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Response of *Diabrotica speciosa* (Coleoptera: Chrysomelidae) to 1,4-Dimethoxybenzene and Analogs in Common Bean Crop

Francisco de Assis Marques[1*], Edison Perevalo Wendler[1], Alexandra Macedo[1], Celso Luiz Wosch[1], Beatriz Helena Sales Maia[1], Adriana Yatie Mikami[2], Iara Cintra Arruda-Gatti[2], Aline Pissinati[2], Fábio Luiz Checchio Mingotte[2], Amilton Alves and Maurício Ursi Ventura[2]

[1]*Departamento de Química; Universidade Federal do Paraná; C. P.: 19.081; 81531-990; Curitiba - PR - Brasil.*
[2]*Departamento de Agronomia; Universidade Estadual de Londrina; C. P. 6001; 86051-970; Londrina - PR - Brasil*

ABSTRACT

Several synthetic and commercial analogs of 1,4-dimethoxybenzene, a kairomone of Diabrotica speciosa*, along with other compounds already shown to be attractive to other species of* Diabrotica*, were tested as attractant to* D. speciosa*. Yellow cup traps were lured with the compounds and installed in a common bean field. Assessments were conducted 24 h later. 1,4-dimethoxybenzene lured traps caught significantly more beetles than the control traps. Captures of traps lured with 1,4-dimethoxybenzene analogs did not differ from the control traps. Results showed that position and nature of the substituents on the aromatic ring played a crucial role in the activity of the natural compound. The aromatic ring was also very important to the activity of the kairomone.*

Key words: *Diabrotica speciosa***,** 1,4-dimethoxybenzene, analogs, kairomone, parakairomone, field test.

INTRODUCTION

Attraction of *Diabrotica* beetles to volatile chemicals from corn (*Zea mays* L.) and pumpkin (C*ucurbita maxima* Duchesne) has been investigated and proposed as a suitable tool for Integrated Pest Management (Metcalf and Metcalf, 1992). The attraction of *D. undecimpunctata howardi* (Barber) to cinnamaldehyde and cinnamyl alcohol baits was reported by Morgan and Crumb (1928). Snapp and Swingle (1929) showed that benzyl alcohol also attracted *D. undecimpunctata*. Ladd et al. (1983) demonstrated that *D. barberi* (Smith) and *D. cristata* (Harris) responded to eugenol, a common floral volatile, which was used as a commercial lure for the Japanese beetle, *Popillia japonica* (Newman). Andersen and Metcalf (1986) and Andersen (1987) isolated several volatile compounds from *Cucurbita* sp. blossoms and tested them for Diabroticite beetles showing that some were attractive.

Analogs of these compounds have also been tested and some of them were attractive and even surpassed the attraction of the original kairomone. Metcalf and Lampman (1989) characterized the attraction of *D. barberi* and *D. v. virgifera* to cinnamyl alcohol analogs and suggested the term parakairomones (active synthetic analog or attractive synthetic bioisosteres) for the 3-phenyl-1-propanol (phenpropanol) that was significantly

* Author for correspondence: tic@ufpr.br

more attractive to *D. barberi* than eugenol. Given these findings, the authors proposed a structure-activity relationship. Eugenol-baited traps caught ca. three times more *D. barberi* adults than methyl eugenol-baited traps; estragole attracted four times more *D. v. virgifera* adults than *E*-anethole; and *ortho*-dimethoxybenzene (veratrole) attracted three times more *D. u. howardi* adults than *meta*-dimethoxybenzene and six times more than *para*-dimethoxybenzene (Ladd, 1984; Lampman et al., 1987). Estragole analogs were demonstrated as exceptional attractants for Diabroticites: 4-methoxycinnamaldehyde and 4-methoxycinnamonitrile for *D. v. virgifera*, cinnamyl alcohol for *D. b*arberi, and cinnamaldehyde for *D. u. howardi* (Metcalf and Metcalf, 1992).

D. v. virgifera are strongly attracted to phenylpropanoids with side chains containing an aldehyde moiety (Metcalf and Metcalf, 1992). *D. v. virgifera* responds to phenylpropanoids with varying hydroxy and methoxy substituents on the phenyl ring (Lampman et al., 1987). Cinnamonitrile and 4-methoxycinnamonitrile have been shown to attract *D. v. virgifera* but neither compound has been reported in the host plants (Metcalf and Lampman 1989; Lance, 1990). Cinnamaldehyde is the most effective lure yet found for *D. u. howardi*. However, this insect also showed attraction to some analogs of this compound (cinnamonitrile, cinnamyl alcohol, 3-phenyl-1-propanol, 4-methoxycinnamaldehyde, 4-methoxycinnamonitrile and 2-phenylethanol (phenethanol) (Metcalf and Lampman,1989; Lampman et al., 1987).

D. barberi beetles are strongly attracted to phenylpropanoids with side chains containing an alcohol moiety, e.g. cinnamyl alcohol (Metcalf and Lampman, 1989). Ladd (1984) tested a series of 2-methoxyphenols and concluded that the 4-alkyl or 4-alkenyl were required in a eugenol-type structure and 3-carbon chain length was the maximum. The *E*-isomer of 2-(1-propenyl)-phenol was highly attractive to *D. barberi*; the *Z*-isomer was only slightly attractive. The 1-propenyl group in conjunction with the hydroxyl group appeared to be especially effective in activating the attractive response to *D. barberi* (Mcgovern and Ladd, 1990). *D. barberi* was attracted by 2-phenyl-1-ethylamine which was not reported to be isolated from corn and squash (*Curcubita* spp.) volatiles (Petroski and Hammack, 1998).

D. speciosa (Germar) (Coleoptera: Chrysomelidae) is a major pest of various crops in South America occurring in many States of Brazil (Krysan, 1986; Arruda-Gatti et al., 20006; Ventura and Ito, 2000). It has been shown that *D. speciosa* is attracted by the floral attractant 1,4-dimethoxybenzene (Ventura et al., 2000). This work had the aim to test some commercial and synthetic analogs of 1,4-dimethoxybenzene to attract *D. speciosa* at the field scale. Moreover, other compounds that were attractive to other species of *Diabrotica*, were also tested.

MATERIAL AND METHODS

Field experiments were carried out at the School Farm of the State University of Londrina, in Londrina (latitude 13°19'S, longitude 51 °12'W), Paraná State, Brazil. Common beans, *Phaseolus vulfaris* L., cv. Pérola (sown on February 23, 2006) was used as the testing crop.

Traps consisted of 750 mL plastic cups, painted with yellow gold 2450-0103 Suvinil paint (BASF S.A., São Bernardo do Campo, SP, Brazil). The cups were externally coated with the clean insect adhesive Tangle Trap (Tangle Foot Co., Grand Rapids, MI, USA).

The compounds (100 µL of liquids or 100 mg of solids) were dissolved in acetone (0.5 mL) and the solutions were applied on dental wicks (40 mm long X 10 mm diameter). Dental wicks soaked with test chemicals were glued to the bottom of the traps which were placed upside down on a wooden stake at a height of 0.25 cm.

.The baited traps were placed in the field at 4:00 p.m. and removed after 24 h. The traps were returned to the laboratory where beetles were identified to the level of species and sexed.

Two experiments were set using the analogs of the 1,4-dimethoxybenzene, *D. speciosa* kairomone, as lures. 1,4-dimethoxybenzene, as a standard treatment, and control (only acetone) were also used in the experiment which was carried out on March 27, 2006.

The experimental design was a completely randomized block with three replicates. The distance between the traps was 5 m within a block, and 10 m between the blocks. Analysis of variance (ANOVA) was performed and Scott-Knott test was used to compare the individual means (Canteri et al., 2001). Data were transformed by log (x + 1)

to normalize them and reduce heterogeneity of variances. Means and standard errors of means are presented for untransformed data.

Compounds 1-3, 7, 10-12, 14, 19, 21-23, 27-28, 31, 33-34 were obtained from Aldrich Chemical, Milwaukee, Connecticut, USA and compounds 4-6, 8-9, 13, 15-18, 20, 24-26, 29-30, 32 were prepared from the O-alkylation of commercial compounds (Enders et al., 1987) (Fig. 1).

Typical procedure employed for the O-alkylation of compounds

To a solution of alcohol (10 mmol) in tetrahydrofuran (THF) (30mL) under nitrogen and magnetic stirring, at -60 ºC, the alkyl halide (13 mmol) was added in one portion, followed by the addition of a suspension of sodium hydride in mineral oil (60% (w/w) (12 mmol). The mixture was allowed to slowly reach room temperature and refluxed for 1 h. The mixture was cooled to room temperature and treated with HCl (2M solution, 10 mL). The phases were separated and the aqueous layer was extracted with ethyl ether (3x15 mL). The combined organic layer was washed with saturated $NaHCO_3$ solution (2x10 mL), saturated $Na_2S_2O_3$ solution (20 mL), 10% aqueous NaOH solution (2x20 mL) and saturated NaCl (30 mL). The organic phase was dried over $MgSO_4$, the solvent was evaporated under the reduced pressure, and the residue was purified by distillation.

1-ethoxy-4-methoxybenzene (4)

Yield: 96%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ : 1.38 (*t*, 3H), 3.75 (*s*, 3H), 3.97 (*q*, 2H), 6.82 (*s*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 14.95, 55.71, 64.00, 114.63, 115.43, 153.11, 153.73; MS (EI) *m/z* (rel. int.): 152 (M^+, 100), 137 (3), 124 (41), 109 (54), 95 (23), 81 (15), 63 (6), 5 (6), 41 (3); IR (KBr, film) ν_{max}/cm^{-1}: 3103, 2952, 2912, 2880, 2832, 1511, 1480, 1456, 1441, 1393, 1243, 1180, 1050, 921, 822, 729.

1-methoxy-4-propoxybenzene (5)

Yield: 85%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.02 (*t*, 3H), 1.78 (*sext*, 2H), 3.76 (*s*, 3H), 3.86 (*t*, 2H), 6.82 (*s*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 10.53, 22.69, 55.72, 70.17, 114.61, 115.44, 153.30, 153.67; MS (EI) *m/z* (rel. int.): 166 (M^+, 100), 149 (1), 135 (1), 124 (14), 109 (13), 95 (3), 81 (1), 63 (2), 53 (1), 39 (3); IR (KBr, film) ν_{max}/cm^{-1}: 3047, 2961, 2932, 2877, 2832, 1508, 1465, 1454, 1441, 1392, 1229, 1180, 1038, 980, 823, 727.

1-(allyloxy)-4-methoxybenzene (6)

Yield: 84%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.76 (*s*, 3H), 4.48 (*dt*, 2H, *J*= 5.28, 1.56 Hz), 5.27 (*dq*, 1H, *J*= 10.56, 1.56 Hz), 5.39 (*dq*, 1H, *J*= 17.41, 1.56 Hz), 6.05 (*ddt*, 1H, J= 17.41, 10.56, 5.28 Hz), 6.78-6.91 (*m*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 55.69, 69.53, 114.61, 115.73, 117.47, 133.63, 152.75, 153.91; MS (EI) *m/z* (rel. int.): 164 (M^+, 100), 149 (94), 133 (7), 121 (26), 103 (24), 91 (14), 77 (10), 65 (12), 53 (9), 43 (12).

1-ethoxy-4-propoxybenzene (8)

Yield: 78%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.02 (*t*, 3H), 1.38 (*t*, 3H), 1.78 (*sext*, 2H), 3.86 (*t*, 2H), 3.97 (*q*, 2H), 6.82 (*s*,4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 10.53, 14.95, 22.71, 64.00, 70.15, 115.41, 153.01, 153.26; MS (EI) *m/z* (rel. int.): 180 (M^+, 100), 165 (1), 153 (2), 138 (25), 121 (1), 110 (35), 95 (1), 81 (3), 63 (4), 53 (2), 39 (8); IR (KBr, film) ν_{max}/cm^{-1}: 3046, 2963, 2926, 2873, 2853, 1508, 1475, 1455, 1442, 1394, 1227, 1151, 1048, 980, 821, 732.

1-(allyloxy)-4-ethoxybenzene (9)

Yield: 64%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.38 (*t*, 3H), 3.96 (*q*, 2H), 4.47 (*dt*, 2H, *J*= 5.28, 1.56 Hz), 5.25 (*dq*, 1H, *J*= 10.56, 1.56 Hz), 5.38 (*dq*, 1H, *J*= 17.41, 1.56 Hz), 6.05 (*ddt*, 1H, *J*= 17.41, 10.56, 5.28 Hz), 6.76-6.88 (*m*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 14.90, 63.94, 69.78, 115.35, 115.68, 117.41, 133.66, 152.89, 153.24; MS (EI) *m/z* (rel. int.): 178 (M^+, 100), 163 (1), 150 (55), 149 (42), 135 (56), 122 (21), 121 (13), 107 (39), 91 (11), 77 (19), 65 (15), 51 (13), 39 (13).

1-ethoxy-4-(ethoxymethyl)benzene (13)

Yield: 72%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.23 (*t*, 3H), 1.40 (*t*, 3H), 3.51 (*q*, 2H), 4.02 (*q*, 2H), 4.43 (*s*, 2H), 6.86 (*d*, 2H), 7.25 (*d*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 14.84, 15.26, 63.43, 65.41, 72.41, 114.35, 129.29, 130.56, 158.50; MS (EI) *m/z* (rel. int.): 180 (M^+, 56), 165 (3), 151 (25), 135 (100), 123 (10), 107 (73), 95 (13), 77 (24), 59 (6), 39 (5); IR (KBr, film) ν_{max}/cm^{-1}: 3033, 2976, 2928, 2870, 2797, 1512, 1475, 1455, 1442, 1390, 1245, 1171, 1096, 1046, 920, 819, 721.

1-methoxy-4-(methoxymethyl)benzene (15)
Yield: 65%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.35 (*s*, 3H), 3.80 (*s*, 3H), 4.39 (*s*, 2H), 6.88 (*d*, 2H), 7.26 (*d*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 55.27, 57.80, 74.37, 113.79, 129.38, 130.31, 159.24; MS (EI) *m/z* (rel. int.): 152 (M^+, 69), 137 (6), 135 (7), 121 (100), 108 (5), 91 (9), 77 (17), 63 (5), 50 (9), 39 (8); IR (KBr, film) ν_{max}/cm^{-1}: 3031, 2955, 2926, 2835, 2816, 1514, 1465, 1456, 1443, 1381, 1248, 1172, 1097, 1035, 917, 819, 717.

anisole (16)
Yield: 75%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.80 (*s*, 3H), 6.85-7.00 (*m*, 3H), 7.20-7.35 (*m*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 55.12, 113.90, 120.64, 129.44, 159.26; MS (EI) *m/z* (rel. int.): 108 (M^+, 100), 93 (11), 85 (2), 78 (49), 65 (44), 51 (17), 44 (4), 39 (23); IR (KBr, film) ν_{max}/cm^{-1}: 3031, 2955, 2835, 1599, 1453, 1433, 1249, 1173, 1038, 753 e 693.

1-methoxy-4-methylbenzene (17): yield: 63%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 2.30 (*s*, 3H), 3.79 (*s*, 3H), 6.82 (*d*, 2H), 7.11 (*d*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 20.38, 55.21, 113.65, 129.76, 129.83, 157.42; MS (EI) *m/z* (rel. int.): 122 (M^+, 100), 107 (53), 91 (22), 79 (22), 77 (38), 65 (15), 51 (24), 39 (9); IR (KBr, film) ν_{max}/cm^{-1}: 3027, 2954, 2857, 1513, 1460, 1378, 1247, 1175, 1040, 817.

1,3-dimethoxybenzene (18)
Yield: 70%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.78 (*s*, 6H), 6.46 (*s*, 1H), 6.51 (*d*, 2H), 7.18 (*t*, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 55.20, 100.40, 106.11, 129.83, 160.79; MS (EI) *m/z* (rel. int.): 138 (M^+, 100), 123 (4), 109 (2), 95 (18), 78 (56), 63 (16), 51 (9), 39 (27); IR (KBr, film) ν_{max}/cm^{-1}: 3000, 2955, 2854, 1592, 1467, 1376, 1212, 1151, 1040, 762 e 685.

1,4-dimethoxycyclohexane (20):
Yield: 94%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.14-1.43 e 1.88-2.11 (2 *m*, 8H, *trans*), 1.47-1.65 e 1.66-1.85 (2 *m*, 8H, *cis*), 3.07-3.39 (*m*, 4H, *cis/trans*), 3.32 (*s*, 6H, *cis*), 3.34 (*s*, 6H, *trans*); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 26.99, 55.48, 76.42 (*cis*), 28.64, 55.90, 78.90 (*trans*); MS (EI) *m/z* (rel. int.): 138 (M^+, 25), 114 (59), 112 (100), 97 (59), 81 (66), 73 (99), 71 (55), 58 (20), 45 (44), 43 (38), 39(41); IR (KBr, film) ν_{max}/cm^{-1}: 2976, 2942, 2862, 2818, 1469, 1448, 1375, 1188, 1104, 749.

1,4-bis(methoxymethyl)benzene (24)
Yield: 77%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.38 (*s*, 6H), 4.45 (*s*, 4H), 7.31 (*s*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 58.05, 74.47, 127.80, 137.65; MS (EI) *m/z* (rel. int.): 165 (M^{-1}, 19), 150 (5), 135 (75), 121 (100), 105 (24), 91 (28), 75 (43), 63 (5), 45 (8); IR (KBr, film) ν_{max}/cm^{-1}: 3054, 2983, 2923, 2848, 2819, 1506, 1471, 1456, 1441, 1377, 1216, 1190, 1020, 915, 810, 756.

1,4-bis(ethoxymethyl)benzene (25)
Yield: 71%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.23 (*t*, 6H), 3.52 (*q*, 4H), 4.50 (*s*, 4H), 7.32 (*s*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 15.23, 65.32, 72.50, 127.76, 137.91; MS (EI) *m/z* (rel. int.): 138 (M^{-1}, 47), 165 (4), 149 (100), 135 (53), 119 (13), 107 (52), 91 (35), 79 (13), 59 (14), 47 (4), 43 (4); IR (KBr, film) ν_{max}/cm^{-1}: 3049, 2975, 2930, 2880, 2849, 1556, 1472, 1456, 1441, 1396, 1212, 1167, 1016, 892, 808, 762.

1,4-bis((allyloxy)methyl)benzene (26)
Yield: 83%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 4.02 (*dt*, 2H, *J*= 5.28, 1.56 Hz), 4.52 (*s*, 2H), 5.20 (*dq*, 1H, *J*= 10.56, 1.56 Hz), 5.30 (*dq*, 1H, *J*= 17.41, 1.56 Hz), 5.95 (*ddt*, 1H, *J*= 17.41, 10.56, 5.28 Hz), 7.33 (*s*, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 71.09, 71.88, 117.12, 127.82, 134.52, 137.69; MS (EI) *m/z* (rel. int.): 217 (M^{-1}, 5), 189 (3), 174 (8), 161 (28), 147 (10), 132 (20), 119 (69), 105 (47), 91 (100), 77 (13), 65 (11), 57 (4), 43 (11).

1-methoxy-4-(2-methoxyethyl)benzene (29)
Yield: 83%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 2.82 (*t*, 2H), 3.35 (*s*, 3H), 3.56 (*t*, 2H), 3.78 (*s*, 3H), 6.83 (*d*, 2H), 7.14 (*d*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 35.31, 55.23, 58.64, 73.90, 113.82, 129.76, 130.99, 158.07; MS (EI) *m/z* (rel. int.): 138 (M^+, 47), 149 (1), 134 (4), 121 (100), 105 (2), 91 (5), 77 (10), 63 (3), 51 (6), 45 (4); IR (KBr, film) ν_{max}/cm^{-1}: 3034, 2973, 2927, 2862, 2831, 1614 e 1512, 1480, 1466, 1436, 1385, 1248, 1177, 1112, 1035, 829, 803, 752.

1-(2-ethoxyethyl)-4-methoxybenzene (30)
Yield: 75%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 1.20 (*t*, 3H), 2.83 (*t*, 2H), 3.50 (*q*, 2H), 3.59 (*t*, 2H), 3.78 (*s*, 3H), 6.83 (*d*, 2H), 7.14 (*d*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 15.20, 35.50, 55.21, 66.20. 71.86, 113.77, 129.80, 131.07, 158.04; MS (EI) *m/z* (rel. int.): 138 (M^+, 49), 165 (1), 153 (1), 134 (4), 121 (100), 105 (2), 91 (9), 77 (14), 65 (6), 50 (4); IR (KBr, film) ν_{max}/cm^{-1}: 3032, 2978, 2934, 2866, 2846, 1614 e 1514, 1475, 1462, 1440, 1375, 1245, 1177, 1111, 1038, 829, 809, 751.

4-allyl-1,2-dimethoxybenzene (32):
Yield: 63%; ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 3.33 (*dt*, 2H, *J*= 6.65, 1.56 Hz), 3.86 (*s*, 3H), 3.87 (*s*, 3H), 5.06 (*dt*, 1H, *J*= 10.36, 1.56 Hz), 5.10 (*dt*, 1H, *J*= 16.23, 1.56 Hz), 5.96 (*ddt*, 1H, *J*= 16.23, 10.36, 6.65 Hz), 6.68-6.93 (*m*, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ: 39.82, 55.79, 111.27, 111.87, 115.60, 120.40, 132.63, 137.70, 147.39, 148.90; MS (EI) *m/z* (rel. int.): 178 (M^+, 100), 163 (50), 147 (23), 135 (13), 131 (7), 119 (10), 107 (45), 103 (28), 91 (21), 77 (5), 63 (7), 51 (7)

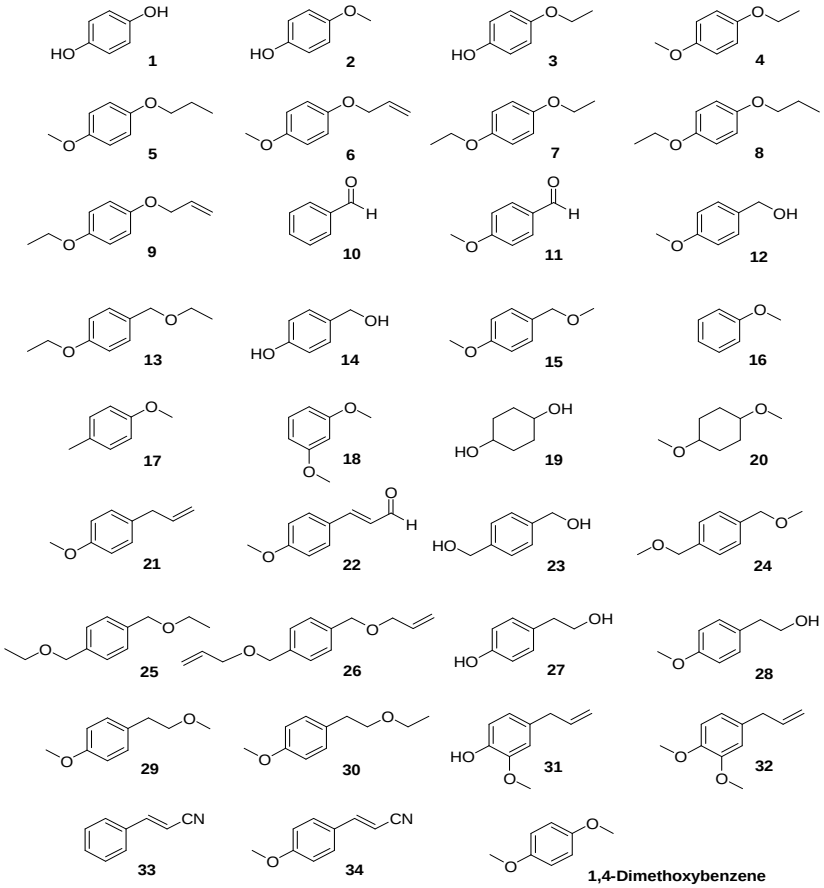

Figure 1 - Compounds tested as attractant for *D. speciosa*: hydroquinone **(1)**, 4-methoxyphenol **(2)**, 4-ethoxyphenol **(3)**, 1-ethoxy-4-methoxybenzene **(4)**, 1-methoxy-4-propoxybenzene **(5)**, 1-(allyloxy)-4-methoxybenzene **(6)**, 1,4-diethoxybenzene **(7)**, 1-ethoxy-4-propoxybenzene **(8)**, 1-(allyloxy)-4-ethoxybenzene **(9)**, benzaldehyde **(10)**, 4-methoxybenzaldehyde **(11)**, (4-methoxyphenyl)methanol **(12)**, 1-ethoxy-4-(ethoxymethyl)benzene **(13)**, 4-(hydroxymethyl)phenol **(14)**, 1-methoxy-4-(methoxymethyl)benzene **(15)**, anisole **(16)**, 1-methoxy-4-methylbenzene **(17)**, 1,3-dimethoxybenzene **(18)**, cyclohexane-1,4-diol **(19)**, 1,4-dimethoxycyclohexane **(20)**, 1-allyl-4-methoxybenzene **(21)**, (*E*)-3-(4-methoxyphenyl)acrylaldehyde **(22)**, 1,4-phenyldimethyl alcohol **(23)**, 1,4-bis(methoxymethyl)benzene **(24)**, 1,4-bis(ethoxymethyl)benzene **(25)**, 1,4-bis((allyloxy)methyl)benzene **(26)**, 4-(2-hydroxyethyl)phenol **(27)**, 2-(4-methoxyphenyl)ethanol **(28)**, 1-methoxy-4-(2-methoxyethyl)benzene **(29)**, 1-(2-ethoxyethyl)-4-methoxybenzene **(30)**, 4-allyl-2-methoxyphenol **(31)**, 4-allyl-1,2-dimethoxybenzene **(32)**, (*E*/*Z*)-cinnamonitrile **(33)**, (*E*/*Z*)-3-(4-methoxyphenyl)acrylonitrile **(34)** and 1,4-dimethoxybenzene.

RESULTS AND DISCUSSION

1,4-dimethoxybenzene lured traps attracted significantly more beetles than the control traps (Table 1).

Captures of *D. speciosa* in the traps lured with 1,4-dimethoxybenzene analogs did not differ from the control traps, showing that all the structural modifications made on the structure of the natural compound resulted in activity loss. Results showed that position and nature of the substituents on the aromatic ring played a crucial role in the activity of the natural compound.

Table 1 - Mean number (± SE) of adults of *Diabrotica speciosa* caught per yellow cup traps in common bean crop after 24 h (March 27, 2006).

Treatment	Beetles[1]
1	4.7 ± 1.3 b
2	15.7 ± 3.9 b
3	10.0 ± 4.1 b
4	5.3 ± 2.1 b
5	4.3 ± 1.8 b
6	8.7 ± 1.5 b
7	8.0 ± 1.5 b
8	8.0 ± 1.8 b
9	3.0 ± 0.6 b
10	7.7 ± 1.5 b
11	9.0 ± 3.1 b
12	7.3 ± 3.9 b
13	7.0 ± 3.0 b
14	4.0 ± 0.6 b
15	6.3 ± 1.8 b
16	5.7 ± 2.2 b
17	4.0 ± 1.7 b
18	14.3 ± 3.2 b
19	7.3 ± 0.7 b
20	8.7 ± 2.1 b
21	5.7 ± 0.7 b
22	8.0 ± 2.7 b
23	4.7 ± 2.1 b
24	8.0 ± 2.7 b
25	3.0 ± 0.0 b
26	7.7 ± 1.2 b
27	8.3 ± 0.0 b
28	12.7 ± 4.5 b
29	6.3 ± 1.2 b
30	8.7 ± 1.9 b
31	10.7 ± 1.5 b
32	7.3 ± 5.0 b
33	4.0 ± 0.6 b
34	4.7 ± 0.3 b
1,4- dimethoxybenzene	46.7 ± 10.0 a
Control	8.7 ± 0.7 b

[1] Means in the same column with different letter are significantly different by Scott-Knott test ($P<0.05$), n = 3.

The aromatic ring was also important to the activity of the kairomone since compound 20 was unattractive. It was also demonstrated that to keep the activity, the heteroatoms, oxygens in this case, have to be bound directly on the aromatic ring since, for instance, compound 15 was unattractive.

D. speciosa showed its own species-specific pattern of response to volatile attractants. The beetle was attracted by *C. maxima* floral attractant, 1,4-dimethoxybenzene (Ventura et al, 2000), which was not reported as attractive for other Diabroticites (Metcalf and Metcalf, 1992). 1,4-dimethoxybenzene is the major component in *C. maxima* cv., True Hubbard (34.54%) and the fourth in the cv. Blue Hubbard (Andersen, 1987). On the other hand, compounds that were attractive to other species of *Diabrotica* (*para*-methoxyphenethanol 28, eugenol 31, methyl eugenol 32, cinnamonitrile 33, *para*-methoxycinnamonitrile 34, estragole 21, *para*-methoxycinnamaldehyde 22) and tested in this work, did not show any attractivity for *D. speciosa*. However, *D. speciosa* shared with North American *Diabrotica sp*. (Lampman and Metcalf, 1987; 1998; Lance et al., 1992) and *Acalymma vittatum* (F.) (Lewis et al, 1990) some attraction by TIC (1,2,4-trimethoxybenzene + indole + cinnamaldehyde) and VIP (veratrole + indole + cinnamaldehyde) mixtures (Ventura et al., 2000). The observed attraction of *D. speciosa* by 1,4-dimethoxybenzene corroborated previous investigations (Ventura et al, 2000).

Several analogs of 1,4-dimethoxybenzene were prepared and tested, among with other commercial compounds, as a possible attractant to *D. speciosa*. Results showed that position and nature of the substituents, along with the aromaticity shown in the structure of the natural compound were crucial for its attractivity. The species-specific pattern of response to the attractants of *D. speciosa* has also been shown since kairomones and parakairomones of other species of *Diabrotica*, did not attract *D. speciosa.*

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RESUMO

Uma série de compostos, sintéticos e comerciais, análogos ao 1,4-dimetoxibenzeno, um cairomônio de *Diabrotica speciosa*, juntamente com outros compostos comerciais atrativos para outras espécies de *Diabrotica*, tiveram suas atividades testadas frente à *D. speciosa.* Armadilhas de copos amarelos contendo os compostos foram instaladas em plantação de feijão. As avaliações foram realizadas 24 horas depois. Armadilhas com 1,4-dimetoxibenzeno capturaram significativamente mais insetos do que armadilhas testemunha. Armadilhas com análogos do 1,4-dimetoxibenzeno não capturaram mais insetos que as armadilhas testemunha. Os resultados mostraram que a posição e a natureza dos substituintes, juntamente com a aromaticidade verificada na estrutura do composto natural, são cruciais para a atratividade.

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