.0090	0.0092	0.0079	0.0090	90	90	92	79	90	90
Plums	0.01	0.0086	0.0085	0.0078	0.0076	0.0081	86	85	78	76	81	81
Prunes	0.01	0.0102	0.0095	0.0083	0.0082	0.0080	102	95	83	82	80	80
Prunes	0.01	0.0104	0.0092	0.0083	0.0084	0.0082	104	92	83	84	82	82
$\bar{x}$ =		0.0104	0.0101	0.0093	0.0090	0.0096	104	101	93	90	96	96
<i>s</i> =		0.0010	0.0011	0.0010	0.0010	0.0012	10	11	10	10	12	12
$(3s)^c$ =		0.003	0.003	0.003	0.003	0.004						
$(10s)^d$ =		0.010	0.011	0.010	0.010	0.012						
RSD =		10%	11%	11%	11%	13%						

Table V. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Stone Fruits

Stone Fruit Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Cherries <sup>a</sup>	0.1	0.112	0.111	0.105	0.104	0.104	112	111	105	104	104
Cherries <sup>d</sup>	0.1	0.112	0.109	0.108	0.104	0.114	112	109	108	104	114
Peaches	0.1	0.121	0.119	0.114	0.112	0.116	121	119	114	112	116
Plums	0.1	0.085	0.084	0.079	0.079	0.081	85	84	79	79	81
Prunes	0.1	0.102	0.090	0.088	0.088	0.088	102	90	88	88	88
	$\bar{x}$ =	0.106	0.103	0.099	0.097	0.101	106	103	99	97	101
	$s$ =	0.014	0.015	0.015	0.013	0.016	14	15	15	13	16
	RSD =	13%	15%	15%	13%	16%					

<sup>a</sup> Sour cherries.

<sup>b</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>c</sup> NA = Not applicable.

<sup>d</sup> Sweet cherries.

Table VI. Summary of Recovery Data for Spinosyns A, D, K, B, and *N*-Demethyl Spinosyn D (Met-D) in Pears and Grapes

Sample Type	$\mu\text{g/g}$ Added	$\mu\text{g/g}$ Found				Percent Recovery						
		A	D	B	Met-D <sup>a</sup>	K <sup>a</sup>	A	D	B	Met-D <sup>a</sup>	K <sup>a</sup>	
Pears	0.0	ND <sup>b</sup>	ND	ND	ND	ND	NA <sup>c</sup>	NA	NA	NA	NA	NA
Grapes	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Pears	0.01	0.0116	0.0127	0.0087	0.0106	0.0106	116	127	87	106	106	106
Pears	0.01	0.0102	0.0107	0.0084	0.0095	0.0095	102	107	84	95	95	95
Grapes	0.01	0.0111	0.0114	0.0092	0.0101	0.0101	111	114	92	101	101	101
Grapes	0.01	0.0107	0.0126	0.0090	0.0100	0.0100	107	126	90	100	100	100
$\bar{x}$ =		0.0109	0.0119	0.0088	0.0101	0.0101	109	119	88	101	101	101
$s$ =		0.0006	0.0010	0.0004	0.0005	0.0005	6	10	4	5	5	5
$(3s)^c$ =		0.002	0.003	0.001	0.002	0.002						
$(10s)^d$ =		0.006	0.010	0.004	0.005	0.005						
RSD =		6%	8%	5%	5%	5%						

Table VI. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Pears and Grapes

Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D <sup>a</sup>	K <sup>a</sup>	A	D	B	Met-D <sup>a</sup>	K <sup>a</sup>
Pears	0.1	0.114	0.125	0.104	0.116	0.116	114	125	104	116	116
Grapes	0.1	0.111	0.121	0.103	0.112	0.112	111	121	103	112	112
	$\bar{x}$ =	0.113	0.123	0.104	0.114	0.114	113	123	104	114	114
	$s$ =	NC <sup>d</sup>	NC	NC	NC	NC	NC <sup>d</sup>	NC	NC	NC	NC
	RSD =	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC

<sup>a</sup> These are averaged results for the total recovery of Met-D and K, because these two analytes were not resolved chromatographically due to inadvertently using the wrong HPLC column.

<sup>b</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>c</sup> NA = Not applicable.

<sup>d</sup> NC = Not calculated due to an insufficient number of data points.

Table VII. Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Unsweetened Grape Juice and Grape Wine

Sample Type	$\mu\text{g/g}$ Added	$\mu\text{g/g}$ Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Grape Juice	0.0	ND <sup>a</sup>	ND	ND	ND	ND	NA <sup>b</sup>	NA	NA	NA	NA
Grape Wine	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA
Grape Juice	0.01	0.0081	0.0091	0.0081	0.0085	0.0090	81	91	81	85	90
Grape Juice	0.01	0.0090	0.0103	0.0084	0.0089	0.0096	90	103	84	89	96
Grape Wine	0.01	0.0096	0.0099	0.0093	0.0099	0.0106	96	99	93	99	106
Grape Wine	0.01	0.0096	0.0106	0.0091	0.0097	0.0101	96	106	91	97	101
	$\bar{x}$ =	0.0091	0.0100	0.0087	0.0093	0.0098	91	100	87	93	98
	$s$ =	0.0007	0.0007	0.0006	0.0007	0.0005	7	7	6	7	5
	(3s) <sup>c</sup> =	0.002	0.002	0.002	0.002	0.002					
	(10s) <sup>d</sup> =	0.007	0.007	0.006	0.007	0.007					
	RSD =	8%	7%	7%	8%	5%					

Table VII. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and *N*-Demethyl Spinosyn D (Met-D) in Unsweetened Grape Juice and Grape Wine

Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Grape Juice	0.1	0.099	0.109	0.093	0.098	0.104	99	109	93	98	104
Grape Wine	0.1	0.101	0.112	0.091	0.098	0.103	101	112	91	98	103
	$\bar{x}$ =	0.100	0.111	0.092	0.098	0.104	100	111	92	98	104
	<i>s</i> =	NC <sup>c</sup>	NC	NC	NC	NC	NC	NC	NC	NC	NC
	RSD =	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC

<sup>a</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>b</sup> NA = Not applicable.

<sup>c</sup> NC = Not calculated due to an insufficient number of data points.

Table VIII. Summary of Recovery Data for Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Whole Potatoes

Potato Sample Type	µg/g Added	µg/g Found					Percent Recovery					
		A	D	B	Met-D	K	A	D	B	Met-D	K	
Irish Potatoes	0.0	ND <sup>a</sup>	ND	ND	ND	ND	NA <sup>b</sup>	NA	NA	NA	NA	NA
Irish Potatoes	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Red Potatoes	0.0	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Irish Potatoes	0.01	0.0100	0.0099	0.0098	0.0089	0.0107	100	99	98	89	107	107
Irish Potatoes	0.01	0.0101	0.0098	0.0095	0.0076	0.0101	101	98	95	76	101	101
Irish Potatoes	0.01	0.0086	0.0089	0.0106	0.0085	0.0113	86	89	106	85	113	113
Irish Potatoes	0.01	0.0101	0.0102	0.0096	0.0113	0.0101	101	102	96	113	101	101
Red Potatoes	0.01	0.0098	0.0088	0.0092	0.0086	0.0107	98	88	92	86	107	107
Red Potatoes	0.01	0.0096	0.0091	0.0089	0.0073	0.0111	96	91	89	73	111	111
	$\bar{x}$ =	0.0097	0.0095	0.0096	0.0087	0.0107	97	95	96	87	107	107
	$s$ =	0.0006	0.0006	0.0006	0.0014	0.0005	6	6	6	14	5	5
	$(3s)^c$ =	0.002	0.002	0.002	0.005	0.002						
	$(10s)^d$ =	0.006	0.006	0.006	0.014	0.005						
	RSD =	6%	6%	6%	16%	5%						

Table VIII. (Cont.) Summary of Recovery Data for Spinosyns A, D, K, B, and *N*-Demethyl Spinosyn D (Met-D) in Whole Potatoes

Potato Sample Type	µg/g Added	µg/g Found					Percent Recovery				
		A	D	B	Met-D	K	A	D	B	Met-D	K
Irish Potatoes	0.1	0.113	0.108	0.098	0.094	0.118	113	108	98	94	118
Irish Potatoes	0.1	0.120	0.118	0.117	0.113	0.128	120	118	117	113	128
Red Potatoes	0.1	0.081	0.075	0.064	0.060	0.091	81	75	64	60	91
	$\bar{x}$ =	0.105	0.100	0.093	0.089	0.112	105	100	93	89	112
	<i>s</i> =	0.021	0.023	0.027	0.027	0.019	21	23	27	27	19
	RSD =	20%	23%	29%	30%	17%					

<sup>a</sup> ND = None detected at a detection limit of 0.003 µg/g.

<sup>b</sup> NA = Not applicable.

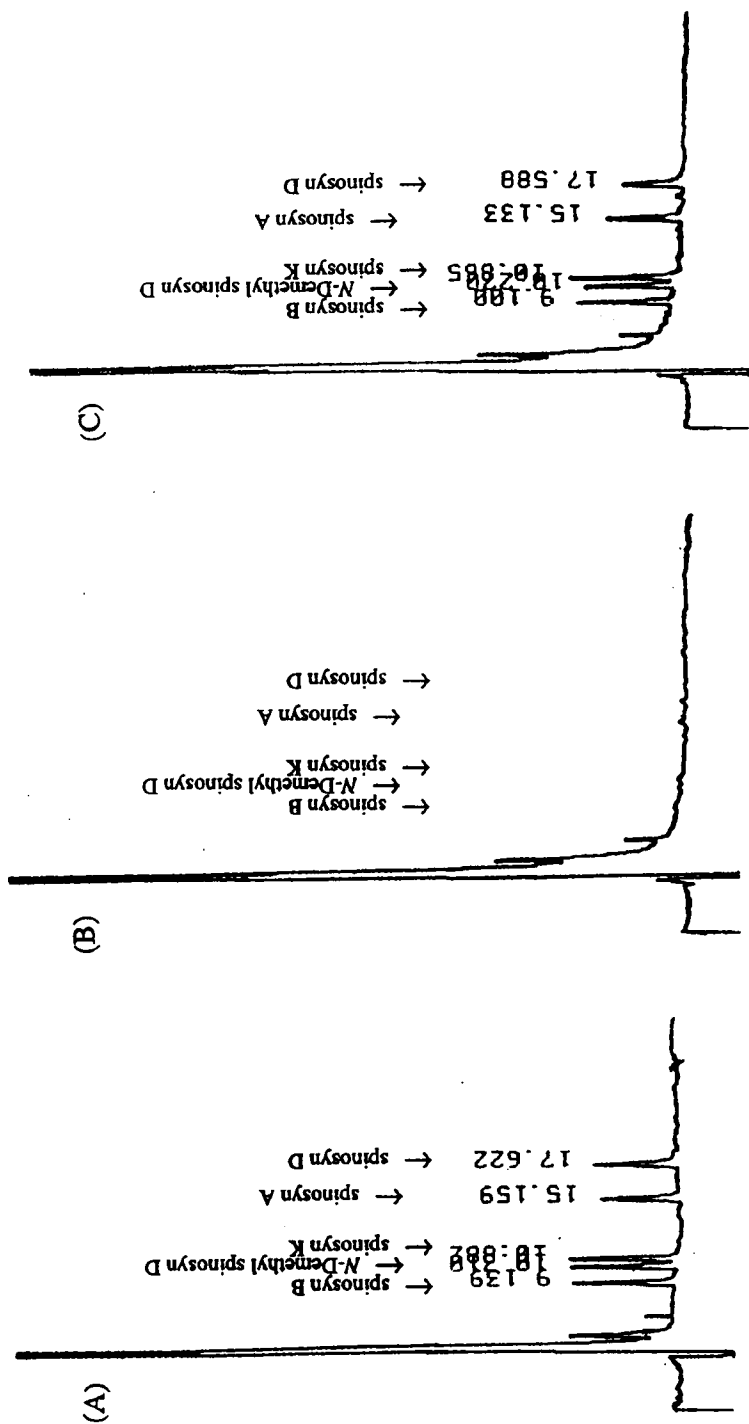
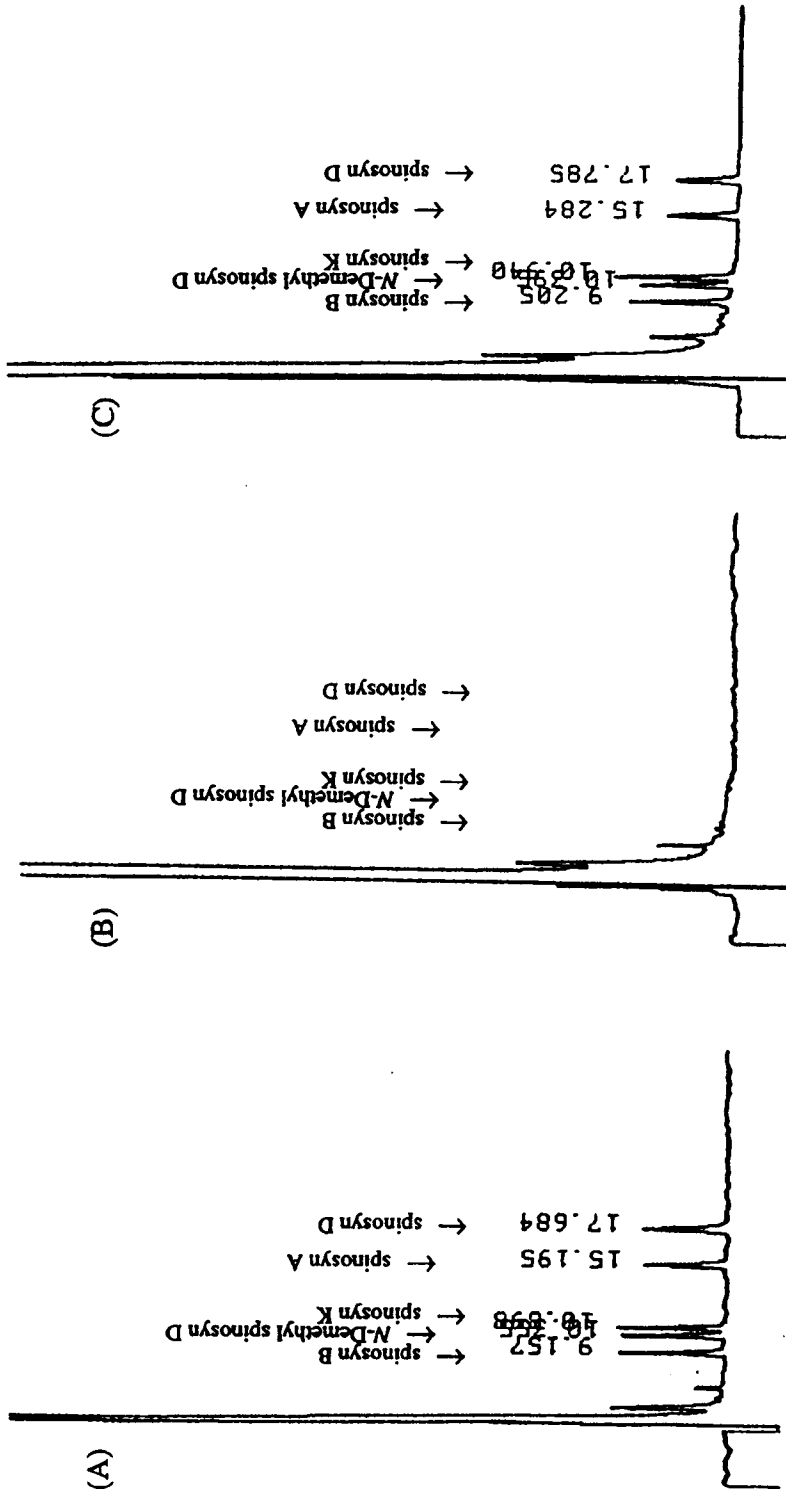
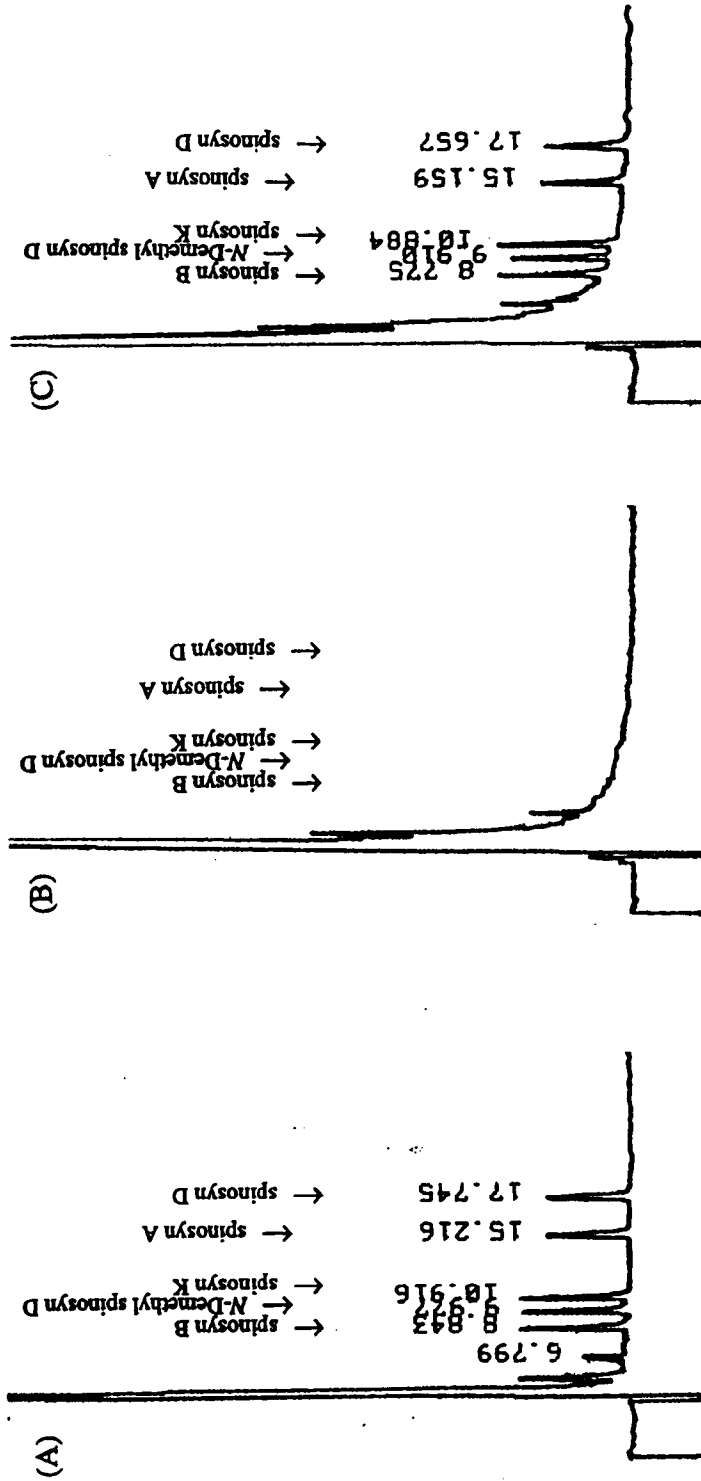


Figure 1. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Summer Squash



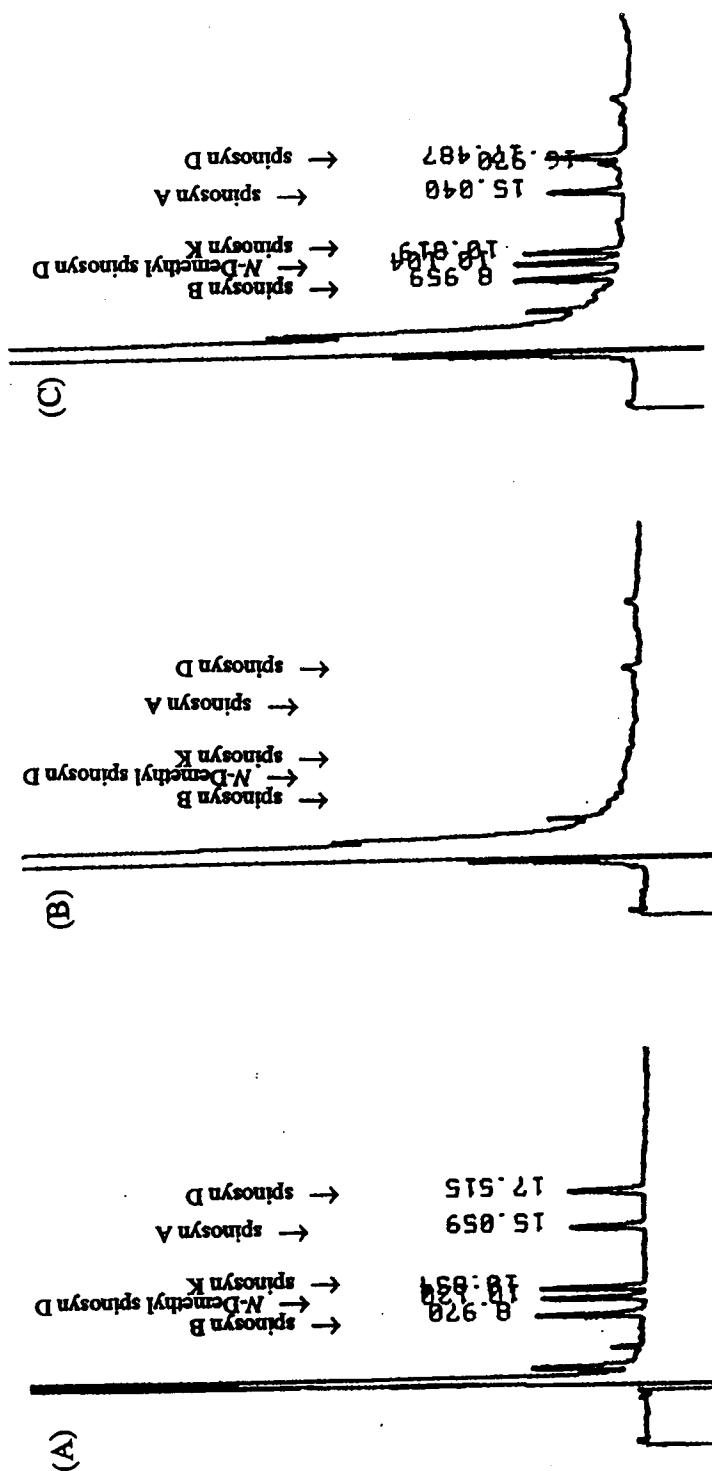
- (A) Standard, 17.5 ng of each analyte injected (equivalent to a theoretical residue of 0.01 µg/g of each).
- (B) Untreated control field corn grain containing no detectable residue of the analytes.
- (C) Untreated control field corn grain fortified with 0.01 µg/g (limit of quantitation), equivalent to recoveries of 88% (spinosyn B), 87% (Met-D), 112% (spinosyn K), 91% (spinosyn A), and 80% (spinosyn D).

Figure 2. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Field Corn Grain



- (A) Standard, 17.5 ng of each analyte injected (equivalent to a theoretical residue of 0.01 µg/g of each).
- (B) Untreated control snow peas containing no detectable residue of the analytes.
- (C) Untreated control snow peas fortified with 0.01 µg/g (limit of quantitation), equivalent to recoveries of 96% (spinosad B), 92% (Met-D), 109% (spinosyn K), 105% (spinosyn A), and 101% (spinosyn D).

Figure 3. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Snow Peas



- (A) Standard, 17.5 ng of each analyte injected (equivalent to a theoretical residue of 0.01 µg/g of each).
- (B) Untreated control sweet corn forage containing no detectable residue of the analytes.
- (C) Untreated control sweet corn forage fortified with 0.01 µg/g (limit of quantitation), equivalent to recoveries of 92% (spinosad B), 98% (Met-D), 91% (spinosyn K), 98% (spinosyn A), and 100% (spinosyn D).

Figure 4. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Sweet Corn Forage

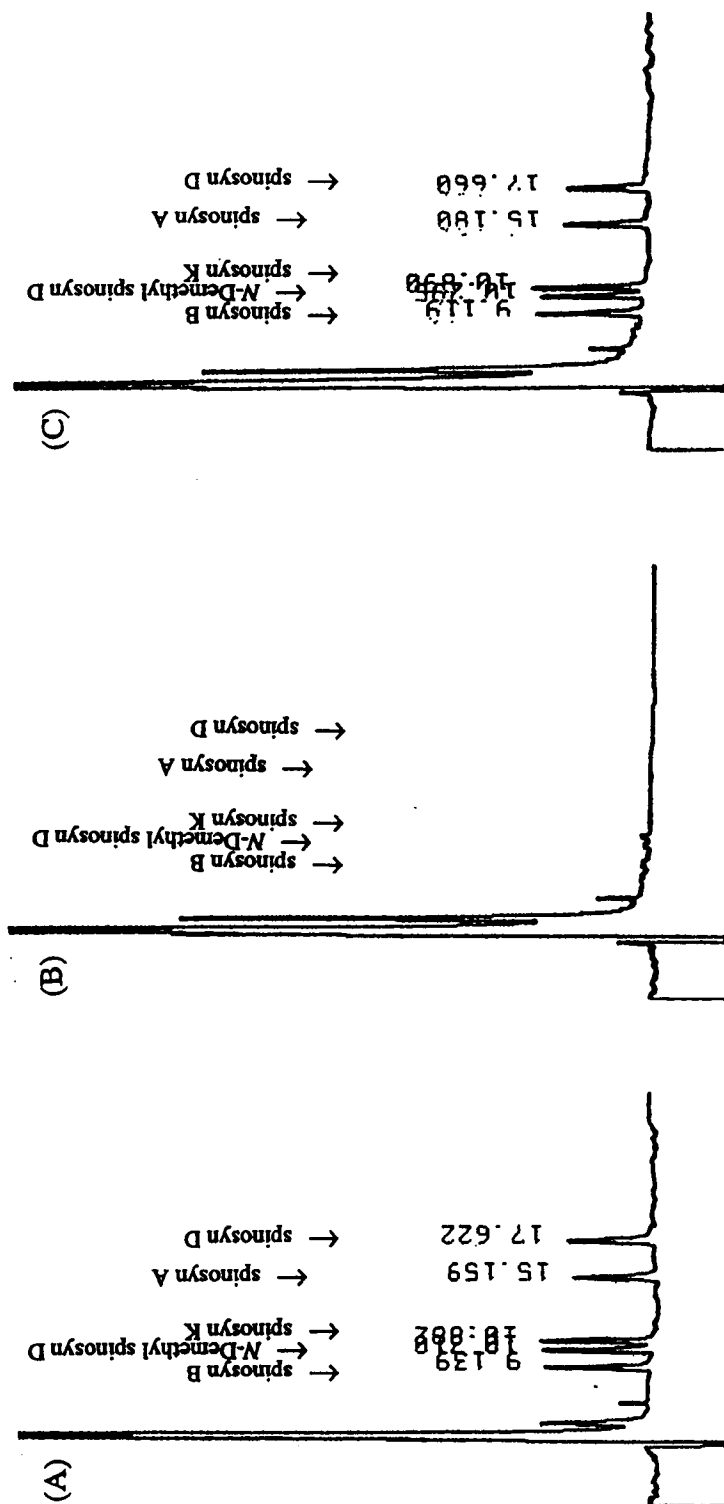


Figure 5. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Sweet Cherries

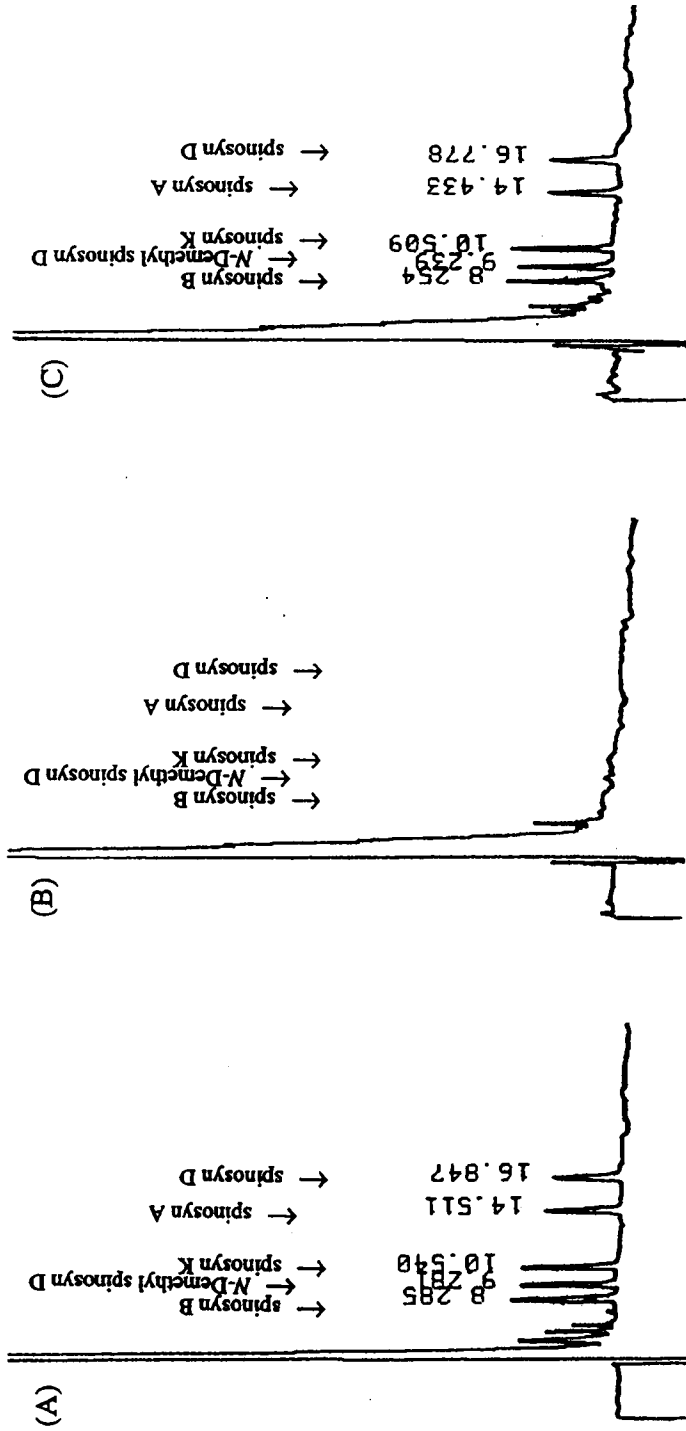


Figure 6. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Grape Wine

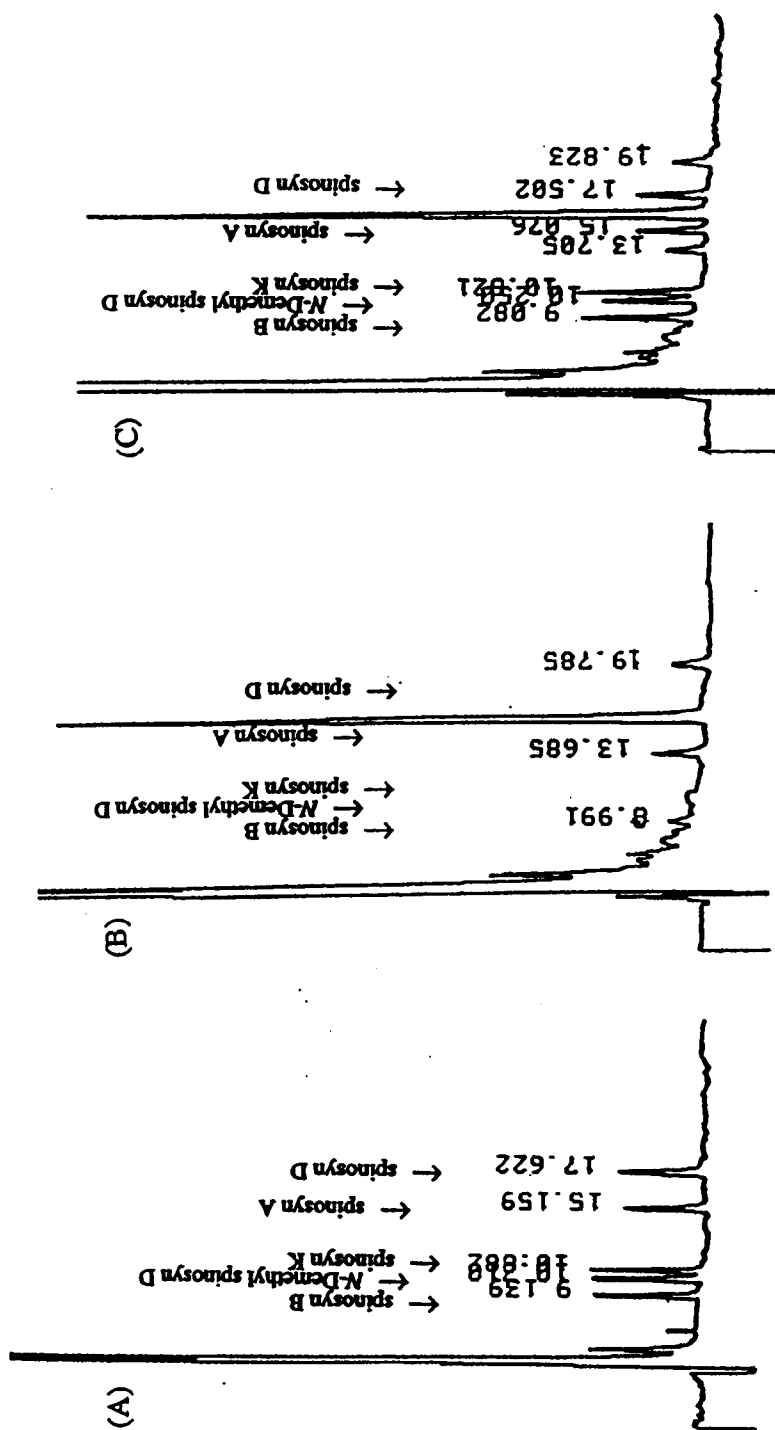


Figure 7. Typical Chromatograms Demonstrating the Determination of Spinosyns A, D, K, B, and N-Demethyl Spinosyn D (Met-D) in Whole Irish Potatoes