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Ultrasound Assisted Synthesis of 5,9-Dimethylpentadecane and 5,9-Dimethylhexadecane – the Sex Pheromones of *Leucoptera coffeella*

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Abstract: Racemic 5,9-dimethylpentadecane and 5,9-dimethylhexadecane, the major and minor constituents, respectively, of the sex pheromone of *Leucoptera coffeella*, have been synthesized from citronellol in 56-58% overall yield through six steps. Ultrasound irradiation efficiently supported tosylation of alcohols (two steps) as well as the subsequent cross coupling reactions with the pertinent Grignard reagents (also two steps).

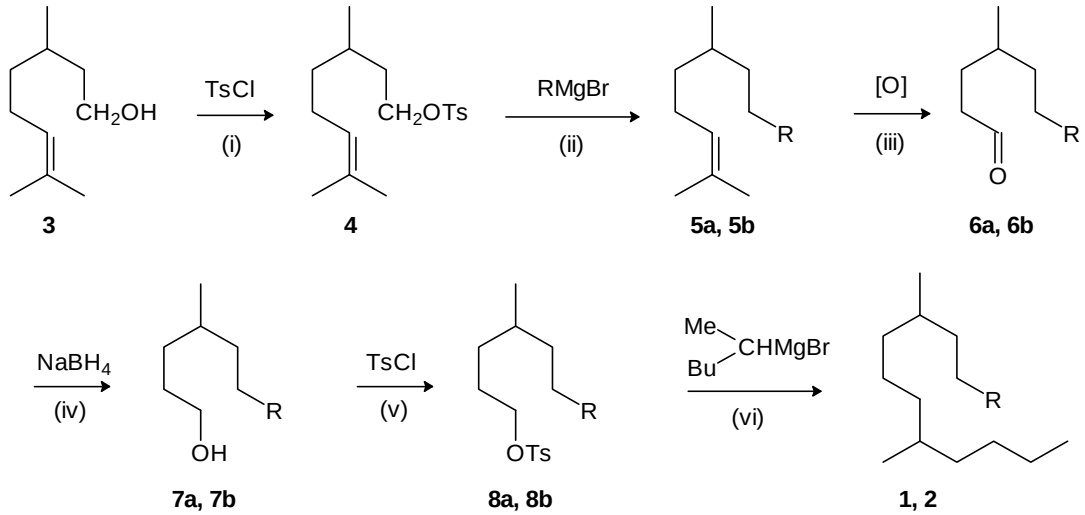
Keywords: 5,9-Dimethylpentadecane; 5,9-Dimethylhexadecane; Ultrasound irradiation; Pheromones; *Leucoptera coffeella*.

Introduction

Recent research has shown that several hydrocarbons with a 1,5-dimethyl skeleton are insect pheromones [1]. 5,9-Dimethylpentadecane (**1**) and 5,9-dimethylhexadecane (**2**) are known as the major and minor constituents, respectively, of the sex pheromone of *Leucoptera coffeella*, a pest of coffee trees [2]. Several ways of synthesizing **1** have been described. Stereoisomers of **1** were synthesized starting from (-)-isopulegol by Moreira and Correa [3] and from methyl (*R*)- and (*S*)-3-hydroxy-2-methylpropanoate by Kuwahara and co-workers [4]. Zarbin *et al*. carried out an unsymmetrical double Wittig olefination as the key reaction to obtain also a stereoisomeric mixture of **1** in a yield of 54% [5]. Using citronellol as the starting material, Liang *et al*. synthesized stereoisomeric mixtures of **1** as well as of **2** in yields of about 25% [6]. Using (R)-citronellol as the starting material, Poppe *et al*. synthesized **1** as a mixture of the (5S,9S) and (5R,9S) stereoisomeric molecules in a related way in an overall yield of 22% [7]. However, the stereochemistry of the natural pheromone is still undetermined [5]. Zarbin *et al*. [5] have tested the biological activity of a synthetic stereoisomeric mixture of **1**. Their field experiments showed, that it was highly attractive to *L. coffeella* males [5].

Ultrasonic irradiation has been found useful as support for quite a few organic reactions [8]. In this paper, we describe a new six-step synthetic route to **1** and **2** (as a mixture of stereoisomers) from citronellol (**3**) (see Scheme 1) in which ultrasound irradiation was used to support the tosylation and cross coupling reactions, which were used repeatedly (four out of six steps, see Scheme 1).

Scheme 1: Synthesis of 5,9-dimethylpentadecane (**1**) and 5,9-dimethylhexadecane (**2**).



a: R = *n*-C_4H_9; **b**: R = *n*-C_5H_{11}; **1**: R = *n*-C_4H_9; **2**: R = *n*-C_5H_{11}.

(i): Tosyl chloride, pyridine, $CHCl_3$, ultrasound; (ii): *n*-C_4H_9MgBr or *n*-$C_5H_{11}MgBr$, Li_2CuCl_4, THF, -78 ^oC, ultrasound; (iii): perphthalic acid, then HIO_4, THF; (iv): $NaBH_4$, MeOH; (v): the same as (i); (vi): BuMeCHMgBr, Li_2CuCl_4, THF, -78 ^oC, ultrasound.

Results and Discussion

Citronellol (**3**), an easily obtainable starting material [9], was tosylated to give the tosylate **4**, which subsequently was coupled with either *n*-butylmagnesium bromide or *n*-pentylmagnesium bromide to give the alkenes **5a** and **5b**, respectively. Upon oxidation, **5a** and **5b** gave the aldehydes **6a** and **6b**, respectively, which in turn were reduced into the corresponding alcohols **7a** and **7b** by $NaBH_4$. Repeated tosylations and cross coupling reactions converted the alcohols **7a** and **7b** into the hydrocarbons **1** and **2** via the tosylates **8a** and **8b** (Scheme 1).

The preparation of the alkyl tosylates **4, 8a** and **8b** were carried out following a Varma-like procedure [10]. According to Kabalka *et al*. [10], alkyl tosylates can be prepared from alcohols and *p*-toluenesulfonyl chloride, in the presence of pyridine, by stirring the reactants together in chloroform solution for 2.5-9.0 hours at 0 ^{o}C. In our procedure, the reactions were supported by ultrasound irradiation from an ultrasonic processor (steps i and v). The results of a series of experiments are shown in Tables 1 and 2.

Table 1: Preparation of the tosylate **4** under ultrasound irradiation.

Entry	3 : TsCl : pyridine (molar ratios)	Time (minutes)	Yield of 4 (%)
1	1:1:1	30	82
2	1:1:1	60	83
3	1:1:2	30	86
4	1:1:2	60	84
5	1:1.5:1	60	80
6	1:1.5:2	30	91
7	1:1.5:2	20	84
8	1:1.5:2	40	92
9	1:1.5:3	30	92
10	1:2:2	20	86
11	1:2:2	30	92

Table 2: Preparation of the tosylates **8a** and **8b** under ultrasound irradiation.

Entry	Tosylate	Time (minutes)	Yield (%)[a]
1	**8a**	30	74
2	**8a**	45	92
3	**8a**	60	93
4	**8b**	30	78
5	**8b**	45	91
6	**8b**	60	91

[a] **7a, 7b** : TsCl : pyridine = 1.0 : 1.5 : 2.0 (molar ratio).

p-Toluenesulfonyl chloride was added to the reaction solutions within a few minutes, *i.e.* not over an extended period, as described by Kabalka's group [10], and with the assistance of ultrasound irradiation, the reactions occurred quickly (within 30-45 minutes) to give the tosylates in good yields (Tables 1 and 2).

In 1974 Fouquet and Schlosser [11] reported the formation of a C-C single bonds by a cross coupling reaction of alkyl tosylates with pertinent Grignard reagents in the presence of lithium tetrachlorocuprate at -78 ^{o}C after overnight stirring. Adopting the reaction conditions of Fouquet and Schlosser, but using ultrasound to promote the reactivity, we were able to perform the cross coupling reactions between the tosylates and the Grignard reagents (steps ii and vi) within 30-45 minutes, while still obtaining the products in high yields (Table 3).

Table 3: Ultrasound assisted cross coupling reactions between tosylates and Grignard reagents.

Entry	Product	Time (minutes)	Yield (%)[a]
1	**5a**	20	80
2	**5a**	30	95
3	**5a**	45	95
4	**5b**	30	94
5	**1**	45	93
6	**2**	45	91

The aldehydes **6a** and **6b** can be prepared from the alkenes **5a** and **5b** by ozonolysis [12]. In this work, the alkenes **5a** and **5b** were oxidized by perphthalic acid, then periodic acid [13], to give **6a** and **6b**, in of 81-82% yields, respectively, The alcohols 7**a** and 7**b** were easily prepared from the aldehydes **6a** and **6b** in yields of 96-97% by reduction of the latter with sodium borohydride in methanol for 15 minutes.

Conclusions

5,9-Dimethylpentadecane was prepared from citronellol in the excellent overall yield of 58% through six steps. By the same procedure, 5,9-dimethylhexadecane was prepared in the overall yield of 56%. The use of ultrasound irradiation combined with the use of optimized repetitive synthetic steps (Scheme 1) offer a convenient method for the synthesis of a variety of related branched hydrocarbons. It should be noticed that also the alkyl groups of the Grignard reagent in steps (ii) and (vi) can be varied.

Acknowledgement

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Experimental

General

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ with TMS as internal reference standard at frequencies 300 MHz and 75 MHz, respectively, on a Varian Mercury 300 NMR spectrometer, or alternatively, at frequencies 600 MHz and 150 MHz, respectively, on a Varian Inova 600 NMR spectrometer. GC-MS analyses were performed on a Hewlett Packard 5890 Series II apparatus with a Hewlett Packard 5791A MS detector (column: RTX-5MS, 30 m, 0.25 mm, 0.25 μm). A Sonics GE130 ultrasonic processor was used both in the tosylation and the cross coupling reactions. All reagents were purchased from Aldrich, while solvents were from Labscan. The chloroform used in the tosylation reactions was filtered through a plug of alumina to remove ethanol (present as stabilizer) [10].

General procedure for the tosylation of alcohols: 3,7-dimethyl-6-octenyl 4-methylbenzenesulfonate (**4**)

A mixture of citronellol (6.24 g, 40 mmol), pyridine (6.32 g, 80 mmol), and chloroform (20 mL) was placed in a 3-neck round flask and cooled to 0 ^{o}C in an ice bath. *p*-Toluenesulfonyl chloride (11.4 g, 60 mmol) was added to the mixture within a few minutes under irradiation from an ultrasonic processor. The reaction was finished within 30 minutes. After adding water (10 mL), the resulting mixture was extracted with diethyl ether (70 mL). The ethereal layer was washed with 2 M aqueous HCl, aqueous $NaHCO_3$, and brine. The solvent was removed by evaporation at reduced pressure, and the residue was chromatographed on a column (24 x 400 mm, 60 g of silica gel, eluent: 2% diethyl ether in hexane) to give 11.46 g (91%) of the tosylate **4**. MS (m/e): 310 (M^{+}); 227; 185; 173; 155; 138; 123; 91 (100%); 81; 69; 55; 41; ^{1}H-NMR (300 MHz) δ: 0.82 (d, *J* = 6.3 Hz, 3H), 1.10-1.65 (m, 5H), 1.57 (s, 3H), 1.67 (d, *J* = 1.5 Hz, 3H), 1.82-1.94 (m, 2H), 2.45 (s, 3H), 4.06-4.07 (m, 2H), 5.00-5.06 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H); ^{13}C-NMR (75 MHz) δ: 17.63, 19.05, 21.63, 25.27, 25.70, 28.88, 35.66, 36.71, 69.06, 124.33, 127.89 (2C), 129.82 (2C), 131.48, 133.26, 144.66.

General procedure for the cross coupling reactions: 2,6-dimethyl-2-dodecene (**5a**)

n-Butylmagnesium bromide was prepared from 1-bromobutane (12.33 g, 90 mmol) and magnesium turnings (2.16 g, 90 mmol) in dry diethyl ether (30 mL) during 30 minutes with assistance of an ultrasonic bath (Branson 1210) at room temperature. The slurry formed was added dropwise to a solution of the tosylate **4** (9.3 g, 30 mmol) in THF (25 mL) at -78 ^{o}C. A solution of 0.1 M Li_2CuCl_4 in THF (3.0 mL) was added to the mixture under ultrasonic irradiation. The mixture was kept at -78 ^{o}C for 10 minutes, after which the temperature was raised slowly to room temperature. The reaction was completed after ultrasound irradiation for a total of 30-45 minutes after the addition of the Li_2CuCl_4 solution. The obtained mixture was poured into a saturated aqueous solution of NH_4Cl containing crushed ice, which was subsequently extracted with diethyl ether (3x50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, with brine, and then dried (anhydrous Na_2SO_4). After removal of the solvent by evaporation at reduced pressure, the crude product was purified by column chromatography (24 x 400 mm, 30 g of silica gel, eluent: *n*-hexane) to give 5.58 g of **5a**

(95%). MS (m/e): 196 (M^+, 14), 126, 111, 98, 83, 69 (100%), 56, 41; ^{1}H-NMR (300 MHz) δ: 0.84-0.88 (m, 6H), 1.06-1.16 (m, 2H), 1.22-1.44 (m, 11H), 1.60 (s, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.93-1.99 (m, 2H), 5.08-5.13 (m, 1H); ^{13}C-NMR (75 MHz) δ: 14.34, 17.83, 19.84, 22.94, 25.83, 25.93, 27.24, 29.93, 32.20, 32.66, 37.23, 37.40, 125.36, 131.13.

2,6-Dimethyl-2-tridecene (**5b**): By the same procedure as described for the cross coupling reaction above, *n*-pentylmagnesium bromide, prepared from 1-bromopentane (9.06 g, 20 mmol) and magnesium turnings (1.44 g, 60 mmol) in 30 mL of dry diethyl ether, was reacted with the tosylate **4** (6.20 g, 20 mmol) to yield 3.95 g (94%) of **5b**. MS (m/e): 210 (M^+, 36), 182, 140, 125, 111, 98, 83, 69 (100%), 56, 41; ^{1}H-NMR (300 MHz) δ: 0.85-0.91 (m, 6H), 1.05-1.16 (m, 2H), 1.26-1.42 (m, 13H), 1.60 (s, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.88-2.04 (m, 2H), 5.04-5.14 (m, 1H); ^{13}C-NMR (75 MHz) δ: 14.14, 17.63, 19.64, 22.73, 25.63, 25.74, 27.09, 29.44, 32.03, 31.98, 32.47, 37.03, 37.19, 125.15, 130.92.

General procedure for oxidation: 4-methyldecanal (**6a**)

A 0.6 M solution of perphthalic acid (70 mL, 42 mmol) in diethyl ether was added dropwise to a solution of **5a** (5.5 g, 28 mmol) in dry diethyl ether (10 mL) at 0 ^{o}C, after which the mixture was placed in a refrigerator overnight. The reaction mixture was washed with aqueous $NaHCO_3$, and dried (anhydrous Na_2SO_4). Then the solvent was removed by evaporation at reduced pressure to leave crude intermediate 2,6-dimethyl-2-dodecene epoxide, which was dissolved in diethyl ether (20 mL) and added dropwise to a stirred solution of HIO_4 (6.84 g, 30 mmol) in THF (30 mL) during 1.5 hours. Removal of the solvents at reduced pressure gave crude **6a**, which was purified by column chromatography (24 x 400 mm, 30 g of silica gel, eluent: 5% diethyl ether in hexane), to yield 3.85 g (81%) of pure **6a** as a light yellow oil. MS (m/e): 155, 142, 126, 111, 95, 85, 69, 56 (100%), 41; ^{1}H-NMR: (300 MHz) δ: 0.84-0.90 (m, 6H), 1.20-1.32 (m, 10H), 1.40-1.47 (m, 2H), 1.60-1.66 (m, 1H), 2.39-2.46 (m, 2H), 9.77 (t, *J* = 1.8 Hz, 1H); ^{13}C-NMR (75 MHz) δ: 14.30, 19.56, 22.87, 27.11, 29.11, 29.77, 32.09, 32.59, 36.89, 41.93, 203.30.

4-Methylundecanal (**6b**): In the same manner as described above for the preparation of **6a**, we obtained 2.80 g (82%) of **6b** from 3.90 g of the alkene **5b**. MS (m/e): 169, 156, 140, 125, 112, 95, 85, 69, 56 (100%), 41; ^{1}H-NMR: (300 MHz) δ: 0.86-0.90 (m, 6H), 1.20-1.34 (m, 12H), 1.37-1.50 (m, 2H), 1.60-1.70 (m, 1H), 2.39-2.46 (m, 2H), 9.77 (t, *J* = 1.8 Hz, 1H); ^{13}C-NMR (75 MHz) δ: 14.31, 19.57, 22.89, 27.16, 29.11, 29.55, 30.08, 32.10, 32.60, 36.90, 41.93, 203.28.

General procedure for reduction: 4-methyl-1-decanol (**7a**)

A solution of sodium borohydride (0.26 g, 6.8 mmol) in methanol (7 mL) was added dropwise to 3.80 g (22 mmol) of **6a** under stirring during 15 minutes at room temperature. The reaction mixture was quenched with 1.0 M aqueous HCl (4 mL), and the resulting mixture was extracted with diethyl ether (3 x 15 mL). The combined organic layers were washed successively with aqueous $NaHCO_3$ and brine, and then dried (anhydrous Na_2SO_4). After removal of the solvent by evaporation at low pressure,

the residue was purified by column chromatography (24 x 400 mm, 30 g of silica gel, eluent: 10% diethyl ether in hexane) to give 3.69 g (96%) of **7a**. MS (m/e): 126, 111, 98, 84, 69 (100%), 56, 41; ^{1}H-NMR (300 MHz) δ: 0.86-0.90 (m, 6H), 1.09-1.42 (m, 13H), 1.52-1.61 (m, 2H), 1.80 (s, br, 1H), 3.63 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (75 MHz) δ: 14.19, 19.72, 22.82, 27.15, 29.81, 30.40, 32.08, 32.79, 33.15, 37.16, 63.20.

4-Methyl-1-undecanol (**7b**): In the same manner as described above for the preparation of **7a**, we obtained 2.74 g (97%) of **7b** from 2.80 g of the aldehyde **6b**. MS (m/e): 140, 125, 112, 97, 84, 69 (100%), 56, 41; ^{1}H-NMR (300 MHz) δ: 0.86-0.90 (m, 6H), 1.11-1.40 (m, 15H), 1.52-1.63 (m, 2H), 1.78 (s, br, 1H), 3.62 (t, *J* = 6.6 Hz, 2H); ^{13}C-NMR (75 MHz) δ: 14.12, 19.65, 22.71, 27.07, 29.40, 29.99, 30.36, 31.94, 32.65, 32.97, 37.01, 63.45.

4-Methyl-1-decanyl 4-methylbenzenesulfonate (**8a**) *and 4-methyl-1-undecanyl 4-methylbenzene-sulfonate* (**8b**): The tosylates **8a** and **8b** were prepared following the general procedure described above for the preparation of the tosylate **4**. We obtained 6.29 g (92%) of **8a** from 3.61 g of **7a**. Data of **8a**: MS (m/e): 207 (10), 173 (74), 154 (39), 126 (49), 111 (34), 97 (36), 91 (100), 84 (46), 69 (91), 56 (65), 41 (61);^{1}H-NMR: (300 MHz) δ: 0.80 (d, *J* = 6.6 Hz, 3H), 0.86-0.90 (m, 3H), 1.01-1.35 (m, 13H), 1.56-1.72 (m, 2H), 2.45 (s, 3H), 4.01 (t, *J* = 6.6 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR: (75 MHz) δ: 14.12, 19.41, 21.63, 22.68, 26.48, 26.90, 29.60, 31.91, 32.28, 32.49, 36.78, 71.12, 127.90 (2C), 129.80 (2C), 133.33, 144.62. Analogously, 4.49 g (91%) of **8b** was obtained from 2.70 g of **7b**. Data of **8b**: MS (m/e): 207 (3), 173 (100), 155, 140, 125, 111, 91, 83, 69, 56, 43, 41; ^{1}H-NMR: (300 MHz) δ: 0.80 (d, *J* = 6.3 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H), 1.07-1.32 (m, 15H), 1.56-1.72 (m, 2H), 2.45 (s, 3H), 4.01 (t, *J* = 6.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H); ^{13}C-NMR: (75 MHz) δ: 14.06, 19.35, 21.58, 22.69, 26.48, 26.95, 29.35, 29.90, 31.91, 32.27, 32.49, 36.77, 71.11, 127.88 (2C), 129.79 (2C), 133.31, 144.60.

5,9-Dimethylpentadecane (**1**): 2-Hexylmagnesium bromide was prepared by reaction of 4.80 g (29 mmol) of 2-bromohexane [14] with magnesium turnings (0.77 g, 32 mmol) in dried diethyl ether (30 mL) for 2 hours. In the same manner as described for the preparation of the alkene **5a** (see general procedure above), we obtained **1,** albeit together with a very small amount of 5,6-dimethyldecane. After removal of 5,6-dimethyldecane by vacuum distillation (65-68 ^{o}C/6 mbar), 2.15 g (93%) of pure **1** could be isolated (from 3.10 g (9.5 mmol) of (**8a**). MS (m/e): 240 (M^{+}, 5), 225 (4), 211 (2), 197 (1), 183 (21), 155 (32), 127 (10), 112 (35), 99 (22), 85 (77), 71 (93), 57 (100), 43 (58); ^{1}H-NMR: (600 MHz) δ: 0.84 (t, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 6.6 Hz, 3H) [15], 0.87-0.90 (m, 6H), 1.02-1.11 (m, 4H), 1.16-1.32 (m, 18H), 1.33-1.39 (m, 2H); ^{13}C-NMR: (150 MHz) δ: 14.14, 14.19, 19.72, 19.78, 22.73, 23.09, 24.50, 27.09 (27.10) [16], 29.38 (29.40) [16], 29.74, 32.01, 32.77 (32.79) [16], 32.80 (32.82) [16], 36.79 (36.89) [16], 37.12 (37.21) [16], 37.43, 37.48.

5,9-Dimethylhexadecane (**2**): In the same manner as described above for the preparation of **1**, 1.43 g (91%) of **2** was obtained from 2.10 g (6.5 mmol) of **8b**. MS (m/e): 254 (M^{+}, 5), 239 (5), 211 (2), 197 (31), 169 (10), 155 (35), 126 (37), 99 (22), 85 (97), 71 (90), 57 (100), 43 (76); ^{1}H-NMR: (300 MHz) δ: 0.84 (d, J = 6.6 Hz, 6H), 0.87-0.91 (m, 6H), 1.02-1.11 (m, 4H), 1.16-1.39 (m, 22H); ^{13}C-NMR: (75

MHz) δ: 14.14, 14.19, 19.72, 19.78, 22.73, 23.08, 24.51, 27.13 (27.14) [16], 29.38 (29.39) [16], 29.44, 30.03, 31.98, 32.77 (32.79) [16], 32.80 (32.82) [16], 36.79 (36.89) [16], 37.11 (37.20) [16], 37.42, 37.48.

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14. Sufficiently pure 2-bromohexane could not be procured commercially, minor contents of the isomeric 3-bromohexane being an apparently unavoidable impurity. Therefore, 2-bromohexane was prepared with the purity of 98% (GC) from 2-hexanol and PBr_3 at a temperature below 5 ^oC ([13]; pp. 559-564).
15. The signals are separated from each other by $\Delta\delta$ = 0.002 ppm.
16. Resolved resonances for the same carbon atom of two diastereomerically different forms.

Sample Availability: Available from the authors.