

4-METHYL-5-NONANOL (FERRUGINEOL) AS AN AGGREGATION PHEROMONE OF THE COCONUT PEST, *RHYNCHOPHORUS FERRUGINEUS* F. (COLEOPTERA: CURCULIONIDAE): SYNTHESIS AND USE IN A PRELIMINARY FIELD ASSAY

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Abstract: 4-Methyl-5-nonanol (ferrugineol), the more attractive component of the aggregation pheromone of *Rhynchophorus ferrugineus* F. (Coleoptera: Curculionidae) was synthesized by a Grignard reaction with butylmagnesiumbromide and 2-methyl-1-pentanal. Oxidation of 2-methyl-1-pentanol in pyridinium chlorochromate was used to obtain 2-methyl-1-pentanal. The overall yield of the synthesis from 2-methyl-1-pentanol was 61%. At a release rate of 0.38 ± 0.08 mg synthetic ferrugineol per day from capillaries suspended in bucket traps filled with soap water, significantly more weevils were caught compared to a control trap (0.23 ± 0.04 weevils/trap/day vs 0.00 weevils/trap/day respectively) in the field. Significant differences were not observed between male and female trap catches using ferrugineol as a bait (0.12 ± 0.02 /trap/day and 0.11 ± 0.01 /trap/day respectively). Ferrugineol remained attractive to weevils for at least 60 d. The weevil response to the bait was observed only between 1800-2000 and 0600-0800 h. In a comparative field assay of synthetic ferrugineol with the coconut bark steam distillate, a known attractant for the red weevil, ferrugineol attracted significantly more weevils than the latter (0.25 ± 0.12 weevils/trap/day vs 0.06 ± 0.04 weevils/trap/day, $p < 0.05$).

Keywords: Coconut pest, ferrugineol, field attractant, red weevil, *Rhynchophorus ferrugineus*.

INTRODUCTION

Recent studies on *Rhynchophorus* species suggest that an aggregation pheromone produced by males plays a substantial role in the colonization of susceptible palms.¹⁻³ Since 1991 five aggregation pheromones of *Rhynchophorus* sp. have been identified as methyl branched secondary alcohols of carbon lengths ranging from C-7 to C-9.^{1,4-6} Aggregation pheromones are more promising than sex pheromones for insect control using baited traps because both males and females are attracted to the former. *Rhynchophorus ferrugineus* F. (Coleoptera: Curculionidae), commonly known as the red weevil is a major pest on the coconut palm in Sri Lanka.⁷ Its detection and control has proved difficult.^{8,9} The male produced aggregation pheromone of *R. ferrugineus* was reported to be a mixture of 4-methyl-5 nonanol (ferrugineol) and 4-methyl-5-nonanone (ferrugineone) whose natural ratio has not been determined.⁴ Laboratory and field studies showed that the alcohol was the more attractive component. However the field activity of a mixture of ferrugineol and ferrugineone at a 10:1 ratio did not differ significantly from that of the individual ferrugineol. Increasing amounts of

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ferrugineone in ferrugineol reduced the weevil catches and therefore the function of ferrugineone in aggregation is not established.⁴ Low volatility, high field stability were other favourable factors for the field use of ferrugineol in preference to a mixture of ferrugineol and ferrugineone. The objective of the present work was to establish a suitable simple route for the synthesis of ferrugineol, and to investigate its use as an attractant in the field for the monitoring and control of red weevils in Sri Lanka.

METHODS AND MATERIALS

General: ¹H NMR and ¹³C NMR spectra were obtained on a Bruker ARX 500 instrument operating at 500 MHz and 125 MHz respectively. CDCl₃ was used as the solvent and tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on a Mattson galaxy FTIR 5000 instrument.

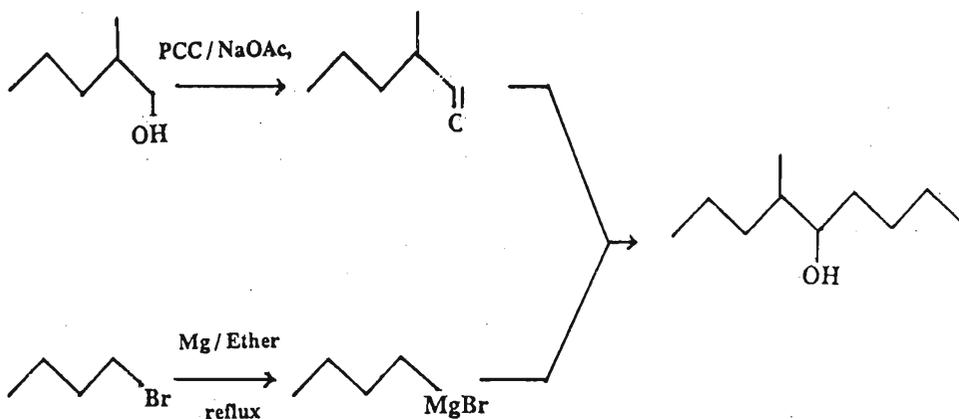


Figure 1: The synthesis of 4-methyl-5-nonanol.

Synthesis of 4-methyl-5-nonanol: 2-Methyl-1-pentanol, (10.00g, 57.86 mmol) in dichloromethane (20 ml) was added to a stirred suspension of pyridinium chlorochromate (PCC)¹⁰ (31.64g, 146.80 mmol) and sodium acetate (2.00g, 24.35 mmol) in dry dichloromethane (150 ml). The resulting dark brown reaction mixture was further stirred for 3 h at room temperature, at which time TLC indicated complete consumption of the starting alcohol. The mixture was filtered through a short column of silica gel. The filtrate was concentrated at 42°C and the crude product subjected to flash chromatography (silica gel, dichloromethane). The removal of dichloromethane in *vacuo* afforded 2-methyl-1-pentanal (7g, 71%) as a pale coloured liquid.

Butylmagnesiumbromide was prepared by the addition of freshly distilled butylbromide (13.7g, 100 mmol) to a stirred suspension of ether and magnesium turnings (2.4g, 100 mmol) at room temperature under a nitrogen atmosphere. A solution of 2-methyl-1-pentanal (5.00g, 50 mmol) in dry ether (25 ml) was

added dropwise *via* a syringe to a stirred solution of butylmagnesiumbromide in ether (50 ml). The resulting mixture was refluxed for 1 h, cooled to room temperature and treated with a saturated solution of NH_4Cl (50 ml). Three ether extractions (25 ml each) were made from the above aqueous solution, and the combined ether solution was dried over MgSO_4 . The removal of ether afforded a crude product which was subjected to flash chromatography (silica gel, ether/hexane 1:1 mixture) and 4-methyl-5-nonanol was obtained in 86% yield (6.8g).

Field experiments: Synthetic 4-methyl-5-nonanol was loaded into capillary tubes (diam 1.5 mm), 22 mg each as a neat liquid. The rate of evaporation of above compound was determined gravimetrically ($n=4$) at 24 h intervals for five days. Open plastic buckets (5 l, 21 cm diam, 17 cm height) filled with soap water were used as traps. Each capillary (diam. 1.5 mm) filled with the test compound was placed inside an open glass vial (2 ml) and the vial suspended on the handle of the bucket just above the water level. The traps 30 m apart were attached at 1.6 m height to coconut palms in a random manner. In these traps the weevils searching for the bait fell into the bucket where they were drowned easily in soap water. Six fields in the Districts of Gampaha (Kadawata, Waragoda, Dalugama) and Kurunegala (Kawdawatta, Uhumeeya, Nikaweratiya) were used and six replicates were run in each field. Empty capillaries were used as controls in these experiments. The weevil catch was noted daily in all traps and the experiments were conducted from 4th to 18th March, 1994. The time dependent response of the weevil was noted at Waragoda fields where the trap catch was registered every 2 h during the day for six days. The experiments at Waragoda fields were extended till 4th May 1994 and the weevil catch was registered daily (Fig. 2). Baits were not replaced until the completion of the experiment. The data were analyzed by Student's *t*-test or ANOVA and Scheffe's test as desired.

For comparing ferrugineol and steam distillate as lures the concentrated steam distillate of the coconut bark (22 mg) prepared by a previously described method¹¹ was loaded into capillaries. Empty capillaries were used as controls. Traps baited with the steam distillate, ferrugineol and controls were hung in Kadawata and Waragoda fields as described before. The trap catch was noted daily from 5th to 19th December 1994.

RESULTS

Spectral characteristics of the synthetic intermediates and ferrugineol were as follows:

2-Methyl-1-pentanal

$^1\text{H NMR}$ δ : 0.93 (t, $J=7\text{Hz}$, 3H), 1.09(d, $J=7\text{Hz}$, 3H), 1.34-1.39 (m,3H), 1.69-1.70 (m, 1H), 9.62 (d, $J=2\text{Hz}$,1H) ppm

$^{13}\text{C NMR}$ δ : 13.19, 13.94, 20.04, 32.62, 46.02, 205.13 ppm

IR (neat) ν : 2961, 2935, 2875, 1709, 1466, 1181, 1148 cm^{-1}

4-Methyl-5-nonanol (ferrugineol)

$^1\text{H NMR}$ δ : 1.00 (m,9H), 1.20-1.60(m,11H), 3.40-3.55 (2m,1H) ppm.

$^{13}\text{C NMR}$ δ : 13.49, 14.00, 14.25, 14.30, 15.18, 20.34, 22.76, 22.77, 28.32, 28.46, 33.04, 34.15, 35.60, 37.90, 38.55, 75.11, 75.97 ppm

IR (neat) ν : 3366, 2958, 2932, 2872, 1465, 1379, 1144, 1117, 1015, 976 cm^{-1}

MS (m/z) : 156 (5%), 114(38%), 85(100%), 71(58%), 57(55%).

Purity of ferrugineol was 98% by GLC (capillary column, DB-5 stationary phase, temp. pr. 60°C (5min.) 60 \rightarrow 240°C at 12°C/min).

Field Assay

Ferrugineol was released from capillaries at a rate of 0.38 ± 0.08 mg/24h (range 0.3-0.5 mg/24h) and the coconut bark steam distillate at a rate of 0.45 ± 0.14 mg/24h (range 0.31-0.60 mg/24h) at a field temperature range of 30-32°C. The weevils were found dead inside traps 4-5 h after falling into the trap. The mean male and female catches for the ferrugineol bait per trap/day were, 0.12 ± 0.01 and 0.11 ± 0.02 respectively, and these values did not differ significantly ($p > 0.05$, Student's t-test). The data for males and females were therefore pooled for subsequent analysis.

Table 1: Field assay of ferrugineol as lure for *R. ferrugineus*.

Field	Total weevil capture/6 traps/14 days	
	Ferrugineol	Control
1. Dalugama	19	00
2. Kadawata	24	00
3. Waragoda	23	00
4. Uhumeeya	14	00
5. Nikaweratiya	17	00
6. Kawdawatta	19	00
Total	116	00
Mean (Weevils/trap/day) (\pm SD)	0.23 (± 0.04)	00

Run 4th to 18th March 1994, 22 mg of ferrugineol was used in a capillary.

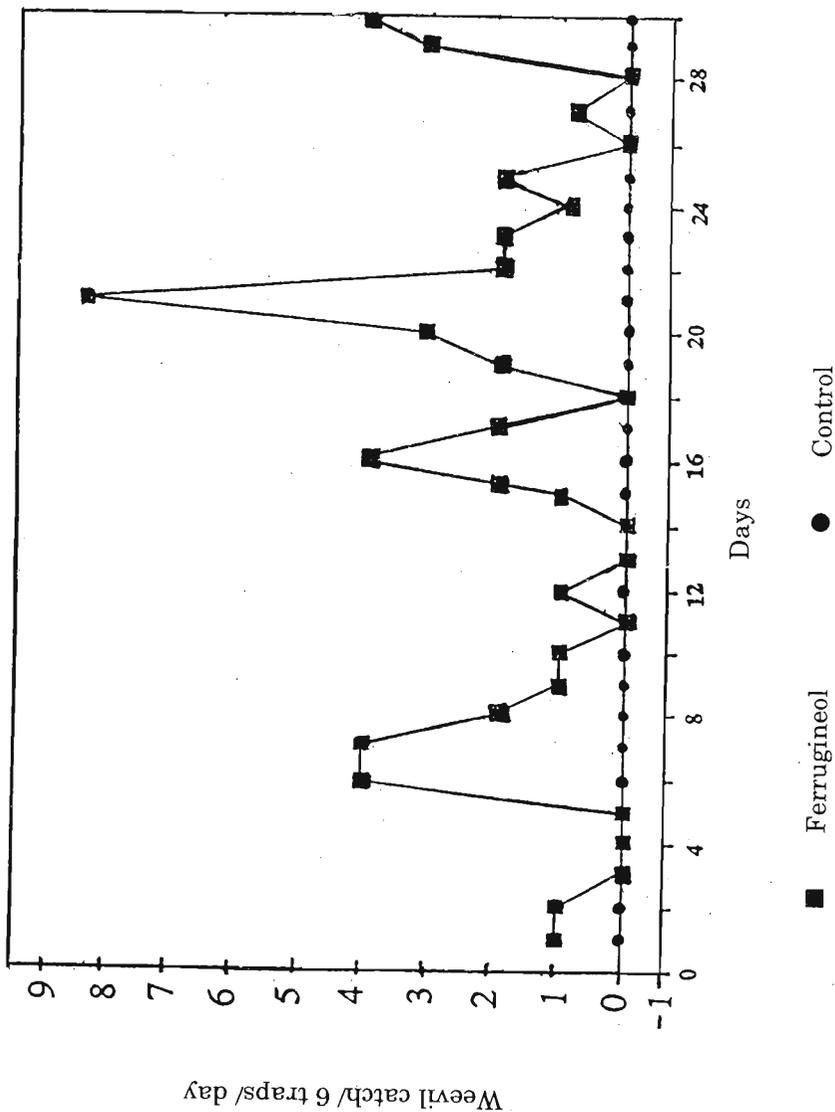


Figure 2: Part of the daily response profile of *R. ferrugineus* to ferrugineol over 60 days. Run 4th March to 4th May, 1994, at Waragoda (Gampaha District).

The weevil catch in the ferrugineol baited and control traps are presented in Table 1. The daily response of the red weevil to ferrugineol is shown in Fig 2. The mean trap catch observed was more or less uniform and the bait remained active for a period of 60 days during which the observations were made. The time dependent attraction of the weevils to the bait revealed that the weevils were attracted to the traps only between 1800-2000 h and 0600-0800 h and a mean number of 7.3 ± 1.5 and 4.0 ± 0.9 weevils/trap respectively were caught for an experimental period of six days.

In a comparison of the activities of ferrugineol and the steam distillate in the field, the former was more effective under the same field conditions (Table 2).

Table 2: Field experiments with ferrugineol vs. the coconut bark steam distillate lure for *R. ferrugineus*.

Field	Total weevil capture/6 traps/ 14 days		
	Ferrugineol	Coconut bark steam distillate	Control
1. Kadawata	24	08	00
2. Waragoda	20	05	00
Total	44	13	00
Mean (Weevils/trap/day) (\pm SD)	0.25 ^a (\pm 0.11)	0.06 ^b (\pm 0.05)	00 ^c

Run December 5th to 19th, 1994; 20 mg of ferrugineol and coconut bark steam distillate as the baits and empty capillary as the blank.

^{a,b,c} Means followed by different superscript letters are significantly different ($p < 0.05$, ANOVA, Scheffe's test).

DISCUSSION

4-Methyl-5-nonanol has been synthesized by a modification of an earlier method.⁴ The alkylation of 2-methyl-1-pentanal was achieved in 84% yield by a conveniently prepared butylmagnesiumbromide and the use of highly sensitive butyllithium was avoided in the present method. The overall yield of this simple route was 61% and this could be adapted to synthesize ferrugineol on a large scale.

The attraction of *Rhynchophorus* species to volatiles from damaged host palms is well known.^{1,5,13} In a laboratory assay *R. ferrugineus* was shown to be attracted to a steam distillate of the coconut bark.¹² However weevil catches for palm wood baited traps have been low.¹

The use of aggregation pheromones as field attractants for *Rhynchophorus* spp. is not yet established. Of the five aggregation pheromones identified^{1,4-6} in *Rhynchophorus*, three^{1,4} have been tested in the field. The synthetic aggregation pheromone in combination with freshly cut palm wood pieces have been better field attractants for palm weevils than the individual attractants.¹⁻⁴ The reason for this was hypothesized¹ as follows. The weevils' aggregation pheromone is the long range attractant and the host palm volatiles provide the short range guidance for the weevils' successful host finding. The aggregation pheromone and the palm volatiles as individual attractants have only previously been compared in *R. cruentatus*. The trap catches for the two attractants were low and not significantly different.¹ In the present study ferrugineol proved to be a better field attractant than the coconut bark steam distillate for *R. ferrugineus* at a release rate of the pheromone as low as 0.38 mg/day. Our trap is economical and operationally simple. The long field stability of ferrugineol is also evident by the continuous trap catch for the entire 60 days. Since trapped weevils are killed in the trap weevils do not contribute to the attraction and the weevil catch is therefore entirely due to ferrugineol. In other weevil traps the trapped weevils are not killed and fresh moistened coconut wood (2 kg) is used alone or in combination with the aggregation pheromone in a closed bucket^{1,4} or box.⁸ Weevils entering the trap through holes are unable to fly out. Such traps are costly and operationally not simple.

Fresh coconut wood for enhancing the attraction of ferrugineol was not used by us for economical and practical reasons. In a large coconut estate, weekly replacement of the fresh coconut is difficult. Instead the use of another chemical attractant of the red weevil in combination with ferrugineol for the enhanced attraction would be ideal keeping the simplicity of the present trap intact. Fermented coconut sap (toddy) and some of its constituents,¹⁴ some monoterpene alcohols¹⁵ etc. have already been reported as attractants for the red weevil and may be investigated with the view of improving the weevil catch of ferrugineol baited traps.

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