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Synthesis of substituted benzyl 2-methyl-2-phenylpropyl ethers and their moth-proofing activity on wool against larvae of *Anthrenus fasciatus*

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Abstract: Synthesis of new moth-proofing agents is necessary to overcome the damage caused by clothes moths and carpet beetles to hosiery and upholstery. In the present paper substituted benzyl 2-methyl-2-phenylpropyl ethers were synthesised and evaluated for moth-proofing activity. Two compounds were found to provide protection against larvae of *Anthrenus fasciatus* at levels of 1.0 and 10 g kg^{-1} respectively. The introduction of a methyl group in the *para* position of the benzene ring attached to C$_2$ of the 2-methylpropyl chain (ring A) increased moth-proofing activity. The introduction of a phenoxy ring at the *meta* position of the benzyl nucleus (ring B) also increased activity, while the presence of a nitro group on the benzyl nucleus (ring B) decreased activity.

Keywords: benzyl propyl ether; wool; *Anthrenus fasciatus*; moth-proofing

1 INTRODUCTION

Clothes moth and carpet beetles cause damage worth millions of dollars annually to clothing, rugs and upholstery. There is therefore great demand for insecticidal protection of these articles. Dieldrin provided a low-cost treatment for wool for many years,[1,2] but continuous extensive use of this single product against moth larvae resulted in moth resistance and it has been phased out because of this and for environmental reasons. Continuous research over the last decade has so far failed to locate any suitable moth-proofing agents for industrial use with the same cost-effectiveness originally enjoyed by dieldrin. Recent investigations[3–7] have revealed synthetic pyrethroids such as permethrin to be promising compounds for the moth-proofing of wool, but they are expensive.

Other insect-resistant formulations contain polychlorodiphenyl ethers, e g Eulan WA new, Eulan U$_{33}$ and Mitin LP based on polychlorodiphenyl ethers or polychloro-2-(chloromethylsulphonamido)diphenyl ethers (PCSD) as active ingredients. All these formulations[8] are based on chlorinated hydrocarbons. Currently around 200 tons of such moth-proofing formulations, representing more than 20 tons of various active ingredients, are used per year in the UK, treating around 45 million kilograms of wool. World-wide, around 230 million kilograms of wool are given an insect-resisting treatment.[9] Continuous discharge from each dye bath provides significant toxic loads to sewage treatment systems and associated down-stream river areas. If this method of application is to be acceptable in the future it must involve the application of insecticides which have low mammalian toxicity and are biodegradable with a very low hazard to aquatic organisms of all kinds.

Fortunately there is a growing awareness in the agricultural chemical industry that there are market opportunities for synthetic pyrethroids with much lower toxicities to aquatic organisms than those highly active compounds that were developed in the 1970s and there have been trends in recent years towards compounds that are environmentally less hazardous.[10] Therefore there is a need for developing moth-proofing preparations free from chlorinated structures and having compounds which have low toxicity to mammals and good biodegradability. As mentioned earlier, following continuous use of a single product in moth-proofing, insects have a tendency to develop resistance to the insecticide, and hence continuous search for new insecticides for moth-proofing is essential, and this requires regular work on the synthetic insecticidal chemistry.

The insecticidal activity of a new generation pyrethroids pesticide, MTI 500,[11] is due to a benzyl ether group and a gem dimethyl structure. A series of benzyl 2-methyl-2-phenylpropyl ethers of similar structure to this have been synthesised and their

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moth-proofing activity on wool against larvae of *Anthrenus fasciatus* evaluated.

2 EXPERIMENTAL METHODS

2.1 General

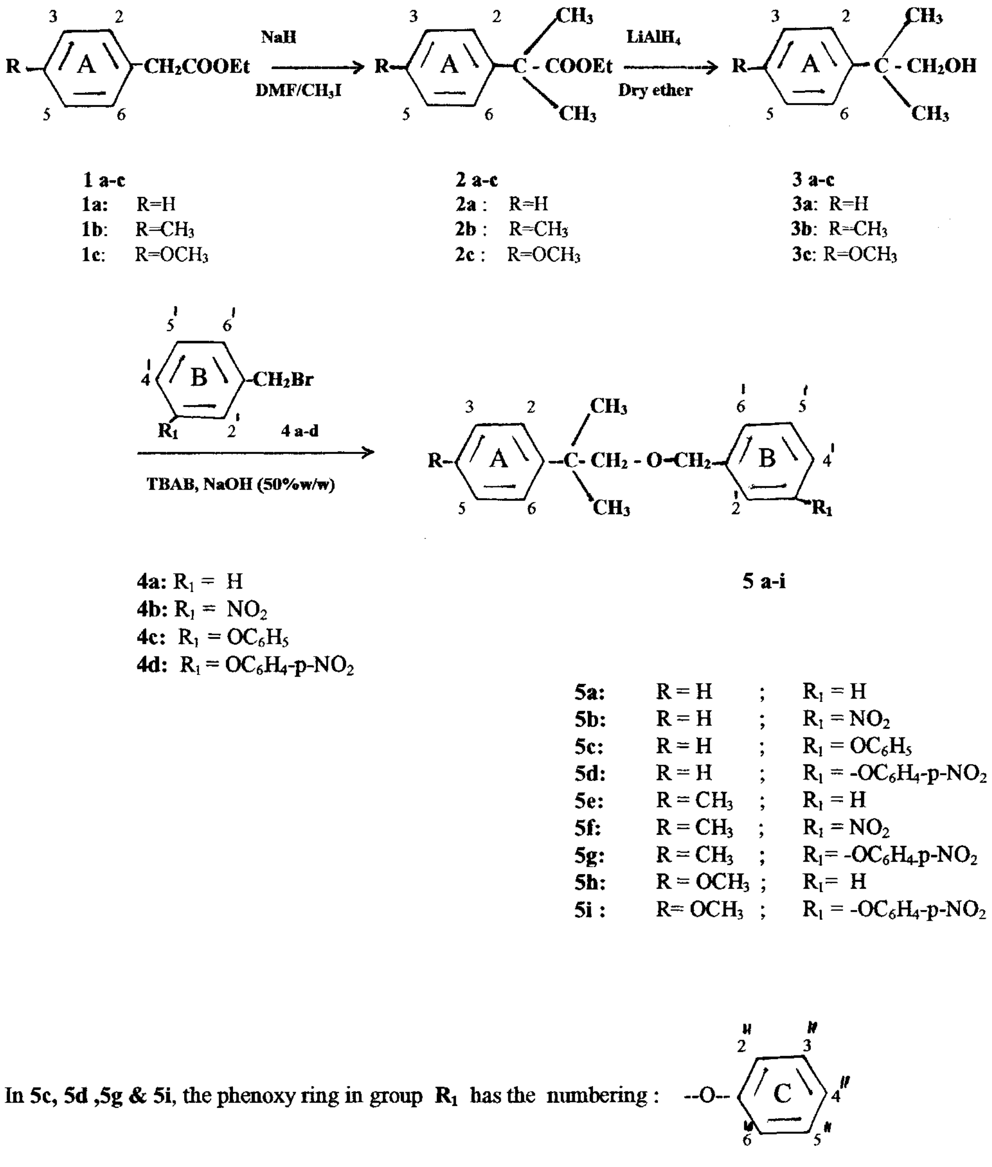
UV spectra were taken on a GBC UV Vis. 918 Spectrophotometer in methanol solution. IR spectra were taken on a Perkin Elmer Spectrophotometer. [^{1}H] NMR spectra were taken on a Varian VXR 300 MHz NMR instrument in deuterochloroform. Mass spectra were taken on a Fison GCMS MD 800 instrument. Melting points were taken in a Thiele tube and are uncorrected. Boiling points were taken under vacuum in a distillation tube.

2.2 Synthesis

The general procedures adopted for the synthesis of different compounds are described below.

2.2.1 *Ethyl 2-methyl-2-phenylpropionate (Fig 1; **2a**)*

To a stirred and cooled (10 °C) suspension of NaH (18.4 g, 0.4 mole, dispersion in mineral oil) in dry dimethylformamide (DMF) was added methyl iodide (56.4 g, 0.4 mole) and the mixture was kept under a slow stream of nitrogen. Subsequently ethyl phenyl acetate **1a** (16.4 g, 0.1 mole) was added drop-wise to the reaction mixture for 1 h. The hydrogen evolved was allowed to escape through a mercury seal and stirring continued at 10 °C for 2 h. The reaction mixture was allowed to come to room temperature and further stirred for 14 h, poured over hydrochloric acid (2 M, 500 ml) and extracted thrice with ether (3 × 40 ml). The combined ether layer was washed with water, dried over anhydrous sodium sulfate and distilled to remove the solvent. The residue was distilled under reduced pressure (10 mm), the fraction distilling between 95 and 105 °C giving a pale yellow liquid of ethyl 2-methyl-2-phenylpropionate **2a** (10 g; 52%).



	R	R₁
5a:	R = H	R_1 = H
5b:	R = H	R_1 = NO_2
5c:	R = H	R_1 = OC_6H_5
5d:	R = H	R_1 = -OC_6H_4-p-NO_2
5e:	R = CH_3	R_1 = H
5f:	R = CH_3	R_1 = NO_2
5g:	R = CH_3	R_1 = -OC_6H_4-p-NO_2
5h:	R = OCH_3	R_1 = H
5i :	R = OCH_3	R_1 = -OC_6H_4-p-NO_2

Figure 1. Syntheses and structures of compounds discussed.

The residue in the flask was dissolved in ether. The ether layer on extraction with sodium hydrogen carbonate solution and neutralisation with dilute hydrochloric acid afforded 2-methyl-2-phenylpropionic acid, m p 75–77 °C, yield 4.75 g (28%).

*Ethyl 2-methyl-2-phenylpropionate **2a**.* UV nm: 204.8 (log ∈, 3.9268) IR (neat) cm^{-1}: 1730 (C=O), 1600, 1498 (phenyl), 1460, 1445 (CH_2), 1385, 1365 (gem $(CH_3)_2$), 1250, 1140, 1025 (C—O—C), 765 and 690 (mono-substituted phenyl); [^{1}H] NMR: δ 1.15 (3H, t, CH_3), 1.60 (6H, s, gem dimethyl), 4.20 (2H, q, CH_2), 7.45 (5H, m, benzene protons); Mass spectrum: M^+ 192 and fragments *m/z* 119 ($C_6H_5C^+(CH_3)_2$), 91 $(C_6H_5CH_2)^+$ and 77 $(C_6H_5)^+$.

2.2.2 *2-Methyl-2-phenylpropanol (**3a**)*

To a stirred and cooled suspension of lithium aluminium hydride (1.6 g, 0.42 mole), in dry ether (300 ml) was added a solution of ethyl 2-methyl-2-phenylpropionate **2a** (8.2 g, 0.42 mole) in dry ether (40 ml) slowly through a dropping funnel to ensure mild reflux. After the addition the mixture was heated under reflux with stirring for 2 h. It was cooled to 0 °C and ethyl acetate (5 ml) was added drop-wise to decompose the excess of lithium aluminium hydride. The organic layer was decanted and the solid residue diluted with water and extracted with ether (3 × 20 ml). The combined ether layer was washed with water, dried over anhydrous sodium sulfate and distilled to remove solvent. The residual liquid was purified by distillation under reduced pressure, bp 105–110 °C/10 mm, to yield 2-methyl-2-phenylpropanol **3a** (5.8 g; 89%). UV nm: 204.8 (log ∈, 3.7916); IR (neat) cm^{-1}: 3375 (—OH), 1602, 1498 (phenyl), 1470, 1450 (—CH_2), 1390, 1360 (gem $(CH_3)_2$), 1045 (C—O), 760 and 690 (mono-substituted phenyl); [^{1}H] NMR: δ 1.4 (6H, s, gem dimethyl), 3.6 (2H, s, —CH_2), 7.5 (5H, m, benzene protons; Mass spectrum: M^+ 150 and fragments at *m/z* 119 ($C_6H_5C^+(CH_3)_2$), 91 $(C_6H_5CH_2)^+$ and 77 $(C_6H_5)^+$.

2.2.3 *Benzyl bromide **4a***

Toluene(1.84 g, 0.02 mole), *N*-bromosuccinimide (3.56 g, 0.02 mole) and 2,2′-azobisisobutyronitrile (0.1 g, 0.00061 mole) were refluxed in dry carbon tetrachloride (100 ml) for 2 h, in the presence of light. The solution was cooled and filtered to remove the precipitated succinimide. Carbon tetrachloride was removed by distillation under reduced pressure. The residual liquid was distilled at 10 mm. The fraction distilling between 105 and 107 °C yielded 2.66 g of pure benzyl bromide (78%). Mass spectrum: M^+170 and fragments at *m/z* 91$(C_6H_5CH_2)^+$ and 65$(C_5H_5)^+$.

2.2.4 *Benzyl 2-methyl-2-phenylpropyl ether **5a***

2-Methyl-2-phenylpropanol 3a (1.65 g, 0.011 mole), benzyl bromide 4a (1.7 g, 0.01 mole), tetrabutyl ammonium bromide (TBAB) (0.35 g, 0.001 mole) and aqueous sodium hydroxide (500 g kg^{-1}; 15 g) were taken up in toluene (20 ml) and vigorously stirred at room temp, for 1 h, and then at 80 °C for 3 h. The reaction mixture was cooled to room temp, diluted with water (20 ml) and the organic layer was separated. The aqueous layer was extracted with toluene (3 × 20 ml). The combined organic extract was washed with water, dried with anhydrous sodium sulfate and distilled under reduced pressure to remove toluene. The crude product was purified by column chromatography on silica gel (200 mesh) using toluene + hexane (1+1 by volume) to give benzyl 2-methyl-2-phenylpropyl ether (**5a**) bp 190–195 °C/10 mm, (2.0 g; 83.3%). UV nm: 206.1 (log ∈, 4.1573); IR (neat) cm^{-1}: 2950, 2850 (CH_2), 1600 (phenyl), 1475, 1450, (CH_2), 1380, 1360 (gem$(CH_3)_2$), 1210 (C—O—C), 1100 (CH_2), 1025 (C—O—C), 730, 690 (mono-substituted phenyl); [^{1}H] NMR: δ 1.35 (6H, s, gem dimethyl), 3.45 (2H, s, —C—CH_2—O), 4.47 (2H, s, O—CH_2-Ar), 7.15 to 7.41 (10H, m, benzene protons); Mass spectrum: M^+ 240 and fragments ions at *m/z* 119 ($C_6H_5C^+(CH_3)_2$), 91 $(C_6H_5CH_2)^+$ and 77 $(C_6H_5)^+$.

2.2.5 *3-(4-Nitrophenoxy)benzyl bromide **4d***

m-Cresol (1.38 g, 0.1 mole), 4-chloronitrobenzene (1.57 g, 0.01 mole) and anhydrous potassium carbonate (1.38 g, 0.1 mole) were refluxed in DMF (20 ml) for 2 h. Dimethylformamide was removed under reduced pressure, water (50 ml) added, the reaction mass was treated with sodium hydroxide solution (50 g $litre^{-1}$; 10 ml) and extracted with ether (3 × 20 ml). The combined ether layer was washed with water and dried over anhydrous sodium sulfate. The ether was removed by distillation. The residue was purified by column chromatography on silica gel (200 mesh) using toluene + hexane (1 + 1 by volume) as eluent. 3-(4-Nitrophenoxy)toluene was crystallised from ethanol into needle-shaped crystals, mp 51 °C, (1.2 g; 52.6%). 3-(4-Nitrophenoxy)toluene (1.03 g, 0.0045 mole), *N*-bromosuccinimide (0.95 g; 0.0053 mole) and benzoyl peroxide (2 mg,) were refluxed in dry carbon tetrachloride (100 ml) for 2 h in the presence of light. The solution was cooled to room temperature and filtered to remove the precipitated succinimide. Carbon tetrachloride was removed under reduced pressure. The solid mass in the flask, on fractional crystallisation, yielded 3-(4-nitrophenoxy)benzyl bromide (**4d**), mp 80–81 °C (alcohol), (0.55 g; 40%). The mother liquor was concentrated to crystallise most of the 3-(4-nitrophenoxy)benzyl bromide, which was filtered. Further evaporation of the mother liquor on a water bath and crystallisation from alcohol afforded a by-product, 2-bromo-5-(4-nitrophenoxy)toluene, mp 91–92 °C, (0.41 g; 29.6%).

When the above procedure of bromination was modified by using 2,2′-azobisisobutyronitrile (0.022 g, 0.000137 mole) as catalyst, 3-(4-nitrophenoxy)benzyl bromide was obtained as a single product in 80% yield.

3-(4-nitrophenoxy)benzyl bromide **4d** UV nm: 204.8 (log ∈, 4.4538), 300.8 (log ∈ 4.0374); IR (neat) cm^{-1}: 3060 (CH str of Ph), 2990 (CH_2), 1580 (phenyl), 1590, 1360 (NO_2), 1490, 1470 (CH def. Ph), 1250 (C—O—C Aryl), 900, 750 (*m*-disubstituted phenyl): [^{1}H]NMR: δ 4.43 (2H, s, —CH_2Br), 7.02 and 7.05 (2H, d, C_2''—H & C_6''—H of C ring, J = 9.34 Hz), 7.02 (1H, d, C_4'—H of B ring), 7.14 (1H, s, C_2'—H of B ring) 7.26(1H, d, C_6'—H of B ring), 7.40 (1H, t, C_5'—H of B ring), 8.20, 8.24 (2H, d, C_3''—H & C_5''—H of C ring, J = 9.34 Hz); Mass spectrum: M$^+$ 307, and fragment ions at *m*/*z* 228 (p-NO_2—C_6H_4—O-m-$C_6H_4CH_2$)$^+$, 181 (C_6H_4—O-m-C_6H_4CH)$^+$, 89 (C_6H_4CH)$^+$, 76 (C_6H_4)$^+$ and 63(C_5H_3)$^+$.

2-bromo-5-(4-nitrophenoxy)toluene: UV nm: 204.8 (log ∈, 4.4457), 300.8 (log ∈, 3.9943); IR (neat) cm^{-1}: 3080 (—CH str of Ph), 2990 (CH_2), 1610, 1585, (phenyl), 1510, 1340 (NO_2), 1240 (C—O—C), 825 (*p*-disubstituted phenyl); [^{1}H]NMR: δ 2.4 (3H, s, methyl), 6.76 to 8.26 (7H, m, benzene protons) Mass spectrum: M$^+$ 307 and fragments ions at *m*/*z* 277 (O—C_6H_4—O-m-$C_6H_3BrCH_3$)$^+$, 198 (O—C_6H_4—O-m-$C_6H_3CH_3$)$^+$ 182 (C_6H_4—O-m-$C_6H_3CH_3$)$^+$, 89 ($C_6H_3CH_2$)$^+$, and 76 (C_6H_4)$^+$.

2.2.6 3-(4-Nitrophenoxy)benzyl 2-methyl-2-phenylpropyl ether, ***5d***

2-Methyl-2-phenylpropanol **3a** (1.65 g, 0.011 mole), 3-(4-nitrophenoxy)benzyl bromide **4d** (3.38 g, 0.01 mole), tetrabutyl ammonium bromide (TBAB) (0.35 g, 0.001 mole) and aqueous sodium hydroxide (500 g kg^{-1}; 15 g) were taken in toluene (20 ml) and vigorously stirred at room temperature for 1 h and then at 80 °C for 3 h. The reaction mixture when worked up as described for **5a** yielded 3-(4-nitrophenoxy)benzyl 2-methyl-2-phenyl propyl ether **5d**, bp 270–275 °C/1 mm, (2.15 g, 57.0%). UV nm: 204.8 (log ∈, 4.3909), 300.8 (log ∈, 3.7553); IR (neat) cm^{-1}: 3060 (CH str of Ph), 2962, 2928 and 2856 (CH_2), 1581, 1343 (NO_2), 1488, 1445(CH_2), 1251 (C—O—C Aryl), 1111 (C—O—C aliphatic), 861, 751 & 699 (substituted benzene) [^{1}H]NMR: δ 1.35 (6H, s, gem dimethyl), 3.48 (2H, s, O—CH_2), 4.45 (2H, s, O—CH_2—Ar), 6.95 (1H, s, C_2'—H of B ring), 6.98(1H, d, C_4'—H of B ring), 7.01, 7.02(2H, d, C_2''—H & C_6''—H of C ring), 7.08 to 7.14 (1H, d, C_6'—H of B ring), 7.25 (3H, t, C_3—H, C_4—H & C_5—H of A ring), 7.35 & 7.37 (3H, t, C_5'-H of B ring & C_2—H & C_6—H of A ring), 8.18 to 8.22 (2H, d, C_3''—H & C_5''—H of C ring); Mass spectrum: M$^+$ 377 and fragments ions at *m*/*z* 228 (p-NO_2—C_6H_4—O-m-$C_6H_4CH_2$)$^+$, 182 (C_6H_4—O-m-$C_6H_4CH_2$)$^+$, 119 (C_6H_5—C^+(CH_3)$_2$), 91 ($C_6H_5CH_2$)$^+$ and 76 (C_6H_4)$^+$.

2.3 Moth-proofing activity

The compounds dissolved in acetone were impregnated on an all-wool serge fabric at 1.0, 5.0 and 10 g kg^{-1}. The fabric samples were air-dried to remove acetone and the dried samples were taken for moth-proofing performance test. The untreated fabric as negative control, permethrin (1.0 g kg^{-1}) treated fabric as positive control, and fabric treated with a corresponding amount of acetone used for dilution were also taken for feeding damage studies. The feeding tests were conducted according to the test procedure of the International Organisations for Standardisation (ISO 3998) for evaluation of the resistance of textiles to the larvae of *Anthrenus fasciatus*.[12] Four discs of about 4 cm diameter and known weight were cut from fabric and placed in contact with 15 *A fasciatus* larvae in glass Petri dishes (50 mm × 18 mm) with a perforated aluminium lid for 14 days in a controlled atmosphere, 27 (±1) °C and 60 (±5)% relative humidity in a dark cabinet. All the fabrics were assessed for damage by visual observation of the extent of cropping, hole formation and by determination of weight loss. The tests were carried out in duplicate.

3 RESULTS & DISCUSSION

3.1 Synthesis

The present paper deals with the synthesis of benzyl ethers which incorporate two structural features, a gem dimethyl moiety and a dibenzyl ether group, which are present in the synthetic pyrethroid MTI 500.[11] Incorporation of these structural features was prompted by a literature report which describes benzyl ethers containing a gem dimethyl group having potential insecticidal activity.[13,14] The insecticidal activity of natural pyrethrins and potent pyrethroids mainly depends on the presence of a gem dimethyl group at the C_2 position of the cyclopropane ring.[15] A number of diphenyl ether compounds have also been reported to have pesticidal and moth-proofing activity.[16,17]

In view of these findings, substituted benzyl 2-methyl-2-phenylpropyl ethers **5a–i** have been synthesised and evaluated for moth-proofing activity. Ethyl phenyl acetates **1a–c** were prepared by esterification of substituted phenyl acetic acids which were obtained from corresponding acetophenones by the Willgerodt reaction.[18] Substituted 2-methyl-2-phenylpropanols **3a–c** were prepared by methylating the corresponding ethyl phenyl acetates **1a–c** in the presence of sodium hydride in dry dimethylformamide and reducing the subsequent products **2a–c** to the corresponding propanols **3a–c**.[19,20] Substituted benzyl bromides **4a–d** needed for condensation were prepared by bromination of the corresponding substituted toluenes using *N*-bromosuccinimide in the presence of 2,2′-azobisisobutyronitrile (AIBN) catalyst. Substituted benzyl 2-methyl-2-phenylpropyl ethers **5a–i** were prepared by the reaction of **3a–c** with **4a–d** under phase-transfer conditions in the presence of aqueous sodium hydroxide (500 g kg^{-1}) using tetrabutyl ammonium bromide (TBAB) catalyst. Compounds **5a–i** were purified by column chromatography. The characterisation data of substituted benzyl ethers are given in Table 1. The structures of the compounds were confirmed by elemental analyses, UV, IR, [^{1}H]NMR and Mass spectra.

Table 1. Characterisation data of substituted benzyl ethers **5a–i**

				Found (calculated) (%)		
Compound	*Boiling point (°C)*	*Yield (%)*	*Molar formula*	*Carbon*	*Hydrogen*	*Nitrogen*
5a	190–195[a]	71	$C_{17}H_{20}O$	84.50	8.70	–
				(85.00)	(8.33)	–
5b	250–252[a]	66.4	$C_{17}H_{19}NO_3$	71.48	6.64	4.88
				(71.58)	(6.60)	(4.91)
5c	245–250[a]	60	$C_{23}H_{24}O_2$	83.65	6.66	–
				(83.13)	(7.23)	–
5d	270–275[b]	57	$C_{23}H_{23}NO_4$	72.50	6.70	3.20
				(73.21)	(6.10)	(3.71)
5e	204–206[a]	68.4	$C_{18}H_{22}O$	84.86	8.74	–
				(85.04)	(8.66)	–
5f	245–250[a]	63.8	$C_{18}H_{21}NO_3$	72.56	7.26	4.07
				(72.24)	(7.02)	(4.68)
5g	285–290[b]	59.5	$C_{24}H_{25}NO_4$	74.00	5.90	3.80
				(73.65)	(6.39)	(3.58)
5h	200–202[b]	64.2	$C_{18}H_{22}O_2$	79.54	8.68	–
				(80.00)	(8.15)	–
5i	305–310[b]	74.5	$C_{24}H_{25}NO_5$	69.95	6.54	3.83
				(70.76)	(6.14)	(3.44)

[a] At 10 mm Hg.
[b] At 1 mm Hg.
All compounds are highly viscous.

3.2. Moth-proofing activity

The moth-proofing activity of the compounds **5a–i** is given in Table 2. The compounds **5c** and **5e** showed positive results above levels of 1.0 and 10 g kg^{-1} respectively.

3.3 Structure–activity relationships

Previous studies have shown that a number of active synthetic pyrethroids contain a gem dimethyl group adjacent to the phenyl ring and an ester or dibenzyl ether group. The recent insecticide MTI 500 has a gem dimethyl group adjacent to a *p*-ethoxyphenyl ring and an *m*-phenoxy substituent on the benzyl moiety. These structural features are mainly responsible for the activity of these compounds. The benzyl substituent could be modified by introduction of nitro, phenoxy, and *p*-nitrophenoxy groups at the meta position. The phenyl ring adjacent to the gem dimethyl group could be modified by introduction of methyl and methoxy groups. The compounds **5a–i**, having different substituents were studied for moth-proofing activity. (Table 2) Compound **5a** has no substitution on either phenyl ring, and the introduction of a nitro group in the *meta* position did not produce any significant increase in the moth-proofing activity, as is evident from the percentage feeding damage in **5b**.

The introduction of a *meta* phenoxy group on the benzyl ring (**5c**) led to moth-proofing activity at a level of 1.0 g kg^{-1} on the fabric weight. Further introduction of a nitro group on the phenoxy ring of **5c** gave **5d**, which showed a marked decrease in moth-proofing activity. Substitution of a methyl group in the phenyl ring adjacent to the gem dimethyl group in **5a** gave compound **5e**, which showed enhanced activity and has been found to be effective at 10 g kg^{-1} level. However the compounds **5f** and **5g** obtained by introduction of nitro and nitrophenoxy groups on the benzyl nucleus showed a decrease in moth-proofing activity. Similarly, compound **5h** containing a methoxy substituent on the phenyl ring adjacent to the gem dimethyl group showed increased insecticidal activity but could not provide adequate moth-proofing over 10 g kg^{-1} fabric weight level. The introduction of a nitrophenoxy group in the compound **5h**, giving compound **5i**, did not produce any increase in activity. In the standard moth-proofing test, compounds **5c** and **5e** provide moth-proofing properties to the fabric. However, all compounds synthesised reduced the feeding damage on the fabric specimen below 24.3% of that observed in case of untreated fabric, indicating positive insecticidal activity imparted to the fabric.

4 CONCLUSION

The application of substituted benzyl 2-methyl-2-phenylpropyl ethers **5a–i** to woollen fabric reduces feeding damage by the larvae of *Anthrenus fasciatus*. However, only compounds having a 4-methyl substituent on the phenyl ring adjacent to the gem dimethyl group (**5e**) or a phenoxy substituent (**5c**) in the benzyl ring of benzyl 2-methyl-2 phenylpropyl ether **5a** were found to provide moth-proofing protection to the wool. The presence of a phenoxy group at the benzyl ring was found to give more pronounced activity than that observed due to presence of a methyl group on the phenyl ring adjacent to gem dimethyl group.

Table 2. Moth-proofing activity of benzyl ethers **5a–i** on all-wool serge fabric

Compound	*Application rate (g kg^{-1} of fabric)*	*Mortality after 15 days*	*Feeding loss*		*Visual damage*[a]	*Proofed/not proofed*[b]	*Remarks*
			mg/% loss I	*mg/% loss II*			
5a	1.0	5, 7	60.9/24.2 ;	37.2/13.7	D/D	Not proofed	
	5.0	10, 10	2.5/1.0 ;	13.0/4.6	D/D	Not proofed	
	10	13, 13	8.6/3.32 ;	9.5/3.6	D/D	Not proofed	
5b	1.0	7, 6	36.2/13.3 ;	40.3/14.4	D/D	Not proofed	
	5.0	6, 3	31.9/12.3 ;	40.3/16.3	D/D	Not proofed	
	10	5, 4	19.3/6.5 ;	35.1/12.4	D/D	Not proofed	
5c	1.0	7, 10	12.0/2.7 ;	0.4/0.9	A/A	Proofed	Effective above 1 g kg^{-1} on fabric wt
	5.0	10, 13	Nil/Nil ;	Nil/Nil	A/A	Proofed	
	10	13, 15	Nil/Nil ;	Nil/Nil	A/A	Proofed	
5d	1.0	10,4	30.1/11.4 ;	44.6/16.8	D/D	Not proofed	
	5.0	3, 5	40.4/15.3 ;	28.2/10.9	D/D	Not proofed	
	10	7, 11	23.0/8.5 ;	23.7/8.8	D/D	Not proofed	
5e	1.0	7, 5	33.0/11.5 ;	50.4/18.4	D/D	Not proofed	Effective above 10 g kg^{-1} on fabric wt
	5.0	5, 6	12.0/4.5 ;	16.6/5.9	C/C	Not proofed	
	10	14, 12	8.1/2.96 ;	7.2/2.7	B/B	Border line	
5f	1.0	3, 3	55.0/18.8 ;	44.6/15.5	D/D	Not proofed	
	5.0	5, 3	34.2/12.1 ;	41.4/14.7	D/D	Not proofed	
	10	3, 6	46.9/16.7 ;	21.6/8.1	D/C	Not proofed	
5g	1.0	10,9	32.0/12.3 ;	27.0/10.1	D/D	Not proofed	
	5.0	12,8	5.4/2.0 ;	40.3/14.8	C/D	Not proofed	
	10	6, 3	20.3/7.7 ;	33.8/12.7	C/D	Not proofed	
5h	1.0	4, 3	52.1/17.4 ;	41.2/13.5	D/D	Not proofed	
	5.0	5, 9	28.0/9.9 ;	11.0/3.9	C/D	Not proofed	
	10	3, 3	26.7/9.7 ;	33.9/12.5	C/D	Not proofed	
5i	1.0	3, 2	50.4/17.9 ;	59.3/20.9	D/D	Not proofed	
	5.0	3, 3	32.3/10.9 ;	10.5/3.9	C/D	Not proofed	
	10	3, 3	32.5/11.6 ;	23.8/8.5	C/D	Not proofed	
Original untreated	(Negative control)	1, 1	48.5/16.7 ;	69.6/24.3	D/D	Not proofed	Fabric structure damaged
Blank fabric with acetone	–	3, 3	48.4/18.6 ;	3.2/11.7	D/D	Not proofed	Fabric structure damaged
Permethrin (1.0 g kg^{-1} treated	(Positive control)	14, 13	Nil/Nil ;	Nil/Nil	A/A	Proofed	No detectable damage

[a] A = no detectable damage, B = yarns or fibres partially severed, C = a few large or several small holes, yarns/fibres severed, D = several large holes.

[b] Proofed = no detectable damage; Not proofed = detectable damage.

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