HL **ISSN: 2231 – 3087(print) / 2230 – 9632(Online)**
http://heteroletters.org **Vol. 4: (1), 2014, 101-107**

FACILE SYNTHESIS OF 8-METHYL-4*H*-FURO[2,3-h]ISOFLAVONES

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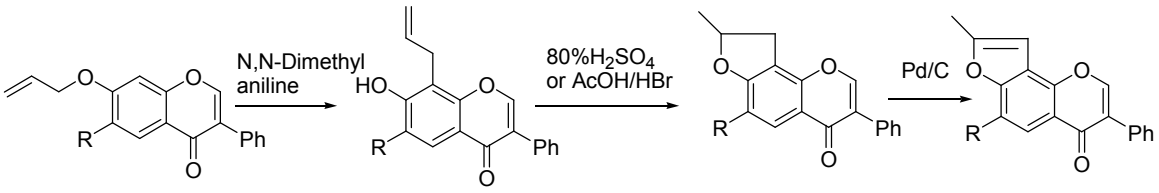
ABSTRACT
A new route for the synthesis of 8-methyl-4*H*-furo[2,3-h]isoflavones 4a-e by the oxidative cyclization of sodium salt of 7-hydroxy-8-allylisoflavones 3a-e using $[PdCl_2(PhCN)_2]$ complex has been developed.

Key words: 7-hydroxy-8-allylisoflavones, $[PdCl_2(PhCN)_2]$complex, 8-methyl-4*H*-furo[2,3-h]isoflavones.

INTRODUCTION
Isoflavones, 3-phenylchromene-4-ones constitute a subclass of flavonoids, a large family of secondary plant metabolites. There are several natural sources of isoflavones but the most important one are soy-bean and red clover (fabaceae family). Isoflavones remain the subject of many scientific studies as illustrated by the more than 1700 scientific publications mentioning isoflavones in their title or abstract. Most of these studies show that isoflavones may have some health benefits. Genistein, is a natural isoflavone occurring in many plants known to possess various biological activities, ranging from phyto-oestrogenic to anti oxidative actions[i,ii]. Recent studies indicated that this isoflavone can also be considered as a drug for as yet untreatable genetic deseases[iii]. Talosin A and B, namely genistein 7-O-α-L-6-deoxy-talopyranoside and genistein 4', 7-di-O-α-L-6-deoxy-talopyranoside are the first isoflavonoid gycosides bearing 6-deoxytalose residue recently isolated from bacteria *Kitasatospora kifunensis* MJM341 exhibited strong antifungal and anti-inflammatory activities[iv]. Ipriflavone, is a synthetic isoflavone used for treatment of postmenopausal, senile osteoporosis[v] and also used to inhibit bone resorption[vi]. Additionally furobenzopyranones were widely distributed in nature and exhibit various biological properties. Khellin a furobenzopyranone isolated from *ammi visnaga* (L) is useful in the treatment of angina pectoris, bronchial asthma and as a coronary vasodilator has been reported, it was also employed for the photochemotheraphy or vitilago[vii].

Earlier we reported a facile route to linear and angular 2-methyl furano chromones, flavones by the oxidative cyclization of 7-hydroxy-6/8-allyl chromones with $[PdCl_2(PhCN)_2]$[vii]. We also reported the synthesis of 2'-methyl furano/pyrano fused coumarins, chromones, flavones and isoflavones starting from their corresponding 7-proprgyloxy derivatives by carrying out Claisen rearrangement[viii-xi].
Joshi.*et.al*[xii] reported synthesis of 2-methylfuroisoflavones (**Scheme-I**) which involves acid catalysed cyclization of 8-allyl-7-hydroxy isoflavones into 2-methyl dihydrofuroisoflavones,

followed by dehydrogenation with Pd/C. The reported yields under these conditions are low and lengthy procedures and require harsh reaction conditions.



Scheme-I

In continuation of our interest in developing new biologically active heterocyclic compounds, we have developed a simple and efficient route for the synthesis of some novel angular 2-methyl furoisoflavones by oxidative cyclisation of 7-hydroxy-8-allyl isoflavones with $[PdCl_2(PhCN)_2]$. The advantages of present methodology are significant improvement in reaction yields, short reaction times and purity of isolated products compare to reported method[xii].

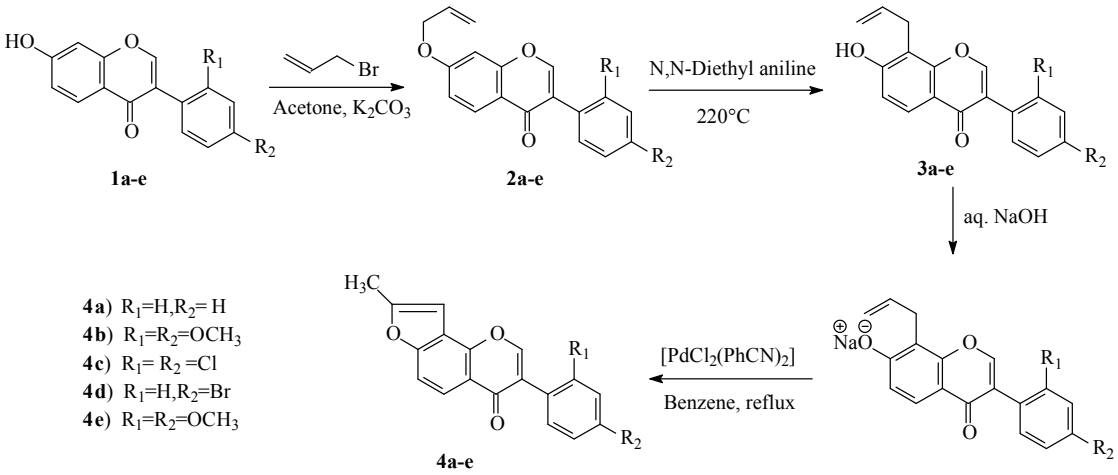
RESULTS & DISCUSSION

7-allyloxyisoflavones **2a-e** were prepared by the allylation of the 7-hydroxyisoflavones **1a-e**. The Claisen rearrangement of **2a-e** in refluxing N,N-diethylaniline (210 °C) afforded the regioselective 7-hydroxy-8-allylisoflavones **3a-e**. In the rearrangement of **2a-e** there is a possibility of migration of allyl group to 6^{th}/ 8^{th} position. Since the aromatic protons of **3a** in ^{1}H-NMR appeared as AB doublets, it is inferred that the allyl group has migrated to 8^{th} position **(Scheme-II)**.

7-hydroxy-8-allylisoflavones **3a-e** were converted into their corresponding sodium salts by dissolving in 0.5M aq NaOH. A suspension of anhy. sodium salt of **3a-e** in benzene was treated with an equimolar quantity of dichlorobis (benzonitrile)palladium and refluxed for 2h. The black metallic palladium which separated out was filtered off. The products 8-methyl-*4H*-furo-[2,3-h] isoflavones **4a-e** of the reaction separated by column chromatography over silica gel. The yield of the reaction products was 95%. There were no traces of starting material in the crude reaction product. Compare to the other methods available for the synthesis of angular 2-methyl furo isoflavones[12], the present method affords a facile route with high overall yields. Reactions are easy to perform and proceed under mild conditions. The structures of products characterized by spectral analysis IR, UV, ^{1}H-NMR, ^{13}C-NMR.

Compound **4a** in its IR showed the carbonyl peak at 1683cm^{-1}. UV of **4a** showed bands at 249 (log ε 4.0), 290 nm (log ε 4.4). The ^{1}H-NMR of **4a** shown characteristic peaks of newly formed methyl furo group fused to 7,8 positions of isoflavone. The furan proton H-9 and methyl proton 8-CH_3 appeared as singlet at δ 6.70 and 2.58 respectively. The isoflavone moiety H-2 protons appeared as a singlet at δ 8.05. The aromatic protons resonated at δ 7.30-7.60 (H-6, 2',3',4',5',6'), δ 8.10(d, J=9.0Hz, H-5).

In its ^{13}C-NMR of **4a** the furan ring carbons resonated at δ156.61 (C-8), 102.79 (C-9), and 12.18 (8-CH_3), 114.94 (C-9a). The other carbons appeared at 176.02 (C-4), 161.42 (C-6a), 152.08 (C-2), 149.88 (C-9b), 131.75 (C-1'), 128.05 (C-2',6'), 127.80 (C-4'), 125.21 (C-3), 125.49 (C-5), 118.32 (C-4a), 109.57 (C-6), 128.86 (C-3',5'). EIMS of **4a** M+ m/z 276.



Scheme-II

Conclusions: In conclusion, an alternative simple and efficient new route was developed for the synthesis of 8-methyl-4*H*-furo[2,3-*h*] isoflavones by the oxidative cyclization of 8-allyl-7-hydroxy isoflavones with $[PdCl_2(Ph(CN)_2]$ complex.

EXPERIMENTAL

General: All melting points were measured on a Polmon digital melting point apparatus (Model No. MP-96) and were uncorrected. IR spectra were recorded on Schimadzu 435 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75.5 MHz on Varian Gemini Unity Spectrometer using $CDCl_3$ solution with TMS as internal standard (chemical shifts in δ ppm). The mass spectra were recorded on a VG micro mass 7070-H instrument and LSIMS spectra were recorded on VG AUTOSPEC mass spectrometer.

General procedure for the synthesis of 7-allyloxyisoflavones 2a-e[12]:

Mixture of 7-hydroxyisoflavones **1a-e** (10 mmol), allylbromide (10mmol), anhy.K_2CO_3 in acetone (40 ml) was refluxed for 6h. After completion of the reaction acetone was evaporated and then ice cold water was added. The solid that separated was filtered and recrystallized from chloroform to get 7-allyoxy isoflavones **2a-e** with 75-90%yields.

7-Allyloxyisoflavone 2a[12]

colorless needles m.p158°C; IR (KBr): 1633 cm^{-1} (C=O); UV (MeOH): 210 nm (log ε5.4), 250 nm (log ε 4.0); ^1H NMR (200 MHz) ($CDCl_3$): δ 4.50 (d, J=6.0 Hz, H-1"), 5.42 (m, H-3"), 6.02 (m, H-2"), 6.05 (d, J=2.5Hz, H-8), 6.99 (d, J=9.0 Hz, H-6), 7.39-7.33 (H-2',6',4',3',5'), 8.00 (s, H-2), 8.02 (d, J= 9.0 Hz, H-5); ^{13}C NMR (50.3 MHz) ($CDCl_3$): δ 69.20 (C-1"), 101.02 (C-8), 114.35 (C-3"), 118.35 (C-4a), 118.65 (C-6), 125.11 (C-3), 127.69 (C-5), 127.96 (C-1'), 128.85 (C-3',5'), 129.31 (C-2',6'), 132.01 (C-4'), 132.01 (C-2"), 152.50 (C-2), 162.84 (C-7), 159.71 (C-8a), 175.38 (C-4),; LSIMS: $[M+H]^+$ m/z 279.

7-Allyloxy-4'-methoxyisoflavone 2b

colorless needles m.p160°C; IR (KBr): 1632 cm^{-1} (C=O); UV (MeOH): 214 nm (log ε 3.6), 260 nm (log ε 3.8); ^1H NMR (200 MHz) ($CDCl_3$) : δ3.78 (s, OCH_3), 4.65 (d, J=6.0 Hz, H-1"), 5.49 (m, H-3"), 6.02 (m, H-2"), 7.0 (d, J= 9.0 Hz, H-6), 6.88 (d, J= 9.0Hz, H-2',6'), 6.08 (d, J=2.5Hz,

H-8), 7.09 (d, J=9.0Hz, H-3',5'), 7.90(s, H-2), 8.20 (d, J=9.0 Hz, H-5); ^{13}C NMR (50.3 MHz) ($CDCl_3$) : δ 55.18 (4'-OCH_3), 69.16 (C-1"), 100.96 (C-8), 113.64 (C-3"), 113.83 (C-3',5'), 114.75 (C-6), 118.31 (C-4a), 124.14 (C-1'), 124.64 (C-3), 127.64 (C-5), 129.98 (C-2',6'), 132.03 (C-2"), 151.93 (C-2), 157.70 (C-7), 159.47 (C-8a), 162.75 (C-4'), 175.62 (C-4); LSIMS: $[M+H]^+$ m/z 309.

7-Allyloxy-2',4'-dichloroisoflavone 2c

colorless needles m.p185°C; IR (KBr):1643 cm^{-1} (C=O); UV (MeOH): 218 nm (log ε 4.3), 248 nm (log ε 4.3); ^{1}H NMR (200 MHz) ($CDCl_3$) : δ 4.69 (d, J=6.0Hz, H-1"), 6.01 (m, H-2"), 5.37 (m, H-3"), 6.05 (d, J=2.5Hz, H-8), 6.80 (d, J=9.0Hz, H-6), 7.91 (s, H-2), 7.25-7.45 (H-6',3',5'), 8.22 (d, J=9.0Hz, H-5); ^{13}C NMR (50.3 MHz) ($CDCl_3$): δ 69.22 (C-1"), 101.14 (C-8), 115.13 (C-6), 115.13 (C-3"),118.12 (C-4a), 118.65 (C-3), 126.99 (C-5'), 127.67 (C-1'), 127.67 (C-5), 129.55 (C-3'), 131.87 (C-6'), 134.84 (C-4'), 135.17 (C-2'), 132.94 (C-2"),153.97 (C-2), 157.87 (C-7), 157.87 (C-8a), 175.60 (C-4); LSIMS: $[M+H]^+$ m/z 347.

7-Allyloxy-4'-Bromoisoflavone 2d

colorless needles m.p.170°C; IR (KBr): 1637 cm^{-1} (C=O); UV (MeOH): 208 nm (log ε 4.5), 250 nm (log ε 4.9); ^{1}H NMR ($CDCl_3$): δ 4.45 (m, H-3"), 4.50 (d, J=6.0 Hz, H-1"), 6.02 (m, H-2"), 6.08 (d, J=2.5Hz, H-8), 6.70 (d, J=9.0 Hz, H-6), 7.20-7.52 (H-2',6',3',5'), 7.90 (s, H-2), 8.25 (d,J= 9.0 Hz, H-5); ^{13}C NMR (50.3 MHz) ($CDCl_3$) : δ69.25 (C-1"), 101.05 (C-8), 114.91 (C-6), 115.07 (C-3"),118.49 (C-4a), 122.23 (C-4'), 124.12 (C-3), 127.70 (C-3',5'), 128.01 (C-5), 128.36 (C-2',6'), 128.63 (C-1'), 131.95 (C-2"),152.01 (C-2), 157.75 (C-7), 152.48 (C-8a), 175.30 (C-4); LSIMS: $[M+H]^+$ m/z 257.

7-Allyloxy-2',4'-dimethoxyisoflavone 2e

colorless needles m.p.190°C; IR (KBr): 1634 cm^{-1} (C=O); UV (MeOH): 248 nm (log ε 4.6), 258 nm (log ε 4.6); ^{1}H NMR ($CDCl_3$) : δ 3.09 (OCH_3x2), 4.65 (d, J=6.0Hz, H-1"), 5.38 (m, H-3"), 6.01(m, H-2"), 6.06 (d, J=2.5 Hz, H-8), 6.80-7.07 (H - 6',3',5'), 6.80 (d, J=9.0 Hz, H-6), 7.91 (s, H-2), 8.22 (d, J=9.0 Hz, H-5)s; ^{13}C NMR ($CDCl_3$) : δ 55.84 and 68.0 (OCH_3x2), 69.15 (C-1"), 111.20 (C-8), 114.78 (C-6), 114.78 (C-3"), 118.28 (C-4a), 120.93 (C-3), 100.98 (C-5'), 100.9 (C-3'), 125.58 (C-5), 132.0 (C-6'), 126.63 (C-1'), 132.0 (C-2"), 152.09 (C-2), 162.79 (C-2'), 157.65 (C-4'), 150.04 (C-7), 162.79 (C-8a), 175.61 (C-4); LSIMS: $[M+H]^+$ m/z 309.

General procedure Synthesis of 8-allyl-7-hydroxyisoflavones 3a-e[12]:

7-Allyloxyisoflavones **2a-e** (10.0 mmol) was taken in *N,N*-diethyl-aniline (20 ml) and refluxed for 6 hrs at 220 °C. The reaction mixture was cooled and poured into dilute hydrochloric acid and extracted with ethyl acetate (200 ml) and then washed with water (100 ml) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The resulting products 8-allyl-7-hydroxy-isoflavones **3a-e** were recrystallized from chloroform in 50-75% yield.

8-allyl-7-hydroxyisoflavone 3a[12]

pale yellow crystals m.p. 198 °C; IR (KBr): 1632 cm^{-1} (C=O); UV (MeOH): 251 nm (log ε 4.8), 282 nm (log ε 4.2); ^{1}H NMR ($CDCl_3$) : δ 3.58 (d,J=6.0Hz,H-1"), 5.0 (m, H-3"), 6.0(m, H-2"), 7.0 (d, J=9.0 Hz, H-6), 7.40 (m, H-3',4',5'), 7.55 (m, 2H, H-2',6'), 7.95 (d, J=9.0 Hz, H-5), 8.00 (s, H-2), 10.00 (7-OH); ^{13}C NMR (DMSO-D_6) : δ 26.48 (C-1"), 114.26 (C-8), 112.87 (C-6), 115.18 (C-3"), 116.71 (C-4a), 123.18 (C-5), 124.60 (C-3), 127.61 (C-4'), 128.04 (C-2',6'), 128.87 (C-

3',5'), 132.11 (C-1'), 135.25 (C-2"), 153.77 (C-8a), 155.30 (C-2), 159.95 (C-7), 174.69 (C-4); LSIMS: $[M+H]^+$ m/z 279.

8-Allyl-7-hydroxy-4'-methoxyisoflavone 3b

pale yellow crystals, m.p.196°C; IR (KBr): 1631 cm^{-1} (C=O); UV (MeOH): 214 nm (log ε 3.7), 210 nm (log ε 3.6); ^1H NMR ($CDCl_3$) : δ3.58 (d, J= 7.0 Hz, H-1"), 3.85 (s, 4'-OCH_3), 6.00 (m, H-2"), 5.00 (m, H-3"), 7.0 (d, J= 9.0 Hz,H-6), 7.85 (d, J=9.0 Hz, H-5), 6.95 (d, J=9.0 Hz, H-3',5'), 7.48 (d, J= 9.0Hz, H-2',6'), 8.10 (s, H-2), 10.35 (s, 7-OH); ^{13}C NMR (DMSO-D_6) : δ 26.48 (C-1"), 55.07 (C-4'-OCH_3), 113.59 (C-3',5'), 114.18 (C-8), 112.79 (C-6), 115.14 (C-"), 116.68 (C-4a), 122.77 (C-5), 124.22 (C-3), 124.57 (C-1'), 129.99 (C-2',6'), 135.28 (C-2"), 153.01 (C-8a), 155.28 (C-2), 158.88 (C-4'), 159.85 (C-7), 174.89 (C-4); EIMS : $M^{+\cdot}$ m/z 308.

8-Allyl-7-hydroxy-2',4'-dichloroisoflavone 3c

pale yellow crystals m.p.156 °C; IR (KBr): 1624 cm^{-1} (C=O); UV (MeOH): 205 nm (log ε 4.9), 220 nm (log ε 4.8); ^1H NMR ($CDCl_3$) : δ 3.60 (d, J=6.0 Hz, H-1"), 6.00 (m,H-2"), 5.00 (m, H-3"), 6.85 (d,J=2.0 Hz, H-3'), 7.03-7.60 (m,H-6',5'), 7.0 (d, J=9.0 Hz,H-6), 7.85 (s, H-2), 8.20 (d, J= 9.0 Hz, H-5), 10.00 (s,7-OH); ^{13}C NMR (DMSO-D_6) : δ 26.53 (C-1"), 114.43 (C-8), 113.11 (C-6), 115.25 (C-3"), 116.34 (C-4a), 121.82 (C-5), 124.49 (C-3), 127.11 (C-1'), 128.63 (C-3'), 130.61 (C-5'), 133.74 (C-4'), 133.66 (C-6'), 135.02 (C-2'), 135.19 (C-2"), 154.73 (C-8a), 155.50 (C-2), 160.21 (C-7), 173.74 (C-4); LSIMS: $[M+H]^+$ m/z 347.

8-Allyl-7-hydroxy-4'-bromoisoflavone 3d

pale yellow crystals m.p 158°C; IR (KBr): 1638 cm^{-1} (C=O); UV (MeOH): 213 nm (log ε 4.7), 220 nm (log ε 4.8); ^1H NMR ($CDCl_3$) : δ 3.6 (d, J=6.0 Hz, H-1"), 6.0 (m, H-2"), 6.99 (d, J=9.0 Hz, H-6), 5.0 (m,H-3"), 7.59-7.72 (m, 4H,H-2',6',3',5'), 7.82 (s, H-2), 8.02 (d, J= 9.0 Hz, H-5), 10.40 (s,7-OH); ^{13}C NMR (DMSO-D_6): δ 26.47 (C-1"), 112.91 (C-6), 114.37 (C-8), 115.13 (C-3"), 116.56 (C-4a), 122.55 (C-5), 124.60 (C-3), 124.60 (C-4'), 124.60 (C-2',6'), 130.89 (C-3',5'), 128.77 (C-1'), 135.21 (C-2"), 154.02 (C-8a), 155.29 (C-2), 159.30 (C-7),174.43 (C-4); LSIMS: $[M+H]^+$ m/z 357.

8-Allyl-7-hydroxy -2',4'-dimethoxyisoflavone 3e

pale yellow crystals m.p. 160 °C; IR (KBr): 1633 cm^{-1} (C=O); UV (MeOH) : 221 nm (log ε 4.7), 206 nm (log ε 7.4); ^1H NMR ($CDCl_3$) : δ 3.64 (d, J=6.0 Hz,H-1"), 3.90 (OCH_3x2), 6.00 (m, H-2"), 5.00 (m, H-3"), 6.08-7.04 (m, 3H, H-6'-3',5'), 6.99 (d, J= 9.0 Hz, H-6), 8.00(s, H-2), 8.02 (d, J= 9.0 Hz, H-5), 10.50 (s, 7-OH); ^{13}C NMR (DMSO-D_6) : δ30.59 (C-1"), 55.51 (OCH_3x2), 101.36 (C-5'), 111.55 (C-1'), 112.78 (C-6), 115.03 (C-3"), 117.65 (C-4a), 118.16 (C-8), 121.19 (C-5), 123.40 (C-3'), 124.33 (C-3), 126.93 (C-6'), 132.75 (C-2"), 148.28 (C-2'), 148.64 (C-4'), 153.56 (C-8a), 157.22 (C-2), 162.47 (C-7), 174.52 (C-4); LSIMS: $[M+H]^+$ m/z 339

Oxidative cyclization of sodium salt of 8-allyl-7- hydroxyisoflavones 3a-e with dichlorobis (benzonitrile) palladium [$PdCl_2(PhCN)_2$]: 8-methyl-*4H*-furo-[2,3-h] isoflavones 4a-e: General procedure:

A suspension of sodium salt of 8-allyl-7-hydroxyisoflavones (10.0 mmols) in benzene (200 ml) containing [$PdCl_2(PhCN)_2$] (10 mmols) was stirred at room temperature for 30 minutes. The suspension became clear and developed intense red color during stirring. The clear solution was refluxed for 2 hrs, black metallic palladium separated out and the solution turned colorless.

Palladium was filtered, and the filtrate concentrated to yield the crude product. The products in each case were purified by column chromatography using silica gel. Elution with benzene gave benzonitrile and subsequent elution with chloroform gave 8-methyl-4*H*-furo-[2,3-*h*]isoflavones **4a-e** which recrystallized from chloroform in 85-90% yield.

8-Methyl-4H-furo[2,3-h] isoflavone 4a[12]
yellow crystals, m.p. 153°C; IR (KBr): 1683 cm^{-1}(C=O); UV (MeOH): 249 nm (log ε 4.0), 290 nm (log ε 4.4); ^{1}H NMR ($CDCl_3$) : δ2.58 (s, CH_3-8), 6.70 (s, H-9), 7.30-7.60 (m, H-6, 2',4',6',3',5'), 8.05 (s, H-2), 8.10 (d, J= 9.0 Hz, H-5); ^{13}C NMR ($CDCl_3$) : δ 12.18 (CH_3-8), 102.79 (C-9), 109.57 (C-6), 114.94 (C-9a), 118.32 (C-4a), 125.49 (C-5), 125.21 (C-3), 127.80 (C-4'), 128.05 (C-2',6'), 128.86 (C-3',5'), 131.75 (C-1'), 149.88 (C-9b), 152.08 (C-2), 156.61 (C-8), 161.42 (C-6a), 176.02 (C-4); EIMS : $M^{+\cdot}$ m/z 276.

8-Methyl-4'-methoxy-4H- furo [2,3-h] isoflavone 4b
yellow crystals, m.p. 166°C; IR (KBr): 1634 cm^{-1}(C=O); UV (MeOH): 257 nm (log ε 4.8), 303 nm (log ε 4.1); ^{1}H NMR ($CDCl_3$): δ 2.55 (s, CH_3-8), 3.82 (s, 4'-OCH_3), 6.70 (s, H-9), 6.90 (d, J= 9.0 Hz, 3',5'), 7.45 (d, J=9.0 Hz, H-6), 7.50 (d, J=9.0 Hz, H-2',6'), 8.00 (s,H-2), 8.10 (d, J=9.0 Hz, H-5); ^{13}C NMR ($CDCl_3$) : δ 13.97 (CH_3-8), 55.20 (4'-OCH_3), 99.77 (C-9), 113.83 (C-3',5'), 109.42 (C-6), 118.25 (C-4a), 119.63 (C-9a), 120.97 (C-5), 124.17 (C-3), 124.99 (C-1'), 130.08 (C-2',6'), 149.83 (C-9b), 151.50 (C-2), 156.49 (C-8), 157.62 (C-4'), 159.48(C-6a), 176.21(C-4); EIMS: $M^{+\cdot}$ m/z 306 (99), 291 (10), 174.

8-Methyl-2',4'-dichloro-4H-furo [2,3-h] isoflavone 4c
yellow crystals, m.p. 150°C; IR (KBr): 1635 cm^{-1}(C=O); UV (MeOH): 241 nm (log ε 4.8), 270 nm (log ε 4.2); ^{1}H NMR ($CDCl_3$) : δ 2.50 (s, CH_3-8), 6.60 (s, H-9), 6.90-7.30 (m, 3H, H-3',5',6'), 7.30 (d, J=9.0 Hz, H-6), 7.45 (s, H-2), 7.65 (d, J=9.0 Hz, H-5),; ^{13}C NMR ($CDCl_3$) : δ 14.04 (CH_3-8), 100.33 (C-9), 100.85 (C-6), 113.58 (C-9a), 119.16 (C-4a), 122.97 (C-5), 125.20 (C-3), 125.19 (C-5'), 129.48 (C-6'), 131.40 (C-3'), 132.52 (C-1'), 133.99 (C-4'), 135.31 (C-2'), 149.80 (C-9b), 155.45 (C-2), 155.43 (C-8), 159.76 (C-6a), 174.54 (C-4),; EIMS : $M^{+\cdot}$ m/z 345.

8-Methyl-4'-bromo-4H-furo-[2,3-h] isoflavone 4d
yellow crystals, m.p. 164°C; IR (KBr): 1684 cm^{-1}(C=O); UV (MeOH): 210 nm (log ε 4.7), 213 nm (log ε 4.0); ^{1}H NMR ($CDCl_3$) : δ 2.56 (s,CH_3-8), 6.70 (s,H-9), 6.90 (d, J=9.0 Hz,2H, H-3',5'), 7.30 (d, J= 9.0 Hz, H-6), 7.60 (d, J= 9.0 Hz, 2H, H-2',6'), 8.00 (s, H-2), 8.20 (d, J= 9.0 Hz, H-5); ^{13}C NMR ($CDCl_3$) : δ 13.85 (CH_3 -8), 99.82 (C-9), 109.58 (C-6), 118.21 (C-4a), 119.36 (C-9a), 120.64 (C-5), 121.99 (C-4'), 124.20 (C-3), 130.39 (C-3',5'), 130.73 (C-1'), 131.28 (C-2',6'), 149.69 (C-9b), 151.78 (C-2), 156.67 (C-8), 157.60 (C-6a), 175.54 (C-4); EIMS: $M^{+\cdot}$ m/z 355.

8-Methyl-2',4'-dimethoxy-4H- furo [2,3-h] isoflavone 4e
yellow crystals, m.p. 160°C; IR (KBr): 1635 cm^{-1}(C=O); UV (MeOH): 214 nm (log ε 4.9), 220 nm (log ε 4.7); ^{1}H NMR ($CDCl_3$) : δ 2.58 (s, CH_3-8), 3.95 (OCH_3x2), 6.90 (d, J=9.0 Hz, H-3'), 6.70 (s, H-9), 7.05 (dd, J=9.0 Hz, H-5'), 7.45 (d, J=9.0 Hz, H-6), 7.25 (d, J=9.0 Hz, H-6'), 8.02 (s, H-2), 8.15 (d, J=9.0 Hz, H-5); ^{13}C NMR ($CDCl_3$) : δ 14.12 (CH_3-8), 55.95 and 55.98 (OCH_3 x2), 100.08 (C-9), 109.67 (C-6), 111.18 (C-5'), 111.18 (C-3'), 118.40 (C-4a), 119.76 (C-9a), 121.12

(C-5), 124.71 (C-3), 112.62 (C-6'), 121.09 (C-1'), 148.79 (C-2'), 149.14 (C-9b), 149.72 (C-8), 151.78(C-2), 156.07 (C-4'), 157.82 (C-6a), 176.42 (C-4); EIMS : $M^{+\cdot}$ m/z 336.

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Received on November 11, 2013.