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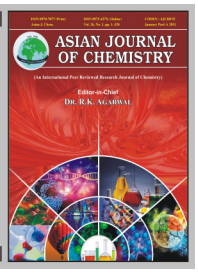


# Synthesis and Ultraviolet Absorption Characteristics of 4-Arylidene Isopinocamphones from α-Pinene

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A new series of 4-arylidene isopinocamphones were synthesized from α-pinene which was a natural chemical from pine tree and their ultraviolet absorption characteristics were investigated. (+)isopinocamphone was obtained from α-pinene by hydroboration-oxidation and then it was reacted with benzaldehyde, *p*-methylbenzaldehyde, *p*-methoxybenzaldehyde, *p*-chlorobenzaldehyde, furfural and *p*-nitrobenzaldehyde in the presence of alkali catalysts to get 4-arylidene isopinocamphones including 2-benzylidene-4,6,6-trimethylbicyclo[3.1.1]heptan-3-one (**1**), 2,6,6-trimethyl-4-(4-methyl benzyl)bicyclo[3.1.1]heptane-3-one (**2**), 2-(4-methoxybenzylidene)-4,6,6-trimethylbicyclo[3.1.1]heptan-3-one (**3**), 2-(4-chlorobenzylidene)-4,6,6-trimethylbicyclo[3.1.1]heptan-3-one (**4**), 2-(furan-2-methylene)-4,6,6-trimethylbicyclic [3.1.1] heptane-3-one (**5**) and 2,6,6-trimethyl-4-(4-nitrobenzylidene)bicyclo[3.1.1]heptan-3-one (**6**). The structures of 4-arylidene isopinocamphones were determined by FT-IR, $^1$H NMR, $^{13}$C NMR and GC-MS technique. Their ultraviolet absorption characteristics and light stability was further examined. The results showed that compounds **1**, **2**, **3** and **5** could be used as B-type UV absorbents, compounds **4** and **6** could be used as A-type UV absorbents and compounds **6** had both functions as UV-A and UV-B types absorbents. The light stability sequence of these compounds was (**2**) > (1) ≈ (3) ≈ (4) ≈ (6) > (5).

**Keywords: α-Pinene, (+)isopinocamphone, 4-Arylidene isopinocamphones, Ultraviolet absorbent, Light stability.**

## INTRODUCTION

Nowadays, the increased ultraviolet radiation that has been becoming one of the global environmental problems in recent years is very harmful to human health[1-3], which leads to sunburn cells, premature skin aging, tanning, DNA and an increased risk for skin cancers[4-12]. Sensitive skin in the sun after continuous UVB and UVA radiation can damage DNA to decreased immunity and even cause skin cancer. So we have no choice but to protect the body from injury and aging from the defense excessive UVA, UVB radiation[13]. Cosmetics ideal UV absorber should have the following properties: including the ability to absorb UV 280-360 nm, high extinction coefficient with less dose, non-toxic light toxicity, no reacting with cosmetics and skin components, good compatibility, low price, no odor, preventing dry skin and so on[14]. Because of the reasons above, we need to obtain new and good sunscreen products to protect the skin from the deleterious effects of the sun[15-17].

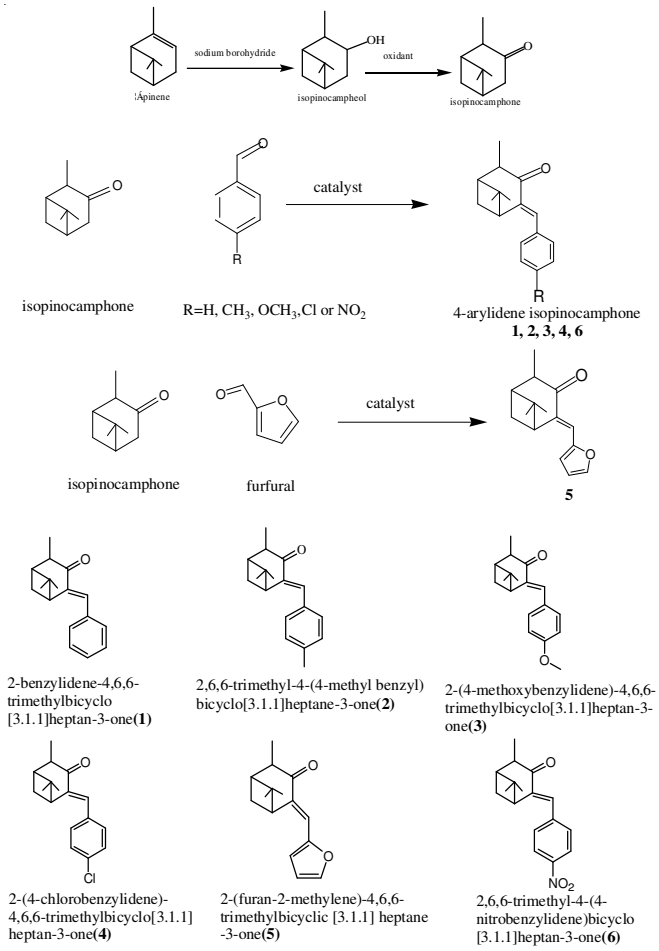
**Many studies have been done in this field:** As a natural product, Camphor derivatives have merits of stable storage, no irritation to skin, no photosensitization, low toxicity, good stability, chemical inertness and low absorption to skin, so they are widely used as UV-B filters in cosmetics[18-21]. However, natural camphor is very expensive, as well as a long process of synthesis routes gives rise to severe environmental pollution[22].

Pinene is another natural product and it has been studied for years as one kind of most important renewable product[23-26]. A new series of 4-arylidene-2-hydroxy-3-pinanones synthesized from (-)-α-pinene could be used as ideal UV absorbents[27]. In this paper, the cheap and abundant renewable resource α-pinene was also used as the raw material to synthesize a series of 4-arylidene isopinocamphones by hydroboration-oxidation and aldol condensation with aromatic aldehydes. The chemical structure, UV absorption and light stability of the synthesized chemicals were studied. The new compounds of 4-arylidene isopinocamphones have a wide range of UV absorption spectra, good stability and high yield.

## EXPERIMENTAL

The structures of compounds were characterized by elemental analysis (Elementar, Germany, Vano EL cube). The raw material α-pinene with a purity of 98.1 % (GC) and $[\alpha]_D^{20}$ + 36.8° (c = 1.0, $CCl_3$) was purchased from Deqing Forest Chemical Plant of China. Flash column chromatography was carried out on silica ge l60 (230-400 mesh). All reactions were

performed under a nitrogen atmosphere with magnetic stirring and the syntheses of 4-arylidene isopinocamphones from α-pinene were shown in **Scheme-I**.




**Scheme-1:** Synthetic route for 4-arylidene isopinocamphones from α-pinene

## General procedure

**Isopinocampheol:** Isopinocampheol was prepared from α-pinene by hydroboration[23]. A 500 mL dried four-necked flask equipped with a thermometer, a condenser and a stirrer was charged with 200 mL tetrahydrofuran, 54.4 g α-pinene, 9.08 g sodium borohydride (purity of 96 %) and cooled with ice bath to under 5 °C. Then, 69.33 mL oboron trifluoride etherate (purity of 46.8 %) was added in portions with the constant of subsection funnel drip in 40 min. The ice bath was removed when the temperature is under 5 °C after finishing addition of oboron trifluoride etherate and the reaction was kept at room temperature for another 3-4 h. Then 38 mL anhydrous ethanol was dropped into the flask for an hour. The reaction system was cooled with ice bath to under 5 °C and the reaction temperature was not higher than 30 °C by controlling dropping speed. Cooled with ice bath to under 5 °C again after finishing addition of anhydrous ethanol, then 40.08 mL 3 mol $L^{-1}$ sodium hydroxide aqueous solution was added for about 30 min and the reaction was kept for at the temperature of 40-45 °C by adding 30 mL hydrogen peroxide (purity of 30 %) and controlling its dropping speed and continued reacting for 1 h after finishing dropping. When the reaction system was cooled to room temperature, added 100 mL *n*-hexane, mixed fully for 0.5 h, filtered, then extraction were finished by adding 12 mL saturated sodium thiosulfate to remove excess $H_2O_2$ firstly and washing with saturated brine to neutral. The organic layer was dried over $Na_2SO_4$ and then concentrated by a rotor evaporator to recover *n*-hexane. The reaction was monitored by GC until the peak of α-pinene was disappeared. Finally, the residue was distilled to collect the fraction at 70-80 °C/266 kPa, a white acicular crystal with a yield over 72 %, purity of 96 % (GC), specific rotation $[\alpha]_D^{20}$ + 0.295° (c = 0.05, $C_2H_5OH$), melting point: 53-55 °C.

**Isopinocamphone:** Isopinocamphone was prepared from isopinocampheol by oxidation[24]. A 250 mL dried three-necked flask equipped with a thermometer, a condenser and a stirrer was charged with 10 g of isopinocampheol, 100 mL of dichloromethane and cooled with ice bath to 0 °C. Then pyridinium chlorochromate (PCC, $CrO_3$ was 2.32 mol/g) was added in the mixture and reacted at the temperature of 20 °C. And it was stopped after the reaction continued for 2 h when the conversion ratio of isopinocampheol was no longer change (monitored with GC). The reacted mixture was diluted with a moderate amount of toluene and filtered 2 or 3 times and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 1000 mL of petroleum ether and 50 mL of ethyl acetate to provide a 99.6 % isolated yield of isopinocamphone as a colourless oily liquid (monitored with GC-MS), specific rotation $[\alpha]_D^{20}$ + 0.459° (c = 0.05, $C_2H_5OH$).

**2-Benzylidene-4,6,6-trimethylbicyclo[3.1.1]heptan-3-one (1):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), benzaldehyde (1.06 g, 0.012 mol) and 1.5 g of powdered sodium methoxide in 15 mL of anhydrous ethanol. The resulting mixture was refluxed at room temperature for14-16 h until the conversion ratio of isopinocamphone reached over 96.7 % (monitored with GC)[25]. The reacted mixture was extracted with 5 % of hydrochloric acid solution and ethyl acetate and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 800 mL of petroleum ether and 100 mL of ethyl acetate to provide a 99.9 % isolated yield of compound **1** as a pale yellow oily liquid (monitored with GC-MS), $[\alpha]_D^{20}$-140.6° (c = 0.005 g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): 0.91 (s, 3H, -$CH_3$), 1.32-1.37 (m, 2H, -$CH_2$-C-C=C-), 1.39-1.40 (d, 3H, *J* = 4.2 Hz, $CH_3$-C-C=O), 2-2.03 (m, 1H, -CH-C=O), 2.57-2.76 (m, 1H, -CH-C-C=O), 2.74-2.76 (t, 1H, *J* = 2.90 Hz, -CH-C=C-), 7.31-7.32 (t, 1H, *J* = 2.19 Hz, -C=CH-), 7.24-7.26 (m, 2H, -CH in -$C_6H_5$), 7.31 (s, 1H, -CH in -$C_6H_5$), 7.33-7.34 (m, 2H, -CH in -$C_6H_5$); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 15.2, 17.0, 21.1, 23.2, 26.1, 26.8, 29.1, 33.9, 41.0, 43.1, 44.5, 44.7, 50.0, 49.4, 52.1, 77.0, 128.1, 131.5, 135.4, 141.7, 203.3; FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 2966 ($CH_3$, $\nu_{as\ C-H}$), 2927 ($CH_2$, $\nu_{as\ C-H}$), 2892 ($CH_3$, $\nu_{s\ C-H}$), 1697 ($\nu_{C=O}$), 1619, 1446 ($C_6H_5$-, $\nu_{as\ C=C}$), 747, 696 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 240.2 ($M^+$, 14), 225(1), 207(2), 199(1),

198(5), 197(20), 195(1), 185(1), 184(2), 183(2), 182(1), 181(1), 180(1), 179(2), 178(1), 1702(1), 169(7), 167(2), 165(3), 158(13), 157(100), 154(6), 153(4), 152(3), 142(4), 141(10), 130(7), 129(64), 128(35), 127(13), 119(2), 115(13), 102(4), 91(10), 83(5), 77(8), 65(3), 63(3), 55(11), 53(3), 51(4); Anal. Calcd for $C_{17}H_{20}O$: C 84.96, H 8.39,O 6.66; found C 84.83, H 8.25,O 6.51.

**2,6,6-Trimethyl-4-(4-methyl benzyl)bicyclo[3.1.1]heptane-3-one(2):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), *p*-methylbenzaldehyde (1.20 g, 0.012 mol) and 1.5 g of powdered sodium methoxide in 15 mL of anhydrous ethanol. The resulting mixture was refluxed at room temperature for 12-15 h until the conversion ratio of isopinocamphone reached over 95.1 % (monitored with GC)[25]. The reacted mixture was extracted with 5 % of hydrochloric acid solution and ethyl acetate and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 1000 mL of petroleum ether and 100 mL of cyclohexane to provide a 99.4 % isolated yield of compound **2** as a pale yellow oily liquid (monitored with GC-MS), $[\alpha]_D^{20}$ -135.8° (c = 0.005 g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.93 (s, 3H, $-CH_3$), 1.32-1.34 (m, 2H, $-CH_2$-C-C=C-), 1.40-1.42 (d, 3H, *J* = 5.79 Hz, $CH_3$-C-C=O), 2.01-2.04 (m, 1H, -CH-C=O, 2.33-2.34 (d, 3H, *J* = 4.23 Hz, $-CH_3-C_6H_4$-), 2.54-2.59 (m, 1H, -CH-C-C=O), 2.74-2.75 (t, 1H, *J* = 1.41 Hz, -CH-C=C-), 7.53 (t, 1H, -C=CH), 7.14-7.17 (m, 2H, -CH in $-C_6H_5$), 7.18-7.25 (m, 2H, -CH in $-C_6H_5$); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 21.2, 26.3, 29.3, 41.1, 43.2, 44.8, 76.8, 77.0, 77.3, 129.0, 129.4, 131.8, 132.7, 138.1, 141.3, 203.7; FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 2967 ($CH_3$, $\nu_{as\ C-H}$), 2931 ($CH_2$, $\nu_{as\ C-H}$), 2876 ($CH_3$, $\nu_{s\ C-H}$), 1695 ($\nu_{C=O}$), 1615, 1510, 1461 ($C_6H_5$-, $\nu_{as\ C=C}$), 1370 (-$CH_3$, $\delta_S$ C-H), 814 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 254 ($M^+$, 12), 212(3), 211(13), 207(3), 195(2), 191(1), 183(7), 178(2), 172(11), 171(90), 169(3), 168(8), 167(7), 166(4), 165(10), 156(7), 155(13), 154(5), 153(13), 152(11), 151(2), 144(6), 143(47), 142(13), 141(42), 139(7), 129(25), 128(100), 127(25), 126(4), 119(3), 117(7), 116(8), 115(43), 105(9), 103(5), 102(7), 91(18), 89(7), 83(14), 79(8), 78(5), 77(15), 69(4), 67(9), 65(11), 63(7), 55(45), 53(12), 51(7); Anal. Calcd for $C_{18}H_{22}O$: C 84.99, H 8.72,O 6.29; found C 84.82, H 8.84,O 6.15.

**2-(4-Methoxybenzylidene)-4,6,6-trimethylbicyclo-[3.1.1]heptan-3-one(3):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), *p*-methoxybenzaldehyde (1.63 g, 0.012 mol) and 1.2 g of powdered sodium methoxide in 15 mL of anhydrous methylbenzene. The resulting mixture was refluxed at room temperature for 12-15 h until the conversion ratio of isopinocamphone reached over 91.3 % (monitored with GC)[25]. The reacted mixture was extracted with 5 % of hydrochloric acid solution and methylbenzene and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 1500 mL of petroleum ether and 100 mL of cyclohexane to provide a 99.4 % isolated yield of compound **3** as a pale yellow oily liquid (monitored with GC-MS), $[\alpha]_D^{20}$ -176° (c = 0.005 g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.91 (s, 3H, $-CH_3$), 1.26-1.34 (m, 2H, $-CH_2$-C-C=C-), 1.34 (d, 3H, $CH_3$-C-C=O), 2.50-2.53 (m, 1H, -CH-C=O), 2.67-2.69 (m, 1H, -CH-C-C=O) 2.68-2.70 (m, 1H, -CH-C=C-), 7.20-7.21 (t, 1H, *J* = 1.68 Hz, -C=CH), 3.73 (s, 3H, -O-$CH_3$), 7.17-7.19 (m, 2H, -CH in $-C_6H_5$), 7.46-7.50 (m, 2H,-CH in $-C_6H_5$); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 15.2, 16.9, 21.1, 23.1, 26.2, 26.8, 29.1, 33.9, 40.9, 43.2, 44.7, 55.0, 77.0, 113.7, 127.8, 130.8, 131.4, 140.2, 159.4, 203.3; FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 2966 ($CH_3$, $\nu_{as\ C-H}$), 2927 ($CH_2$, $\nu_{as\ C-H}$), 2892 ($CH_3$, $\nu_{s\ C-H}$), 1697 ($\nu_{C=O}$), 1619, 1446 ($C_6H_5$-, $\nu_{as\ C=C}$), 1377 (-$CH_3$, $\delta_{S\ C-H}$), 747, 696 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 270 ($M^+$, 11), 227(5), 207(1), 199(4), 195(1), 188(13), 187(100), 185(2), 184(3), 173(1), 171(4), 159(34), 158(4), 157(3), 153(4), 152(4), 146(2), 145(10), 144(16), 143(4), 141(6), 133(5), 128(23), 127(14), 121(6), 116(14), 115(32), 103(4), 102(9), 91(9), 89(7), 81(5), 79(7), 78(4), 77(11), 65(5), 63(5), 55(27), 53(7), 51(4); Anal. Calcd for $C_{18}H_{22}O_2$: C 79.79, H 8.20,O 11.84; found C 79.65, H 8.16, O 11.71.

**2-(4-Chlorobenzylidene)-4,6,6-trimethylbicyclo-[3.1.1]heptan-3-one(4):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), *p*-chlorobenzaldehyde (1.40 g, 0.012 mol) and 1.2 g of powdered sodium methoxide in 15 mL of anhydrous methylbenzene. The resulting mixture was refluxed at room temperature for 12-14 h until the conversion ratio of isopinocamphone reached over 96.3 % (monitored with GC)[25]. The reacted mixture was extracted with 5% of hydrochloric acid solution and methylbenzene and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by recrystallization in mixed solvent containing 24 mL of ethyl acetate and 3 mL of petroleum ether for several days at room temperature to afford a 99.9 % isolated yield of compound **4** as a colourless transparent crystal, m.p. 55-57 °C, $[\alpha]_D^{20}$ -190.4° (c = 0.005 g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.91 (s, 3H, $-CH_3$), 1.33-1.35 (m, 2H, $-CH_2$-C-C=C-), 1.33-1.35 (d, 3H, *J* = 5.58 Hz, $CH_3$-C-C=O), 2.03-2.06 (m, 1H, -CH-C=O), 2.57-2.78 (m, 1H, -CH-C-C=O), 2.67-2.69 (m, 1H, -CH-C=C-) 7.27-7.32 (t, 1H, *J* = 5.58 Hz, -C=CH), 7.18-7.26 (m, 2H, -CH in $-C_6H_5$), 7.48 (m, 2H, -CH in $-C_6H_5$); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 15.4, 21.3, 26.3, 29.2, 41.2, 43.2, 44.7, 44.8, 76.7, 77.3, 128.6, 130.5, 134.0, 142.4, 203.5; FT-IR (KBr, $\nu_{max}$ $cm^{-1}$): 2964 ($CH_3$, $\nu_{as\ C-H}$), 2935 ($CH_2$, $\nu_{as\ C-H}$), 2885 ($CH_3$, $\nu_{s\ C-H}$), 1693 ($\nu_{C=O}$), 1620, 1487 ($C_6H_5$-, $\nu_{as\ C=C}$), 899, 822, 803, 768 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 274 ($M^+$, 13), 233(6), 232(4), 231(15), 217(1), 207(6), 203(5), 197(1), 196(6), 195(3), 191(100), 181(2), 177(2), 176(1), 168(7), 167(6), 166(5), 165(18), 164(5), 163(36), 162(4), 156(4), 155(4), 153(8), 152(10), 151(5), 149(8), 141(10), 139(6), 129(8), 128(50), 127(35), 126(6), 125(10), 115(11), 77(10), 75(6), 67(5), 63(6), 55(28), 53(7), 51(6); Anal. Calcd for $C_{17}H_{19}ClO$: C 74.31, H 6.97,O 5.82; found C 74.15, H 6.78,O 5.64.

**2-(Furan-2-methylene)-4,6,6-trimethylbicyclic [3.1.1] heptane-3-one (5):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), furfural (1.52 g, 0.012 mol) and 0.8 g of powdered sodium methoxide in 20 mL of anhydrous ethanol under a nitrogen atmosphere and the resulting mixture was refluxed at room temperature for 14-16 h until the conversion ratio of isopinocamphone reached over 93.8 % (monitored with GC)[25]. The reacted mixture was extracted with 5 % of hydrochloric acid solution and ethyl acetate and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 1500 mL of *n*-hexane and 100 mL of ethyl acetate to provide a 99.9 % isolated yield of compound **5** as a pale yellow oily liquid (monitored with GC-MS), $[\alpha]_D^{20}$ -138°(c = 0.005g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.86 (s, 3H, $-CH_3$), 1.43-1.45 (m, 2H, $-CH_2$-C-C=C-), 1.34-1.36 (d, 3H, *J* = 6.45 Hz, $CH_3$-C-C=O), 2.01-2.03 (m, 1H, -CH-C=O), 2.03-2.17 (m, 1H, -CH-C-C=O), 2.59-2.64 (m, 1H, -CH-C=C-), 7.46 (s, 1H, -C-C=CH), 6.42-6.43 (d, 1H, *J* = 1.05 Hz, CH in furyl), 6.43 (d, 1H, *J* = 1.08 Hz, CH in furyl), 7.46 (s, 1H, CH in furfuryl); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 15.3, 17.0, 21.1, 23.2, 26.4, 28.8, 33.8, 41.1, 43.8, 44.2, 44.5, 44.8, 45.1, 49.4, 77.0, 115.6, 118.0, 138.8, 143.6, 151.9; FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 2967 ($CH_3$, $\nu_{as\ C-H}$), 2933 ($CH_2$, $\nu_{as\ C-H}$), 2879 ($CH_3$, $\nu_{s\ C-H}$), 1695 ($\nu_{C=O}$), 1615, 1551 ($C_6H_5$-, $\nu_{as\ C=C}$), 743 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 230 ($M^+$, 22), 215(1), 188(3), 187(21), 174(1), 173(2), 159(7), 148(10), 147(100), 145(2), 144(3), 131(6), 120(3), 119(26), 117(4), 116(4), 115(9), 105(7), 104(2), 103(4), 95(1), 92(2), 91(37), 89(4), 81(5), 79(4), 78(4), 77(11), 65(15), 55(19), 53(6), 52(2), 51(8); Anal. cald for $C_{15}H_{18}O_2$: C 78.23, H 7.88, O 13.89; found C 78.09, H 7.75,O 13.76.

**2,6,6-Trimethyl-4-(4-nitrobenzylidene)bicyclo[3.1.1]-heptan-3-one(6):** A 100 mL dried flask equipped with an agitator, a thermometer and a condenser was charged with (+)-isopinocamphone (1.52 g, 0.01 mol), *p*-nitrobenzaldehyde (1.51 g, 0.012 mol) and 0.8 g of powdered sodium methoxide in 20 mL of anhydrous ethanol. The resulting mixture was refluxed at room temperature for 8-10 h until the conversion ratio of isopinocamphone reached over 91.7 % (monitored with GC)[25]. The reacted mixture was extracted with 5 % of hydrochloric acid solution and ethyl acetate and the combined organic layers were washed with water and saturated brine to neutrality, dried over $Na_2SO_4$ and concentrated to afford the yellow crude product, which was purified by thin layer silica gel chromatography column with mixed solvent containing 1500 mL of petroleum ether and 100 mL of ethyl acetate to provide a 96.1 % isolated yield of compound **6** as as a white crystal, m.p. 121.8-131.8 °C, $[\alpha]_D^{20}$ -197.6° (c = 0.005 g $mL^{-1}$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.93 (s, 3H, $-CH_3$), 1.22-1.37 (m, 2H, $-CH_2$-C-C=C-), 1.39-1.40 (d, 3H, *J* = 3.27 Hz, $CH_3$-C-C=O), 2.07-2.08 (m, 1H, -CH-C=O), 2.09-2.10 (m, 1H, -CH-C-C=O), 2.61-2.66 (m, 1H, -CH-C=C-), 7.27-7.41 (m, 1H, -C-C=CH), 8.20-8.22 (m, 2H, -CH in $-C_6H_5$), 7.41-7.54 (m, 2H, -CH in $-C_6H_5$); $^{13}C$ NMR (500 MHz, $CDCl_3$): δ (ppm) 15.3, 17.1, 21.4, 23.5, 26.3, 26.9, 29.0, 33.9, 41.4, 43.5, 44.8, 45.0, 49.7, 77.0, 123.6, 129.0, 130.0, 142.5, 144.8, 147.1, 203.1; FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 2964 ($CH_3$, $\nu_{as\ C-H}$), 2912 ($CH_2$, $\nu_{as\ C-H}$), 1694 ($\nu_{C=O}$), 1617, 1593 ($C_6H_5$-, $\nu_{as\ C=C}$), 911, 847, 691 ($C_6H_5$-, $\tau_{C-H}$); EI-MS *m/z* (%): 285 ($M^+$, 17), 281(3), 270(3), 268(3), 256(3), 255(7), 244(3), 243(16), 242(16), 242(21), 229(5), 228(4), 226(6), 215(2), 214(4), 207(8), 204(4), 203(28), 202(26), 197(5), 196(6), 186(8), 181(7), 174(12), 173(6), 172(30), 169(7), 168(18), 167(18), 166(8), 165(19), 157(11), 156(15), 155(10), 154(10), 153(24), 153(24), 152(28), 151(7), 144(18), 143(16), 142(8), 141(34), 140(6), 139(15), 131(6), 130(14), 129(25), 128(98), 127(50), 126(11), 117(15), 116(15), 115(67), 114(10), 113(11), 107(5), 106(10), 105(10), 103(10), 102(28), 101(9), 93(9), 92(5), 91(27), 89(20), 83(65), 81(13), 79(18), 78(18), 77(33), 76(12), 75(11), 69(15), 67(31), 65(18), 63(19), 60(12), 55(100), 54(11), 53(28), 51(19); Anal. Calcd for $C_{17}H_{19}NO_3$: C 71.56, H 6.71,O 16.82; found C 71.44, H 6.59,O 16.70.

**UV spectroscopy of compound 1-6:** $\lambda_{max}$ and molar extinction coefficient (ε) of synthesized compounds **1-6** were determined as follows: the solutions of **1**, **2**, **3**, **4**, **5** and **6** in the concentration range $10^{-4}$-$10^{-5}$ mol/L (or 0.0015 %, weight percent) were prepared in 50 % ethanol and their absorbance (A) was recorded at respective peak wavelengths ($\lambda_{max}$) using quartz cuvettes of 1 cm path length (L). A plot of A *versus* molar concentration at $\lambda_{max}$ was prepared and ε value was obtained from the slope of straight line.

**Photodegradation experiments of compound 1-6:** Photochemical measurements were carried out as follows: three the same conical flasks with stoppers were charged with 50 mL of the afore prepared solution, respectively for compound 1 and one was kept in dark place, one was put indoor and the last one was shown in sunlight using 50 % ethanol as the blank. The other compounds were done according to the same procedure and their UV absorbance was measured at the maximum absorption wavelength lmax at the same time on every day using the 50 % ethanol as the control. Photo stability of the synthesized compounds was compared by calculating their degradation rate[26,27].

NMR spectra were recorded in $CDCl_3$ solution on a Bruker AV 500 spectrometer at 300 MHz for $^1H$ and 500 MHz for $^{13}C$, respectively. The chemical shifts were expressed in ppm (δ scale) relative to the reference compound tetramethylsilane (TMS). Electronic impact (EI) gas chromatography-mass spectrometry (GC-MS) was conducted on an Agilent 6890N GC coupled to an Agilent Technologies 5973 inert mass selective detector using a 30 m × 0.25 mm i.d., 0.25 mm file thickness HP-5MS capillary column (Agilent Technologies, Wilmington, DE) with helium as carrier gas (36 cm/s, 80 °C for 2 min and then programmed to 280 °C at 15 °C/min and held for 20 min). A 70 eV electron beam was employed for sample ionization. GC analyses were performed on an Agilent 6890 GC equipped with a flame ionization detector (FID) using a 30 m × 0.32 mm i.d., 0.25 mm file thickness HP-5 capillary column with nitrogen as carrier gas (38 cm/s, 80 °C for 2 min and then programmed to 280 °C at 10 °C/min and held for 20 min) in the split mode and the split ratio was 50:1. Fourier-transform infrared (FT-IR) spectra of samples were recorded from potassium bromide disks prepared with each crystalline sample on a Nicolet 380 FT-IR spectrophotometer in the scan range of 4000-400 $cm^{-1}$. Melting points and specific rotation were

measured using X-6 microscopic melting point apparatus and W22-2S digital automatic polarimeter.

## RESULTS AND DISCUSSION

**UV ray absorption ability analysis of the 4-arylidene isopinocamphone derivatives:** UV ray absorption abilities of compounds **1** to **6** which are the E-isomers were listed in Table-1. It was known from Table-1 that compounds **1** to **6** had strong UV absorption. For compound **1**, its UV absorption range, $\lambda_{max}$ and ε value were 202-313 nm, 295 nm and 24640 L/mol cm, respectively. It completely meets the requirement of UV-B absorbent. For compounds **2**, **3** and **5** and they can also be used as UV-B absorber. For compound **4**, it also meet the conditions of UV-A absorbents because its UV absorption range, $\lambda_{max}$ and ε value were 249-490 and 298 nm, 33821 L/mol × cm, respectively. For compound **6**, it had wide range of UV absorption and $\lambda_{max}$ reached 313 nm, which was suitable for UV-A and B absorbent. The sequence of UV ray absorption ability of compounds **1** to **6** was (6) > (4) > (3) > (5) > (2) > (1) according to the ε value.

TABLE-1
UV ABSORPTION RANGES, $\lambda_{max}$ AND ε OF THE 4-ARYLIDENE ISOPINOCAMPHONE DERIVATIVES

| Compounds | UV absorption range (nm) | $\lambda_{max}$ (nm) | ε (L/mol cm) |
|---|---|---|---|
| 1 | 202-313 | 295 | 24640 |
| 2 | 238-310 | 304 | 25888 |
| 3 | 214-318 | 310 | 31115 |
| 4 | 249-490 | 298 | 33821 |
| 5 | 202-312 | 296 | 26687 |
| 6 | 238-536 | 313 | 37453 |

**Photodegradation studies of 4-arylidene isopinocamphone derivatives:** The photostability of compounds **1** to **6** was examined by comparing their molar extinction coefficient change at different conditions including dark, indoor and sunlight circumstance. The test results were shown in Fig. 1, 2 and 3, respectively.

Fig. 1 showed that all of these compounds were stable in dark circumstance because their molar extinct coefficients had little change even after 7 days. It was found from Fig. 2 and 3 that the molar extinct coefficients of all the synthesized compounds were decreased in different extent. ε of compounds **4** and **6** were obviously decreased during the first two days under strong sunlight irradiation and the molar extinct coefficients was decreased by 6.3 and 6.7 %, respectively. However, the ε values of compounds **1**, **2**, **3**, **4**, **5** and **6** were scarcely changed after two days. All of the six compounds were stable after two days. Therefore, the photostability sequence of the synthesized compounds was **(2)** > **(1)** ≈ **(3)** ≈ **(4)** ≈ **(6)** > **(5)**.

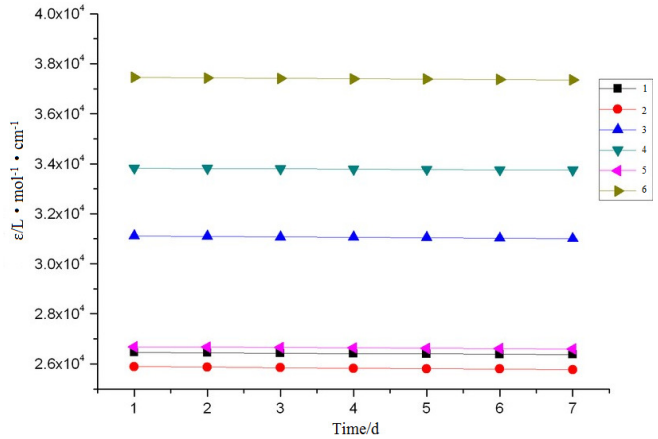



Fig. 1. ε Variation of compounds **1** to **6** along with the time in dark circumstance

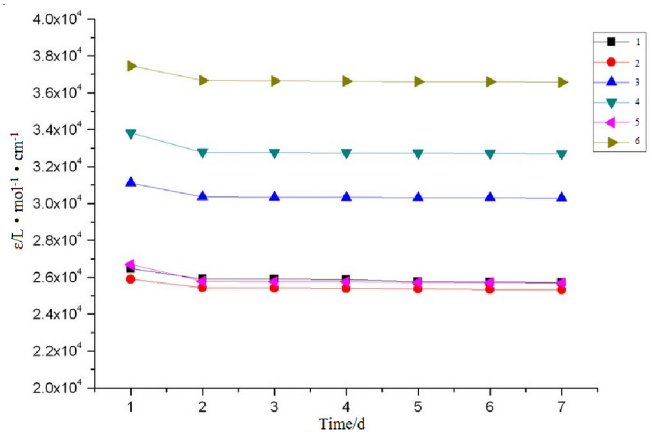



Fig. 2. ε Variation of compounds **1** to **6** along with the time in indoor circumstance

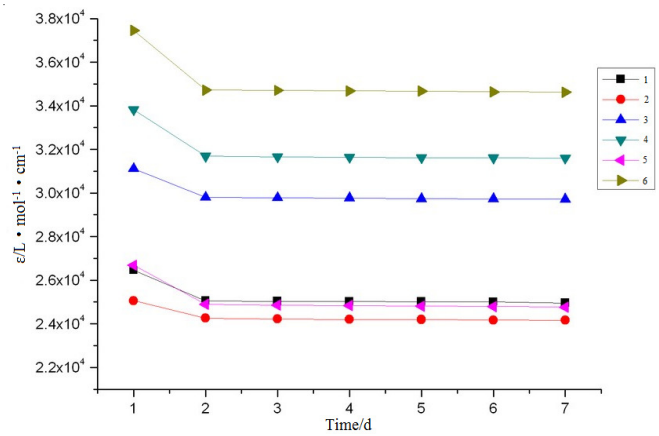



Fig. 3. ε Variation of compounds **1** to **6** along with the time in sunlight circumstance

## Conclusion

In conclusion, the results presented in this paper clearly illustrated that 4-arylidene isopinocamphone derivatives prepared from α-pinene possessed not only good UV ray absorption ability but also good photostability. Furthermore, their UV absorption abilities were all much better than that of *p*-methylbenzylidene camphor (UV max in 95 % ethanol was 301 nm and ε value was 20500 L/mol cm). More interesting thing is that 2-(furan-2-methylene)-4,6,6-trimethylbicyclic [3.1.1] heptane-3-one is a completely green product because the starting materials furfural and α-pinene are totally natural renewable resource. This research results also provide a completely new pathway for developing new type of UV filter.

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## REFERENCES


1. M.E. Ghitany and N.F. El-Nashar, *Int. J. Sustain. Energy*, **24**, 167 (2005).
2. S.Y. Yu, M.W. Scott, P.C. George and D.M. Jonathan, *Sci. Total Environ*., **75**, 481 (2014).
3. C. Soliman and M.A. Hussein, *Radiat. Eff. Defect*., **165**, 23 (2010).
4. R. K. Sivamani, L. A. Crane and R. P. Dellavalle, *Dermatol. Clin*., **2**, 149 (2009).
5. S.J. Moon A.A. Fryer R.C. Strange. S.J. Moon, A.A. Fryer and R.C. Strange, *Mutat. Res-Fund. Mol*., **571**, 207 (2005).
6. K.L. Cooper, B.S. King, M.M. Sandoval, K.J. Liu and L.G. Hudson, *Toxicol. Appl. Pharmacol*., **269**, 81 (2013).
7. E. Chatelain and B. Gabard, *Photochem. Photobiol*., **74**, 401 (2001).
8. V. Vanquerp, C. Rodriguez, C. Coiffard, L.J.M. Coiffard and Y. De Roeck-Holtzhauer, *J. Chromatogr. A*, **832**, 273 (1999).
9. M. Wlaschek, L. Tantcheva-Poor, L. Naderi, W. Ma, L.A. Schneider, Z. Razi-Wolf, J. Schüller and K. Scharffetter-Kochanek, *J. Photochem. Photobiol. B*, **63**, 41 (2001).
10. H.Y. Youn, A.P. Cullen, B.R. Chou and J.G. Sivak, *The Open Toxicol. J*., **4**, 13 (2010).
11. B.R. Das, *The Open Textile J*., **3**, 14 (2010).
12. J.M. Kuchel, R.St.C. Barnetson, L. Zhuang, F.M. Strickland, R. Pelley and G. Halliday, *Lett. Drug Des. Discov*., **2**, 165 (2005).
13. N. Tarras-Wahlberg, G. Stenhagen, O. Larko, A. Rosen, A.M. Wennberg and O. Wennerstrom, *J. Invest. Dermatol*., **113**, 547 (1999).
14. W. Christof-Kandzia and N. Horst-Westenfelder, R.V olker-Schehlmann, US Patent 6086857 (2000).
15. C. Couteau, A. Faure, J. Fortin, E. Paparis and L.J.M. Coiffard, *J. Pharm. Biomed. Anal*., **44**, 270 (2007).
16. J. Hojerova, A. Medovcikova and M. Mikula, *Int. J. Pharm*., **408**, 27 (2011).
17. N. Serpone and D. Dondi and A. Albini, *Inorg. Chim. Acta*, **3**, 794 (2007). Available:.
18. J. Nowicka-Scheibe, *Synth. Commun*., **43**, 2198 (2013).
19. L. Gerard, D. Andre and B. Irena, US Patent 4950478 (1990).
20. L. Gerard, F. Serge and M. Claudine, US Patent 5000961 (1991).
21. L.M. Yuan and D.Q. Deng, *J. Dermatol. Venereal*, **31**, 20 (2009).
22. Z. Zhao and L. Bi, *Bio. Chem. Eng*., **43**, 1 (2009).
23. P.R. Venkata, K. Rajasekhar and M. Veerendeer, US Patent 2010226597 (2010). 24. M.P. Krzeminski and A. Wojtczak, *Tetrahedron Lett*., **46**, 8299 (2005).
25. A.V. Malkov, A.J.P. Stewart-Liddon and F. Teply, *Tetrahedron*, **64**, 4022 (2008).
26. S.F. Wang, Y.P. Li and M.G. Zhang, *J. Org. Chem*., **27**, 1612 (2007).
27. B.S. Wei, X. Xu, Y.Q. Yang, X.Q. Cao and S.F. Wang, *Chin. J. Org. Chem*., **32**, 2287 (2012).
28. Q.Y. Meng, M.J. Wu, L.J. Zhang and G.X. Cai, *Chin. J. Appl. Chem. Ind*., **3**, 314 (2008).