

1 **Published in: Journal of Heterocyclic Chemistry: 48(4); 2011; 952-956.**

2  
3 First synthesis of 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthol & 3-  
4 (2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl) )-2-naphthol from 1- and 2-naphthol  
5  
6 derivatives  
7  
8  
9

10  
11  
12 Jose C. J. M. D. S. Menezes\*, Shashikumar K. Paknikar<sup>a</sup> & Shrivallabh P. Kamat

13  
14  
15 Department of Chemistry, Goa University, Taleigao Goa 403 206 India

16  
17  
18 <sup>a</sup>Siddharth Chemicals, Kundaim Industrial Estate, Ponda Goa 403 115, India

19  
20  
21  
22  
23  
24  
25 Abstract

26  
27 Two new structurally isomeric, 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-  
28 naphthol (**1**) & 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl) )-2-naphthol (**3**) have  
29  
30 been synthesized from 2-acetyl-1-naphthol and ethyl-3-hydroxy-2-naphthoate respectively  
31  
32 involving Grignard reaction, dehydration of the corresponding tertiary alcohols and hetero Diels-  
33  
34 Alder dimerization. The two benzochromenes (**1** & **3**) have been fully characterized by IR,  
35  
36 NMR and HRESIMS data. Their structures are further supported by crystallography of their  
37  
38 corresponding acetates (**2** & **4**).  
39  
40  
41  
42  
43  
44  
45

46  
47 Keywords: benzochromenes, Grignard, hetero Diels-Alder, naphthol, structural isomers  
48  
49

50  
51 Introduction  
52  
53  
54  
55

56  
57 

---

\* e-mail: [jose\\_menz@yahoo.co.in](mailto:jose_menz@yahoo.co.in)  
58  
59  
60

Naturally occurring 2-phenylchromans commonly called flavans, characterized by the presence of a benzopyran core, exist widely in the plant kingdom and exhibit many important biological and pharmacological activities [1]. Flavans substituted in the heterocyclic ring (3- and 4-positions, eg catechins) are frequently encountered in nature, but natural flavans with methyl substituents at 2- and 4-positions on the heterocyclic ring are comparatively rare [2].

To our knowledge there is only one report on a naturally occurring flavan of this type called inulavosin [2-(2'-hydroxy)-2,4',4,4,7-penta methyl flavan] isolated [2] from *Inula nervosa* (Compositae) having piscicidal activity [2] and recently discovered as a melanogenesis inhibitor [3]. The flavan inulavosin is a dimer of thymol and was prepared [4] from *m*-cresol and acetone much before its isolation as a natural product. Several synthetic methyl substituted flavans similar to inulavosin have also been prepared from *o*-cresol [5], *p*-cresol [5,6,7], resorcinol [8,7], 2,3-dimethyl phenol and 3,4-dimethyl phenol [7] but so far no such compounds from naphthols have been reported.

In this paper we describe the synthesis of 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthol **1** & 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthol **3** and their acetates (**2** & **4**) from 1- and 2-naphthol derivatives using Grignard reaction followed by dehydration of the corresponding tertiary alcohols and hetero Diels-Alder dimerization. The numbering pattern is given for clarity (Figure 1).

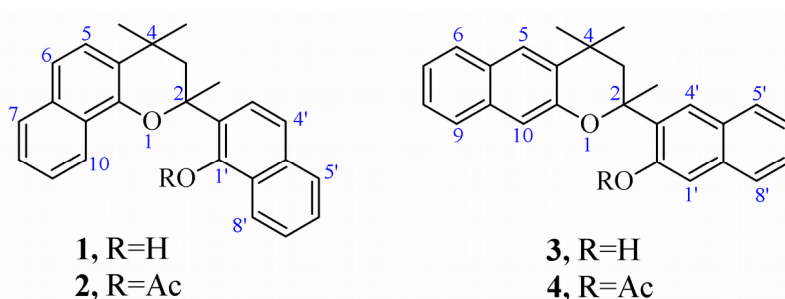


Figure 1

## Results and Discussion

We chose to prepare **1** by using a simple approach (Figure 2). Grignard reaction on 2-acetyl-1-naphthol [9] **5** afforded 2-(1'-hydroxy-1'-methyl ethyl)-1-naphthol [10] **6** as colorless oil in quantitative yield. Heating **6** with maleic anhydride on water bath gave 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthol **1** as viscous oil which solidified on standing.

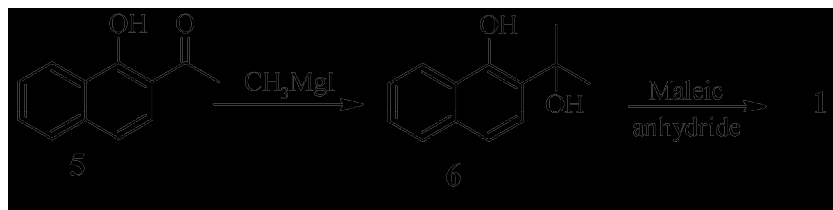


Figure 2

IR spectrum of **1** showed peak at  $3364\text{ cm}^{-1}$  indicating the presence of hydroxyl group. In its  $^1\text{H}$  NMR three singlets at  $\delta$  1.21, 1.48 and 1.83 integrating for 3H each were assigned to the three methyl groups. Equally spaced doublets at  $\delta$  2.17 and 2.63 with  $J = 14.5\text{ Hz}$  were assigned to geminal protons of C-3. Its  $^{13}\text{C}$  NMR showed in all 26 proton decoupled carbon signals, which comprised of 20  $sp^2$  and 6  $sp^3$  carbons. From DEPT 135 experiment it showed that 2  $sp^3$  carbons are quaternary one of which is bearing oxygen atom ( $\delta$  83.2). Among the aromatic signals, the two downfield signals at  $\delta$  144.4 and 149.9 are attributed to oxygen bearing  $^2sp$  carbon atoms. HRESIMS data on **1** showed the presence of a peak at  $m/z$  369.1853 [ $\text{M}^{\dagger}\text{H}$ ] indicating the formation of pseudomolecular ion of **1**.

The dehydration of tertiary alcohol **6** using maleic anhydride gives **7** which dimerizes with its tautomer **7a** to give the benzochromene **1** (Figure 3). Maleic anhydride was converted to maleic acid by water molecule released during the dehydration reaction and was identified by comparison with an authentic sample (m.p., co-TLC and IR).

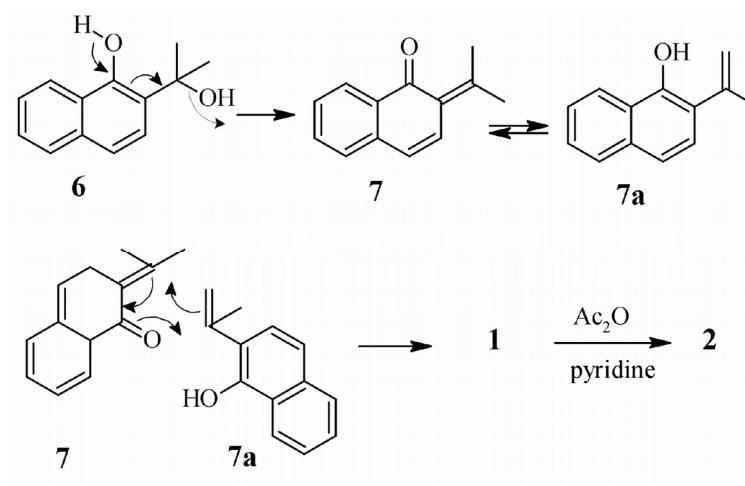
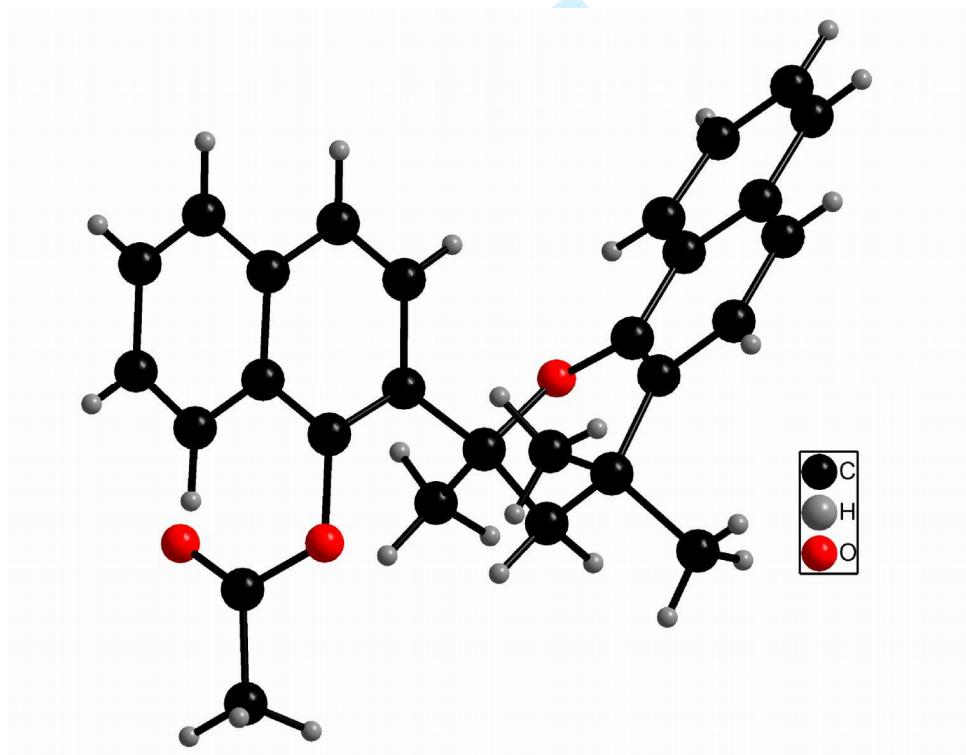


Figure 3

Acetylation of the phenolic hydroxyl in **1** using acetic anhydride and pyridine gave 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate **2** as a crystalline solid having mp 168 °C. Single crystal X-ray studies [11] of benzochromene acetate **2** further supported the structure for the benzochromene **1** (Figure 4).

Figure 4 – Crystallographic structure of benzochromene acetate **2**

Dehydration of **6** using *p*-TsOH in refluxing benzene [12] gave two compounds, 7,7-dimethyl-7*H*-dibenzo[*c,h*]xanthene **8** and benzochromene **1** (Figure 5). The benzoxanthene **8** was obtained as silvery white flakes (m.p. 180 °C). GCMS showed molecular ion peak at *m/z* 310.1 [*M*<sup>+</sup>] and a base peak at *m/z* 295 [*M* – 15]<sup>+</sup> due to the doubly benzylic ion formed by the loss of one methyl group. Benzoxanthene **8** is reported in literature [13] and prepared by the reaction of 1-naphthol with acetone in presence of POCl<sub>3</sub>. No spectroscopic data was reported on **8** hence, it was characterized by spectral data and is included in experimental section. The identity of **8** was further confirmed by its synthesis from 1-naphthol and acetone in the presence of *p*-TsOH [14].

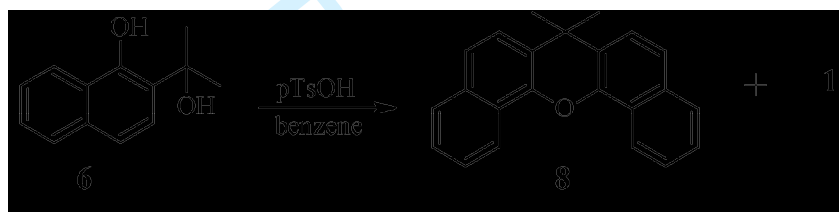


Figure 5

Grignard reaction on ethyl-3-hydroxy-2-naphthoate [15] **9** gave 3-(1'-hydroxy-1'-methyl ethyl)-2-naphthol [16] **10** as solid in 98% yield. Although **10** is reported in literature [16], no spectroscopic data was reported hence it was characterized by detail NMR and MS data. GCMS of **10** gave peak at *m/z* 184 [*M* – 18]<sup>+</sup> indicating loss of water molecule. Heating **10** with maleic anhydride on water bath gave 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthol **3** as viscous oil which solidified on standing (Figure 6).

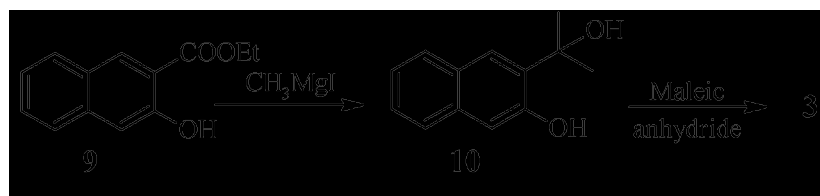


Figure 6

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRESIMS (given in experimental section) on **3** were similar to that observed for **1** since both compounds are structural isomers. The formation of benzochromene **3** is based on a similar mechanism as for the formation of benzochromene **1**. Acetylation of the phenolic hydroxyl in **3** gave 3-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*g*]chromen-2-yl)-2-naphthyl acetate **4** as greenish crystalline solid (m.p. 136 °C) which on single crystal X-ray diffraction studies [11] provided further support to the structure of benzochromene **3** (Figure 7). Dehydration of **10** using *p*-TsOH in refluxing benzene [12] gave benzochromene **3** as the sole product.

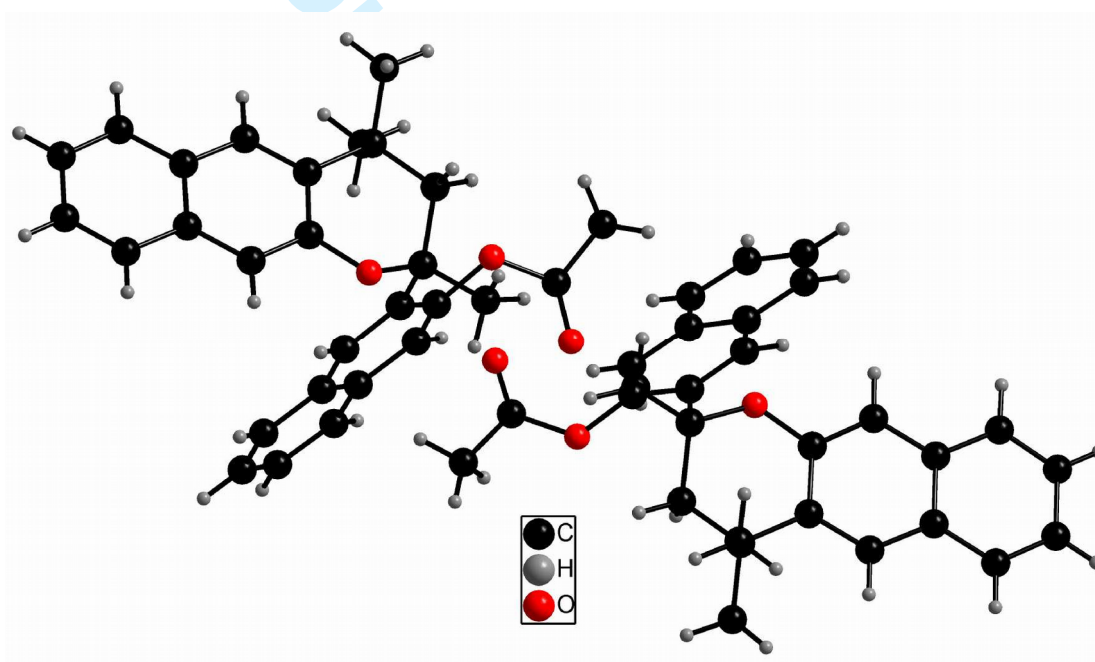


Figure 7 – Crystallographic structure of benzochromene acetate **4**

## Experimental

Melting points were determined in open capillary tubes and are uncorrected. UV spectra were recorded on a Shimadzu UV-2450 UV-VISIBLE spectrophotometer. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FTIR spectrophotometer in the range 4000-400  $\text{cm}^{-1}$  as KBr diluted pellets in the solid state or as film in NaCl plates. NMR spectra were

1  
2  
3 recorded on a Bruker WT 300 MHz FTNMR spectrophotometer with TMS as the internal  
4 standard. The multiplicities of carbon signals were obtained from a distortionless enhancement  
5 by polarization transfer (DEPT-135). Coupling constants ( $J$ ) are expressed in Hz. Diethyl ether  
6 was distilled and stored over sodium wire.  
7

8  
9  
10  
11  
12 **2-(1'-hydroxy-1'-methyl ethyl)-1-naphthol (6).** Grignard reagent was prepared by dropwise  
13 addition of methyl iodide (1.7 mL, 3.82 g, 27 mmol) in ether (5 mL) to a stirred suspension of  
14 magnesium metal (0.65 g, 27 mmol) in ether (5 mL) containing a crystal of  $I_2$ . After addition  
15 was complete (30 min), the mixture was refluxed for additional 30 min. The Grignard reagent  
16 was cooled in ice bath and to this a solution of **5** (2.0 g, 11 mmol) in ether (5 mL) was added  
17 dropwise with vigorous stirring. After addition was completed, the resulting mixture was  
18 refluxed for 2 h, cooled and added to a saturated solution of  $NH_4Cl$  in crushed ice. This was  
19 extracted with ether, washed with water, brine and dried over anhydrous  $Na_2SO_4$ . Evaporation  
20 of the ether afforded 2-(1'-hydroxy-1'-methyl ethyl)-1-naphthol **6** as oil in quantitative yield; IR:  
21 3520, 3258, 1574, 1464, 1385, 1304, 1107, 955, 876  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  1.63  
22 (s, 6H,  $2 \times CH_3$ ), 2.49 (s, 1H, 1' OH), 7.01 (d, 1H, H-4,  $J = 8.7$  Hz), 7.25 (d, 1H, H-3,  $J = 8.7$   
23 Hz), 7.37-8.25 (m, 4H, H-5, 6, 7, 8), 9.78 (s, 1H, OH).  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

34  
35  
36  
37  
38  
39  
40  
41 **2-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[h]chromen-2-yl)-1-naphthol (1).** A mixture of **6**  
42 (0.662 g, 3.27 mmol) and maleic anhydride (0.482 g, 4.9 mmol) was heated on a water bath for 1  
43 h. Reaction mixture was cooled, diluted with water and extracted with ether. The organic  
44 extract was washed with saturated  $NaHCO_3$ , water and dried over anhydrous  $Na_2SO_4$ .  
45 Evaporation of the ether afforded 2-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[h]chromen-2-yl)-1-  
46 naphthol **1** as oil. Purification by silica gel column chromatography using benzene and  
47 petroleum ether (1:1) as eluant gave pure **1** (0.6 g, 99.5%) which solidified on standing, mp 68-  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

70 °C; UV (MeOH): 296, 235, 213 nm; IR: 3364, 2963, 1574, 1387, 1074, 806, 748, 677 cm<sup>-1</sup>;  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.21 (s, 3H, CH<sub>3</sub>), 1.48 (s, 3H, CH<sub>3</sub>), 1.83 (s, 3H, CH<sub>3</sub>), 2.17 (d, 1H, H-3, *J* = 14.5 Hz), 2.63 (d, 1H, H-3, *J* = 14.5 Hz), 7.17-7.47 (m, 8H, Ar-H), 7.68-7.76 (m, 2H, Ar-H), 8.19 (d, 2H, Ar-H, *J* = 9 Hz), 9.26 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 27.3 (CH<sub>3</sub>), 31.5 (CH<sub>3</sub>), 32.9 (CH<sub>3</sub>), 48.5 (C-3), 75.5 (C-4), 83.2 (C-2), 119.1 (C-4'), 121.2 (C-6), 121.8 (C-7'), 122.3 (C-2'), 122.5 (C-9), 124.2 (C-6'), 124.4 (C-8), 125.3 (C-5'), 125.7 (C-4a, 10a, 8'a), 126.1 (C-3'), 126.2 (C-7), 126.5 (C-5), 127.0 (C-10), 127.7 (C-8'), 133.1 (C-4'a), 133.8 (C-6a), 144.4 (C-1a), 149.9 (C-1'); HRESIMS: *m/z* [M + H]<sup>+</sup> Found: 369.1853, Calcd. for C<sub>26</sub>H<sub>25</sub>O<sub>2</sub>: 369.1849.

**2-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*h*]chromen-2-yl)-1-naphthyl acetate (2).** A mixture of benzochromene **1** (0.3 g, 0.8 mmol), acetic anhydride (4 mL) and pyridine (2 mL) was heated on a water bath for 5 min and kept overnight. The reaction mixture was poured over crushed ice to which few drops of conc. HCl were added, stirred and extracted with ether. The ethereal layer was washed with water, brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of ether afforded 2-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*h*]chromen-2-yl)-1-naphthyl acetate **2** (0.27 g, 80.8%) as colorless solid; mp 168 °C (hexane); IR: 1769 (CO), 1385, 1366, 1198, 1082, 810, 750 cm<sup>-1</sup>.

**Dehydration of 6 with *p*-TsOH, formation of 7,7-dimethyl-7H-dibenzo[*c,h*]xanthene (8) and benzochromene (1).** A mixture of **6** (0.516 g, 2.5 mmol) and catalytic amount of *p*-TsOH (0.05 g) was heated under reflux in benzene (10 mL) for 7 h (monitored by TLC). The reaction mixture was cooled, diluted with water and extracted with ether. The organic extracts were washed with saturated NaHCO<sub>3</sub>, water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of ether gave crude oil (0.529 g). TLC of the oil in benzene showed 2 spots which were separated by silica gel column chromatography. Elution with petroleum ether gave silvery white flakes of



1  
2  
3 7,7-dimethyl-7*H*-dibenzo[*c,h*]xanthene **8** (0.09 g, 22.7%); mp 180 °C (hexane) (lit [13] 186 °C);  
4  
5 IR: 2966, 1566, 1393, 1371, 1211, 1111, 808, 746, 677 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ  
6  
7 1.80 (s, 6H, 2 × CH<sub>3</sub>), 7.55-7.67 (m, 8H, Ar-H), 7.85 (d, 2H, H-5, 9, *J* = 8.1 Hz), 8.64 (d, 2H, H-  
8  
9 6, 8, *J* = 8.1 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 33.2 (CH<sub>3</sub> × 2), 34.1 (C-7), 121.8 (C-5, 9),  
10  
11 122.7 (C-2, 12), 123.1 (C-6a, 8a), 124.2 (C-3, 11), 124.3 (C-1a, 13a), 126.0 (C-4, 10), 126.2 (C-  
12  
13 6, 8), 127.4 (C-1, 13), 133.1 (C-4a, 9a), 144.2 (C-14a, 14b); GCMS: *m/z* 310.1 [*M*] 295.  
14  
15 Further elution with benzene:petroleum ether (3:7) gave **1** (0.233 g, 49.6%) as oil and found to  
16  
17 be identical with that obtained earlier.  
18  
19  
20  
21

22 **7,7-Dimethyl-7*H*-dibenzo[*c,h*]xanthene (8)**. To a mixture of acetone (0.25 mL, 3.5 mmol) and  
23  
24 distilled 1-naphthol (1.0 g, 6.9 mmol), *p*-TsOH (13.3 mg, 0.07 mmol) was added and stirred at  
25  
26 125°C for 1 h. The progress of the reaction was monitored by TLC. The reaction mixture was  
27  
28 cooled, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with dilute  
29  
30 NaOH, water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave crude solid  
31  
32 (1.08 g). Purification through a small bed of silica using petroleum ether as eluant gave **8** (0.766  
33  
34 g, 71.2%) as silvery white flakes, mp 180 °C (hexane) (lit [13] 186 °C).  
35  
36  
37  
38

39 **3-(1'-hydroxy-1'-methyl ethyl)-2-naphthol (10)**. Grignard reagent was prepared by dropwise  
40  
41 addition of methyl iodide (6.2 mL, 14.2 g, 0.1 mol) in ether (10 mL) to a stirred suspension of  
42  
43 magnesium metal (2.4 g, 0.1 mol) in ether (10 mL) containing a crystal of I<sub>2</sub>. After addition was  
44  
45 complete (30 min), the mixture was refluxed for additional 30 min. The Grignard reagent was  
46  
47 cooled in ice bath and to this a solution of **9** (2.14 g, 0.01 mol) in ether (10 mL) was added  
48  
49 dropwise with vigorous stirring. After addition was complete, the resulting mixture was refluxed  
50  
51 for 5 h, cooled and added to a saturated solution of NH<sub>4</sub>Cl in crushed ice. This was extracted  
52  
53 with ether, washed with water, brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the ether  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 afforded 3-(1'-hydroxy-1'-methyl ethyl)-2-naphthol **10** (1.96 g, 98%) as solid; mp 140 °C  
4 (benzene) (lit [16] 140 °C); IR: 3418, 2982, 1634, 1599, 1369, 1240, 1199, 947, 874, 748 cm<sup>-1</sup>;  
5  
6  
7  
8 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.77 (s, 6H, 2 × CH<sub>3</sub>), 2.56 (bs, 1H, 1' OH), 7.23 (s, 1H, H-1),  
9  
10 7.25-7.39 (m, 2H, H-6,7), 7.56 (s, 1H, H-4), 7.65 (d, 1H, H-8, *J* = 8.3 Hz), 7.70 (d, 1H, H-5, *J* =  
11  
12 8.3 Hz), 8.97 (bs, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 30.3 (C-2', 3'), 75.9 (C-1'), 111.9 (C-  
13  
14 1), 123.5 (C-6), 124.5 (C-7), 125.9 (C-4), 126.4 (C-8), 127.8 (C-5), 128.0 (C-3), 133.4 (C-4a),  
15  
16 134.4 (C-8a), 153.9 (C-2); GCMS: *m/z* 184 [M-18]<sup>+</sup>.  
17  
18  
19

20  
21 **3-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*g*]chromen-2-yl)-2-naphthol (3)**. A mixture of **10**  
22 (0.2 g, 0.9 mmol) and maleic anhydride (0.11 g, 1.48 mmol) was heated on a water bath for 1 h.  
23  
24 Reaction mixture was cooled, diluted with water and extracted with ether. The organic extract  
25  
26 was washed with saturated NaHCO<sub>3</sub>, water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of  
27  
28 the ether afforded 3-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*g*]chromen-2-yl)-2-naphthol **3** as oil.  
29  
30 Purification by silica gel column chromatography using benzene and petroleum ether (1:1) as  
31  
32 eluant gave pure **3** (0.153 g, 84%) which solidified on standing, mp 82-84 °C; UV (MeOH): 333,  
33  
34 320, 278, 269, 244 nm; IR: 3381, 2961, 1634, 1504, 1444, 1339, 1252, 1165, 1060, 947, 868,  
35  
36 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.31 (s, 3H, CH<sub>3</sub>), 1.59 (s, 3H, CH<sub>3</sub>), 1.88 (s, 3H,  
37  
38 CH<sub>3</sub>), 2.30 (d, 1H, H-3, *J* = 14.4 Hz), 2.89 (d, 1H, H-3, *J* = 14.4 Hz), 3.50 (s, 1H, OH), 7.24-7.76  
39  
40 (m, 12H, Ar-H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 28.9 (CH<sub>3</sub>), 32.6 (CH<sub>3</sub>), 32.8 (CH<sub>3</sub>), 47.5 (C-3),  
41  
42 77.2 (C-4), 81.7 (C-2), 111.9 (C-1'), 113.0 (C-10), 123.5 (C-6'), 124.1 (C-7), 125.6 (C-7'), 125.7  
43  
44 (C-8), 125.9 (C-4'), 126.2 (C-5), 126.3 (C-8'), 126.4 (C-9), 127.4 (C-5'), 127.9 (C-6), 128.2 (C-  
45  
46 3'), 129.9 (C-4a), 132.7 (C-4'a), 133.2 (C-5a), 134.1 (C-8'a), 134.3 (C-9a), 149.7 (C-10a), 152.7  
47  
48 (C-2'); HRESIMS: *m/z* [M + H]<sup>+</sup> Found: 369.1851, Calcd. for C<sub>26</sub>H<sub>25</sub>O<sub>2</sub>: 369.1849.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 **3-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*g*]chromen-2-yl)-2-naphthol (3)** by *p*-TsOH  
4  
5 **method.** (Procedure as followed for compound **1**). Found to be identical (mp, IR, NMR) with  
6  
7  
8 that obtained earlier.  
9

10 **3-(2,4,4-trimethyl-3,4-dihydro-2H-benzo[*g*]chromen-2-yl)-2-naphthyl acetate (4).**  
11  
12 (Procedure as followed for compound **2**) greenish crystals, mp 136 °C (hexane); IR: 2970, 1757,  
13  
14 1633, 1599, 1500, 1442, 1369, 1255, 1199, 1037, 950 cm<sup>-1</sup>.  
15  
16  
17

## 18 19 20 Conclusion

21  
22 A simple and convenient synthesis of two new substituted benzochromenes **1** and **3** has been  
23  
24 achieved. They have been fully characterized by IR, NMR, HRESIMS data and supported by  
25  
26 crystallographic structures of their corresponding acetates (**2** & **4**).  
27  
28

## 29 30 Acknowledgment

31  
32 The authors wish to thank B. R. Srinivasan, Department of Chemistry, Goa University for  
33  
34 helpful discussions and L. D'Souza, Scientist, NIO, Goa for recording spectral data.  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## References and Notes

- 1  
2  
3  
4  
5  
6 [1] Saini, K. S.; Ghosal, S. *Phytochemistry* 1984, 23, 2415.  
7  
8 [2] Yoshida, T.; Mori, K.; He, G. *Heterocycles* 1995, 41, 1923 and references cited therein.  
9  
10 [3] Fujita, H.; Motokawa, T.; Katagiri, T.; Yokota, S.; Yamamoto, A.; Himeno, M.; Tanaka,  
11  
12 Y. *J Invest Derm* 2009, 129, 1489.  
13  
14 [4] Baker, W.; Curtis, R. F.; Mcomie, J. F. W. *J Chem Soc* 1951, 76 and references cited  
15  
16 therein.  
17  
18 [5] Baker, W.; Curtis, R. F.; Mcomie, J. F. W. *J Chem Soc* 1952, 1774.  
19  
20 [6] Dinge, A. S.; Kirtany, J. K.; Paknikar, S. K. *Indian J Chem* 1981, 20B, 245.  
21  
22 [7] Kamat, V. P.; Asolkar, R. N.; Kirtany, J. K. *Synth Commun* 1998, 28, 4581.  
23  
24 [8] Livant, P.; Webb, T. R.; Xu, W. *J Org Chem* 1997, 62, 737.  
25  
26 [9] Crouse, D. J.; Hurlbut, S. L.; Wheeler, D. M. S. *J Org Chem* 1981, 46, 374.  
27  
28 [10] Broyles, D. A.; Carpenter, B. K. *Org Biomol Chem* 2005, 3, 1757.  
29  
30 [11] Srinivasan, B. R.; Ragavaiah, P.; Menezes, J. C. J. M. D. S.; Kamat, S. P. *J Chem*  
31  
32 *Crystallogr*, submitted.  
33  
34 [12] Scretta, C. G.; Smonou, I. C. *J Org Chem* 1988, 53, 893.  
35  
36 [13] Saint-Ruf, G.; Poupelin, J. P. *Synthesis* 1975, 10, 661 and reference cited therein.  
37  
38 [14] Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. *Synlett* 2005, 6, 955.  
39  
40 [15] *Dictionary of Organic Compounds*; Pollock, J. R. A., Stevens, R., Ed.; Eyre and  
41  
42 Spottiswoode: London, 1965, Vol. 3, pp 1750.  
43  
44 [16] Lammer, P. *Monatshefte fuer Chemie* 1914, 35, 171. (Chem Abstr 1914, 8, 1574).  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60