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ISOFLAVANS FROM *MILLETTIA RACEMOSA*

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Key Word Index—*Millettia racemosa*; Leguminosae; stems; 3*R*(+)-millinol; 3*R*(+)-millinol-B; 3*R*(+)-cyclomillinol; isoflavans insecticidal activity.

Abstract—From the stems (without bark) of *Millettia racemosa*, new isoflavans- 3*R*(+)-millinol, 3*R*(+)-millinol-B and 3*R*(+)-cyclomillinol were isolated. Their structures were determined by analytical and spectroscopic methods. All these compounds showed promising insecticidal activity.

INTRODUCTION

Several plants in the genus *Millettia* are well known for fish poisoning and insecticidal properties [1–4]. Rotenoids, flavonoids, isoflavonoids and 3-phenyl-4-hydroxycoumarins were isolated from these plants [5, 6]. We report herein the chemical investigation of the stems without bark of *Millettia racemosa* (Benth.) procured from Mannanoor forest of Andhra Pradesh, India. Except for the isolation of stigmasterol from the roots and β-sitosterol and stigmasterol from the bark of this plant [7], no other compounds responsible for insecticidal activity have been reported.

RESULTS AND DISCUSSION

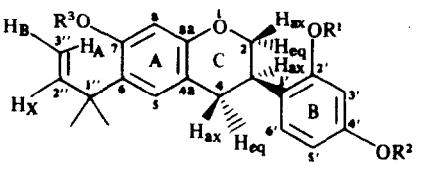
Procedures for the isolation of isoflavans 3R(+)-millinol (**1**), 3R(+)-millinol-B (**5**) and 3R(+)-cyclomillinol (**7**), the analytical and spectral characteristics of these compounds and their derivatives are given in the Experimental.

Millinol (**1**) formed a triacetate (**2**) mp 123° and a dimethyl ether (**3**) by ethereal diazomethane. Millinol (**1**) on prolonged methylation (Me_2SO_4, Me_2CO, K_2CO_3, 12 hr) formed a trimethyl ether (**4**). Thus the presence of three phenolic hydroxyls, one of which is a hindered phenolic hydroxyl, is indicated. The UV spectral data is characteristic of isoflavans [5]. ^{1}H NMR (500 MHz, $CDCl_3$) of **1** clearly indicated the complex ABMXX' system for the five proton isoflavan heterocyclic ring assigned to the H_ACH_B–CH_M–$H_XCH_{X'}$ [8, 9]. The well resolved coupling constants of heterocyclic protons $J_{2eq,3ax} = 3.0$ Hz, $J_{2eq,2ax} = 10.1$ Hz, $J_{2ax,3ax} = 10.1$ Hz, $J_{3ax,4ax} = 10.6$ Hz, $J_{3ax,4eq} = 5.1$ Hz and $J_{4ax,4eq} = 15.7$ Hz are characteristic of the isoflavan skeleton. In the ^{1}H NMR (500 MHz) spectra the C_4-methylene protons of **1** are well resolved and appeared as two clear double doublets whereas it was earlier reported [10–13] as a doublet of AA'B system. The signal due to H-3ax was very clearly resolved and appeared as an octet (δ3.49). Further the ^{1}H NMR spectrum revealed the presence of 1,1-dimethylallyl group [14]. Based on the chemical shifts of protons and coupling constants in ^{1}H NMR and on biogenetic grounds the three phenolic hydroxyl groups in **1** are assigned to C-7, C-2' and C-4' positions. Millinol (**1**) gave a position Gibbs test [15] (deep blue colour) indicating that the aromatic position *para* to 2'-OH is unsubstituted. ^{13}C NMR data also confirmed the structure assigned to millinol (**1**) [16].

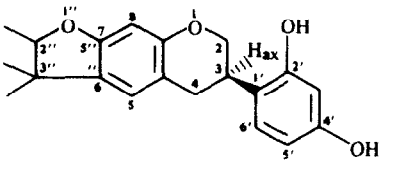
3*S*-Isoflavans were found to exhibit a negative CD Cotton effect in the region 270–300 nm whilst 3*R*-isoflavans were found to exhibit a positive CD Cotton effect in the same region [8, 17, 18]. Since millinol exhibited a positive CD Cotton effect in the region (at 287 nm), a 3*R*-configuration is indicated. However, ^{1}H NMR spectral data is not helpful in assigning the configuration at C_3 as '*S*' or '*R*' because of their identical chemical shifts and coupling constants in the stable half chair conformation of the heterocyclic C-ring [8–13]. A study of molecular models, using Karplus equation [19] and on the basis of the observed coupling constants of C-2, C-3 and C-4 protons of 3*R*(+)-Millinol (**1**) suggested that the heterocyclic C-ring is in a half chair conformation with the 3-aryl group occupying β-equatorial position [20].

In mass spectra, RDA fragmentation at *m/z* 136 (**8**) and *m/z* 191 (**10**) supported the placement of 1,1-dimethylallyl substituent in ring-A [9, 18, 21]. Due to this substituent at C_6, 7-OH is hindered and as such found to undergo methylation with difficulty. Acid catalysed cyclization of **1** furnished a compound (**7**). It gave a positive Gibbs test indicating aromatic position *para* to 2'-OH is unsubstituted. ^{1}H NMR spectral data indicated the formation of α,β,β-trimethyldihydrofurano ring system [22]. In the ^{1}H NMR spectra of millinol (**1**) as well as in compound **7**, the H-5 and H-8 resonated as singlets. Therefore in millinol (**1**), 1,1-dimethylallyl group is placed at C_6, while in compound **7**, the fused dihydrofurano ring is linear.

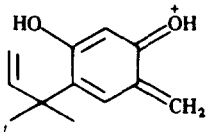
Millinol-B (**5**) formed a dimethyl ether identical (superimposable IR and co-TLC) with tri-*O*-methylmillinol (**4**). Millinol-B (**5**) gave a negative Gibbs test indicating the lone methoxyl group is located at 2' rather than at 4' in the ring-B. Cyclomillinol was found to be identical (superimposable IR and co-TLC) with **7**, the acid catalysed cyclization product of 3*R*(+)-millinol (**1**). All the three isoflavans (**1**, **5**, **7**) were found to exhibit insecticidal activity against fourth instar larvae of *Spodoptera litura* F.



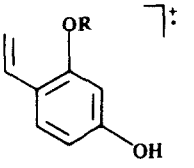
1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = R^3 = Ac$
3 $R^1 = R^2 = Me$, $R^3 = H$
4 $R^1 = R^2 = R^3 = Me$
5 $R^1 = Me$, $R^2 = R^3 = H$
6 $R^1 = Me$, $R^2 = R^3 = Ac$



7



10 *m/z* 191



8 R = H; *m/z* 136
9 R = Me; *m/z* 150

EXPERIMENTAL

The air-dried and powdered stems (without bark) of *Millettia racemosa* (6 kg) collected from the forests of Mannanoor, Andhra Pradesh, India were extracted with MeOH (20 l) under cold conditions and the extract concd under red. pres. to give a dark reddish gummy residue (90 g) which was redissolved in minimum amount of MeOH (600 ml) and adsorbed on the previously extracted plant material (500 g). The adsorbed plant material dried and re-extracted successively with petrol (bp 60–80°, 4 l) and $CHCl_3$ (4 l) in a Soxhlet. The extracts were concd to yield the following semisolids: petrol extract, light brown semisolid (8 g), $CHCl_3$ extract, dark red gummy substance (18 g).

The petrol extract on CC over silica gel afforded only sitosterol (2.3 g) mp 138°. The TLC examination ($CHCl_3$–EtOAc, 9:1) and spray reagent 2% H_2SO_4) of $CHCl_3$ extract revealed the presence of a number of closely related compounds. The $CHCl_3$ extract was separated into an ether-soluble fraction as a dark red gum (12 g) and an ether-insoluble fraction as a light brown solid (6 g). Both these fractions are soluble in dil. aq. NaOH indicating their phenolic nature. TLC examination of ether insoluble fraction ($CHCl_3$–EtOAc, 9:1) revealed that it was a complex mixture of compounds having close R_f values and therefore was not worked out.

The ether soluble portion was column chromatographed over silica gel (180 g, 200 mesh). Fractions of 50 ml each were collected by eluting successively with $CHCl_3$–EtOAc (9:1). The fractions were mixed on the basis of their identical behaviour on TLC. Fractions 1–4 did not yield any product. Fractions 5–18 afforded a light yellow gummy substance (0.2 g) which on rechromatography over silica gel (10 g, 200 mesh) gave a colourless gummy compound designated as cyclomillinol (**7**, 0.15 g). Fractions 19–28 afforded a light yellow gummy substance (1.4 g) which on rechromatography over silica gel (44 g, 200 mesh) gave a colourless gummy compound designated as millinol-B (**5**, 0.8 g). Fractions 29–54 afforded a light yellow gummy substance (3.3 g) which on rechromatography over silica gel (110 g, 200 mesh) afforded a colourless gummy compound designated as millinol (**1**, 2.1 g).

3R(+)-Millinol[3R(+)-*2′,4′,7-trihydroxy-* 6(1,1-*dimethylallyl*) *isoflavan*] (**1**). Colourless gum, $[\alpha]_D^{25} + 3.7°$ ($CHCl_3$; *c* 0.216) (Found: C, 73.68; H, 6.72. $C_{20}H_{22}O_4$ requires: C, 73.62; H, 6.75%.) Gibbs reagent–deep blue colour. UV λ_{max}^{MeOH} nm (log ε): 228 (4.17), 283 (3.91), 287 (3.91); no NaOAc, H_3BO_3 + NaOAc, $AlCl_3$ shifts; $\lambda_{max}^{MeOH+NaOMe}$ nm (log ε): 234 (4.07), 293 (3.92). ^{1}H NMR (500 MHz, $CDCl_3$): δ3.98 (1H, *t*, H-2ax, $J_{2ax,3ax} = 10.1$ Hz, $J_{2ax,2eq} = 10.1$ Hz), 4.29 (1H, *dd*, H-2eq, $J_{2eq,3ax} = 3.0$ Hz, $J_{2eq,2ax} = 10.1$ Hz), 3.49 (1H, octet, H-3ax), 2.98 (1H, *dd*, H-4ax, $J_{4ax,3ax} = 10.6$ Hz, $J_{4ax,4eq} = 15.7$ Hz), 2.87 (1H, *dd*, H-4eq, $J_{4eq,3ax} = 5.1$ Hz, $J_{4eq,4ax} = 15.7$ Hz), 6.93 (1H, *s*, H-5), 6.38 (1H, *s*, H-8), 6.30 (1H, *d*, H-3′, $J_{3'H,5'H} = 2.2$ Hz), 6.36 (1H, *dd*, H-5′, $J_{5'H,6'H} = 10.7$ Hz, $J_{5'H,3'H} = 2.2$ Hz), 6.92 (1H, *d*, H-6′, $J_{6'H,5'H} = 10.7$ Hz), 1.41 (6H, *s*, Me_2-1″), 6.17 (1H, *dd*, H_X-2″, $J_{2''Hx,3''HA} = 17.7$ Hz, $J_{2''Hx,3''HB} = 10.6$ Hz), 5.29 (1H, *dd*, H_A-3″, $J_{3''HA,2''Hx} = 17.7$ Hz, $J_{3''HA,3''HB} = 1.1$ Hz), 5.27 (1H, *dd*, H_B-3″, $J_{3''HB,2''Hx} = 10.6$ Hz, $J_{3''HB,3''HA} = 1.1$ Hz), 3.75 (2H, *s*, 2′,4′-OH), 5.78 (1H, *s*, 7-OH), ^{13}C NMR (22.63 MHz, $CDCl_3$): δ69.73 (C-2), 31.81 (C-3), 30.40 (C-4), 114.00 (C-4a), 128.10 (C-5), 125.00 (C-6), 154.66 (C-7), 104.86 (C-8), 153.20 (C-8a), 119.84 (C-1′), 154.22 (C-2′), 103.04 (C-3′), 153.50 (C-4′), 107.73 (C-5′) 127.00 (C-6′), 39.72 (C-1″), 27.04 (C-1″Me_2), 147.90 (C-2″), 112.68 (C-3″), MS *m/z* (rel. int.): 326 [M^+] (15), 311 (6), 257 (5), 191 (18), 175 (14), 136 (20), 124 (5), 123 (18), 121 (10), 69 (15), 43 (100). CD (MeOH; *c* 1×10^{-3}): $[\theta]_{232} -4.2 \times 10^4$, $[\theta]_{265} -0.49 \times 10^4$, $[\theta]_{272}$O, $[\theta]_{287} + 1.4 \times 10^4$, $[\theta]_{298}$O, $[\theta]_{307} -0.7 \times 10^4$.

*2′,4′,7-Tri-*O*-acetyl-*3R(+)-*millinol* (**2**). (**1**, Ac_2O-pyridine, room temp. 24 hr). Colourless amorphous solid, mp 123° (Found: C, 69.11; H, 6.09. $C_{26}H_{28}O_7$ requires: C, 69.03; H, 6.19%). UV λ_{max}^{MeOH} nm (log ε): 222 (4.19), 280 (3.85). ^{1}H NMR (90 MHz, $CDCl_3$): δ3.97 (1H, *t*, H-2ax, $J_{2ax,3ax} = 9.7$ Hz, $J_{2ax,2eq} = 9.7$ Hz), 4.26 (1H, *dd*, H-2eq, $J_{2eq,3ax} = 3.1$ Hz, $J_{2eq,2ax} = 9.7$ Hz), 3.34 (1H, *m*, H-3ax), 2.93–3.01 (2H, *m*, H-4ax, H-4cq), 7.22 (1H, *s*, H-5), 6.92 (1H, *s*, H-8), 6.52 (1H, *d*, H-3′, $J_{3'H,5'H} = 2.1$ Hz), 7.05 (1H, *dd*, H-5′, $J_{5'H,6'H} = 9.4$ Hz, $J_{5'H,3'H} = 2.1$ Hz), 7.23 (1H, *d*, H-6′, $J_{6'H,5'H} = 9.4$ Hz), 1.40 (6H, *s*, Me_2-1″), 5.96 (1H, *dd*, H_X-2″, $J_{2''Hx,3''HA} = 17.9$ Hz, $J_{2''Hx,3''HB} = 10.3$ Hz), 4.98 (1H, *dd*, H_A-3″, $J_{3''HA,2''Hx} = 17.9$ Hz, $J_{3''HA,3''HB} = 1.1$ Hz), 4.97 (1H, *dd*, H_B-3″, $J_{3''HB,2''Hx} = 10.3$ Hz, $J_{3''HB,3''HA} = 1.1$ Hz), 2.20 (3H, *s*, 7-OAc), 2.33 and

2.29 (6H, two *s*, 2′,4′-OAc). MS *m/z* (rel. int.): 452 [M^+] (12), 410 (25), 395 (20), 367 (5), 353 (10), 326 (5), 311 (5), 191 (18), 178 (15), 175 (20), 149 (10), 136 (20), 123 (25), 107 (8), 43 (100).

2′,4′-Di-O-methyl-3R(+)-millinol (**3**). (**1**, ethereal soln of CH_2N_2, 7 days) Colourless gum (Found: C, 74.63; H, 7.31. $C_{22}H_{26}O_4$ requires: C, 74.58; H, 7.34%). UV λ_{max}^{MeOH} nm (log ε): 215 (4.16), 285 (3.88); $\lambda_{max}^{MeOH+NaOMe}$ nm (log ε): 225 (4.25), 285 (3.72), ^{1}H NMR (90 MHz, $CDCl_3$): δ3.96 (1H, *t*, H-2ax, $J_{2ax,3ax}$ = 10.3 Hz, $J_{2ax,2eq}$ = 10.3 Hz), 4.21 (1H, *dd*, H-2eq, $J_{2eq,3ax}$ = 3.1 Hz, $J_{2eq,2ax}$ = 10.3 Hz), 3.50 (1H, *m*, H-3ax), 2.83–2.97 (2H, *m*, H-4ax, H-4eq), 6.92 (1H, *s*, H-5), 6.41 (1H, *s*, H-8), 6.49 (1H, *d*, H-3′, $J_{3'H,5'H}$ = 2.1 Hz), 6.36 (1H, *dd*, H-5′, $J_{5'H,6'H}$ = 9.3 Hz, $J_{5'H,3'H}$ = 2.1 Hz), 7.01 (1H, *d*, H-6′, $J_{6'H,5'H}$ = 9.3 Hz), 1.41 (6H, *s*, Me_2-1″), 6.13 (1H, *dd*, H_X-2″, $J_{2''Hx,3''H_A}$ = 17.6 Hz, $J_{2''Hx,3''H_B}$ = 10.2 Hz), 5.25 (1H, *dd*, H_A-3″, $J_{3''H_A,2''Hx}$ = 17.6 Hz, $J_{3''H_A,3''H_B}$ = 1.1 Hz), 5.23 (1H, *dd*, H_B-3″, $J_{3''H_B,2''Hx}$ = 10.2 Hz, $J_{3''H_B,3''H_A}$ = 1.1 Hz), 5.71 (1H, *br s*, 7-OH), 3.80 (6H, *s*, 2′,4′-OMe) MS *m/z* (rel. int.): 354 [M^+] (20), 339 (80), 285 (5), 191 (5), 175 (24), 164 (100), 152 (28), 151 (62), 149 (56), 121 (40), 69 (10).

2′,4′,7-Tri-O-methyl-3R(+)-millinol (**4**). (**1**, Me_2SO_4, Me_2CO, K_2CO_3, reflux, 12 hr). Colourless gum (Found: C, 75.12; H, 7.58. $C_{23}H_{28}O_4$ requires: C, 75.00; H, 7.61%). UV λ_{max}^{MeOH} nm (log ε): 220 (4.22), 283 (3.96); ^{1}H NMR (90 MHz, $CDCl_3$): δ3.98 (1H, *t*, H-2ax, $J_{2ax,3ax}$ = 10.2 Hz, $J_{2ax,2eq}$ = 10.2 Hz), 4.25 (1H, *dd*, H-2eq, $J_{2eq,3ax}$ = 3.2 Hz, $J_{2eq,2ax}$ = 10.2 Hz), 3.50 (1H, *m*, H-3ax), 2.86–2.96 (2H, *m*, H-4ax, 4-eq), 6.94 (1H, *s*, H-5), 6.40 (1H, *s*, H-8), 6.48 (1H, *d*, H-3′, $J_{3'H,5'H}$ = 2.0 Hz), 6.41 (1H, *dd*, H-5′, $J_{5'H,6'H}$ = 9.4 Hz, $J_{5'H,3'H}$ = 2.0 Hz), 7.02 (1H, *d*, H-6′, $J_{6'H,5'H}$ = 9.4 Hz), 1.43 (6H, *s*, Me_2-1″), 6.14 (1H, *dd*, H_x-2″, $J_{2''Hx,3''H_A}$ = 17.6 Hz, $J_{2''Hx,3''H_B}$ = 10.3 Hz), 4.82–5.01 (2H, *m*, H_A-3″, H_B = 3″), 3.80, 3.79 and 3.74 (9H, three *s*, 2′,4′,7-OMe). MS *m/z* (rel. int.): 368 [M^+] (100), 353 (15), 299 (8), 205 (5), 189 (48), 164 (73), 152 (15), 151 (72), 149 (30), 135 (10), 69 (5).

3R(+)-Millinol-B[3R(+)-2′- *methoxy*-4′,7- *dihydroxy*- 6(1,1-*dimethylallyl*)*isoflavan*] (**5**). Colourless gum, [α] +4.16° ($CHCl_3$; *c* 0.240). (Found: C, 74.21; H, 7.01. $C_{21}H_{24}O_4$ requires: C, 74.12; H, 7.06%). Gibbs reagent-no reaction. UV λ_{max}^{MeOH} nm (log ε): 215 (4.17), 281 (3.92), 286 (3.92); $\lambda_{max}^{MeOH+NaOMe}$ nm (log ε): 223 (4.24), 294 (3.94). ^{1}H NMR (90 MHz, $CDCl_3$): δ4.03 (1H, *t*, H-2ax, $J_{2ax,3ax}$ = 10.1 Hz, $J_{2ax,2eq}$ = 10.1 Hz), 4.33 (1H, *dd*, H-2eq, $J_{2eq,3ax}$ = 3.1 Hz, $J_{2ax,2eq}$ = 10.1 Hz), 3.35–3.65 (1H, *m*, H-3ax), 2.90–3.05 (2H, *m*, H-4ax, H-4eq), 6.96 (1H, *s*, H-5), 6.50 (1H, *s*, H-8), 6.52 (1H, *d*, H-3′, $J_{3'H,5'H}$ = 2.4 Hz), 6.36 (1H, *dd*, H-5′, $J_{5'H,3'H}$ = 2.4 Hz, $J_{5'H,6'H}$ = 10.8 Hz), 6.99 (1H, *d*, H-6′, $J_{6'H,5'H}$ = 10.8 Hz) 1.42 (6H, *s*, Me_2-1″), 6.16 (1H, *dd*, H_X-2″), $J_{2''Hx,3''H_A}$ = 17.7 Hz, $J_{2''Hx,3''H_B}$ = 10.5 Hz), 5.30 (1H, *dd*, H_A-3″, $J_{3''H_A,2''Hx}$ = 17.7 Hz, $J_{3''H_A,3''H_B}$ = 1.1 Hz), 5.28 (1H, *dd*, H_B-3″, $J_{3''H_B,2''Hx}$ = 10.5 Hz, $J_{3''H_B,3''H_A}$ = 1.1 Hz), 3.76 (3H, *s*, 2′-OMe), 3.81 (1H, *s*, 4′-OH), 5.75 (1H, *s*, 7-OH), ^{13}C NMR (22.63 MHz, $CDCl_3$): δ70.19 (C-2), 32.04 (C-3), 30.61 (C-4), 114.77 (C-4a), 128.48 (C-5), 125.82 (C-6), 155.45 (C-7), 105.28 (C-8), 153.70 (C-8a), 120.29 (C-1′), 155.06 (C-2′), 103.71 (C-3′), 153.83 (C-4′), 108.14 (C-5′), 127.70 (C-6′), 61.15 (C-2′ OMe), 39.96 (C-1″), 27.36 (C-1″ Me_2), 148.50 (C-2″), 113.08 (C-3″). MS *m/z* (rel. int.): 340 [M^+] (85), 325 (20), 271 (5), 191 (58), 175 (42), 150 (100), 138 (12), 137 (64), 135 (10), 121 (14), 69 (28). c.d. (MeOH: *c* 1×10^{-3}): $[\theta]_{233} - 3.25 \times 10^3$, $[\theta]_{267} - 0.65 \times 10^4$, $[\theta]_{276}0$, $[\theta]_{288} + 1.25 \times 10^4$, $[\theta]_{298}0$, $[\theta]_{308} - 0.6 \times 10^4$.

4′,7-Di-O-acetyl-3R(+)-millinol-B (**6**). (**5**, Ac_2O-pyridine, room temp. 24 hr). Colourless gum (Found: C, 70.84; H, 6.56. $C_{25}H_{28}O_6$ requires: C, 70.75, H, 6.60%). UV λ_{max}^{MeOH} nm (log ε): 225 (4.19), 283 (3.87). ^{1}H NMR (90 MHz, $CDCl_3$): δ3.93 (1H, *t*, H-2ax, $J_{2ax,3ax}$ = 10.2 Hz, $J_{2ax,2eq}$ = 10.2 Hz), 4.20 (1H, *dd*, H-2eq, $J_{2eq,3ax}$ = 3.0 Hz, $J_{2ax,2eq}$ = 10.2 Hz), 3.34 (1H, *m*, H-3ax), 2.86–2.95 (2H, *br d*, H-4ax, H-4eq), 7.07 (1H, *s*, H-5), 6.42 (1H, *s*, H-8), 6.63 (1H, *d*, H-3′, $J_{3'H,5'H}$ = 2.3 Hz), 6.81 (1H, *dd*, H-5′, $J_{5'H,3'H}$ = 2.3 Hz, $J_{5'H,6'H}$ = 9.3 Hz), 7.11 (1H, *d*, H-6′, $J_{6'H,5'H}$ = 9.3 Hz), 1.39 (6H, *s*, Me_2-1″, 5.97 (1H, *dd*, H_X-2″, $J_{2''Hx,3''H_A}$ = 17.8 Hz, $J_{2''Hx,3''H_B}$ = 10.4 Hz), 4.99 (1H, *dd*, H_A-3″, $J_{3''H_A,2''Hx}$ = 17.8 Hz, $J_{3''H_A,3''H_B}$ = 1.2 Hz), 4.96 (1H, *dd*, H_B-3″, $J_{3''H_B,2''Hx}$ = 10.4 Hz, $J_{3''H_B,3''H_A}$ = 1.2 Hz), 3.79 (3H, *s*, 2′-OMe), 2.63 (3H, *s*, 4′-OAc), 2.39 (3H, *s*, 7-OAc). MS *m/z* 424 [M^+].

3R(+)-2″,3″-Dihydro-2″,3″,3″ -trimethyl-2′,4′- dihydroxyfuro [4″,5″,:6,7]*isoflavan* (**7**). (**1**, HOAc, H_2SO_4, warm) Colourless gum, $[\alpha]_D^{25}$ +3.9° ($CHCl_3$, *c* 0.212) (Found: C, 73.72; H, 6.74. $C_{20}H_{22}O_4$ requires: C, 73.62; H, 6.75%). Gibbs reagent–deep blue colour. UV λ_{max}^{MeOH} nm (log ε): 215 (4.08), 283 (3.94), 288 (3.94). ^{1}H NMR (90 MHz, $CDCl_3$): δ3.91–4.34 (2H, *m*, H-2ax, H-2eq), 3.42–3.54 (1H, *m*, H-3ax), 2.84–2.99 (2H, *m*, H-4ax, H-4eq), 6.95 (1H, *s*, H-5), 6.21 (1H, *s*, H-8), 6.25–6.90 (3H, *m*, H-3′, H-5′, H-6′), 1.12 and 1.30 (6H, 2*s*, Me_2-3″), 1.38 (3H, *d*, Me-2″, *J* = 7.0 Hz), 4.42 (1H, *q*, H-2″, *J* = 7.0 Hz), 3.78 (2H, *s*, 2′,4′-OH). MS *m/z* 326 [M]$^+$. CD (MeOH; *c* 1×10^{-3}): $[\theta]_{230} - 4.25 \times 10^4$, $[\theta]_{269} - 0.7 \times 10^4$, $[\theta]_{278}$O, $[\theta]_{288} + 1.1 \times 10^4$, $[\theta]_{298}$O, $[\theta]_{309} - 1.0 \times 10^4$.

4′,7-Di-O-methyl-3R(+)-millinol-B. (**5**, Me_2SO_4, Me_2CO, K_2CO_3, reflux, 12 hr). The analytical and spectral characteristics are similar to **4**. Direct comparison (superimposable IR and co-TLC) revealed its identity to **4**.

3R(+)-Cyclomillinol. The analytical and spectral characteristics of this compound are similar to 3*R*(+)-2″,3″-dihydro-2″,3″,3″-trimethyl-2′,4′-dihydroxyfuro [4″,5″:6,7] isoflavan (**7**), the acid catalysed cyclized product of 3R(+)-millinol (**1**). Direct comparison (superimposable IR and co-TLC) revealed its identity to **7**.

The insecticidal activity of the isoflavan (**1**, **5**, **7**) was assessed by a modification of the non-choice test method of ref. [23] using IV instar larvae of *Spodoptera litura* F. and freshly cut castor leaves. The percentage of insecticidal activity was determined by the method of ref. [24] using fenvalerate as standard. With 3*R* (+)-millinol (**1**), 3R(+)-millinol-B (**5**), 3R(+)-cyclomillinol (**7**) the larvae suffered mortality (*c* 1000 mg/l) at the end of 36 hr due to stomach poison with the % protection of castor leaves 98.85, 98.32 and 98.74 respectively. Thus the insecticidal nature of the *Millettia racemosa* may be due to the presence of these compounds.

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