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Metabolites of Lesser Grain Borer in Grains

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Many volatile alcohol and ester metabolites of the lesser grain borer (LGB, *Rhyzopertha dominica*) cultured on wheat grain were identified. Volatiles from infested samples at 80 °C were collected on Tenax absorbent, thermally desorbed, and analyzed by gas chromatography (GC) using infrared (IR) and mass (MS) detectors for component identification. A solid-phase microextraction (SPME) technique was used to analyze selected samples with a GC-MS system set up for obtaining chemical ionization mass spectra. SPME was also used in a synthesis process required to identify ester metabolites. Predominant compounds in LGB-infested grains were 2-pentanol and its esters of 2-methyl-2-pentenoic (**A**) and 2,4-dimethyl-2-pentenoic (**B**) acids, which are known aggregation pheromones, dominicalures 1 and 2. 2-Pentanol esters of saturated A, β-keto- and β-hydroxy derivatives of **A** and **B**, homologues of **A** and **B**, and acid moieties lacking the 2-methyl substitution were found. Other straight- and branched-chain secondary alcohols and their esters were also observed. Reexamination of GC-MS-IR data acquired in previous investigations of LGB cultured on sorghum grain and commercial samples in a grain odor study showed the presence of many LGB metabolites in addition to the known dominicalures.

KEYWORDS: Insect metabolites; grain; wheat; sorghum

INTRODUCTION

The lesser grain borer (LGB, *Rhyzopertha dominica*) is an insect that causes major physical and off-odor damage to grain in storage (*1*). Aggregation pheromones of male LGB, dominicalure 1 [Dom1, 1-methylbutyl (*E*)-2-methyl-2-pentenoate] and dominicalure 2 [Dom2, 1-methylbutyl (*E*)-2,4-dimethyl-2-pentenoate], have been described (*2*). A homologue of Dom1, 1-methylbutyl (*E*)-2-hexenoate, and other esters were previously found in grain sorghum inoculated with LGB (*3*). Also, commercial wheat samples collected for a grain odor study contained many dominicalure-related compounds when the samples contained relatively high levels of the dominicalures. The objective of this work was to identify these compounds using chromatographic and spectroscopic (MS and IR) data coupled with a simple method for synthesis of selected compounds.

MATERIALS AND METHODS

Samples. Cultures of LGB on wheat were provided by the Biological Research Unit at our Center. About 500 adults were added to 500 g of whole wheat in a quart-size jar with a porous lid. A dusting of flour was added for neonates. The cultures were incubated for at least 25 days at 25 °C and 60% relative humidity with a 12 h light/dark cycle. Cultures were frozen to kill the insects before analyses were conducted. The material analyzed contained a mixture of whole kernels, damaged kernels, fine material, frass, and insect carcasses. The commercial wheat sample H266W was from a collection of samples for a grain odor study (*4*).

Analysis of Volatiles. Volatiles from cultures of LGB on whole wheat were analyzed by using purge and trap (P&T) and gas chromatography (GC) instrumentation described below and similar to that described previously (*3*, *5*). Samples of culture material (usually ~30 g) in U-shape sparge tubes (without glass frit) were attached to a Hewlett-Packard Co. (Palo Alto, CA) P&T instrument (model G1901A-60500) equipped with a sample pocket heater (model 14-5737-020) and a capillary interface module (model G1908-60500). The P&T instrument was modified to make it as inert as possible as described previously (*5*). Each sample was preheated to 80 °C for 3 min, and then the volatiles from the heated samples were purged with helium at 40 mL/min onto a glass-lined Tenax trap, type 1G (Tekmar Co., Cincinnati, OH). After a 10-min sample purge, a 10-min dry purge was performed to remove excess moisture from the Tenax trap. After the trap was preheated at 175 °C, the volatiles were desorbed at 200 °C for 4 min. With the capillary interface module, the desorbed volatiles were cryofocused at −140 °C (liquid N_2), and the cryofocused zone was heated at 200 °C for 0.85 min before initiation of the analytical run. The temperature of the injector zone under the capillary interface was maintained at 200 °C.

The solid-phase microextraction technique (SPME) was also used to collect volatiles from the headspace above the culture materials and grain samples. About 13 g of sample was placed in a 40-mL vial with a screw-cap lid containing a Teflon-faced septum. A 100-μm polydimethylsiloxane (red) fiber (Supelco, Bellefonte, PA) was placed in the upper portion of the headspace just below the septum. The lower portion of the vial up to a height only slightly above the sample was heated in a water bath at 80 °C for 30−45 min. Then the compounds

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were desorbed from the fiber in the GC injector at 250 °C for 1.5 min. A black fiber (Carboxen/polydimethylsiloxane, Supelco) was also found to have a high affinity for the ester metabolites.

A model 5890 series II gas chromatograph (GC) coupled with a model 5965B FTIR detector (IRD) and a model 5970 mass selective detector (MSD), all from Hewlett-Packard Co. (HP), were used to analyze the volatiles collected by the P&T and SPME techniques. A BPX-5 column (50 m × 0.32 mm i.d. × 0.25 μm film thickness) from Scientific Glass Engineering Inc. (Austin, TX) was used for separation. Column head pressure was 124 kPa (18 psi) at 50 °C. Carrier gas was helium at a constant flow rate of ~1.7 mL/min. Oven temperature was held at 50 °C for 2 min, increased to 90 °C at a rate of 7 °C/min, to 170 °C at 3.5 °C, and then to 230 °C at 17.5 °C/min. Effluent from the column first passed through the IRD and then into the MSD. Transfer lines and flow cell temperatures of the IRD were maintained at 250 °C. MSD conditions for obtaining electron ionization mass spectra (EI-MS) were as follows: direct transfer line temperature, 280 °C; ion source temperature, 280 °C; ionization voltage, 70 eV; mass range, 33−300 amu; scan rate, 1.78 scans/s; and electron multiplier voltage, 2600 V.

Identification of compounds was aided by comparing experimental IR and mass spectra of compounds with standard spectra in four IR vapor-phase libraries [HP 59963A EPA; HP 59964A flavors and fragrances; and Bio-Rad (Sadtler Division, Philadelphia, PA), Vol. 1 and 2] and in the *Wiley Registry of Mass Spectral Data*, 6th ed. (Palisade Corp., Newfield, NY), respectively. A mass spectral database from The National Institute of Standards and Technology (NIST/EPA/NIH), PC version 4.5, U.S. Department of Commerce) also was used when necessary. Further details regarding the use of IR and EI-MS information for identification of compounds is discussed under Results and Discussion.

Chemical ionization mass spectra (CI-MS) of LGB metabolites were obtained by using a model 5890 series II GC coupled with a model 5971 MSD (both from HP) with the chemical ionization source installed. The ionization gas was methane. The column was a DB5 (30 m × 0.25 mm i.d. × 0.25 μm film thickness) from HP. Carrier gas was helium at ~1 mL/min flow rate. Column temperature was programed from 40 (held for 2 min) to 230 at 5 °C/min. Because this instrument did not have an attached P&T instrument, the SPME technique described above was used to collect the volatile compounds from the samples and inject them into the GC.

Synthesis of Selected Esters. The esters marked with "X" in **Table 1** were synthesized by mixing the appropriate acid (13 μL) and alcohol (60 μL) in 5−6 drops of dimethyl sulfoxide and 2−3 drops of concentrated HCl as catalyst. These reagents were placed in a 40-mL vial with a Teflon-faced septum screw-cap lid and heated in a water bath at 65 °C for 30−45 min. The synthesized ester was collected and transferred to the GC by using the SPME technique. A 100-μm polydimethylsiloxane (red) fiber (Supelco) was exposed to the upper portion of the headspace above the mixture for ~7 min. Then the compounds were desorbed from the fiber in the GC injector at 250 °C for 1.5 min. As expected, the reactions were not complete, but enough product was observed to establish retention times and obtain good MS and IR data. Other synthetic methods involve several steps and additional chemicals (*6*).

RESULTS AND DISCUSSION

We have analyzed many cultures of LGB on wheat, and results from those analyses were in general agreement with previous results in a study of LGB cultured on sorghum grain (*3*). Typically, the cultures contained (a) numerous ester compounds in addition to the known aggregation pheromones Dom1 and Dom2; (b) many alcohols, mostly secondary, especially including high levels of 2-pentanol, and lower amounts of 2-butanol, 3-pentanol, 3-methyl-2-pentanol, 2-methyl-3-pentanol, 2-hexanol, and 3-hexanol; (c) ketones corresponding to most of the observed alcohols; and (d) usually relatively little or none of the free Dom1 and Dom2 acid moieties. As discussed below, some of these alcohols and esters were detected in commercial grain (mostly wheat) samples with various degrees of LGB infestation. To aid identification of the minor metabolites produced by LGB, we utilized cultures to obtain enhanced amounts of compounds such that useful mass and IR spectra could be obtained.

Typical results from a GC-EI-MS-IR analysis of volatiles collected by the P&T technique from a culture of LGB on wheat are shown in **Figure 1** and **Table 1**. Compounds were identified by comparing retention times and spectra (EI-MS and IR) among compounds, especially including comparisons with known compounds such as Dom1, Dom2, and the synthesized esters. Results from CI-MS analyses of volatiles in cultures (discussed below) and the presence of significant amounts of certain straight- and branched-chain secondary alcohols in the cultures provided important pieces of information to consider in the identification of compounds. Variation among compounds came from (a) modifications in acid or alcohol moieties of the ester, (b) absence of the double bond, and (c) keto or hydroxyl derivatization of the acid moiety (**Table 1**). Trans stereochemistry about the double bond was predominant. Compounds normally found in wheat (*7*) were relatively minor in these cultures, and only a few of them are included in **Table 1**.

EI-MS and IR spectral data for ester compounds listed in **Table 1** are shown in **Table 2**. The abundant compounds that were eluted at 17.40 and 18.44 min were the known pheromones Dom1 (**59**) and Dom2 (**63**) because the EI-MS data of these compounds were essentially identical to the EI-MS data reported (*2*) and to the EI-MS and IR spectra for these compounds observed in a previous study of LGB in grain sorghum (*3*). Also, EI-MS and IR spectra, as well as relative retention time, indicated that compound **74** was the homologue of Dom1 reported in the grain sorghum study. Compounds that were positively identified by comparing EI-MS and IR spectra of the synthesized compounds with compounds observed in cultures are marked in **Table 1**. EI-MS and IR spectra of these compounds also provided spectral features that helped to identify other related compounds when considered along with retention time. In addition, the EI-MS of compound **39** was very similar to the spectrum reported for the male aggregation pheromone of the larger grain borer (*Prostephans truncatus*) identified as 1-methylethyl (2*E*)-2-methyl-2-pentenoate (*8*). The spectrum of the cis (*Z*) isomer of this compound synthesized (*8*) did not match the spectrum we observed for **39**.

Certain EI-MS features relating to the acid moieties were utilized to identify the ester compounds (**Table 2**). Dom1 had major ions *m*/*z* 97 and 115, which arose from the acid moiety of the ester. Likewise, compounds with the acid moiety identical to that of Dom1 (2-methyl-2-pentenoate, **59**) also had ions *m*/*z* 97 and 115 as observed with compounds **30** (97 only), **37** (low 115 intensity), **39**, **46**, **49**, **52**, **57**, **58**, **65**, **66**, **71**, **73**, and **75**. Acid moiety homologues of Dom1 with major ions that differed from the Dom1 major ions by 14 or 28 mass units (equivalent to one or two CH_2 units) were characterized by pairs of ions such as *m*/*z* 83 and 101 for 2-methyl-2-butenoate (**47**, **51**, and **61**), *m*/*z* 111 and 129 for 2-methyl-2-hexenoate [**38** (lacks 129), **74**, **87**, **88**, and **89**), *m*/*z* 125 and 143 for 2-methyl-2-heptenoate (**90**, **93**, and **94**), and *m*/*z* 139 and 157 for 2-methyl-2-octenoate (**92**). Esters of the Dom2 acid moiety (2,4-dimethyl-2-pentenoate, **63**) had ions *m*/*z* 111 and 128 as observed with compounds **34** (low 128 intensity), **40**, **43**, **48**, **53**, **55**, **56**, **60**, **62**, **70**, **72**, **77**, **78**, and and **81**. The only homologue of the Dom2 acid moiety observed was 2-pentyl 2,4-dimethyl-2-hexenoate (**79**), which exhibited the expected pairs of major ions *m*/*z* 125 and 142. The latter can be compared with the

Table 1. Compounds Found in Cultures of LGB Grown on Wheat

compd no.	TIC area[a]	RT[b]	ID[c]	CI[d]	MW[e]	compd name
1	713	3.08			72	2-methylpropanal
2	21	3.14			70	2-methylpropenal
3	285	3.27			72	2-butanone
4	48	3.35			82	2-methylfuran
5	485	3.49			74	2-butanol
6	135	3.68			74	2-methyl-1-propanol
7	1752	3.76			86	3-methylbutanal
8	721	3.85			86	2-methylbutanal
9	6918	4.19			86	2-pentanone
10	1057	4.25			86	3-pentanone
11	1691	4.39			88	3-pentanol
12	33830	4.79			88	2-pentanol
13	2288	5.03			100	2-methyl-3-pentanone
14	1121	5.09			100	3-methyl-2-pentanone
15	175	5.15			88	2/3-methyl-1-butanol
16	4226	5.57			102	2-methyl-3-pentanol
17	249	5.68			100	2-hexanone
18	1567	5.86			100	hexanal
19	3078	5.96			102	3-methyl-2-pentanol
20	584	6.01			102	3-hexanol
21	2598	6.09			102	2-hexanol
22	84	6.57			114	4-methyl-3-hexanone
23	33	7.29			116	2-heptanol
24	196	7.38			102	1-hexanol
25	81	7.54			116	2-methyl-2-hexanol
26	54	7.72			104	styrene
27	72	7.89			116	3-heptanol
28	10	7.95			112	heptanal
29	24	7.99			116	3-methyl-2-hexanol
30	29	9.06		C	128	methyl 2-methyl-2-pentenoate
31	59	9.48			158	2-pentyl 2-methylpropanoate
32	246	9.82			128	1-octen-3-ol
33	545	9.92			126	6-methyl-5-hepten-2-one
34	292	10.04		C	142	methyl 2,4-dimethyl-2-pentenoate
35	441	10.18			128	6-methyl-5-hepten-2-ol
36	96	10.37			128	octanal
37	58	10.82		C	142	ethyl 2-methyl-2-pentenoate
38	34	11.52			142	methyl 2-methyl-2-hexenoate
39	200	11.60	X	C	156	2-propyl 2-methyl-2-pentenoate
40	247	11.80		C	156	ethyl 2,4-dimethyl-2-pentenoate
41	304	11.89		C	144	2-propyl 2-methylbutanoate
42	42	12.03			126	*E*-2-octenal
43	850	12.52		C	170	2-propyl 2,4-dimethyl-2-pentenoate
44	141	13.27			142	nonanal
45		N		C	170	ethyl 2,4-dimethyl-2-hexenoate
46	47	13.53		C	156	1-propyl 2-methyl-2-pentenoate
47	30	14.06			170	3-methyl-2-butyl 2-methyl-2-butenoate
48	52	14.26			170	1-propyl 2,4-dimethyl-2-pentenoate
49	377	14.33	X	C	170	2-butyl 2-methyl-2-pentenoate
50	84	14.39		C	158	2-propyl 2-methylpentanoate
51	1439	14.60		C	170	2-pentyl 2-methyl-2-butenoate
52	136	15.22		C	170	2-methyl-1-propyl 2-methyl-2-pentenoate
53	373	15.27		C	184	2-butyl 2,4-dimethyl-2-pentenoate
54	257	15.38			186	2-pentyl 2-methylpentanoate
55	189	16.23		C	184	2-methyl-1-propyl 2,4-dimethyl-2-pentenoate
56	23	16.34				Dom2 related (high *m/z* 128 relative to 111)
57	674	16.53	X	C	184	3-methyl-2-butyl 2-methyl-2-pentenoate
58	128	16.92	X	C	184	3-pentyl 2-methyl-2-pentenoate
59	20715	17.40	K	C	184	2-pentyl 2-methyl-2-pentenoate (Dom1)
60	698	17.53		C	198	3-methyl-2-butyl 2,4-dimethyl-2-pentenoate
61	226	17.70		C	184	2-hexyl 2-methyl-2-butenoate
62	271	17.82		C	198	3-pentyl 2,4-dimethyl-2-pentenoate
63	25009	18.44	K	C	198	2-pentyl 2,4-dimethyl-2-pentenoate (Dom2)
64	1277	18.58	X	C	184	2-pentyl 2-hexenoate
65	259	18.81	X	C	184	3-methyl-1-butyl 2-methyl-2-pentenoate
66	300	18.85	X		198	2-methyl-3-pentyl 2-methyl-2-pentenoate
67	576	19.11		C	200	2-pentyl 3-oxo-2-methylpentanoate
68	166	19.36			152	4-ethyl-2-methoxyphenol
69	516	19.49			202	2-pentyl 3-hydroxy-2-methylpentanoate
70	30	19.58			212	unknown alcohol 2,4-dimethyl-2-pentenoate
71	680	19.68	X	C	198	3-hexyl 2-methyl-2-pentenoate
72	166	19.79		C	198	3-methyl-1-butyl 2,4-dimethyl-2-pentenoate
73	1726	19.95	X	C	198	3-methyl-2-pentyl 2-methyl-2-pentenoate
74	4946	20.27		C	198	2-pentyl 2-methyl-2-hexenoate
75	582	20.31	X	C	198	2-hexyl 2-methyl-2-pentenoate

Table 1. (Continued)

compd no.	TIC area[a]	RT[b]	ID[c]	CI[d]	MW[e]	compd name
76	1250	20.39		C	214	2-pentyl 3-oxo-2,4-dimethylpentanoate
77	482	20.47		C	212	2-methyl-3-pentyl 2,4-dimethyl-2-pentenoate
78	1654	20.75		C	212	3-methyl-2-pentyl 2,4-dimethyl-2-pentenoate
79	428	20.93		C	212	2-pentyl 2,4-dimethyl-2-hexenoate
80		N		C	198	3-pentyl 2-heptenoate
81	1361	21.11		C	212	2-hexyl 2,4-dimethyl-2-pentenoate
82	34	21.20			216	2-pentyl 3-hydroxy-2,4-dimethylpentanoate
83	63	21.24			198	3-methyl-2-pentyl 2-hexenoate
84	71	21.62		C	198	2-hexyl 2-hexenoate
85	126	21.80			228	2-hexyl 3-oxo-2,4-dimethylpentanoate
86	450	21.95		C	198	2-pentyl 2-heptenoate
87	79	22.67		C		branched alcohol 2-methyl-2-hexenoate
88	149	22.92		C	212	3-methyl-2-pentyl 2-methyl-2-hexenoate
89	133	23.23		C	212	2-hexyl 2-methyl-2-hexenoate
90	544	23.47		C	212	2-pentyl 2-methyl-2-heptenoate
91	113	25.00				unknown, ms 95, 125, 140
92	91	25.50			226	2-pentyl 2-methyl-2-octenoate
93	81	26.18				branched acohol 2-methyl-2-heptenoate
94	94	26.48				unknown alcohol 2-methyl-2-heptenoate

[a] TIC area $\times 10^5$. [b] Retention time (min); N = not observed in EIMS analysis using P&T sampling. [c] X = compound synthesized; K = known compound, Dom1 and Dom2. [d] C = ester compound observed in CIMS analysis using SPME sampling (see **Table 3**). [e] Molecular weight.

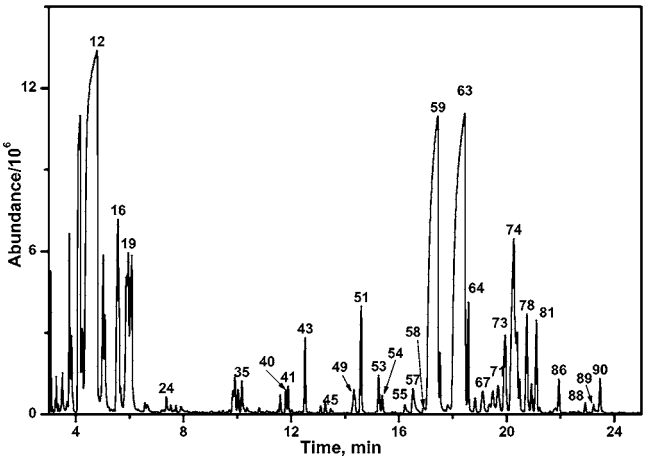

Figure 1. Total ion chromatogram of volatiles purged from a culture of LGB on wheat. Numbers above peaks refer to compounds listed in **Table 1**.

corresponding Dom1 homologue, that is, 2-pentyl 2-methyl-2-hexenoate (**74**). Esters with saturated acid moieties related to Dom1 (**50** and **54**) were observed as indicated by major ions *m*/*z* 99 and 117. No esters with saturated acid moieties related to Dom2 were found.

Intensity ratios of the diagnostic ions from the acid moieties and relative retention times were affected by the alcohol moiety. In general, branching in the alcohol moiety caused the low-mass/high-mass intensity ratio to increase substantially. For example, that ratio was 5.8 and 1.8, respectively, for compounds **47** and **51** with ions *m*/*z* 83 and 101; 9.1, 1.6, and 20.0 for **57**, **59**, and **73** with ions *m*/*z* 97 and 115; 1.2 and 14.3 for **74** and **88** with ions *m*/*z* 111 and 129; and 2.3, 0.9, and 3.6 for **60**, **63**, and **78** with ions *m*/*z* 111 and 128. In addition, certain ions appeared as the size of the alcohol moiety increased. For example, ions *m*/*z* 84 and 101 were enhanced in the 2-hexyl ester of the Dom1 and Dom2 acid moieties (**75** and **81**) compared to Dom1 (**59**) and Dom2 (**63**), which are 2-pentyl esters. Also, the M − 43 ion *m*/*z* 169 was observed in **75**, whereas the corresponding ion in Dom1 (**59**) was *m*/*z* 155. In a comparison of retention times for esters of a given acid moiety linked to secondary alcohol moieties containing the same number of carbons, those with branching in the alcohol moiety were generally eluted first, as, for example, with **57** compared to Dom1 (**59**) and **60** compared to Dom2 (**63**). The 3-pentyl esters of the Dom1 and Dom2 acid moieties were eluted slightly ahead of Dom1 (**59**) and Dom2 (**63**). Esters with primary alcohol moieties were eluted later than corresponding esters with secondary alcohol moieties, as, for example, with **65** compared with Dom1 (**59**) and **72** compared with Dom2 (**63**).

Certain IR frequencies were associated with structural features of the esters, especially on the acid moiety, as illustrated in selected spectra shown in **Figures 2** and **3**. Compounds with both the 2-methyl substitution and the C2−C3 unsaturation in the acid moiety, such as Dom1 (**59**) and Dom2 (**63**), had a strong, sharp carbonyl peak at 1725−1727 cm^{-1} and a much smaller peak at 1653 cm^{-1}. All Dom1- and Dom2-related compounds mentioned above had this characteristic with the exception that the carbonyl peak for methyl, ethyl, and larger primary esters of Dom1 and Dom2 acid moieties were increased to the 1730−1736 cm^{-1} range (**30**, **34**, **37**, **40**, **48**, **52**, **55**, **65**, and **72**). Saturated esters had carbonyl peaks near 1750 cm^{-1}, and there was no small peak in the 1653−1657 cm^{-1} region (for example, **54** in **Figure 2**). Also, appearances of spectra in the 2800−3000 and 750−1600 cm^{-1} regions were indicators of certain features in the alcohol and acid moieties of the esters. All esters of the Dom2 acid moiety had a distinct peak at 1306 cm^{-1} (**Figure 3**). With both Dom1 and Dom2 esters, a straight-chain alcohol moiety in length from 2-butyl to 2-hexyl showed a peak at or near 1127 cm^{-1}. However, if the alcohol moiety was methyl branched, that peak would not be prominent or perhaps shifted to a position under one of the adjacent major peaks (for example, compare **59** and **73** in **Figure 2** and refer to listings in **Table 2**). Enhanced absorbance at ∼980 cm^{-1} was observed for compounds lacking the 2-methyl group (**64** and **86**) and at 936 cm^{-1} for the 3-pentyl ester of the Dom1 acid moiety (**58**).

Compounds lacking the 2-methyl substitution on the acid moiety were observed [2-pentyl 2-hexenoate (**64**), 2-hexyl 2-hexenoate (**84**), and 2-pentyl 2-heptenoate (**86**)]. The EI-MS data of these compounds were somewhat similar to those of Dom1 and its homologues (**Table 2**). However, the IR spectra showed distinguishing characteristics in that the carbonyl absorbance was at 1736 cm^{-1} and the associated smaller peak was at 1657 cm^{-1} as compared to about 1725 and 1653 cm^{-1}

Table 2. EI-MS and IR Spectra of Esters and Other Selected Compounds Listed in **Table 1**

compd no.	IR spectrum, cm^{-1} (intensity)	*m/z* (abundance)
30	1734 very weak	39 (39), 41 (100), 42 (14), 43 (44), 59 (26), 67 (20), 68 (11), 69 (74), 79 (7), 81 (6), 91 (10), 95 (8), 96 (14), 97 (21), 98 (4), 99 (5), 113 (9), 128 (46), 129 (3)
31	1750 very weak	41 (29), 42 (12), 43 (86), 45 (18), 55 (6), 70 (17), 71 (100), 72 (6), 89 (11), 105 (6), 115 (9), 143 (2)
34	2969 (59), 2883 (13), 1736 (100), 1653 (9), 1440 (17), 1368 (9), 1306 (29), 1253 (70), 1159 (44), 1096 (30), 1006 (7), 982 (7), 820 (4)	39 (64), 41 (88), 43 (46), 51 (7), 53 (25), 55 (100), 59 (21), 67 (72), 69 (14), 73 (96), 79 (17), 81 (27), 82 (24), 83 (79), 93 (11), 95 (44), 99 (10), 109 (15), 110 (14), 111 (36), 127 (22), 128 (2), 142 (55), 143 (4)
37	2979 (96), 1732 (100), 1250 (86), 1148 (87), 1100 (74)	39 (46), 41 (100), 42 (38), 42 (55), 45 (27), 53 (14), 55 (26), 67 (15), 68 (10), 69 (86), 70 (19), 71 (14), 85 (7), 96 (10), 97 (46), 113 (18), 114 (22), 115 (2), 127 (4), 142 (26), 143 (2)
38	1736 (100), 1282 (96), 1149 (71), 1101 (70)	39 (28), 41 (28), 43 (31), 53 (26), 54 (10), 55 (100), 56 (12), 59 (25), 67 (22), 69 (21), 71 (10), 73 (18), 81 (21), 82 (39), 83 (24), 85 (18), 88 (37), 95 (11), 99 (8), 101 (38), 109 (11), 111 (26), 127 (18), 142 (34), 143 (4)
39	2984 (48), 2949 (22), 2887 (14), 1727 (99), 1653 (19), 1383 (26), 1252 (71), 1147 (58), 1113 (57), 1035 (15), 931 (16)	39 (27), 41 (90), 43 (64), 53 (9), 59 (13), 67 (13), 68 (12), 69 (100), 70 (13), 85 (6), 96 (9), 97 (73), 98 (6), 99 (8), 114 (31), 115 (16), 127 (33), 156 (3)
40	2972 (55), 2883 (14), 1731 (100), 1653 (10), 1460 (12), 1371 (14), 1306 (35), 1251 (80), 1156 (60), 1097 (45), 1007 (11)	39 (48), 41 (86), 43 (67), 53 (21), 55 (100), 59 (46), 67 (52), 68 (8), 69 (9), 70 (18), 79 (10), 81 (36), 82 (25), 83 (90), 87 (28), 95 (35), 109 (46), 110 (16), 111 (62), 112 (6), 113 (39), 127 (18), 128 (16), 141 (4), 156 (52), 157 (6)
41	2977 (58), 2947 (39), 2888 (21), 1745 (100), 1468 (18), 1381 (20), 1241 (32), 1186 (76), 1153 (53), 1125 (46), 1081 (21), 1021 (12)	39 (22), 41 (55), 43 (95), 55 (28), 56 (15), 57 (100), 70 (34), 71 (65), 74 (15), 85 (98), 86 (7), 87 (11), 91 (11), 103 (36), 129 (9), 144 (2)
43	2974 (60), 2946 (28), 2884 (16), 1727 (100), 1653 (10), 1468 (12), 1383 (18), 1306 (32), 1252 (83), 1157 (52), 1114 (52), 1010 (11), 954 (9), 910 (5), 858 (3), 832 (3)	39 (41), 41 (82), 43 (90), 53 (13), 55 (70), 59 (64), 67 (35), 70 (42), 82 (18), 83 (74), 95 (23), 109 (6), 110 (8), 111 (65), 112 (7), 113 (45), 128 (100), 129 (8), 170 (2)
46	2968 (58), 2940 (50), 1734 (100), 1645 (24), 1279 (85), 1225 (54), 1152 (70), 1143 (66), 1104 (50), 1089 (40)	39 (34), 41 (100), 43 (44), 53 (14), 54 (9), 55 (14), 67 (2), 68 (10), 69 (81), 70 (13), 74 (10), 79 (9), 85 (8), 87 (8), 96 (12), 97 (53), 98 (6), 99 (6), 109 (11), 114 (32), 115 (23), 127 (24), 156 (2)
47	very weak	39 (31), 41 (15), 43 (22), 55 (54), 56 (11), 70 (40), 71 (16), 82 (10), 83 (100), 84 (9), 91 (9), 101 (8), 126 (6), 127 (6)
48	1730 (100) very weak	39 (50), 41 (68), 43 (94), 55 (100), 59 (23), 67 (12), 69 (13), 71 (6), 74 (21), 82 (21), 83 (31), 87 (90), 99 (14), 110 (5), 111 (68), 112 (8), 113 (7), 127 (20), 128 (41), 129 (14), 170 (3)
49	2980 (64), 2944 (41), 2888 (29), 1727 (100), 1654 (12), 1463 (15), 1384 (18), 1361 (13), 1250 (76), 1150 (64), 1124 (42), 1097 (57)	39 (27), 41 (94), 43 (17), 53 (10), 55 (12), 56 (19), 57 (30) 67 (9), 68 (7), 69 (67), 73 (11), 96 (5), 97 (100), 98 (8), 99 (7), 114 (9), 115 (65), 116 (5), 141 (6), 155 (1), 170 (1)
50	2976 (51), 2946 (35), 2887 (17), 1745 (100), 1685 (63), 1653 (68), 1559 (74), 1541 (73), 1522 (70), 1508 (75), 1472 (73), 1458 (78), 1265 (82), 1244 (88), 1180 (98), 1151 (96), 1124 (95), 1003 (76)	39 (13), 41 (36), 43 (100), 55 (18), 56 (7), 57 (6), 69 (13), 70 (23), 71 (94), 74 (38), 85 (4), 87 (10), 97 (13), 99 (54), 115 (9), 116 (4), 117 (27), 143 (4), 144 (5)
51	2973 (42), 2942 (37), 2885 (19), 1727 (86), 1657 (12), 1461 (10), 1387 (17), 1349 (7), 1261 (100), 1142 (59),1077 (29)	39 (20), 41 (16), 43 (38), 53 (9), 54 (6), 55 (69), 56 (4), 70 (28), 71 (6), 82 (6), 83 (100), 84 (7), 100 (6), 101 (57), 127 (2), 155 (1), 170 (1)
52	very weak	39 (32), 41 (98), 56 (14), 57 (19), 69 (100), 71 (10), 96 (10), 97 (99), 98 (21), 114 (14), 115 (61), 116 (7), 155 (3)
53	2975 (73), 2944 (39), 2884 (23), 1727 (100), 1653 (14), 1468 (18), 1384 (22), 1307 (34), 1250 (81), 1157 (58), 1094 (52), 1005 (22)	39 (40), 41 (98), 43 (42), 55 (70), 56 (21), 57 (31), 59 (34), 67 (27), 69 (30), 70 (29), 83 (51), 111 (95), 112 (7), 113 (27), 128 (100), 129 (16), 141 (4)
54	2969 (85), 2945 (63), 2881 (40), 1749 (100), 1465 (36), 1383 (43), 1335 (40), 1253 (54), 1178 (81), 1117 (63), 1003 (36), 955 (36)	39 (17), 41 (38), 43 (100), 55 (32), 56 (12), 57 (21), 60 (8), 69 (9), 70 (41), 71 (35), 81 (42), 83 (7), 87 (9), 99 (81), 100 (6), 101 (9), 116 (10), 117 (27), 143 (5), 171 (1)
55	2972 (100), 2941 (36), 2887 (21), 1731 (100), 1654 (6), 1468 (10), 1384 (9), 1307 (31), 1260 (69), 1248 (74), 1155 (67), 1092 (38), 1010 (17)	39 (33), 41 (85), 43 (40), 53 (18), 55 (56), 56 (9), 57 (30), 59 (42), 67 (29), 70 (35), 82 (15), 83 (58), 84 (7), 95 (19), 111 (70), 112 (10), 113 (37), 128 (100), 129 (24), 141 (3), 184 (1)
56	very weak	39 (19), 41 (43), 43 (30), 55 (43), 56 (11), 57 (19), 59 (14), 67 (16), 69 (12), 70 (11), 82 (8), 83 (23), 84 (5), 95 (6), 110 (6), 111 (22), 113 (13), 127 (8), 128 (100), 129 (15)
57	2976 (69), 2941 (47), 2891 (34), 1727 (100), 1653 (26), 1461 (29), 1385 (34), 1305 (sh) (34), 1248 (77), 1150 (63), 1094 (61), 1040 (33), 925 (23)	39 (18), 41 (59), 43 (43), 53 (6), 54 (4), 55 (12), 67 (6), 68 (4), 69 (37), 70 (51), 71 (15), 87 (5), 97 (100), 98 (7), 99 (4), 115 (11), 141 (1)

Table 2. (Continued)

compd no.	IR spectrum, cm^{-1} (intensity)	*m/z* (abundance)
58	2977 (64), 2944 (36), 2894 (20), 1726 (100), 1653 (16), 1248 (62), 1149 (46), 1094 (38), 937 (20) weak	39 (15), 41 (58), 43 (30), 53 (9), 54 (4), 55 (10), 67 (7), 68 (5), 69 (47), 70 (17), 71 (3), 97 (100), 98 (5), 115 (66), 116 (4), 155 (4), 170 (1)
59	2976 (69), 2946 (48), 2888 (28), 1726 (100), 1653 (13), 1464 (14), 1385 (16), 1248 (79), 1148 (61), 1097 (45), 937 (7),	39 (32), 41 (98), 43 (67), 45 (11), 53 (12), 54 (6), 55 (22), 67 (10), 68 (5), 69 (65), 70 (45), 71 (12), 87 (7), 96 (5), 97 (100), 98 (7), 114 (8), 115 (64), 116 (4), 155 (4), 169 (1), 184 (1)
60	2973 (86), 2945 (34), 2887 (20), 1726 (100), 1653 (11), 1469 (15), 1388 (20), 1306 (33), 1253 (90), 1158 (70), 1093 (68), 1043 (16), 1008 (16)	39 (18),41 (45), 43 (70), 53 (9), 55 (47), 59 (12), 67 (13), 69 (7), 70 (48), 71 (16), 82 (5), 83 (27), 84 (4), 85 (4), 87 (5), 95 (5), 110 (4), 111 (100), 112 (9), 113 (17), 128 (43), 129 (14)
61	1727 (100), 1261 (96), 1141 (60) very weak	39 (8), 41 (10), 43 (14), 55 (35), 56 (18), 57 (9), 83 (100), 84 (27), 85 (9), 101 (61), 102 (8)
62	2973 (93), 2919 (49), 2888 (46), 1726 (100), 1653 (16), 1465 (15), 1305 (25), 1252 (98), 1160 (70), 1096 (59), 1017 (15)	39 (13), 41 (39), 42 (11), 43 (54), 53 (12), 55 (47), 59 (20), 67 (21), 69 (5), 70 (36), 71 (8), 82 (6), 83 (16), 87 (8), 95 (16), 111 (100), 112 (9), 113 (24), 128 (59), 129 (30)
63	2972 (89), 2945 (49), 2884 (47), 1726 (100), 1653 (9), 1487 (14), 1386 (15), 1306 (34),1250 (81), 1157 (57), 1127 (35), 1094 (44), 1008 (16), 951 (6)	39 (35), 41 (79), 43 (100), 45 (8), 53 (15), 55 (71), 59 (33), 67 (24), 68 (5), 69 (8), 70 (38), 71 (9), 81 (5), 82 (13), 83 (49), 87 (6), 95 (11), 111 (71), 112 (7), 113 (25), 128 (77), 129 (22),155 (4), 169 (1), 183 (1), 198 (1)
64	2973 (63), 2944 (53), 2886 (28), 1736 (100), 1657 (27), 1463 (14), 1383 (16), 1310 (35), 1263 (66), 1228 (33), 1178 (79), 1121 (48), 1056 (18), 1005 (21), 979 (27)	39 (18), 41 (31), 43 (32), 45 (7), 53 (5), 55 (71), 68 (11), 69 (8), 70 (28), 71 (6), 73 (14), 87 (8), 97 (100), 98 (7), 115 (47), 116 (3), 141 (4), 184 (1)
65	2974 (72), 2948 (50), 2892 (27), 1730 (100), 1652 (20), 1468 (37), 1388 (35), 1273 (66), 1247 (81), 1147 (85), 1094 (49)	39 (31), 41 (100), 43 (54), 53 (14), 54 (5), 55 (34), 67 (13), 68 (6), 69 (67), 70 (96), 71 (16), 97 (100), 98 (8), 99 (7), 114 (10), 115 (46), 116 (4), 155 (4)
66	very weak	39 (16), 41 (62), 43 (39), 53 (7), 55 (16), 57 (5), 67 (7), 69 (47), 70 (30), 83 (3), 84 (24), 85 (4), 97 (100), 98 (6), 115 (22), 129 (4), 155 (1), 169 (1)
67	2985 (49), 2948 (53), 2888 (27), 1747 (98), 1733 (100), 1461 (37), 1384 (36), 1321 (39), 1226 (50), 1193 (72), 1119 (60), 1066 (43)	39 (9), 41 (19), 43 (37), 55 (12), 56 (40), 57 (100), 58 (4), 68 (5), 69 (5), 70 (7), 71 (11), 74 (32), 75 (4), 101 (10), 113 (24), 130 (16), 144 (2), 153 (2)
68	very weak	39 (10), 41 (10), 43 (11), 51 (9), 52 (5), 53 (9), 55 (6), 65 (8), 66 (6), 77 (9), 91 (10), 109 (5), 122 (13), 137 (100), 138 (7), 152 (34), 153 (4)
69	3585 (10), 2977 (54), 2946 (47), 2889 (26), 1734 (57), 1463 (34), 1383 (40), 1180 (100), 1121 (59), 1057 (35), 979 (31)	39 (11), 41 (23), 43 (52), 45 (17), 55 (15), 56 (15), 57 (24), 58 (5), 59 (19), 69 (15), 70 (8), 71 (15), 73 (5), 74 (100), 75 (5), 85 (16), 87 (4), 97 (8), 103 (43), 115 (39), 137 (2), 144 (4), 173 (3)
70	very weak	39 (17), 41 (43), 43 (57), 55 (41), 56 (8), 57 (14), 58 (4), 59 (13), 67 (9), 69 (16), 70 (16), 71 (7), 74 (25), 83 (14), 84 (21), 85 (10), 103 (10), 111 (100), 112 (8), 113 (7), 127 (4), 128 (17), 129 (10), 137 (4), 142 (2), 152 (2), 173 (2)
71	2975 (83), 2946 (57), 2888 (35), 1728 (98), 1653 (20), 1463 (26), 1387 (28), 1248 (77), 1149 (69), 1094 (50)	39 (18), 41 (62), 43 (48), 53 (7), 55 (18), 56 (10), 57 (10), 69 (45), 70 (11), 74 (16), 84 (32), 85 (8), 97 (100), 98 (6), 103 (6), 115 (26), 141 (2), 169 (2)
72	very weak	39 (10), 41 (10), 43 (78), 53 (12), 55 (57), 59 (29), 67 (16), 68 (8), 70 (50), 71 (15), 74 (10), 82 (21), 83 (50), 95 (8),103 (5), 110 (5), 111 (52), 112 (5), 113 (30), 128 (100), 129 (23), 137 (4), 155 (4), 169 (2)
73	2977 (81), 2945 (50), 2889 (35), 1726 (100), 1653 (15), 1464 (18), 1387 (22), 1364 (10), 1248 (79), 1148 (63), 1095 (61), 1052 (24), 920 (5)	39 (13), 41 (51), 43 (31), 53 (6), 55 (6), 56 (5), 57 (6), 67 (5), 69 (43), 70 (3), 81 (4), 84 (42), 85 (7), 97 (100), 98 (7), 114 (2), 115 (5), 125 (2), 141 (2)
74	2973 (72), 2944 (61), 2884 (34), 1726 (100), 1653 (16), 1463 (17), 1386 (20), 1363 (16), 1274 (67), 1144 (53), 1129 (46), 1098 (49), 1024 (14)	39 (29), 41 (59), 43 (78), 53 (14), 54 (11), 55 (97), 56 (6), 67 (9), 69 (12), 70 (52), 71 (14), 74 (8), 82 (10), 83 (14), 87 (41), 95 (4), 111 (100), 112 (8), 128 (8), 129 (83), 130 (6), 155 (6), 198 (2)
75	2976 (73), 2945 (60), 2886 (29), 1727 (100), 1653 (16), 1460 (25), 1386 (25), 1361 (18), 1305 (sh) (30), 1246 (72), 1148 (59), 1129 (50), 1098 (50), 1013 (23), 929 (13)	39 (26), 41 (93), 43 (87), 53 (11), 54 (6), 55 (32), 56 (26), 57 (11), 67 (10), 68 (5), 69 (72), 70 (12), 71 (22), 84 (29), 85 (8), 97 (100), 98 (8), 114 (10), 115 (71), 116 (5), 169 (3), 198 (2)
76	2979 (92), 2948 (66), 2887 (34), 1750 (85), 1728 (100), 1463 (35), 1385 (37), 1312 (36), 1239 54), 1194 (64), 1118 (65), 1067 (39), 1011 (40)	39 (7), 41 (23), 43 (96), 55 (9), 56 (16), 57 (3), 70 (7), 71 (100), 72 (5), 73 (3), 74 (20), 101 (18), 126 (3), 127 (13), 144 (11), 153 (2), 171 (2)

Table 2. (Continued)

compd no.	IR spectrum, cm^{-1} (intensity)	*m/z* (abundance)
77	2973 (93), 2945 (54), 2887 (37), 1726 (100), 1653 (16), 1468 (16), 1388 (17), 1363 (10), 1306 (29), 1260 (85), 1248 (91), 1158 (70), 1093 (63), 1013 (37), 944 (28), 901 (28)	39 (18), 41 (51), 43 (79), 53 (8), 55 (46), 56 (14), 57 (10), 59 (12), 67 (16), 68 (3), 69 (19), 70 (14), 71 (14), 82 (6), 83 (24), 84 (33), 85 (9), 95 (4), 110 (4), 111 (100), 112 (8), 113 (11), 128 (36), 129 (16), 144 (4), 169 (2), 212 (1)
78	2972 (100), 2945 (49), 2887 (33), 1726 (100), 1653 (10), 1467 (18), 1387 (20), 1363 (10), 1306 (36), 1250 (85), 1157 (60), 1094 (58), 1053 (17), 1012 (18), 901 (5), 862 (5)	39 (14), 41 (40), 43 (55), 53 (7), 55 (35), 56 (7), 57 (9), 59 (8), 67 (11), 68 (3), 69 (17), 70 (8), 83 (19), 84 (41), 85 (9), 95 (4), 111 (100), 112 (8), 113 (9), 128 (28), 129 (8), 151 (2)
79	2973 (80), 2942 (45), 2886 (29), 1726 (100), 1656 (7), 1463 (16), 1385 (20), 1318 (18), 1271 (48), 1238 (74), 1156 (45), 1127 (30), 1097 (42), 1031 (14), 1000 (14), 935 (8)	39 (30), 41 (73), 43 (99), 45 (10), 53 (16), 54 (5), 55 (76), 56 (40), 57 (12), 67 (32), 68 (9), 69 (47), 70 (30), 71 (14), 73 (28), 87 (64), 95 (21), 96 (35), 97 (21), 109 (24), 113 (41), 124 (7), 125 (81), 126 (9), 127 (10), 142 (100), 143 (24), 155 (3), 212 (2)
81	2970 (90), 2942 (62), 2881 (31), 1726 (100), 1653 (10), 1467 (16), 1386 (17), 1307 (35), 1248 (78), 1158 (58), 1129 (30), 1094 (42), 1013 (17), 951 (5)	39 (22), 41 (65), 43 (86), 53 (10), 55 (61), 56 (18), 57 (9), 59 (33), 67 (20), 68 (5), 69 (12), 70 (25), 82 (12), 83 (50), 84 (16), 85 (7), 95 (9), 101 (3), 110 (6), 111 (75), 112 (7), 113 (29), 128 (100), 129 (38), 169 (3), 212 (1)
82	very weak	39 (10), 41 (44), 43 (68), 53 (7), 54 (5), 55 (26), 56 (20), 57 (37), 58 (8), 59 (13), 67 (7), 69 (5), 71 (20), 73 (20), 74 (100), 83 (20), 85 (34), 103 (98), 104 (6), 129 (23), 130 (6), 144 (6), 173 (6)
83	2973 (85), 1735 (100), 1260 (66), 1179 (83), 1115 (42)	39 (17), 41 (39), 43 (52), 53 (8), 55 (69), 56 (8), 68 (7), 69 (26), 83 (10), 84 (37), 85 (13), 97 (100), 98 (9), 113 (3), 115 (5), 126 (2), 129 (8), 141 (3)
84	1734 (100) very weak	39 (15), 41 (32), 43 (34), 55 (58), 56 (26), 68 (6), 69 (37), 73 (8), 84 (33), 97 (100), 98 (8), 114 (9), 115 (47), 116 (5), 141 (5)
85	1751 (100), 1722 (90) very weak	39 (6), 41 (28), 43 (78), 55 (11), 56 (22), 57 (12), 70 (7), 71 (100), 72 (6), 74 (37), 83 (4), 101 (10), 111 (8), 127 (12), 144 (13), 171 (2)
86	2972 (66), 2941 (62), 2883 (30), 1736 (100), 1657 (28), 1383 (14), 1361 (16), 1466 (12), 1313 (sh) (31), 1263 (66), 1211 (35), 1175 (62), 1123 (46), 1028 (18), 982 (23)	39 (17), 41 (32), 43 (39), 53 (6), 54 (3), 55 (81), 56 (5), 68 (13), 69 (5), 70 (37), 71 (8), 73 (17), 81 (3), 83 (5), 87 (11), 99 (3), 111 (100), 112 (8), 129 (59), 130 (5), 141 (3), 155 (2)
87	very weak	39 (27), 41 (32), 43 (49), 53 (10), 54 (8), 55 (71), 56 (15), 57 (12), 67 (6), 69 (25), 81 (5), 82 (6), 83 (15), 84 (33), 85 (7), 87 (8), 95 (6), 97 (7), 111 (100), 112 (6), 129 (28)
88	2972 (70), 2944 (45), 2888 (29), 1726 (100), 1653 (30), 1271 (66), 1148 48), 1095 (68)	39 (16), 41 (36), 43 (41), 53 (7), 54 (6), 55 (52), 56 (8), 57 (8), 67 (5), 69 (23), 83 (8), 84 (55), 85 (7), 87 (5), 101 (3), 111 (100), 112 (9), 129 (7), 143 (1), 155 (1)
89	2970 (77), 2941 (61), 2883 (21), 1726 (100), 1653 (19), 1272 (67), 1244 (61), 1225 (52), 1138 (58), 1097 (58), 1021 (21)	39 (31), 41 (56), 43 (75), 53 (12), 54 (13), 55 (90), 56 (35), 57 (27), 67 (10), 68 (3), 69 (28), 74 (11), 82 (9), 83 (14), 84 (40), 85 (18), 87 (27), 95 (7), 101 (9), 111 (100), 112 (8), 113 (6), 128 (8), 129 (98), 130 (9), 141 (2), 169 (5)
90	2971 (74), 2942 (69), 2884 (36) 1726 (100), 1653 (11)	39 (24), 41 (44), 43 (70), 53 (10), 54 (10), 55 (100), 56 (12), 67 (9)
91	very weak	39 (16), 41 (30), 43 (49), 55 (27), 67 (18), 77 (10), 79 (12), 93 (5), 94 (7), 95 (32), 96 (6), 97 (6), 111 (8), 120 (4), 123 (17), 124 (3), 125 (100), 126 (13), 140 (34), 210 (4)
92	very weak	39 (20), 41 (60), 43 (78), 55 (58), 56 (40), 69 (90), 70 (100), 87 (62), 139 (60), 157 (65)
93	very weak	39 (40), 41 (44), 43 (84), 55 (58), 56 (22), 57 (40), 67 (16), 69 (22), 71 (22), 84 (80), 85 (28), 125 (100), 143 (18)
94	very weak	39 (31), 41 (76), 43 (75), 53 (33), 55 (100), 56 (37), 67 (39), 68 (26), 69 (20), 71 (13), 82 (23), 87 (26), 93 (80), 125 (93), 143 (70), 144 (14)

for compounds with the 2-methyl group (**64**, **Figure 2**). Also, the absence of the 2-methyl group enhanced the intensity of the 1657 cm^{-1} peak relative to the intensity of the carbonyl peak as compared with corresponding intensities when the 2-methyl substitution was present. Primary evidence for identification of these compounds came from retention time, EI-MS, and IR spectra of synthesized 2-pentyl 2-hexenoate, which were identical to those of compound **64** observed in the cultures. Also, the EI-MS of **64** was similar to spectra reported for propyl esters of 2-hexenoic acid synthesized by Cork et al. (*8*), especially the relative intensities of *m/z* 55, 73, 97, and 115.

Molecular weight information was needed to aid compound identifications. However, EI-MS did not definitively indicate molecular weight because molecular ions from the esters were usually either nonexistent or very low in intensity. Therefore, chemical ionization (CI-MS) was utilized to obtain information

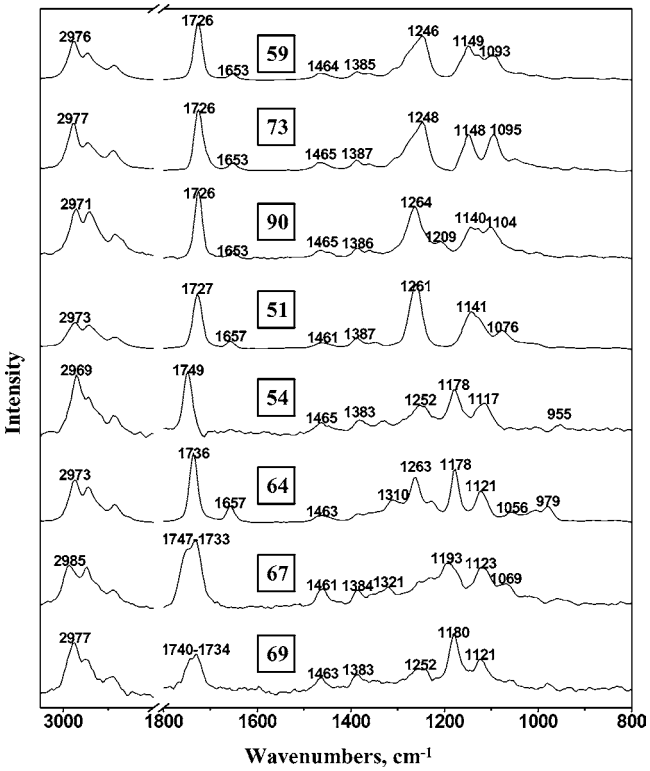

Figure 2. IR spectra of Dom1 (**59**) and related esters. Numbers in boxes refer to compounds listed in **Table 1**.

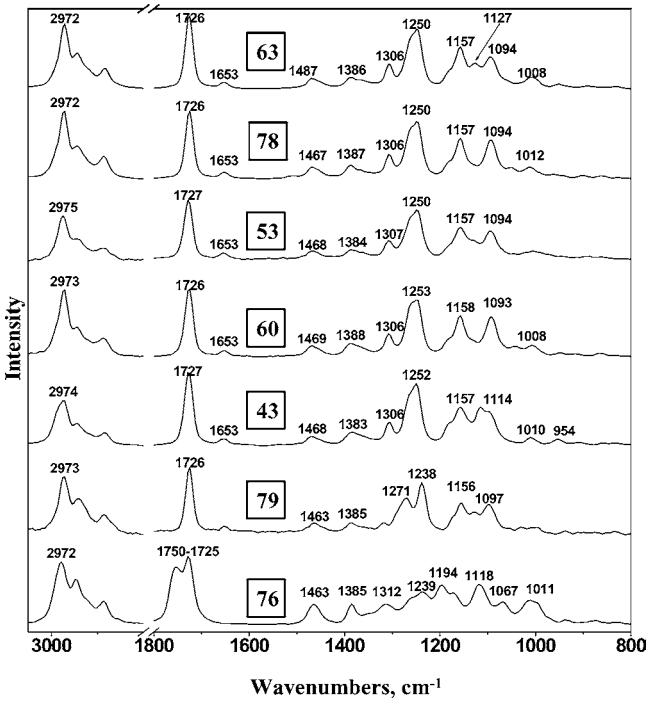

Figure 3. IR spectra of Dom2 (**63**) and related esters. Numbers in boxes refer to compounds listed in **Table 1**.

on molecular weight. The available CI instrument was in another laboratory at our Center and did not have an attached P&T instrument for introducing volatile compounds into the GC. Consequently, the SPME technique was used to collect volatiles from the headspace above LGB cultures and inject them into the CI-MS instrument.

The CI-MS data from esters collected by SPME from LGB cultured on wheat is summarized in **Table 3**. Fewer compounds were observed with SPME sampling than with P&T sampling, and the compounds observed in the SPME-CI experiment are marked in **Table 1** (see more discussion of P&T vs SPME below). Even though CI using methane is relatively soft compared to EI, considerable fragmentation occurred. With Dom1 and Dom2, $(M + 1)^+$ ions of *m*/*z* 185 and 199, respectively, were observed, and minor intensities of $(M - 1)^+$ ions were also present. The pattern of $(M + 1)^+$ and $(M - 1)^+$ ions was evident and utilized to determine molecular weight. For some compounds intensities of $(M + 1)^+$ and $(M - 1)^+$ ions were fairly similar. The intensity of the $(M + 1)^+$ ion relative to fragment ions was enhanced when the amount of compound introduced into the instrument was relatively high. Also, it appeared that CI-MS of compounds with straight-chain alcohol moieties gave enhanced $(M + 1)^+$ ions compared to corresponding compounds with branched alcohol moieties. Major fragment ions *m*/*z* 97 and 115 in Dom1 remained the same mass in CI-MS and EI-MS, whereas with Dom2 the major ion *m*/*z* 111 remained the same, but ion *m*/*z* 128 was protonated to *m*/*z* 129 in the CI-MS. Esters collected by SPME from LGB cultures were also analyzed on the GC-EI-MS-IR instrument. Number and relative amounts of compounds observed and relative retention times, along with MS and IR spectra, were all consistent with the compounds listed in **Table 3**.

Five esters with additional oxygen in the acid moiety were observed. These included β-ketone and β-hydroxy derivatives of Dom1 (**67** and **69**) and Dom2 (**76** and **82**). In addition, a minor amount of 2-hexyl ester of the keto-Dom2 acid moiety (**85**) was indicated by EI-MS. The EI-MS of **69** showed a fairly good match with an entry in the Wiley6 database labeled propyl ester of 3-hydroxy-2-methylpentanoic acid. The EI-MS of keto-Dom1 (**67**) had ions *m*/*z* 101 (M − 99), 113 (M − 87), and 130 (M − 70). The former two ions corresponded to ions *m*/*z* 103 (M − 99) and 115 (M − 87) observed in the hydroxy-Dom1 compound, whereas the corresponding M − 70 ion was very weak. The CI-MS of **67** showed major ions *m*/*z* 131,113, 87, and 69 and lacked some major ions such as *m*/*z* 74 and 101 that were present in the EI-MS (**Tables 2** and **3**). Masses consistent with keto and hydroxy derivatives of Dom2 were also observed (**Tables 2** and **3**). Interestingly, only the keto derivatives of Dom1 and Dom2 were observed in the CI-MS analysis, apparently because the hydroxy derivatives were not picked up by SPME. The IR spectrum of keto-Dom1 (**67**, **Figure 2**) had nearly equally intense carbonyl peaks at 1747 and 1733 cm^{-1}, whereas the spectrum of hydroxy-Dom1 (**69**, **Figure 2**) had only one carbonyl peak at 1734 cm^{-1} and a broadened hydroxyl peak centered at 3585 cm^{-1}. Similarly, keto-Dom2 (**76**, **Figure 3**) had carbonyl peaks at 1750 and 1728 cm^{-1} of similar intensities. Not enough hydroxy-Dom2 (**82**) was present to provide an IR spectrum.

Some commercial samples collected in a grain odor study contained Dom1, Dom2, and some of the other compounds listed in **Table 1**. A wheat sample (H266W) with LGB-type of "insect" odor was analyzed as described above for the culture samples. Evaluation of retention times and spectra (EI-MS and IR) showed that the sample contained 29 of the ester compounds, including **40**, **43**, **50**−**55**, **57**, **59**, **60**, **62**, **63**−**66**, **71**−**79**, **81**, **86**, **88**, and **90**. Also, the H266W sample contained the six esters listed in **Table 4**, which involved the primary alcohols pentanol and hexanol esterified to the Dom1, Dom2, pentanoic, and hexanoic acid moieties. Compared to most commercial grain and culture samples infested with LGB, this sample was unusual in that the 2-pentanol level was relatively low and the 1-hexanol level was relatively high. Because the sample was cleaned before

Table 3. Chemical Ionization Spectra of Esters Listed in **Table 1**

compd no.	TIC area[a]	RT[b]	MW[c]	compd name	*m/z* (abundance)
30	trace	8.35	128	methyl 2-methyl-2-pentenoate	129
34	trace	9.63	142	methyl 2,4-dimethyl-2-pentenoate	143
37	10	10.56	142	ethyl 2-methyl-2-pentenoate	55 (5), 71 (5), 97 (17), 115 (33), 141 (5), 142 (5), 143 (100), 144 (10)
39	3	11.53	156	2-propyl 2-methyl-2-pentenoate	55 (18), 97 (12), 99 (11), 115 (100), 143 (20), 55 (9), 157 (16)
40	5	11.77	156	ethyl 2,4-dimethyl-2-pentenoate	83 (7), 111 (18), 127 (11), 129 (21), 141 (7), 155 (6), 157 (100), 158 (10)
41	3	11.90	144	2-propyl 2-methylbutanoate	57 (11), 59 (10), 69 (14), 71 (28), 85 (15), 103 (100), 131 (12), 143 (7), 145 (2)
43	7	12.62	170	2-propyl 2,4-dimethyl-2-pentenoate	111 (23), 113 (7), 128 (8), 129 (100), 130 (9), 157 (16), 169 (9), 171 (11)
45	6	13.17	170	ethyl 2,4-dimethyl-2-hexenoate	55 (9), 57 (22), 67 (9), 69 (100), 71 (8), 81 (10), 83 (58), 109 (6), 111 (3), 123 (17), 125 (30), 141 (12), 143 (34), 171 (10)
46	4	13.51	156	1-propyl 2-methyl-2-pentenoate	59 (11), 69 (40),97 (31), 109 (15), 111 (5), 113 (15), 115 (100), 143 (28), 155 (6), 157 (94), 158 (8)
49	6	14.37	170	2-butyl 2-methyl-2-pentenoate	55 (9), 57 (29), 97 (17), 99 (6), 115 (100), 116 (8), 129 (20), 143 (15), 155 (4), 169 (3), 171 (6)
50	1	14.49	158	2-propyl 2-methylpentanoate	55 (30), 57 (32), 71 (45), 99 (26), 115 (25), 117 (100), 125 (10), 128 (2), 145 (18), 155 (6), 157 (45), 159 (8)
51	23	14.59	170	2-pentyl 2-methyl-2-butenoate	55 (5), 57 (5), 69 (17), 71 (29), 83 (21), 101 (100), 129 (15), 141 (5), 169 (2), 171 (6)
52	3	15.21	170	2-methyl-1-propyl 2-methyl-2-pentenoate	55 (10), 57 (48), 97 (18), 99 (7), 115 (100), 116 (9), 143 (13), 155 (8), 169 (4), 171 (18)
53	7	15.32	184	2-butyl 2,4-dimethyl-2-pentenoate	55 (14), 57 (59), 71 (8), 85 (7), 111 (13), 113 (6), 115 (6), 129 (100), 130 (8), 143 (4), 157 (15), 169 (5) 185 (6)
55	3	16.20	184	2-methyl-1-propyl 2,4-dimethyl-2-pentenoate	57 (50), 111 (23), 113 (7), 129 (100), 130 (9), 157 (18), 169 (8), 183 (4), 185 (18)
57	8	16.42	184	3-methyl-2-butyl 2-methyl-2-pentenoate	57 (17), 69 (17), 70 (10), 71 (72), 97 (23), 99 (6), 113 (6), 115 (100), 116 (8), 143 (16), 155 (7), 183 (2), 185 (2)
58	5	16.75	184	3-pentyl 2-methyl-2-pentenoate	56 (8), 57 (14), 59 (5), 69 (14), 71 (38), 85 (12), 95 (8), 97 (20), 115 (100), 116 (6), 121 (9), 143 (16), 155 (9), 185 (3)
59	1344	17.20	184	2-pentyl 2-methyl-2-pentenoate [DOM1]	69 (3), 70 (2), 71 (6), 97 (32), 113 (3), 115 (100), 116 (7), 143 (14), 155 (5), 183 (2), 185 (59), 186 (7)
60	29	17.32	198	3-methyl-2-butyl 2,4-dimethyl-2-pentenoate	55 (4), 57 (6), 69 (7), 71 (26), 111 (23), 129 (100), 130 (9), 157 (15), 169 (8), 198 (2), 199 (4)
61	trace	17.44	184	2-hexyl 2-methyl-2-butenoate	59 (22), 83 (26), 85 (24), 101 (100)
62	18	17.60	198	3-pentyl 2,4-dimethyl-2-pentenoate	57 (17), 83 (8), 111 (22), 129 (100), 153 (40), 157 (12), 181 (9)
63	1417	18.09	198	2-pentyl 2,4-dimethyl-2-pentenoate [DOM2]	55 (2), 69 (2), 71 (4), 83 (2), 111 (38), 112 (3), 113 (4), 127 (4), 128 (8), 129 (100), 130 (7), 157 (15), 169 (5), 183 (2), 197 (3), 199 (65), 200 (8)
64	46	18.17	184	2-pentyl 2-hexenoate	69 (4), 71 (9), 97 (18), 115 (100), 116 (7), 143 (14), 155 (6), 183 (2), 185 (5)
65	20	18.36	184	3-methyl-1-butyl 2-methyl-2-pentenoate	55 (3), 69 (6), 70 (8), 71 (29), 97 (21), 99 (5), 115 (100), 116 (7), 143 (20), 155 (6), 169 (3), 183 (2), 185 (29), 186 (3)
67	8	18.53	200	2-pentyl 3-oxo-2-methylpentanoate	55 (27), 69 (40), 71 (30), 87 (22), 97 (4), 113 (41), 115 (17), 131 (100), 132 (11), 159 (11), 171 (8), 183 (4), 201 (3)
71	19	19.08	198	3-hexyl 2-methyl-2-pentenoate	57 (2), 69 (10), 71 (7), 83 (22), 85 (50), 97 (24), 115 (100), 116 (7), 129 (24), 143 (20), 155 (6), 157 (4), 169 (2), 197 (3), 199 (2)
72	19	19.12	198	2-methyl-1-butyl 2,4-dimethyl-2-pentenoate	69 (7), 71 (18), 111 (22), 128 (8), 129 (100), 130 (6), 157 (19), 169 (5), 197 (3), 199 (16), 200 (3)
73	61	19.29	198	3-methyl-2-pentyl 2-methyl-2-pentenoate	57 (3), 69 (6), 71 (3), 83 (10), 84 (8), 85 (48), 86 (3), 97 (27), 98 (2), 99 (4), 113 (4), 115 (100), 116 (7), 143 (17), 155 (6), 197 (2), 199 (2)
74	498	19.63	198	2-pentyl 2-methyl-2-hexenoate	69 (3), 71 (8), 111 (25), 127 (6), 129 (100), 130 (8), 157 (15), 169 (5), 197 (2), 199 (26), 200 (3)
75	80	19.66	198	2-hexyl 2-methyl-2-pentenoate	69 (4), 71 (4), 83 (6), 85 (8), 97 (22), 115 (100), 116 (7), 129 (18), 143 (15), 155 (7), 169 (3), 183 (2), 197 (3), 200 (4)
76	56	19.69	216	2-pentyl 3-oxo-2,4-dimethylpentanoate	71 (38), 101 (13), 127 (34), 129 (18), 145 (100), 173 (13), 185 (5), 199 (13), 215 (9)
77	20	19.80	212	2-methyl-3-pentyl 2,4-dimethyl-2-pentenoate	57 (7), 69 (8), 71 (6), 83 (17), 84 (6), 85 (38), 95 (3), 111 (26), 113 (8), 127 (6), 129 (100), 130 (8), 157 (17), 169 (6), 197 (2), 211 (2), 213 (2)
78	51	20.01	212	3-methyl-2-pentyl 2,4-dimethyl-2-pentenoate	57 (4), 69 (5), 71 (3), 83 (11), 84 (7), 85 (36), 111 (28), 113 (5), 127 (5), 129 (100), 130 (8), 157 (16), 169 (7), 197 (2), 211 (2), 213 (3)
79	25	20.17	212	2-pentyl 2,4-dimethyl-2-hexenoate	55 (5), 69 (9), 71 (16), 125 (21), 127 (5), 141 (7), 142 (7), 143 (100), 144 (9), 171 (14), 183 (6), 211 (2), 213 (4)
80	16	20.23	198	3-pentyl 2-heptenoate	71 (30), 111 (32), 129 (100), 157 (17), 199 (51), 200 (9), 201 (4)
81	82	20.32	212	2-hexyl 2,4-dimethyl-2-pentenoate	55 (2), 57 (2), 69 (3), 83 (9), 85 (10), 111 (21), 113 (4), 127 (4), 128 (5), 129 (100), 130 (8), 157 (15), 169 (5), 197 (2), 211 (2), 213 (7)
86	21	20.87	198	2-pentyl 2-heptenoate	55 (2), 57 (3), 69 (10), 71 (24), 111 (21), 129 (100), 130 (9), 157 (19), 169 (5), 197 (2), 199 (3)
87	5	21.69	212	branched alcohol 2-methyl-2-hexenoate	57 (13), 69 (20), 71 (11), 83 (31), 84 (12), 85 (73), 111 (28), 113 (6), 127 (6), 129 (100), 130 (8), 157 (19), 169 (9), 211 (3), 213 (2)
88	10	21.97	212	3-methyl-2-pentyl 2-methyl-2-hexenoate	57 (10), 69 (11), 71 (8), 83 (21), 84 (5), 85 (26), 111 (17), 113 (4), 127 (6),129 (100), 130 (9), 157 (17), 169 (6), 211 (4), 213 (2)
84	9	22.04	198	2-hexyl 2-hexenoate	57 (10), 69 (12), 71 (9), 83 (15), 84 (4), 85 (18), 97 (24), 99 (5), 113 (5), 115 (100), 116 (7), 143 (20), 155 (5), 169 (2), 197 (4), 199 (39), 200 (5)
90	27	22.15	212	2-pentyl 2-methyl-2-heptenoate	55 (6), 57 (5), 69 (10), 70 (5), 71 (20), 97 (2), 99 (3), 125 (20), 141 (8), 143 (100), 144 (9), 171 (15), 183 (5), 211 (2), 213 (4)
89	3	22.83	212	2-hexyl 2-methyl-2-hexenoate	55 (20), 57 (28), 69 (21), 71 (7), 83 (32), 85 (26), 95 (10), 111 (29), 121 (7), 127 (7), 128 (8), 129 (100), 130 (8), 157 (16), 185 (4), 197 (8), 213 (53), 214 (5)

[a] TIC area $\times 10^5$. [b] Retention time (min). [c] Molecular weight.

analysis, it contained little or no frass or fine material. Essentially all of the kernels were whole, but many of them had visible insect damage (mostly exit holes). From reexamination of data obtained from a group of grain samples in an odor study (*4*), which included the wheat sample H266W, we found Dom1 and Dom2 in ~100 samples, mostly wheat. About one-third of those

Table 4. Esters Found in a Commercial Wheat Sample (H266W) That Were Not Present in LGB Cultures

compd	MW[a]	RT[b]	IR spectrum, cm^{-1} (intensity)	*m/z* (abundance)
1-pentyl hexanoate	186	19.18	2966 (100), 2937 (96), 2877 (67), 1753 (90), 1469 (39), 1240 (63), 1174 (81)	39 (22), 41 (72), 43 (100), 55 (34), 56 (19), 57 (24), 58 (7), 60 (17), 61 (16), 67 (10), 69 (19), 70 (65), 71 (32), 73 (12), 81 (9), 85 (12), 87 (10), 99 (40), 100 (6), 116 (3), 117 (52), 118 (4), 130 (3), 186 (2)
1-hexyl pentanoate	186	19.23	2964 (70), 2935 (100), 2872 (35), 1753 (50) weak	39 (24), 41 (66), 43 (100), 55 (51), 56 (53), 57 (65), 58 (11), 60 (14), 61 (12), 69 (38), 73 (8), 75 (5), 84 (33), 85 (67), 103 (60), 104 (3), 129 (2), 144 (2)
1-pentyl 2-methyl-2-pentenoate	184	20.03	2961 (68), 2937 (100), 2873 (42), 1733 (80), 1655 (24), 1465 (27), 1385 (22), 1253 (52), 1204 (20), 1144 (51), 1094 (35)	39 (25), 41 (100), 43 (68), 53 (9), 54 (9), 55 (44), 56 (17), 57 (40), 67 (20), 68 (20), 69 (73), 70 (29), 71 (18), 81 (12), 82 (18), 83 (13), 84 (8), 85 (10), 95 (9), 96 (11), 97 (43), 98 (9), 99 (5), 109 (4), 110 (4), 111 (4), 112 (2), 113 (4), 114 (17), 115 (51), 116 (4), 123 (2), 124 (3), 126 (3), 155 (12), 156 (2), 184 (2)
1-hexyl hexanoate	200	22.54	2967 (91), 2941 (100), 2876 (47), 1754 (94), 1466 (22), 1387 (19), 1237 (45), 1171 (78), 1104 (29)	39 (13), 41 (52), 43 (100), 55 (35), 56 (49), 57 (12), 60 (13), 61 (20), 69 (28), 70 (8), 71 (24), 73 (12), 84 (41), 85 (10), 87 (12), 89 (4), 97 (3), 99 (42), 100 (4), 116 (5), 117 (60), 118 (5), 129 (2), 144 (2), 157 (2)
1-hexyl 2-methyl-2-pentenoate	198	23.37	2967 (82), 2943 (77), 2886 (49), 1730 (100), 1652 (29), 1464 (30), 1248 (82), 1148 (79), 1097 (50)	39 (28), 41 (100), 43 (65), 45 (11), 53 (9), 54 (4), 55 (23), 56 (31), 57 (16), 59 (4), 67 (13), 68 (9), 69 (92), 70 (12), 73 (6), 83 (3), 84 (7), 85 (6), 95 (6), 96 (9), 97 (52), 98 (6), 99 (8), 114 (17), 115 (100), 116 (8), 169 (7)
1-hexyl 2,4-dimethyl-2-pentenoate	212	24.31	2970 (100), 2935 (79), 2869 (44), 1730 (86), 1657 (16), 1469 (25), 1399 (22), 1306 (33), 1272 (59), 1249 (63), 1157 (58), 1092 (41)	39 (22), 41 (73), 43 (82), 53 (10), 55 (63), 56 (16), 57 (36), 59 (36), 67 (23), 68 (7), 69 (21) ,70 (35), 71 (13), 81 (9), 82 (17), 83 (63), 84 (7), 85 (15), 95 (15), 109 (6), 110 (11), 111 (25), 112 (5), 113 (34), 114 (4),127 (7), 128 (100), 129 (21), 136 (2), 141 (2), 154 (2), 155 (2), 169 (2), 183 (3), 184 (2), 212 (8), 213 (2)

[a] Molecular weight. [b] Retention time (min).

samples had sufficiently high LGB infestation, as indicated by relative Dom1 and Dom2 levels, such that a number of minor ester compounds could be observed, including **53**, **55**, **60**, **64**, **73**, **74**, **77**, **78**, **79**, **81**, **86**, and **90**. Further information concerning relative levels of these compounds and other insect metabolites in the group of grain-odor samples will be included in a separate publication.

Reexamination of the data obtained in the study of LGB in grain sorghum was undertaken to identify compounds in addition to Dom1, Dom2, and the Dom1 homologue previously reported (*3*). Results reported in the 1996 publication were based on volatile analyses using a Supelcowax-10 (Supelco Co.) column and a sample purge temperature of 60 °C. Later, the 10-week incubation sorghum sample was reanalyzed using a BPX-5 column and a 60 °C purge temperature. The chromatogram with the BPX-5 column was similar to that obtained from LGB cultures on wheat (**Figure 1**), except that fewer of the minor ester compounds were observed because the sample purge temperature was 20 °C lower than that used for the analyses of the cultures in wheat described above. By comparison of retention times along with EI-MS and IR spectral data obtained in the sorghum study with the same information collected from the wheat cultures, the following compounds were identified in the cultures of LGB in sorghum: **39**, **40**, **43**, **49**−**51**, **53**, **54**, **57**, **59**, **60**, **63**, **64**, **73**−**76**, **78**, **79**, **81**, **86**, and **90**. In addition, **65**, **66**, **71**, **72**, and **77** were tentatively identified. The relative amounts of these compounds in the sorghum samples were similar to those in the wheat cultures (**Table 1**). All of these compounds were found in sorghum incubated with LGB for 7 and 10 weeks (*3*), whereas **43**, **49**, **50**, and **54** were not found in samples representing 5 weeks of incubation. The list of identified compounds includes one oxygenated acid moiety (**76**), three Dom1-acid homologues (**51**, **74**, **90**), the Dom2-acid homologue (**79**), and two homologous compounds lacking the 2-methyl group (**64**, **86**). Also, the order in which compounds were eluted from the Supelcowax column was different from that of the BPX column. For example, with the Supelcowax column, Dom2 was eluted very sightly ahead of Dom1, as opposed to Dom1 being eluted well ahead of Dom2 with the BPX column (**Figure 1**). Similar differences were observed with other alcohol moiety homologues of Dom1 and Dom2.

The P&T technique was generally more effective than SPME for collecting and concentrating the wide range of volatiles from the LGB cultures and grain samples. It was especially more effective for detecting the alcohols, aldehydes, and ketones that were eluted early in the analysis. Also, more of the very minor ester compounds were observed when the P&T technique was used.

The focus of this paper was to identify compounds observed in LGB-infested grain samples. Determination of how these compounds related to insect behavior was beyond the scope of this investigation. The fact that some of the minor compounds were observed in grain samples collected from grain storage and handling facilities showed that the compounds were produced in natural environments and not just in laboratory cultures. It appears that detection of the minor compounds in samples taken from grain storage facilities would indicate a high LGB population and/or presence of infestation for an extended time.

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