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# ABSOLUTE CONFIGURATIONS OF ISOFLAVANS*

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**Key Word Index**—*Cyclolobium*; *Dalbergia*; *Machaerium*; Leguminosae–Lotoideae; isoflavans; isoflavanquinones; absolute configurations.

**Abstract**—The absolute configurations of isoflavans and isoflavanquinones isolated from *Cyclolobium, Dalbergia* and *Machaerium* species were established by comparison of their ORD curves with that of (3*S*)-5,7,3′,4′-*tetra*-methoxyisoflavan and (3*S*)-7,4′-dimethoxyisoflavan-2′,5′-quinone, respectively. The assignments were checked by the ozonolysis of the isoflavan (−)-duartin to (*R*)-paraconic acid and the oxidation of isoflavans to isoflavanquinones. The PMR spectra of the dihydropyran ring of the isoflavans are discussed in terms of the preferred conformation of this ring.

## INTRODUCTION

A number of isoflavans was isolated from *Cyclolobium, Dalbergia* and *Machaerium* species (Table 1). The determination of the absolute configuration of these compounds, already reported in preliminary form [9], was necessary, both as part of the structural elucidation and in order to examine relationships of possible biogenetic significance [10, 11].

## RESULTS

The ORD curves of the natural compounds **1**–**4** (Table 1), as well as those of the animal metabolite (3*S*)-equol (**12a**) [9, 12] and of (3*S*)-5,7,3′,4′-tetramethoxyisoflavan [13, 14], all exhibited a negative Cotton effect in the 260–300 nm region, in opposition to the ORD curves of the isolates **7**–**9** (Table 1) which exhibited a positive Cotton effect in this region. Comparing additionally the UV spectra of these compounds, we conclude that the isoflavans **1**–**4** and **7**–**9** have, respectively, the 3*S*- and 3*R*-configuration.

The validity of this assignment for (−)-duartin (**4**) was checked by degradation. The absolute configuration of dihydrotrifolirhizin tetraacetate (**13**) has been established [15] by ozonolysis to (*S*)-(−)-paraconic acid (**14a**) [16]. Similar ozonolyses of the isoflavan **12b**, whose *S*-configuration was assigned on basis of its synthesis [13] and relationship with (*S*)-(−)-methylsuccinic acid [13, 14], and of **4** gave (*R*)-(+)-paraconic acid (**14b**) [17].

As a further check on the validity of the use of ORD characteristics for the assignment of configurations to the isoflavans of Table 1, the ORD curves of some of the corresponding isoflavanones were examined. It was anticipated that the aroyl chromophore of the isoflavanones would result in more pronounced Cotton effects than the aryl group of the isoflavans. The preparation of

*Part 6 in the series 'Isoflavonoid Constituents of *Dalbergia* and *Machaerium* Species'. For Part 5 see ref. [1].

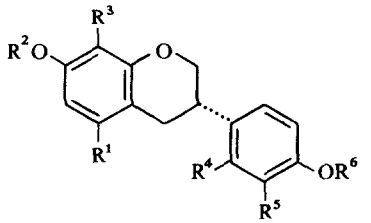
Table 1. Isoflavans of *Cyclolobium, Dalbergia* and *Machaerium* species.

| Isoflavan | Substituents at position 3 | 7 | 8 | 2′ | 3′ | 4′ | 5′ | Plant Source* |
|---|---|---|---|---|---|---|---|---|
| **1** (+)-Vestitol | *S* | OH | — | OH | — | OMe | — | Dec, Dva, Mve |
| **2** 7-*O*-Methylvestitol | *S* | OMe | — | OH | — | OMe | — | Dec |
| **3** (−)-Mucronulatol | *S* | OH | — | OMe | OH | OMe | — | Mmu, Mop, Mve, Mvi |
| **4** (−)-Duartin | *S* | OH | OMe | OMe | OH | OMe | – | Mmu, Mop, Mve, Mvi |
| **5** (−)-Mucroquinone | *S* | OH | OMe | =O | — | OMe | =O | Mmu |
| **6** (±)-Mucronulatol | — | OH | — | OMe | OH | OMe | — | Dva, Mmu |
| **7** Vestitol | *R* | OH | — | OH | — | OMe | — | Ccl |
| **8** Mucronulatol | *R* | OH | — | OMe | OH | OMe | — | Dce |
| **9** α,α-Dimethylallylcyclolobin | *R* | OH | — | OMe | OH | OH | X | Ccl |
| **10** Mucroquinone | *R* | OH | OMe | =O | — | OMe | =O | Ccl |
| **11** Claussequinone | *R* | OH | — | =O | — | OMe | =O | Ccl, Cve |

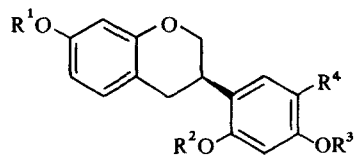
* Key: Ccl *C. clausseni* Benth. [2]; Cve *C. vecchii* A. Samp. [2]; Dcc *D. cearensis* Ducke [3]; Dec *D. ecastophyllum* (L.) Taub. [4]; Dva *D. variabilis* Vog. [5]; Mmu *M. mucronulatum* (Mart.) Benth. [6]; Mop *M. opacum* Vog. [7]; Mve *M. vestitum* Vog. [8]; Mvi *M. villosum* Vog. [6]; X = 1,1-dimethylallyl.

the isoflavanone **15a** from (−)-equol dimethyl ether (**12c**) has been described [18] and the isoflavanones **15b**, **15c** and **15d** were prepared, similarly by oxidation with $KMnO_4$, from respectively (−)-mucronulatol dimethyl ether (**12d**), (−)-duartin dimethyl ether (**12e**) and (+)-7,2′,4′-trimethoxyisoflavan (**12f**). All four isoflavanones showed intense negative Cotton effects in the 330–350 nm spectral region.

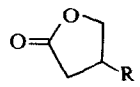
The isoflavan **12f** was prepared from natural (6*aS*, 11*aS*)-3,9-dimethoxypterocarpan [(+)-homopterocarpin] [6, 8] by hydrogenation to **12g**, followed by methylation. Both, **12f** and **12g**, are thus (3*S*)-isoflavans



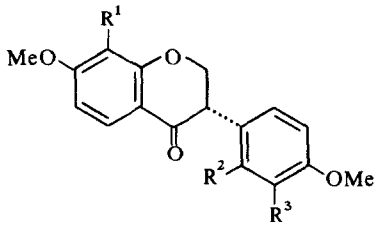
**12a** $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$
**12b** $R^1 = R^5 = OMe$, $R^2 = R^6 = Me$, $R^3 = R^4 = H$
**12c** $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = R^6 = Me$
**12d** $R^1 = R^3 = H$, $R^2 = R^6 = Me$, $R^4 = R^5 = OMe$
**12e** $R^1 = H$, $R^2 = R^6 = Me$, $R^3 = R^4 = R^5 = OMe$
**12f** $R^1 = R^3 = R^5 = H$, $R^2 = R^6 = Me$, $R^4 = OMe$
**12g** $R^1 = R^3 = R^5 = H$, $R^2 = R^6 = Me$, $R^4 = OH$



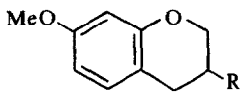
**13a** $R^1$ = tetraacetylglucosyl, $R^2 = H$, $R^3 - R^4 = CH_2O$
**13b** $R^1 = R^3 = Me$, $R^2 = R^4 = H$
**13c** $R^1 = R^2 = R^3 = Me$, $R^4 = H$



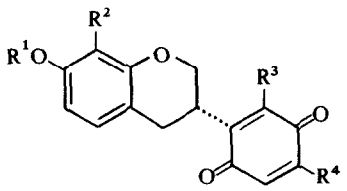
**14a** $R = \beta\text{-}CO_2H$
**14b** $R = \alpha\text{-}CO_2H$



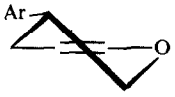
**15a** $R^1 = R^2 = R^3 = H$
**15b** $R^1 = H$, $R^2 = R^3 = OMe$
**15c** $R^1 = R^2 = R^3 = OMe$
**15d** $R^1 = R^3 = H$, $R^2 = OMe$



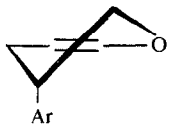
**16a** $R = \alpha\text{-}CO_2H$
**16b** $R = \beta\text{-}CO_2H$



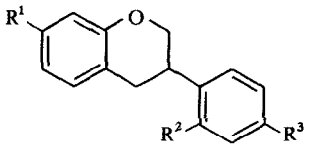
**17a** $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = OMe$
**17b** $R^1 = H$, $R^2 = R^3 = R^4 = OMe$
**17c** $R^1 = Me$, $R^2 = R^3 = R^4 = OMe$



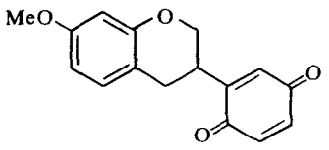
**18a**



**18b**



**19a** $R^1 = R^2 = R^3 = H$
**19b** $R^1 = R^3 = OMe$, $R^2 = H$
**19c** $R^1 = R^3 = OAc$, $R^2 = H$
**19d** $R^1 = R^2 = OMe$, $R^3 = H$
**19e** $R^1 = OMe$, $R^2 = OAc$, $R^3 = H$
**19f** $R^1 = OMe$, $R^2 = OH$, $R^3 = H$



**20**

and show, as expected, negative Cotton effects in the 260–300 nm region. Oxidation of (+)-dihydrohomopterocarpin (**12g**) with $KMnO_4$ gave (−)-7-methoxychroman-3-carboxylic acid (**11a**) with a similar mp but opposite $[\alpha]_D$ to the acid **16b** obtained by the oxidation of (−)-dihydrohomopterocarpin (**13b**) [19, 20].

The ORD characteristics of the quinonoid isoflavans **5**, **10** and **11** (Table 1) were very different from those of the simple isoflavans. The *S*-configuration of **5** and the *R*-configuration of **10** and **11** were established respectively by the similarity and dissimilarity of their ORD curves with that of (3*S*)-(−)-7,4′-dimethoxyisoflavan-2′,5′-quinone (**17a**). The *S*-configuration of **17a** follows from its synthesis by the oxidation of (+)-dihydrohomopterocarpin (**12g**) with Fremy's salt [21].

This empirical use of ORD to compare absolute configurations of related aromatic compounds, however, is potentially misleading when applied to isoflavans which have complex aromatic chromophores and some conformational freedom [9, 22]. Thus the isoflavanquinones **17b** and **17c** were prepared by oxidation of (3*S*)-duartin (**4**) and must therefore both have the *S*-configuration; the ORD curves of **17b** and **17c** are, nevertheless, almost enantiomeric in the 400–500 nm region with those of the (3*S*)-isoflavanquinones **5** and **17a**. This difference could just be a consequence of the different chromophores of the two pairs of quinones [cf. 23], but examination of the PMR spectra of the dihydropyran ring protons revealed an interesting conformational situation. This ring is expected to assume a half-chair conformation by analogy with cyclohexene and on general considerations of the minimisation of torsional strain [24]. It is not possible to state which of the two possible conformations **18a** or **18b** is expected to be of lower free energy, since the axial 3-aryl substituent in **18b** does not result in the destabilising 1,3-diaxial interaction of axially substituted cyclohexane and cyclohexene systems [24]. The PMR lines of the dihydropyran ring protons of isoflavans form an ABMXY or ABMXX′ system which is complex at 60 MHz. At 220 MHz, however, coupling constants were readily obtained for the natural (**1**, **3**, **4**) and synthetic (**19a–e**) isoflavans and the natural (**5**) and synthetic (**17b**, **c**, **20**) isoflavanquinones. The models **19a–e** and **20** were prepared, respectively by reduction of the appropriate isoflavones and by oxidation of 2′-hydroxy-7-methoxyisoflavan (**19f**) with Fremy's salt. The vicinal proton coupling constants for the isoflavans **1**, **3**, **4** and **19a–e** are similar in magnitude to those of the isoflavanquinones **17b** and **17c** and are consistent with the values expected for the half-chair conformation **18a** in which the 3-aryl or 3-quinonyl substituent occupies an equatorial position ($J_{2,3}$ = 2–3.5 and 10–10.5 Hz; $J_{3,4}$ = 5–7 and 10.5–12.5 Hz, for ABMXX′ systems: average $J_{3,4}$ = 7.5–8 Hz). The observed vicinal coupling constants for the isoflavanquinones **5** and **20** are, however, quite different and are consistent with the values expected from a conformational equilibrium in which **18b**, with an axial 3-quinonyl substituent, is the major contributor ($J_{2,3}$ = 2.5–3 and 6–6.5 Hz; $J_{3,4}$ = 6 and 6.5 Hz). These conformational differences between the pairs of quinones **5** and **20**, which lack the 6′-methoxy substituent, and **17b** and **17c**, which have a 6′-methoxy substituent, are clearly related to the atypical ORD characteristics shown by (−)-mucroquinone (**5**) and **17a**.

## DISCUSSION

The correlation of structure and source of pterocarpans [1] and isoflavans is consistent with their postulated biosynthetic connection [11]. (6*aS*, 11*aS*)-Pterocarpans and (3*S*)-isoflavans occur in all *Machaerium* and some *Dalbergia* species examined. In contradistinction, (6*aR*, 11*aR*)-pterocarpans and (3*R*)-isoflavans were isolated only from some special *Dalbergia* and closely related *Cyclolobium* species.

## EXPERIMENTAL

Unless otherwise stated spectra were measured in EtOH (UV), $CHCl_3$ (IR), $CHCl_3$ (60 MHz PMR) and MeOH (ORD). All evapns of volatile material were performed under diminished pressure.

*Ozonolyses of* (−)-5,7,3′,4′-*tetramethoxyisoflavan* (**12b**) *and of* (−)-*duartin* (**4**). Ozonised oxygen was passed through **12b** [13] in HOAc (20 ml) (room temp., 20 hr). After evap of the HOAc, 3% aq. $H_2O_2$ (10 ml) was added and the mixture was heated (100°, 10 min). Acidification and evap gave a residue which was triturated with $CHCl_3$. Evap of the $CHCl_3$ soln gave (+)-paraconic acid (**14b**, 30 mg), $[\alpha]_D^{20°}$ +17.3° (*c* 1.18, MeOH), identical (IR) with an authentic sample [16]. Ozonolysis of **4** (200 mg) also gave **14b** (47 mg).

*Synthesis of* (+)-7,2′,4′-*trimethoxyisoflavanone* (**15d**). (a) *Preparation of* (+)-2′-*hydroxy*-7,4′-*dimethoxyisoflavan* (**12g**). (+)-Homopterocarpin [6, 8] (730 mg) in HOAc (100 ml) was hydrogenated (room temp., 1 atm) over 10% Pd/C (200 mg). Filtration and evap of the HOAc gave a residue which was purified by TLC (Si gel, $CHCl_3$) and cryst. to **12g** (550 mg), rhombs, mp 154° (EtOH–$H_2O$), $[\alpha]_D^{20°}$ +13.3° (*c* 0.306, MeOH). $\nu_{max}$ ($cm^{-1}$): 3500, 1600, 1580. [Lit. [18] data for the (−)-isomer **13b**, mp 154°, $[\alpha]_D^{20°}$ −12.7° (*c* 0.295, EtOH)]. (b) *Preparation of* (+)-7,2′,4′-*trimethoxyisoflavan* (**12f**). MeI-methylation of **12g** (550 mg) gave **12f** (200 mg), rhombs, mp 63° (EtOH–$H_2O$) [lit. [25] mp for the (−)-isomer **13c** 61° (EtOH–$H_2O$)]. (c) *Preparation of* (+)-7,2′,4′-*trimethoxyisoflavanone* (**15d**). **12f** (200 mg) in $Me_2CO$ (30 ml) was stirred (room temp., 14 hr) with 5% aq. $KMnO_4$ (20 ml) and treated with excess $SO_2$. Evap of the $Me_2CO$ gave a residue which, by extraction with $CHCl_3$, evap and TLC (Si gel, $C_6H_6$–$CHCl_3$), gave **15d** (20 mg), needles, mp 127° (petrol) (lit. [18] mp for the (−)-isomer 127°), $[\alpha]_D^{20°}$ + 39° (*c* 0.7, $CHCl_3$).

*Oxidation of* (+)-*dihydrohomopterocarpin* (**12g**) *to* (−)-7-*methoxychroman*-3-*carboxylic acid* (**16a**). **12g** (320 mg) in $Me_2CO$ (50 ml) was stirred (room temp., 25 min) with 5% aq. $KMnO_4$ (40 ml) and treated with excess $SO_2$. Evap of the $Me_2CO$ gave a residue which, by extraction with $CHCl_3$, evap and sublimation, gave **16a** (170 mg), plates, mp 152° (lit. [18] mp for the (+)-isomer **16b** 149°), $[\alpha]_D^{20°}$ −37° (*c* 0.80, $CHCl_3$), identical (IR) with (±)-7-methoxychroman-3-carboxylic acid obtained by the analogous reaction on (±)-2′-hydroxy-7-methoxyisoflavan (**19f**).

*Oxidations of isoflavans to isoflavanquinones* with Fremy's salt were as described for the synthesis of (±)-mucroquinone [6]. (a) *Preparation of* 2-(7-*methoxychroman*-3-*yl*)-1,4-*benzoquinone* (**20**). Oxidation (13 hr) of **19f** (200 mg) in MeOH (10 ml) with $ON(SO_3K)_2$ (500 mg) in $H_2O$ (10 ml) gave **20** (27 mg), yellow needles, mp 125° (EtOH). [Found: C, 70.87; H, 5.25. $C_{16}H_{14}O_4$ requires: C, 71.10; H, 5.22%]. $\lambda_{max}$ (nm): 230, 249, 283, 289, 315 (ε 13200, 16000, 3800, 3450, 600). $\nu_{max}$ ($cm^{-1}$): 1600, 1625, 1585. PMR (τ): 3.52 (*dd*), 3.60 (*d*), 3.06 (*d*) (ABX system, $J_{AB}$ = 2.5 Hz, $J_{AX}$ = 8.5 Hz, H-6, H-8, H-5), 3.43 (*d*, *J* = *ca* 1 Hz, quinonoid H-3), 3.24 (*s*, quinonoid H-5, H-6), 5.5–7.5 (*m*, 2H-2, H-3, 2H-4), 6.25 (*s*, OMe). (b) *Preparation of* (+)-2-*methoxy*-5-(7-*methoxychroman*-3-*yl*)-1,4-*benzoquinone* (**17a**). Oxidation (16 hr) of **12g** (60 mg) in MeOH (10 ml) with $ON(SO_3K)_2$ (300 mg) in $H_2O$ (10ml) gave **17a** (25 mg), yellow platelets, mp 179° (lit. [18] mp for (−)-isomer 177.5–178.5°), $[\alpha]_D^{20°}$ +45° (*c* 0.81, $CHCl_3$). [Found: C, 67.77; H, 5.51. $C_{17}H_{16}O_5$ requires: C, 67.99; H, 5.37%]. $\lambda_{max}$ (nm): 225, 266, 357 (ε 11300, 16000, 950). $\nu_{max}$ ($cm^{-1}$): 1680, 1650, 1625, 1605, 1590. ORD (*c* 0.081): $[\phi]_{500}$

$-219$, $[\phi]_{400}$ $+1310$, $[\phi]_{345}$ $-435$, $[\phi]_{299}$ $+3600$, $[\phi]_{290}$ $+2400$, $[\phi]_{278}$ $+4800$. (c) *Preparation of* (−)-2,6-*dimethoxy*-3-(7-*hydroxy*-8-*methoxychroman*-3-*yl*)-1,4-*benzoquinone* (**17b**). Oxidation (20 hr) of **4** (2 g) in MeOH (100 ml) with $ON(SO_3K)_2$ (8 g) in $H_2O$ (150 ml) gave **17b** (1.4 g), orange platelets, mp 190° (EtOH), $[\alpha]_D^{20°}$ −85° (*c* 0.90, $CHCl_3$). [Found: C, 62.68; H, 5.27. $C_{18}H_{18}O_7$ requires: C, 62 42; H, 5.24%]. $\lambda_{max}$ (nm): 225, 287, 360 (ε 20000, 17100, 700). $\nu_{max}$ ($cm^{-1}$): 3500, 1685, 1645, 1600. PMR (τ): 3.36 (*d*), 3.50 (*d*) (AB system, $J_{AB}$ = 9 Hz, H-5, H-6), 4.12 (*s*, quinonoid H-5), 4.22 (*br. s*, OH), 5.35–7.7 (*m*, 2H-2, H-3, 2 H-4), 6.01, 6.10, 6.19 (3*s*, 3OMe). ORD (*c* 0.098): $[\phi]_{500}$ −334, $[\phi]_{417}$ −911, $[\phi]_{328}$ −3010, $[\phi]_{299}$ −836. (d) *Preparation of* (−)-2,6-*dimethoxy*-3-(7,8-*dimethoxychroman*-3-*yl*)-1,4-*benzoquinone* (**17c**). **17b** (90 mg), $Me_2SO_4$ (200 mg), $K_2CO_3$ (200 mg) in $Me_2CO$ (20 ml) were heated under reflux (12 hr). Evap of the $Me_2CO$, addition of $H_2O$ and $CHCl_3$ extraction gave **17c** (25 mg), orange plates, mp 137° (EtOH), $[\alpha]_D^{20}$ −55° (*c* 1 02, $CHCl_3$). [Found: C, 63.04; H, 5.77. $C_{19}H_{20}O_7$ requires: C, 63.33; H, 5.59%]. $\lambda_{max}$ (nm): 285, 3500 (ε 12000, 850). $\nu_{max}$ ($cm^{-1}$): 1685, 1645, 1600. PMR (τ): 3.29 (*d*), 3.49 (*d*) (AB system, $J_{AB}$ = 9 Hz, H-5, H-6), 4.13 (*s*, quinonoid H-5), 5.3–7.6 (*m*, 2H-2, H-3, 2H-4), 6.02, 6.12, 6.16, 6.18, (4*s*, 4OMe). ORD (*c* 0.084): $[\phi]_{464}$ −300, $[\phi]_{417}$ −500, $[\phi]_{385}$ −300, $[\phi]_{333}$ −2200, $[\phi]_{393}$ −1590.

*Reduction of isoflavones to isoflavans* with hydrogen (1 atm., room temp.) were carried out as described for the synthesis of (±)-duartin [7]. (a) *Preparation of* (±)-*isoflavan* (**19a**). Hydrogenation of isoflavone (60 mg) in HOAc (20 ml) over 10% Pd/C (50 mg) gave **19a** (35 mg), needles, mp 56° (MeOH) (lit. [25] mp 55°). [Found: C, 85.23; H, 6.70. $C_{15}H_{14}O_4$ requires: C, 85.68; H, 6.70%]. $\nu_{max}$ ($cm^{-1}$): 1604, 1585, 1490, 1450. PMR (τ): 2.5–3.3 (*m*, 9ArH), 5.69 (*dd*, *J* = 10.5 and 3 Hz, H-2), 5.98 (*dd*, *J* = 10.5 and 8.6 Hz, H-2), 6.6–7.3 (*m*, H-3, 2H-4). (b) *Preparation of* (±)-2′-*hydroxy*-7-*methoxyisoflavan* (**19f**) Hydrogenation of 2′-hydroxy-7- methoxyisoflavone (28 g) [26] in HOAc (200 ml) over 10% Pd/C (4 g) gave by fractional cryst. **19f** (12 g), needle clusters, mp 119° ($C_6H_6$–petrol). [Found: C, 75.21; H, 6.37. $C_{16}H_{16}O_3$ requires: C, 74.98; H, 6.29%]. PMR (τ): 3.56 (*dd*), 3.58 (*d*), 2.75 (*d*) (ABX system, $J_{AB}$ = 2.5 Hz, $J_{AX}$ = 8.5 Hz, H-6, H-8, H-5), 2.9–3.5 (*m*, 4ArH), 4.6 (*br. s*, OH), 5.5–6.8 (*m*, 2H-2, H-3), 6.25 (*s*, OMe), 7.05 (*br. d*, *J* = 7.5, 2H-4). TLC (Si gel, $CHCl_3$) of the mother liquors gave (±)-3-methoxypterocarpan (2 g), mp 95° (EtOH). [Found: C, 76.22; H, 5.64. $C_{16}H_{14}O_3$ requires: C, 75.58; H, 5.55%]. PMR (τ): 3.41 (*dd*), 3.56 (*d*), 2.60 (*d*) (ABX system, $J_{AB}$ = 2.5 Hz, $J_{AX}$ = 8 Hz, H-2, H-4, H-1), 2.7–3.6 (*m*, 4ArH), 4.54 (*br. d*, *J* = 7 Hz, H-11a), 5.6–6.7 (*m*, 2H-6, H-6a), 6.25 (*s*, OMe). (c) *Preparation of* (±)-7,2′-*dimethoxyisoflavan* (**19d**). MeI methylation of **19f** (200 mg) gave **19d** (135 mg), oil. [Found: M (HRMS), 270.1256. $C_{17}H_{18}O_3$ requires: M, 270.1256]. $\nu_{max}$ ($cm^{-1}$): 1615, 1585. PMR (τ): 2.7–3.5 (*m*, 5ArH), 3.58 (*dd*), 3.61 (*d*) (AB part of ABX system, $J_{AB}$ = 2.5 Hz, $J_{AX}$ = 8.5 Hz, H-6, H-8), 5.5–6.7 (*m*, 2H-2, H-3), 6.24, 6.32 (2*s*, 2OMe), 7.13 (*d*, *J* = 7.5 Hz, 2H-4). (d) *Preparation of* (±)-2′-*acetoxy*-7-*methoxyisoflavan* (**19e**). $Ac_2O$ acetylation of **19f** (200 mg) gave **19e** (102 mg), plates, mp 105° (MeOH). [Found: C, 72.78; H, 5 78. $C_{18}H_{18}O_4$ requires: C, 72.46; H, 6.08%]. $\nu_{max}$ ($cm^{-1}$): 1760, 1620, 1590 PMR (τ): 2.6–3.2 (*m*, 5ArH), 3.52 (*dd*), 3.56 (*d*) (AB component of ABX system, $J_{AB}$ = 2.5 Hz, $J_{AX}$ = 8 5 Hz), 5.5–6.9 (*m*, 2H-2, 3-H), 6.28 (*s*, OMe), 7.12 (*d*), *J* = 7.5 Hz, 2H-4), 7.74 (*s*, OAc).

*ABMXY or ABMXX′ PMR systems of isoflavanquinones and isoflavans.* (200 MHz, τ). **5**: 5.68 (*q*), 5.91 (*q*), 6.55 (*m*), 6.98 (*q*), 7.28 (*q*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 2.5 Hz, $J_{BM}$ = 6.5 Hz, $J_{MX}$ = 6 Hz, $J_{MY}$ = 6.5 Hz, $J_{XY}$ = 16 Hz). **17b**: 5.55 (*t*), 5.79 (*q*), 6.41 (*m*), 6.88 (*q*), 7.37 (*q*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 10.5 Hz, $J_{BM}$ = 2 Hz, $J_{MX}$ = 12.5 Hz, $J_{MX}$ = 5 Hz, $J_{XY}$ = 15.5 Hz). **17c**: 5.55 (*t*), 5.76 (*o*), 6 43 (*m*), 6.84 (*q*), 7.34 (*o*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 10.5 Hz, $J_{BM}$ = 3 Hz, $J_{BY}$ = 2 Hz, $J_{MX}$ = 12 Hz, $J_{MY}$ = 5 Hz, $J_{XY}$ = 15.5 Hz). **20**: 5.75 (*q*), 5.97 (*q*), 6.58 (*m*), 6.97 (*q*), 7.27 (*q*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3 Hz, $J_{BM}$ = 6 Hz, $J_{MX}$ = 6 Hz, $J_{MY}$ = 6.5 Hz, $J_{XY}$ = 16 Hz). **19a**: 5.66 (*o*), 5.99 (*t*), 6.77 (*m*), 6.98 (*d*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3.5 Hz, $J_{BM}$ = 10.5 Hz, $(J_{MX} + J_{MX'})/2$ = 8 Hz). **19b**: 5.68(*q*), 6.00 (*t*), 6.81 (*m*), 7.03 (*d*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3 Hz, $J_{BM}$ = 10.5 Hz, $(J_{MX} + J_{MX'})/2$ = 8 Hz). **19c**: 5.68, 6.01 (*t*), 6.78 (*m*), 7.02 (*d*) / $J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3 Hz, $J_{BM}$ = 10 5 Hz ($J_{MX} + J_{MX'}$)/2 = 8 Hz). **19d**: 5.67 (*o*), 5.97 (*t*), 6.35 (*m*), 7.00 (*q*), 7.13 (*q*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3 Hz, $J_{AH-5}$ = 1.5 Hz, $J_{BM}$ = 10.5 Hz, $J_{MX}$ = 10.5 Hz, $J_{MY}$ = 5.5 Hz, $J_{XY}$ = 15.5 Hz). **19e**: 5.73 (*o*), 6.02 (*t*), 6.68 (*m*), 7.05 (*q*), 7.10 (*q*) ($J_{AB}$ = 10.5 Hz, $J_{AM}$ = 3.5 Hz, $J_{AH-5}$ = 1.5 Hz, $J_{BM}$ = 10.5 Hz, $J_{MX}$ = 10.5 Hz, $J_{MX}$ = 7 Hz, $J_{XY}$ = 15.5 Hz).

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