Comparison among 18 Hexyl Esters of 1-Naphthylacetic Acid Used on Grapevine

Marcello Dolci,*,† Giancarla Navissano,§ Giuliana Gay,§ Anna Eynard,† and Mauro Rangone†

Dipartimento di Valorizzazione e Protezione delle Risorse Agroforestali, Università di Torino, Via L. da Vinci 44, 10095 Grugliasco (TO), Italy, and Centro per il Miglioramento Genetico e la Biologia della Vite, CNR, Via L. da Vinci 44, 10095 Grugliasco (TO), Italy

Eighteen esters derived from 1-naphthylacetic acid (NAA) and from hexyl isomer alcohols were synthesized and sprayed on grapevine suckers at 1, 2, 4, and 8% w/w concentrations to test their sucker control efficiency 2, 10, and 30 days and 1 year after their application. All compounds gave a prompt control of suckers. After 1 year, sucker growth was inhibited by the derivatives from primary and secondary alcohols, whereas the number of suckers was reduced only by application of naphthyl acetates of tertiary alcohols.

Keywords: *NAA; hexyl esters of 1-naphthylacetic acid; sucker control; grapevine*

INTRODUCTION

Among plant growth regulators, 1-naphthylacetic acid (NAA) is widely used in agriculture for rooting of cuttings, inhibition of fruit-set, fruit abscission, and induction and control of flowering. Recently, NAA has also been employed effectively for the control of suckers in many fruit tree species. Because of its low solubility, experiments were carried out with the sodium salt and ethyl ester of NAA (Antognozzi, 1978; Morris and Cawthon, 1981; Ahmedullah and Wolfe, 1982; Forlani and Di Vaio, 1990; Reynolds et al., 1991). Addition of a wetting agent (Tween 20) has been found to increase the effectiveness of the esters (Lownds et al., 1987). Use of some esters derived from NAA with methyl and ethyl alcohols and propyl, butyl, and pentyl isomer alcohols for sucker control has been reported (Eynard et al., 1986a,b; Dolci et al., 1992, 1993, 1994). Predominant symptoms on treated suckers after a few days were withering, distortion, and narrowing of leaves and shoots, usually followed by necrosis and drying. The observation of shoot sections a few days after application showed strong red browning and narrowing of vessels; these narrow parts blocked the sap flow and caused shoot drying (data not published).

The present work aims to measure the effect of some isomeric hexyl 1-naphthylacetates on grapevine sucker control.

MATERIALS AND METHODS

Chemical Methods. Eighteen esters, 17 of which were new, were synthesized from NAA. The products were prepared according to the following well-known reactions.

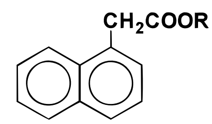
for primary and secondary alcohols

$$ArCH_2COOH + R'OH \overset{H^+}{\rightleftarrows} ArCH_2COOR' + H_2O$$

for tertiary alcohols

$$ArCH_2COCl + R'OH \xrightarrow{\text{pyridine}} ArCH_2COOR' + HCl$$

Table 1. Physical Data of Synthesized Compounds



no.	R	yield (%)	bp, °C/mbar
1	$(CH_2)_5CH_3$	94	133/1 × 10^{-5}
2	$(CH_2)_3CH(CH_3)_2$	95	120/1 × 10^{-5}
3	$(CH_2)_2CH(CH_3)C_2H_5$	92	114/1 × 10^{-5}
4	$CH_2CH(CH_3)C_3H_7$	93	129/6 × 10^{-6}
5	$(CH_2)_2C(CH_3)_3$	94	123/1 × 10^{-5}
6	$CH_2C(CH_3)_2C_2H_5$	92	119/5 × 10^{-6}
7	$CH_2CH(CH_3)CH(CH_3)_2$	90	113/1 × 10^{-5}
8	$CH_2CH(C_2H_5)_2$	91	139/6 × 10^{-4}
9	$CH(CH_3)C_4H_9$	86	127/6 × 10^{-6}
10	$CH(CH_3)CH_2CH(CH_3)_2$	91	138/2 × 10^{-5}
11	$CH(CH_3)CH(CH_3)C_2H_5$	82	115/8 × 10^{-6}
12	$CH(C_2H_5)C_3H_7$	81	138/6 × 10^{-4}
13	$CH(CH_3)C(CH_3)_3$	83	120/6 × 10^{-6}
14	$CH(C_2H_5)CH(CH_3)_2$	81	118/3 × 10^{-5}
15	cyclo-C_6H_{11}	92	142/8 × 10^{-6}
16	$C(CH_3)_2C_3H_7$	58	103/6 × 10^{-6}
17	$C(CH_3)_2CH(CH_3)_2$	52	109/7 × 10^{-6}
18	$C(CH_3)(C_2H_5)_2$	52	105/1 × 10^{-5}

All compounds were characterized by NMR spectroscopy. The synthesized compounds, their yields, and their boiling points are shown in Table 1.

Synthesis from Primary and Secondary Alcohols. A mixture of NAA (0.35 mol) and primary or secondary alcohol (0.385 mol), carbon tetrachloride (400 mL), and 96% sulfuric acid (2 mL) was placed in a three-neck flask, complete with Soxhlet containing anhydrous sodium sulfate. The mixture was refluxed for 5−6 h until NAA disappeared (TLC, petroleum ether/ethyl ether, 80:20 v/v). Carbon tetrachloride was removed under vacuum; the mixture was extracted with ethyl ether and washed with 3% NaOH and with water, and then dried with anhydrous sodium sulfate, and treated with animal charcoal. The product was purified on a silica gel column, using petroleum ether/ethyl ether (80:20 v/v) as the eluent to yield the resultant ester, which was distilled under high vacuum.

Synthesis from Tertiary Alcohols. A solution of tertiary alcohol (0.33 mol), pyridine (70 mL), and benzene (50 mL) was combined with 1-naphthylacetyl chloride (0.3 mol) in benzene (50 mL) with stirring at 10−15 °C. The reaction was allowed to progress under continuous stirring at room temperature until the acyl chloride disappeared (TLC, petroleum ether/ethyl

* Author to whom correspondence should be addressed [fax 39-(0)11-4031819; e-mail gay@cvt.to.cnr.it].

† Università di Torino.

§ CNR.

10.1021/jf980316e CCC: $18.00
Published on Web 04/02/1999

Table 2. Wilting Index Scale with Descriptions of Symptoms

score	effect
0	no symptoms
1	apex drooping
2	shoots drooping and a few leaves rolled
3	shoots drooping and all leaves rolled without necrosis
4	shoots drooping and leaves generally rolled into a cone with marginal necrosis
5	apical leaves with sides reddened or dried, apex not yet dried, internodes browned
6	a few leaves completely reddened or with large necrotic areas, apex generally dried
7	basal leaves partially reddened or with necrotic areas, distal internodes dried, medial internodes browned or starting to dry
8	apical leaves dried, basal leaves strongly reddened and necrotic, distal and medial internodes dried
9	last leaves starting to dry, distal and medial internodes dried, basal internodes strongly browned
10	internodes and leaves all dried

ether, 80:20 v/v). The mixture was carefully poured into 15% hydrochloric acid (300 mL) at 0 °C, extracted with ethyl ether, washed with 3% NaOH and with water, then dried with anhydrous sodium sulfate, and treated with animal charcoal. Ether and benzene were removed under vacuum. The product was purified on a silica gel column, using petroleum ether/ethyl ether (80:20 v/v) as the eluent to yield the resultant ester, which was distilled under high vacuum.

Biological Methods. The experiment was carried out on three plants per treatment of *Vitis vinifera* L. cv. Barbera, double-curtain trained, with 1.50 m high trunks. The esters were sprayed at 1, 2, 4, and 8% w/w concentrations corresponding to 0.0370, 0.0740, 0.1479, and 0.2959 mol/L for compounds **1**−**14** and **16**−**18** and 0.0373, 0.0745, 0.1491, and 0.2981 mol/L for compound **15**. All compounds were suspended in 400 mL of deionized water with 1% (w/w) of surfactant (Tween 20), and all solutions were sprayed by hand on 0.10−0.40 m long suckers.

Sucker control was evaluated after 2, 10, and 30 days by applying a wilting index (WI) with scores ranging from 0 (no symptoms) to 10 (complete wilting) (Table 2).

The time of leaf persistence (Lp) in the same year of the treatment was calculated by summing the products of the complement of WI by the number of days after ester application (d_n) at 4% rate:

$$\mathrm{Lp} = \Sigma(10 - \mathrm{WI})d_n$$

At harvest, the number of clusters and the yield were recorded. The pH, the total acidity, and the soluble solids of the grape juice were measured. In addition, the winter pruning wood was weighed.

The persistence of sucker control was evaluated by counting the number of the suckers (Sn) originated from the trunk in the first spring after treatment.

All data were processed by analysis of variance and Duncan's multiple-range test. Linear correlation between the leaf persistence in the same year of the treatment (Lp) and the number of suckers produced in the following year (Sn) was calculated and the coefficient compared with values of Fisher and Yates [Table 6 of Little and Hill, (1978)].

RESULTS AND DISCUSSION

Tables 3−5 show the effect of treatments on the suckers 2, 10, and 30 days after application.

Two days after treatment (Table 3), a few compounds (**13**, **14**, **16**−**18**) at 1% induced bending of the apex of the shoots. Other compounds at the same concentration caused leaf roll. It was determined that **5** and **6** were most active and significantly different from compounds **9**−**14** and **16**−**18**. At 8% concentration, compounds **1**−**5**, **8**−**10**, and **12** changed the color of some leaves and produced wide necrotic areas and drying of the apex. They differed from many other compounds. The effect of intermediate concentrations (2 and 4%) varied with the compound. For example, compound **10** showed increasing response with the concentration, that is, in 2, 3, 5, and 6 scores from 1 to 8%. Other compounds, such as **1**, **5**, **6**, **8**, and **12**, were very active even at 4% (score 5 or 6).

Ten days after treatment (Table 4), the symptoms did not change from the first observations in the case of **13**, **14**, **16**, and **17** at 1%, but the WI of many compounds (**1**−**6**, **8**−**12**, **15**, and **18**) increased even at 1% concentration. Almost all compounds at 4% induced a more advanced withering than at the highest concentration

Table 3. Wilting Index 2 Days after Treatment[a]

	concentration			
compd	1%	2%	4%	8%
1	2.33 ABC	4.33 A	5.00AB	6.33A
2	3.00 AB	3.33 A	4.33 ABCD	6.00 AB
3	3.00 AB	3.33 AB	4.33 ABCD	6.00 AB
4	2.67 AB	3.67 A	4.67 ABC	6.67 A
5	3.33 A	3.67 A	5.00 AB	6.00 AB
6	3.33 A	3.33 AB	5.00 AB	5.00 ABCD
7	3.00 AB	3.00 ABC	3.67 BCD	3.67 CD
8	2.33 ABC	3.00 ABC	6.00 A	6.33 A
9	2.00 BCD	3.00 ABC	4.00 ABCD	6.67 A
10	2.00 BCD	3.00 ABC	4.67 ABC	6.00 AB
11	2.00 BCD	2.67 ABC	3.33 BCD	4.33 BCD
12	2.00 BCD	3.00 ABC	5.00 AB	6.33 A
13	1.00 D	2.67 ABC	3.33 BCD	3.67 CD
14	1.00 D	1.00 C	2.33 D	4.00 CD
15	2.67 AB	3.00 ABC	4.00 ABCD	5.33 ABC
16	1.00 D	1.33 BC	2.33 D	3.33 D
17	1.00 D	1.33 BC	2.67 CD	4.33 BCD
18	1.33 CD	1.33 BC	2.33 D	3.33 D

[a] Average for all treated suckers (means followed by the same letter were not significantly different, $P \leq 0.01$).

Table 4. Wilting Index 10 Days after Treatment[a]

	concentration			
compd	1%	2%	4%	8%
1	3.67 ABC	5.67 A	7.00 A	7.67 A
2	4.00 AB	4.67 AB	7.00 A	7.67 A
3	4.00 AB	4.67 AB	6.33 AB	7.33 AB
4	3.00 ABCD	4.67 AB	5.33 ABC	7.67 A
5	4.33 AB	5.33 A	7.00 A	7.00 ABC
6	4.00 AB	5.00 AB	6.33 AB	7.00 ABC
7	3.00 ABCD	4.00 ABCD	4.67 BC	6.00 ABCD
8	5.00 A	5.33 A	7.00 A	7.67 A
9	2.67 BCD	4.67 AB	5.67 ABC	7.33 AB
10	3.33 ABC	5.00 AB	5.67 ABC	6.67 ABC
11	2.67 BCD	4.33 ABC	5.67 ABC	6.67 ABC
12	3.00 ABCD	4.67 AB	6.67 AB	7.00 ABC
13	1.00 D	3.00 BCDE	5.33 ABC	7.00 ABC
14	1.00 D	2.33 CDE	5.00 ABC	6.00 ABCD
15	4.33 AB	5.00 AB	6.33 AB	6.67 ABC
16	1.00 D	1.67 E	4.00 C	5.67 BCD
17	1.00 D	1.33 E	4.00 C	4.67 D
18	1.67 CD	2.00 DE	4.00 C	5.33 CD

[a] Average for all treated suckers (means followed by the same letter were not significantly different, $P \leqslant 0.01$).

Table 5. Wilting Index 30 Days after Treatment[a]

	concentration			
compd	1%	2%	4%	8%
1	7.33 ABCD	8.67 AB	10.00 A	10.00 A
2	8.00 AB	9.67 A	9.67 A	10.00 A
3	7.67 ABC	9.33 A	9.67 A	10.00 A
4	6.67 ABCD	8.00 ABC	9.00 A	9.67 A
5	9.33 A	10.00 A	10.00 A	10.00 A
6	8.33 AB	9.67 A	10.00 A	10.00 A
7	7.00 ABCD	8.33 AB	9.67 A	10.00 A
8	7.67 ABC	8.67 AB	10.00 A	10.00 A
9	7.00 ABCD	8.33 AB	9.67 A	10.00 A
10	6.33 BCD	8.67 AB	10.00 A	10.00 A
11	5.00 CDE	6.33 BCD	7.67 ABC	9.00 A
12	6.67 ABCD	9.33 A	9.67 A	10.00 A
13	4.67 DE	5.67 CD	8.33 AB	9.00 A
14	5.00 CDE	5.67 CD	8.67 A	9.67 A
15	6.67 ABCD	7.67 ABC	10.00 A	10.00 A
16	1.67 F	2.33 EF	5.00 D	6.00 B
17	1.00 F	1.67 F	6.00 CD	6.67 B
18	3.33 EF	4.67 DE	6.33 BCD	7.00 B

[a] Average for all treated suckers (means followed by the same letter were not significantly different, $P \leqslant 0.01$).

Table 6. Number of Suckers Grown 1 Year after Treatment[a]

	concentration			
compd	1%	2%	4%	8%
1	6.3 CD	7.0 BCDE	2.0 CD	0.0 D
2	4.7 CD	3.7 CDE	1.3 CD	0.3 D
3	10.0 ABCD	6.7 BCDE	2.3 BCD	0.3 D
4	6.0 CD	3.7 CDE	1.3 CD	0.3 D
5	4.7 CD	3.7 CDE	0.3 D	0.0 D
6	4.0 CD	0.0 E	0.0 D	0.0 D
7	4.3 CD	1.7 CDE	0.0 D	0.0 D
8	2.7 CD	4.0 CDE	0.3 D	0.0 D
9	8.0 BCD	1.3 DE	1.0 CD	1.0 D
10	2.7 CD	0.0 E	0.0 D	0.0 D
11	0.3 D	0.0 E	0.0 D	0.0 D
12	4.0 CD	0.7 DE	0.0 D	0.0 D
13	17.7 AB	5.7 BCDE	3.7 BCD	1.7 CD
14	8.0 BCD	3.7 CDE	1.0 CD	1.3 CD
15	3.7 CD	2.7 CDE	1.3 CD	0.0 D
16	10.7 ABCD	11.7 B	6.3 BC	7.0 BCD
17	12.3 ABC	8.3 BCD	8.0 B	9.0 B
18	9.7 ABCD	9.3 BC	8.0 B	8.0 BC
control	18.7 A	18.7 A	18.7 A	18.7 A

[a] Means followed by the same letter were not significantly different, $P \leqslant 0.01$.

2 days after treatment. At 8% concentration all compounds, except **16**−**18**, showed a similar activity, that is, basal leaves reddened or necrotic, apex dried, distal and medial internodes browned or dried.

Thirty days after treatment (Table 5), almost all of the suckers treated with compound **5** at 1% wilted. It was not so in the case of most esters from secondary and tertiary alcohols (except **9**, **12**, and **15**). At 4 and 8% concentrations, all compounds showed very good effects except esters prepared from tertiary alcohols. At 8% concentration, the WI were 9−10, that is, leaves and internodes dried or strongly reddened.

None of the compounds damaged leaves of productive canes or changed grape quality and quantity.

After 1 year, even at the lowest rate most of the esters reduced the sprouting of suckers in comparison with the untreated plants (Table 6). It was observed that some compounds, **3** among the primary esters, **13** among the secondary esters, and all of the tertiary esters, at 1% did not significantly differ from the control plants. At 2% concentration, all of the compounds reduced the sprouting of new suckers. At the highest concentrations (4−8%), except for the tertiary alcohol derivatives, all other esters showed an almost complete anti-bud-break action.

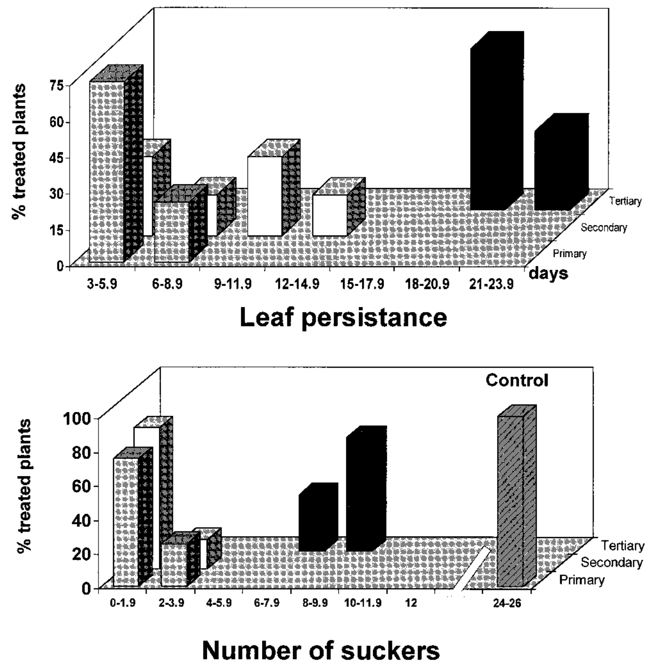


Figure 1. Time of leaf persistence during the first month after treatment with 4% NAA derivative (top) and number of suckers grown after 1 year (bottom). Both values are expressed as percent of treated plants.

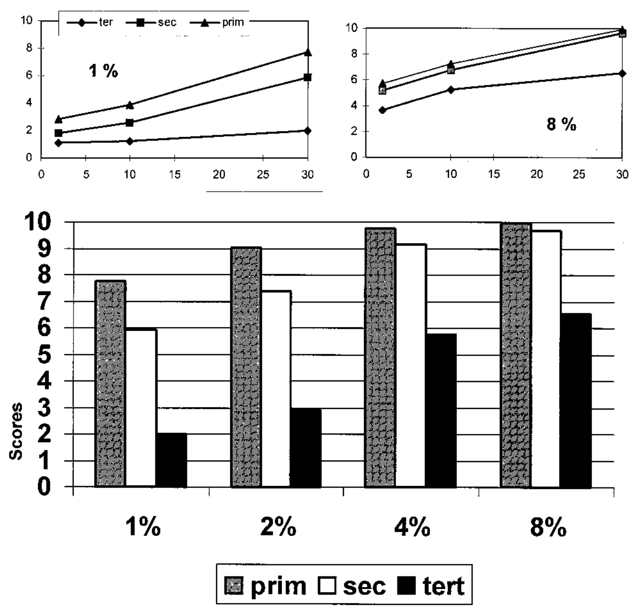


Figure 2. Wilting index during the first month after treatment at 1 and 8% (top) and 30 days after treatment at different concentrations (bottom).

In the year of treatment at 4%, the leaf persistence (Lp) was <9 days in the case of esters from primary alcohol (Figure 1) and 3−15 days in the case of esters from secondary alcohol, whereas tertiary alcohol derived esters took >18 days for complete wilting of suckers.

The linear correlation between Lp in the year of the treatment and Sn sprouting during the following year was positive and highly significant ($r = 0.765$***) (Figure 1).

In the year of treatment the effects of increasing concentration for the three groups of esters are shown in Figure 2. In the case of primary and secondary alcohol derived esters, the wilting index was similar and higher than in case of tertiary alcohol derived esters.

CONCLUSIONS

The chemical structure of NAA hexyl isomer esters and their biological activity, measured by sucker wilting and anti-bud-break effect on grapevine, appeared to be related. The application of esters of primary and secondary hexyl alcohols and NAA at concentrations of 4−8% wilted suckers in a similar way and inhibited the sprouting of suckers in the year following the treatment. The compounds derived from tertiary alcohols were less effective even at 4−8% concentrations, yet all esters reduced the number of suckers the year after treatment in comparison with untreated plants. The anti-bud-break effect makes it possible to apply esters every 2 years, to reduce the cost of distribution and the environmental impact. Because of their efficiency at low rates, the esters derived from primary and secondary alcohols appear to be most suitable for sucker control in viticulture.

LITERATURE CITED

Ahmedullah, M.; Wolfe, W. H. Control of sucker growth on *Vitis vinifera* L. cultivar Sauvignon Blanc with naphthaleneacetic acid. *Am. J. Enol. Vitic.* **1982**, *33*, 198−200.

Antognozzi, E. Effetti dell'estere etilico dell'NAA nel controllo dei succhioni in piante potate di melo, pero, susino e pesco (Effects of ethyl ester of NAA on the sucker control of pruned plants of apple, pear, plum, and peach). *Ann. Fac. Agraria Univ. Perugia* **1978**, *32*, 753−760.

Dolci, M.; Navissano, G.; Gay, G.; Eynard, I. Attività su vite di nuovi derivati dell'acido 1-naftilacetico (Effects of new derivatives of 1-naphthylacetic acid on grapevine). *Atti Accad. Ital. Vite Vino Siena* **1992**, *44*, 245−255.

Dolci, M.; Navissano, G.; Gay, G.; Eynard, I. Impiego di esteri dell'acido 1-naftilacetico in viticoltura (Use of 1-naphthylacetic acid esters in viticulture). *Ann. Accad. Agric. Torino* **1993**, *135*, 87−94.

Dolci, M.; Navissano, G.; Gay, G.; Eynard, I. Attività su vite di esteri dell'acido 1-naftilacetico (Esters of 1-naphthylacetic acid applied to grapevine). *Atti XI Conv. SICA*, Cremona, Sept 21−23, 1993; Patren: Bologna, 1994; pp 242−247.

Eynard, I.; Gay, G.; Occelli, P.; Dolci, M.; Martini, A. Effects of different NAA derivatives for suckering control in grapevine. *Acta Hortic.* **1986a**, *179*, 289−290.

Eynard, I.; Gay, G.; Vallania, R.; Occelli, P.; Botta, R.; Dolci, M.; Martini, A. Control of sucker growth on *Vitis vinifera* cv Merlot with NAA derivatives. *Vitis* **1986b**, *25*, 169−177.

Forlani, M.; Di Vaio, C. Impiego dell'NAA per il controllo della crescita dei succhioni di vite (NAA used for sucker growth control in grapevine). *L'Inform. Agr.* **1990**, *46* (15), 105−106.

Little, T. M.; Hill, F. G. *Agricultural Experimental Design and Analysis*; Wiley: New York, 1978.

Lownds, N. K.; Leon, J. M.; Bukovac, M. I. Effect of surfactants on foliar penetration of NAA and NAA-induced ethylene evolution in cowpea. *J. Am. Soc. Hortic. Sci.* **1987**, *112*, 554−560.

Morris, E. M.; Cawthon, D. L. Control of trunk shoots on "Concord" grapevines (*Vitis labrusca* L.) with naphthaleneacetic acid. *HortScience* **1981**, *16*, 321−322.

Reynolds, A. G.; Contrell, A. C.; Wardle, D. A.; Gaunce, A. P. NAA and Paclobutrazol control grapevine suckers: vine performance and fruit tissue residues. *HortScience* **1991**, *26*, 1286−1287.

Received for review March 27, 1998. Revised manuscript received November 20, 1998. Accepted November 23, 1998.

JF980316E