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MUCRONULATOL, MUCROQUINONE AND MUCRONUCARPAN, ISOFLAVONOIDS FROM *MACHAERIUM MUCRONULATUM* AND *M. VILLOSUM**

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Key Word Index—*Machaerium mucronulatum*; *M. villosum*; Leguminosae–Lotoideae; isoflavans; isoflavanquinone; pterocarpan.

Abstract—Additionally to the cinnamylphenols described in a previous paper, wood samples of *Machaerium mucronulatum* and *M. villosum* contain isoflavones, besides (−)-duartin, (−)- and (±)-mucronulatol [(3*S*)- and rac-7,3′-dihydroxy-2′,4′-dimethoxyisoflavan], (−)-mucroquinone [(3*S*)-2-methoxy-5-(7-hydroxy-8-methoxychroman-3-yl)-1,4-benzoquinone] and (+)-mucronucarpan [(6a*S*,11a*S*)-2,10-dihydroxy-3,9-dimethoxypterocarpan]. The constitutions of mucronulatol, mucroquinone and mucronucarpan were deduced by spectra and degradations, and confirmed by syntheses.

INTRODUCTION

In a previous paper [2] we described the elucidation of structure and synthesis of mucronustyrene, mucronulastyrene and villostyrene, cinnamylphenols which occur in the wood of *Machaerium mucronulatum* Mart. ex Benth. and *M. villosum* Vog. (Leguminosae–Lotoideae). The concomitant isolation of the isoflavonoids (−)-duartin, (−)-mucronulatol, (±)-mucronulatol, (−)-mucroquinone, (+)-mucronucarpan and 3′-hydroxyformononetin from *M. mucronulatum* was reported at the same time, but their study was deferred to a later paper. (−)-Duartin, (−)-mucronulatol and 3′-hydroxyformononetin, accompanied by daidzein, 3′-hydroxydaidzein, formononetin, isoformononetin and (+)-homopterocarpin, occur also in *M. villosum*, and the entire group of isoflavonoids is now considered in detail. Further heartwood constituents of this species include the chalcones butein and isoliquiritigenin and the flavanone butin. The sapwood contains sitosterol, 3-*O*-acetyl-β-amyrin and 3-*O*-acetylerythrodiol. These two triterpenoids have also been isolated from other *M.* species, including *M. incorruptibile* Fr. Allem. [3] and *M. triste* Vog. [4].

ISOFLAVANS

Four of the mentioned isoflavonoids were recognized as isoflavans [5] by the characteristic complex PMR signals [1, 5] assignable to the CH_2—CH—CH_2 grouping of the 3-arylchroman system. One isoflavan was identified with (−)-duartin (**1a**, α-Ar) by direct comparison with a sample isolated from *M. opacum* [1].

Another isoflavan, (−)-mucronulatol, $C_{15}H_{10}O(OH)_2$, mp 145°, was also isolated as the racemate, mp 227°. The relationship between these two products was established by their identical spectroscopic (UV, IR, PMR) properties in solution. Oxidation of (±)-mucronulatol dimethyl ether gave the corresponding tetramethoxyisoflavanone which was hydrolysed to a tetramethoxy-2-hydroxydeoxybenzoin. The PMR signals of the aromatic protons of mucronulatol and its derivatives showed that the aromatic rings are 1,2,4-(ABX systems, J_{AB} = 2.5 Hz, J_{AX} = 9 Hz) and 1.2,3,4-(AB systems, J_{AB} = 9 Hz) substituted. The ABX system of the isoflavanone produced a low field doublet (τ 2.09, J = 9 Hz) showing that hydrogen atoms are located at positions 5, 6 and 8. By analogy with the structure of duartin (**1a**) it therefore seemed probable that mucronulatol dimethyl ether, the isoflavanone and the deoxybenzoin are represented respectively by **1b**, **2** and **3a**. This hypothesis was shown to oe correct by the synthesis of **3a**.

The remaining constitutional problem concerned the relative OH/OMe positions in mucronulatol. The shift to low field of all aromatic proton signals of mucronulatol diacetate, relative to those of mucronulatol, indicated that one hydroxyl is associated with each of the aromatic rings. Again in analogy with duartin, constitution **1c** was proposed for mucronulatol and confirmed by the synthesis of the racemic diethyl ether **1d**.

The synthesis of isoflavans may be effected by hydrogenation of the corresponding isoflavones in AcOH using a Pd/C catalyst [1]. The synthesis of the required isoflavone was achieved using conventional methods. 3-Ethoxy-2,4-dimethoxybenzaldehyde was prepared from 2,6-dimethoxyphenetole [6] using the Vilsmeier procedure. The aldehyde was condensed with rhodanine to give the derivative **5a** which was hydrolysed with aq.

* Part 2 in the series 'Isoflavonoid Constituents of *Dalbergia* and *Machaerium* Species'. For Part 1 see ref. [1].

$NaOH/Na_2S$ to the 3-aryl-2-thionopropionic acid **6a**. This was converted by the action of Ac_2O on its oxime into the nitrile **6b**. Hoesch condensation of **6b** and resorcinol gave the deoxybenzoin **3b**, which by reaction with $HC(OEt)_3$ yielded the isoflavone **4b**. Ethylation of **4b** gave the required isoflavone **4a** which was hydrogenated into the isoflavan **1d**, identical (mp, IR, PMR) with the diethyl ether of natural (±)-mucronulatol.

The synthesis of (±)-mucronulatol itself (**1c**) required the initial synthesis of 3-hydroxy-2,4-dimethoxyphenylacetic acid (**6c**). This was achieved either by hydrolysis and de-ethylation of **6b** or, more satisfactorily, by the Wilgerodt reaction of 2,3,4-trimethoxyacetophenone (prepared by the reaction of pyrogallol with BF_3–AcOH and methylation of the product) to the phenylacetic acid **6d** and demethylation. Reaction of **6c** with resorcinol in BF_3–Et_2O gave the deoxybenzoin **3c** which was converted into the isoflavone **4c**. Hydrogenation of **4c** gave the isoflavan **1c**, identical in all respects with natural (±)-mucronulatol. The absolute configuration of (−)-mucronulatol was shown to be 3*S*, (**1c**, α-Ar) by comparison of its ORD characteristics with those of other isoflavans [1, 7].

The orange colour, UV and IR spectra suggested a quinonoid structure for the fourth isoflavonoid, $C_{15}H_9O_3.OH(OMe)_2$, accordingly named (−)-mucroquinone. The PMR spectrum shows signals assignable to the CH_2—CH—CH_2 grouping of an isoflavan, although the vicinal coupling constants differ from those observed for duartin [1], mucronulatol and their derivatives. Additional signals are assignable to two *para*-related protons on a 4-methoxy-2,5-benzoquinonyl grouping [8], and to two *ortho*-related aromatic protons. The low field quinonoid proton (τ 3.54, H-6) shows long range coupling (J = 1.5 Hz) to a methine hydrogen at C-1. Similar long range coupling has been observed in the PMR spectra of dalbergiones [8]. The existence of the quinonyl moiety received further support by the MS of mucroquinone which shows prominent peaks at *m/e* 153 (**7**) and 164 (**8**). Of the four structures for mucroquinone consistent with the evidence above, constitution **9** was preferred by analogy with the co-occurring duartin (**1a**). This proposal was proved to be correct by synthesis of racemic **9**.

By the procedure described above, 3-hydroxy-4-methoxybenzaldehyde was transformed through the intermediates **5b**, **6e** and **6f** into **6g**. BF_3-catalysed condensation of this arylacetic acid with pyrogallol 2-methylether gave the deoxybenzoin **3d** which was converted, via the isoflavone **4d**, into the isoflavan **1e**. This was oxidised with Fremy's salt [9] to give the isoflavanquinone **9** with UV, IR and PMR properties identical with those of natural (−)-mucroquinone. The 3*S*-configuration for (−)-mucroquinone (**9**, α-quinonyl) was established by the close similarity of its ORD curve with that of (3*S*)-7,4′-dimethoxyisoflavan-2′,5′-quinone [7].

PTEROCARPAN

The PMR spectrum of (+)-mucronucarpan, $C_{15}H_8O_2(OMe)_2$, shows the characteristic multiplets [10, 11] associated with the CH—CH—CH_2 grouping of the pterocarpan skeleton, besides signals assignable to pairs of *ortho*- and *para*-related protons. MS fragment ions of *m/e* 177 (**10**) and 164 (**11**) indicate the location of one hydroxyl and one methoxyl on each of the aromatic rings. This evidence and the co-occurrence of mucronucarpan with duartin (**1a**) and mucronulatol (**1e**) on one hand, and mucroquinone (**9**) on the other, suggested the existence of, respectively, either the 3,4,8,9- or the 2,3,9,10-oxygenation pattern. The latter alternative was shown to be correct by catalytic reduction of (+)-mucronucarpan to (+)-dihydromucronucarpan whose trimethyl ether proved to be spectroscopically identical with synthetic (±)-6,7,2′,3′,4′-pentamethoxyisoflavan (**1f**).

The route described in the preceding isoflavan syntheses was employed. 2,3,4-Trimethoxyphenylacetic acid (**6d**) was reacted with 3,4-dimethoxyphenol in the presence of BF_3–Et_2O to give the deoxybenzoin **3e**, which was converted, via the pentamethoxyisoflavone **4e**, into **1f**.

The constitution of mucronucarpan was finally established by the spectroscopic identity with synthetic (±)-2,10-dihydroxy-3,9-dimethoxypterocarpan (**12a**). The synthesis was carried out as for a number of other pterocarpan derivatives [12, 13]. The deoxybenzoin **3f**, prepared by the BF_3-catalysed reaction between **6c** and 4-hydroxy-3-methoxyphenol, was transformed into the isoflavone **4f**. This was selectively demethylated using $AlCl_3$ in MeCN to **4g**, characterized as its triacetate (**4h**). Hydrogenation of **4g** under controlled conditions, using a Pd/C catalyst in AcOH, gave **12a** with IR and PMR properties identical with those of natural (+)-mucronucarpan. If the hydrogenation of **4g** was continued for a longer period, (±)-dihydromucronucarpan (**1g**) was isolated as the only reaction product.

The 6*aS*, 11*aS*-configuration of (+)-mucronucarpan (**12a**, β-6aH, β-11aH) follows from the comparison of its ORD and PMR characteristics with those of other pterocarpans of established relative and absolute configuration [14].

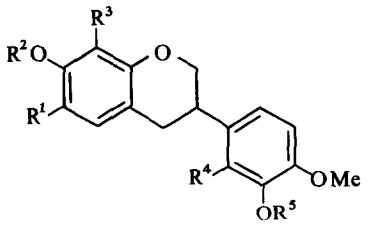
ISOFLAVONES

The five isoflavones were assigned to two groups by their oxygenation pattern, attributed in each case by PMR spectra. The first group of 7,4′-dioxygenated compounds was characterised by methylation of all its representatives, daidzein (**4i**), formononetin (**4j**) and isoformononetin (**4k**) into di-*O*-methyldaidzein (**4l**), previously isolated from *Dalbergia miscolobium* Benth. [15]. The second group of 7,3′,4′-trioxygenated compounds was characterised by methylation of its representatives, 3′-hydroxydaidzein (**4m**) and 3′-hydroxyformononetin (**4n**), into cabreuvin (**4o**), previously isolated from *Myroxylon balsamum* Fr. Allem.[16]. 7,4′-Dihydroxy-3′-methoxyisoflavone, an isomer of **4n**, has not so far been isolated from a natural source, all previous reports of its occurrence [17] referring in fact to 7,3′-dihydroxy-4′-methoxyisoflavone, as shown by the identity of all isolates with **4n** and a positive Gibbs test [18].

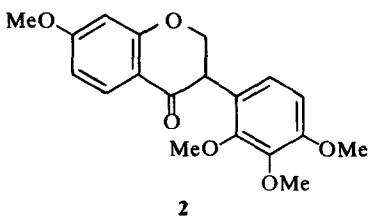
EXPERIMENTAL

Unless otherwise stated spectra were measured in EtOH (UV), $CHCl_3$ (IR), $CDCl_3$ (60 MHz PMR) and MeOH (ORD). All evaporations of volatile material were performed under diminished pressure.

Isolation of the constituents of M. villosum. A specimen was collected near Caldas, MG, Brasil, and identified by Apparício Pereira Duarte. Ground sapwood (8.5 kg) was continuously



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



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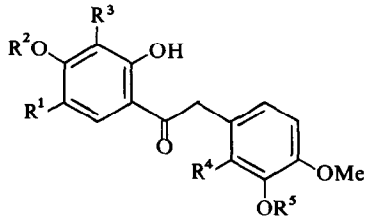
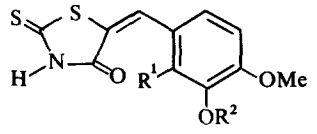
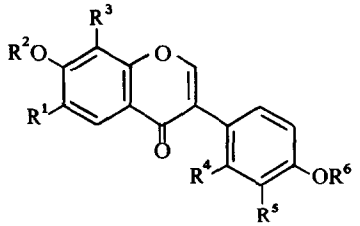


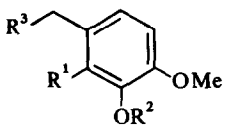
3a $R^1 = R^3 = H$, $R^2 = R^5 = Me$, $R^4 = OMe$
3b $R^1 = R^2 = R^3 = H$, $R^4 = OMe$, $R^5 = Et$
3c $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = OMe$
3d $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OMe$
3e $R^1 = R^4 = OMe$, $R^2 = R^5 = Me$, $R^3 = H$
3f $R^1 = OH$, $R^2 = Me$, $R^3 = R^5 = H$, $R^4 = OMe$



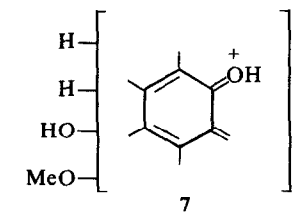
5a $R^1 = OMe$, $R^2 = Et$
5b $R^1 = R^2 = H$



4a $R^1 = R^3 = H$, $R^2 = Et$, $R^4 = OMe$, $R^5 = OEt$, $R^6 = Me$
4b $R^1 = R^2 = R^3 = H$, $R^4 = OMe$, $R^5 = OEt$, $R^6 = Me$
4c $R^1 = R^2 = R^3 = H$, $R^4 = OMe$, $R^5 = OH$, $R^6 = Me$
4d $R^1 = R^2 = R^4 = H$, $R^3 = OMe$, $R^5 = OH$, $R^6 = Me$
4e $R^1 = R^4 = R^5 = OMe$, $R^2 = R^6 = Me$, $R^3 = H$
4f $R^1 = R^5 = OH$, $R^2 = R^6 = Me$, $R^3 = H$, $R^4 = OMe$
4g $R^1 = R^4 = R^5 = OH$, $R^2 = R^6 = Me$, $R^3 = H$
4h $R^1 = R^4 = R^5 = OAc$, $R^2 = R^6 = Me$, $R^3 = H$
4i $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$
4j $R^1 = R^2 = R^3 = R^4 = R^5 = H$, $R^6 = Me$
4k $R^1 = R^3 = R^4 = R^5 = R^6 = H$, $R^2 = Me$
4l $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = R^6 = Me$
4m $R^1 = R^2 = R^3 = R^4 = R^6 = H$, $R^5 = OH$
4n $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OH$, $R^6 = Me$
4o $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OMe$, $R^6 = Me$



6a $R^1 = OMe$, $R^2 = Et$, $R^3 = CS.CO_2H$
6b $R^1 = OMe$, $R^2 = Et$, $R^3 = CN$
6c $R^1 = OMe$, $R^2 = H$, $R^3 = CO_2H$
6d $R^1 = OMe$, $R^2 = Me$, $R^3 = CO_2H$
6e $R^1 = R^2 = H$, $R^3 = CS.CO_2H$
6f $R^1 = R^2 = H$, $R^3 = CN$
6g $R^1 = R^2 = H$, $R^3 = CO_2H$



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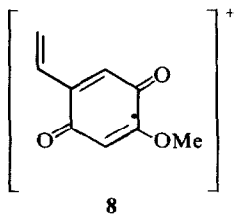

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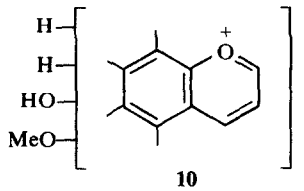

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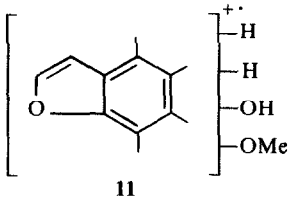

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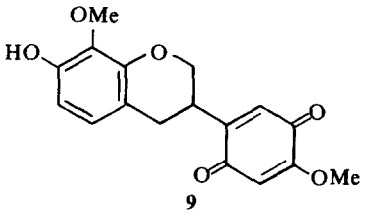

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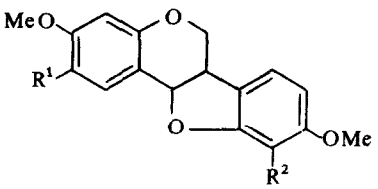

12a $R^1 = R^2 = OH$
12b $R^1 = R^2 = H$

extracted with hot C_6H_6. Evapn. of C_6H_6 gave a residue (56 g) which was extracted with petrol. The extract (22 g) was chromatographed on Si gel (600 g) to the following products (eluant, method of purif. and quantity indicated): fatty oil (C_6H_6), 3-*O*-acetyl-*β*-amyrin (C_6H_6–$CHCl_3$ (4:1) cryst. from C_6H_{14}, 106 mg), sitosterol (C_6H_6–$CHCl_3$ (3:2) cryst. from C_6H_{14}, 443 mg), 3-*O*-acetylerythrodiol (C_6H_6–$CHCl_3$ (2:3) cryst. from MeOH, 33 mg).

Ground heartwood (12 kg) was continuously extracted with hot C_6H_6. Concn. of the soln gave a ppt. (25 g) which was cryst. from EtOH to (−)-**1a** (15.3 g). Evapn of the C_6H_6 from the filtrate gave residue (125 g) which was extracted with petrol. Part (20 g) of the extract (66 g) was chromatographed on Si gel (600 g) to the following products (eluant, method of purif. and quantity indicated): fatty oil (C_6H_{12}–C_6H_6 (3:2) 3.9 g), (+)-**12b** (C_6H_{14}–C_6H_6 (1:4) cryst. from C_6H_{14}, 170 mg), villostyrene (C_6H_6, TLC, 2 g), sitosterol (C_6H_6–$CHCl_3$ (9:1) cryst. from MeOH, 170 mg). Part (40 g) of the petrol. insoluble fraction (56 g) was chromatographed on Si gel (1 kg) to the following products (eluant, method of purif, and quantity indicated): (+)-**12b** (C_6H_6, cryst. from C_6H_{14}, 180 mg), villostyrene (C_6H_6–$CHCl_3$, 19:1), mucronulastyrene (C_6H_6–$CHCl_3$ (4:1) TLC, 110 mg), (−)-**1a** (C_6H_6–$CHCl_3$ (7:3) cryst. from EtOH, 6.4 g), (−)-**1c** (C_6H_6–$CHCl_3$ (1:1) TLC, 2.4 g). The ground heartwood, after extraction with C_6H_6 (above) was then continuously extracted with hot EtOH. The extract was washed with C_6H_6 and the insoluble part treated with cold AcOEt. The AcOEt soln was evapd and the residue (69 g) was chromatographed on Si gel (1.3 kg) to the following products (eluant, method of purif. and quantity indicated): (−)-**1a** (C_6H_6–$CHCl_3$ (1:4) cryst. from EtOH, 14.7 g), (−)-**1c** (C_6H_6–$CHCl_3$ (1:9) cryst. from EtOH, 1.8 g), **4k** ($CHCl_3$; cryst. from EtOH–H_2O, 220 mg), isoliquiritigenin ($CHCl_3$–MeOH (99:1) sephadex LH-20 chromatography, 25 mg). **4n** ($CHCl_3$–MeOH (49:1) cryst. from MeOH, 490 mg), **4m**, **4i** and butein ($CHCl_3$–MeOH (97:3) sephadex LH-20 chromatography, resp. 9, 4 and 90 mg), butin and butein ($CHCl_3$–MeOH (19·1) sephadex LH-20 chromatography, resp. 25 and 31 mg).

Identifications. Sitosterol, 3-*O*-acetyl-*β*-amyrin [3], 3-*O*-acetylerythrodiol [3], butein [19], isoliquiritigenin [20], butin [19], daidzein (**4i**) [21], formononetin (**4j**) [22], isoformononetin (**4k**) [23], (+)-homopterocarpin (**12b**), (−)-duartin (**1a**) [1], villostyrene [2] and mucronulastyrene [2] were identified by direct comparison with authetic samples. A sample of butein was kindly supplied by Prof. T. A. Geissman. Butin was prepared by acid catalysed cyclization of butein. (+)-Homopterocarpin was prepared by methylation of (+)-medicarpin [24].

3′-Hydroxydaidzein (7,3′,4′-trihydroxyisoflavone, **4m**). Crystals, mp 262–265° (EtOH–H_2O) (lit. [21] mp 245–250°). [Found: M (MS), 270. $C_{15}H_{10}O_5$ requires: M, 270]. λ_{max} (nm): 249, 292 (ε 19500, 13300). ν_{max} (KBr, cm^{-1}): 3490, 3210, 1635, 1602. Me_2SO_4-methylation gave cabreuvin [16].

3′-Hydroxyformononetin (7,3′-dihydroxy-4′-methoxyisoflavone, **4n**). Crystals, mp 228–231° and 240–242° (MeOH) (lit. [25] mp 245–247°). [Found: M (MS), 284. $C_{16}H_{12}O_5$ requires: M, 284]. λ_{max} (nm): 249, 261 infl., 292 (ε 23100, 22000, 14900). Gibbs test [18]: positive. ν_{max} (KBr, cm^{-1}): 3400, 3165, 1625. PMR ($CF_3 \cdot CO_2H$, τ): 1.28 (*s*, H-2), 2.59 (*d*), 2.49 (*dd*), 1.52 (*d*) (ABX system, J_{AB} = 3 Hz, J_{BX} = 8.5 Hz, H-8, H-6, H-5), 2.86 (*s*, H-2′, H-5′, H-6′), 5.94 (*s*, OMe). Me_2SO_4-methylation gave cabreuvin [16].

(−)-Mucronulatol, [(3S)-7,3′-dihydroxy-2′,4′-dimethoxyisoflavan, **1c**, α-Ar]. Microcrystals, mp 145° (MeOH), $[\alpha]_D^{20}$ −18.5° (*c* 0.58, Me_2CO).[Found: C, 67.41: H, 6.05. $C_{17}H_{18}O_5$ requires: C, 67.54; H, 6.00%]. λ_{max} (nm): 225, 282, 290 (ε 15500, 5400, 4150). ν_{max} (cm^{-1}): 3500, 3300, 1620, 1595. PMR [$(CD_3)_2SO$, τ]: 3.70 (*dd*), 3.80 (*d*) (ABX system, J_{AB} = 2.5 Hz, J_{AX} = 8.5 Hz, H-6, H-8, H-5), 3.33, 3.44, (AB system, J_{AB} = 9 Hz, H-5′, H-6′), 5.8–7.0 (*m*, OCH_2), 7.25 (*br. d*, CH_2), 6.6 (*br. s*, 2 OH), 6.19, 6.23 (2 *s*, 2 OMe). ORD (*c* 0.08): $[\phi]_{303}$ −890, $[\phi]_{290}$ −2500, $[\phi]_{267}$ +3500, $[\phi]_{263}$ +3070, $[\phi]_{244}$ +4430, $[\phi]_{238}$ +8000. *Diacetate*, needles, mp 95° (C_6H_6–petrol.), $[\alpha]_D^{20}$ − 19.1 (*c* 0.40, $CHCl_3$). [Found: C, 65.31; H, 5.80. $C_{21}H_{22}O_7$ requires: C, 65.28; H, 5.74%]. λ_{max} (nm): 224, 278, 284 (ε 17600, 4500, 4150). ν_{max} (cm^{-1}); 1765, 1610. ORD (*c* 0.0075); $[\phi]_{400}$ +1200; $[\phi]_{313}$ +1600, $[\phi]_{286}$ +580, $[\phi]_{278}$ +8900, $[\phi]_{250}$ +300.

(±)-*Mucronulatol* (**1c**). Platelets, mp 227° (MeOH) [Found: C, 67.46; H, 5.97; M (MS), 302. $C_{17}H_{18}O_5$ requires: C, 67.54; H, 6.00%; M, 302]. λ_{max} (nm): 225, 282, 289 (ε 14900. 5350, 4000). ν_{max} (KBr, cm^{-1}): 3400, 1620, 1595. *Diacetate*, fine needles, mp 131° (MeOH). [Found: C, 65.67; H, 6.10. $C_{21}H_{22}O_7$ requires: C, 65.28; H, 5.74%]. λ_{max} (nm): 224, 278, 284, (ε 17100, 4700, 4100). IR identical with IR of diacetate above. PMR (τ): 3.39 (*dd*), 3.40 (*d*), 2.95 (*d*) (ABX system, $J_{AB} = 2.5$ Hz, $J_{AX} = 8.5$ Hz, H-6, H-8, H-5), 3.29, 3.07 (AB system, $J_{AB} = 9$ Hz, H-5', H-6'),5.5–6.8 (*m*, 2 H-2, H-3), 7.07 (*br. d*, $J = 7.5$ Hz, 2 H-4), 6.18 (*s*, 2 OMe), 7.65, 7.73 (2*s*, 2 OAc). *Dimethyl ether* (**1b**) (**1c**, MeI, K_2CO_3, Me_2CO), needle clusters. [Found: C, 68.58; H, 6.59. $C_{19}H_{22}O_5$ requires: C, 69.07; H, 6.71%]. λ_{max} (nm): 227, 282, 289 (ε 17800, 5400, 4700). ν_{max} (cm^{-1}): 1620, 1590. PMR (τ): 3.58 (*dd*), 3.59 (*d*), 3.08 (*d*) (ABX system, $J_{AB} = 2.5$ Hz, $J_{AX} = 9$ Hz, H-6, H-8, H-5), 3.41, 3.26 (AB system, $J_{AB} = 8.5$ Hz, H-5', H-6'), 5.5–6.8 (*m*, 2 H-2, H-3), 7.10 (*br. d*, $J = 7.5$ Hz, 2 H-4), 6.13, 6.17, 6.20, 6.26 (4 *s*, 4 OMe). *7-Ethyl ether and diethyl ether* (**1d**). **1c** (100 mg). EtI (500 mg), K_2CO_3 (500 mg) in Me_2CO (30 ml) were heated under reflux (2 days) giving a mixture which was separated by TLC (Si gel, $CHCl_3$) into (±)-mucronulatol 7-ethyl ether (26 mg) and **1d** (36 mg). *7-Ethyl ether*, needles, mp 151° (EtOH–petrol). [Found: C, 69.06; H, 6.53. $C_{19}H_{22}O_5$ requires: C, 69.07; H, 6.71%]. λ_{max} (nm) 226, 283, 290 (ε 16100, 4100, 3400). ν_{max} (cm^{-1}): 3500, 1620, 1590. PMR (τ): 3.53 (*dd*), 3.56 (*d*), 3.02 (*d*) (ABX system, $J_{AB} = 2.5$ Hz, $J_{AX} = 9$ Hz, H-6, H-8, H-5), 3.38 (*s*, H-5', H-6'), 5.5–6.8 (*m*, 2 H-2, H-3), 7.09 (*br. d*, $J = 7.5$ Hz, 2 H-4), 4.2 (*br. s*. OH), 6.08, 6.16 (2*s*, 2 OMe), 5.98 (*q*), 8.60 (*t*), (*J*-7 Hz, OEt). **1d**, platelets, mp 87° (petrol). [Found: C, 70.07; H, 7.19. $C_{21}H_{26}O_5$ requires: C, 70.37; H, 7.31%]. λ_{max} (nm): 227, 283, 289 (ε 17500, 3850, 3650). ν_{max} (cm^{-1}): 1615, 1580. PMR (CCl_4, τ): 3.67 (*dd*), 3.76 (*d*), 3.16 (*d*) (ABX system, $J_{AB} = 2.5$ Hz, $J_{AX} = 9$ Hz, H-6, H-8, H-5), 3.45, 3.23 (AB system, $J_{AB} = 9$ Hz, H-5', H-6'), 5.5–6.8 (*m*, 2 H-2, H-3), 7.20 (*br. d*, $J = 7.5$ Hz, 2 H-4), 6.10, 6.21 (2*s*, 2 OMe), *ca* 6.1 (2 *q*), 8.63 (*t*) (2 OEt).

(3S)-*Mucroquinone* (**9**, α-*quinonyl*). Orange needles, mp 92° (EtOH) $[\alpha]_D^{20} - 15.4°$ (*c* 0.42, Me_2CO). [Found: C, 64.66; H, 5.44; M (MS), 316. $C_{17}H_{16}O_6$ requires: C, 64.55; H, 5.10; M, 316]. λ_{max} (nm): 230 infl., 264, 360 (ε 10300. 13400, 1010). ν_{max} (cm^{-1}): 3500, 1680, 1650, 1600. PMR (220 MHz, τ): 3.34, 3.50 (AB system, $J_{AB} = 8.5$ Hz, H-5, H-6), 3.54 (*d*, $J = 1.5$ Hz, H-6'), 4.02 (*s*, H-3'), 6.13, 6.19 (2 *s*, 2 OMe), 5.68 (*q*, H-2), 5.91 (*q*, H-2), 6.54 (*m*, H-3), 6.98 (*q*, H-4), 7.28 (*q*, H-4) (ABMXY system, $J_{AB} = 10.5$ Hz, $J_{AM} = 2.5$ Hz, $J_{BM} = 6.5$ Hz, $J_{MX} = 6$ Hz, $J_{MY} = 6.5$ Hz, $J_{XY} = 16$ Hz). ORD (*c* 0.103): $[\phi]_{475} - 180$, $[\phi]_{400} + 724$, $[\phi]_{357} - 898$, $[\phi]_{323} + 1090$, $[\phi]_{303} + 2740$.

(6aS,11aS)-*Mucronucarpan* (**12a**, β-6aH, β-11aH). Oil, $[\alpha]_D^{20}$ +114° (*c* 0.64, $CHCl_3$). [Found: M (HRMS), 316.0948. $C_{17}H_{16}O_6$ requires: M, 316.0947]. λ_{max} (nm): 230, 294 (ε 16700, 6750). ν_{max} (cm^{-1}): 3500, 1620, 1595. PMR (τ): 2.90 (*s*, H-1), 3.56 (*s*, H-4), 3.28, 3.57 (AB system, $J_{AB} = 8.5$ Hz, H-7, H-8), 4.7 (*br. s*, 2 OH), 6.18 (*s*, 2 OMe), 4.4–6.7 (ABCX system, 2 H-6, H-6a, H-11a). ORD (*c* 0.107): $[\phi]_{345} + 3090$, $[\phi]_{313}$ 0, $[\phi]_{278} + 20100$, $[\phi]_{263} + 19000$, $[\phi]_{250} + 30900$, $[\phi]_{238} + 41000$. *Diacetate*, oil, $[\alpha]_D^{20}$ + 75° (*c* 0.59, $CHCl_3$) [Found: M (HRMS), 400.1162. $C_{21}H_{20}O_8$ requires: M, 400.1158]. λ_{max} (nm): 230, 285 (ε 12000, 5300). ν_{max} (cm^{-1}): 1760, 1620. PMR (τ): 2.82 (*s*, H-1), 3.50 (*s*, H-4), 2.98, 3.54 (AB system, $J_{AB} = 8.5$ Hz, H-7, H-8), 6.21 (*s*, 2OMe), 7. 70, 7.71 (2 *s*, 2 OAc), 4.4–6.7 (ABCX system, 2 H-6, H-6a, H-11a). *Dihydro-derivative* (**1g**, α-Ar). Hydrogenation (room temp., 1 atm., 48 hr) of **12a** (100 mg) over 10% Pd/C catalyst (50 mg) in AcOH (20 ml), followed by filtration and evapn of the AcOH gave (+)-*dihydromucronucarpan*, $[\alpha]_D^{20}$ + 12.1° (*c* 0.45, MeOH). λ_{max} (nm): 225, 298 (ε 18000, 6350). ν_{max} (cm^{-1}): 3500, 1620, 1600. MeI-Methylation of this derivative gave the *trimethyl ether* (**1f**, α-Ar), λ_{max} (nm): 225, 296 (ε 17200, 6250). PMR (τ): 3.42 (*s*, H-5), 3.56 (*s*, H-8), 3.38, 3.23 (AB system, $J_{AB} = 8.5$ Hz, H-5', H-6'), 5.5–6.8 (*m*, 2 H-2, H-3), 7.10 (*br. d*, *J ca* 7.5 Hz, 2 H-4), 6.09, 6.11 (2 *s*, 2 OMe), 6.15 (*s*, 2 OMe), 6.17 (*s*, OMe).

Degradation of (±)-*mucronulatol dimethyl ether* (**1b**). (a) *Formation of* 7,2',3',4'-*tetramethoxyflavanone* (**2**). $KMnO_4$-oxidation of **1b** (400 mg) as in ref. [1] gave **2** (140 mg), plates, mp 133–134° (EtOH). [Found: C, 65.78; H, 6.01. $C_{19}H_{20}O_6$ requires: C, 66.28; H, 5.84%]. λ_{max} (nm): 228, 274, 314 (ε 23600, 17300, 8950). ν_{max} (cm^{-1}): 1655, 1595. PMR (τ): 2.89 (*dd*), 3.56 (*d*), 2.09 (*d*), (ABX system, $J_{AB} = 2.5$ Hz, H-6, H-8, H-5), 3.37, 3.22 (AB system, $J_{AB} = 8.5$ Hz, H-5', H-6'), 5.48 (*m*), 5.81 (*dd*) (AA'B system, average of J_{AB} and $J_{A'B} = 9.6$ Hz, H-2, H-3, H-2). (b) *Formation of* 2,3,4-*trimethyoxybenzyl* 2-*hydroxy*-4-*methoxyphenyl ketone* (**3a**). KOH-hydrolysis of **2** (140 mg) as in ref. [1] gave **3a** (35 mg), needles, mp 116° (EtOH). [Found: C, 64.46; H, 5.89. $C_{18}H_{20}O_6$ requires: C, 65.05; H, 6.07%]. λ_{max} (nm): 228, 266, 317 (ε 9250, 8500, 4450). ν_{max} (cm^{-1}): 1625, 1575. This degradation product proved to be identical, by direct comparison, with the product of MeI-methylation of synthetic 2,3,4-trimethoxybenzyl 2,4-dihydroxyphenyl ketone [26].

Synthesis of (±)-*mucronulatol diethyl ether* (**1d**). (a) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzaldehyde*. 2,6-Dimethoxyphenetole [6] (106 mg), DMF (64 g) and $POCl_3$ (130 g) were heated 100°, 3 hr), cooled, poured into iced H_2O and extracted with $CHCl_3$. Dist. (130–132°, 1 mm) gave the aldehyde (70 mg), mp 32°. [Found: C, 62.61; H, 6.80. $C_{11}H_{14}O_4$ requires: C, 62.85; H, 6.71%]. ν_{max} (film, cm^{-1}): 2700, 1670, 1590. (b) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzylidene rhodanine* (**5a**). The aldehyde (70 mg), rhodanine (60 g) and NaOAc (210 g) in AcOH (280 ml) were heated (100°, 3 hr), cooled and poured into H_2O. The ppt. was collected and recryst. giving **5a** (75 g), yellow prisms, mp 183° (AcOEt). [Found: C, 51.93; H, 4.63; N, 4.57; S, 19.85. $C_{14}H_{15}NO_4S$ requires: C, 51.68; H, 4.67; N, 4.31; S, 19.61%]. ν_{max} (cm^{-1}): 1715, 1590. (c) *Formation of* 3-(3-*ethoxy*-2,4-*dimethoxyphenyl*)-2-*thionopropionic acid* (**6a**). **5a** (32 g), NaOH (19 g) and $Na_2S.9H_2O$ (15 g) in H_2O (125 ml) were heated (100°, 20 min), cooled, poured into iced H_2O and acidified. AcOEt extraction gave **6a** (19 g), yellow microcrystals, mp 195° (MeOH). [Found: C, 54.84; H, 5.52; S, 11.53. $C_{13}H_{16}O_5S$ requires: C, 54.85; H, 5.67; S, 11.27%]. (d) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzylcyanide* (**6b**). To NaOEt (3.1 g Na) in EtOH (200 ml) $NH_2OH.HCl$ and **6a** (19 g) were added. The mixture was heated (100°, 3 hr), the EtOH evapd and 6 N HCl added to the residue. AcOEt extraction gave 3-(3-ethoxy-2,4-dimethoxyphenyl-2-oximinopropionic acid (15 g), oil. This was heated (100°, 20 min) with Ac_2O (100 ml). Fractional dist. gave **6b** (7.5 g) oil, bp 120–123°, 0.2 mm. [Found: C, 65.09; H, 6.66; N, 6.54. $C_{12}H_{15}NO_3$ requires: C, 65.14, H, 6.83; N, 6.33%]. ν_{max} (cm^{-1}): 2250, 1665. (e) *Formation of* 3-*ethoxy*-2,4-*dimethoxybenzyl* 2,4-*dihydroxyphenyl ketone* (**3b**). **6b** (10 g), resorcinol (10 g), freshly fused $ZnCl_2$ in anh. Et_2O (50 ml) were satd with HCl at 0° and kept 4 days at room temp. The soln was decanted from the oily ketimine hydrochloride, which was then hydrolysed (50 ml H_2O, 100°, 1 hr). The soln was cooled, the ppt. collected and recryst. to **3b** (1.08 g), needles, mp 172° (EtOH). [Found: C, 64.93; H, 6.33. $C_{18}H_{20}O_6$ requires: C, 65.05, H, 6.07%]. ν_{max} (cm^{-1}): 3500, 3200, 1630. (f) *Formation of* 3'-*ethoxy*-7-*hydroxy*-2',4'-*dimethoxyisoflavone* (**4b**). (1.2 g) and $HC(OEt)_3$ (30 ml), acc. to a described procedure [1], gave **4b** (320 mg), microcrystals, mp 122° (EtOH–petrol). [Found: C, 66.42; H, 5.62. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%]. ν_{max} (cm^{-1}): 1640, 1625, 1600. (g) *Formation of* 7,3'-*diethoxy*-2',4'-*dimethoxyisoflavone* (**4a**). EtI-Ethylation of **4b** (100 mg) gave **4a** (80 mg), needles, mp 128° (EtOH–petrol). [Found: C, 68.12; H, 6.30. $C_{21}H_{22}O_6$ requires: C, 68.10; H, 5.99%]. ν_{max} (cm^{-1}): 1640, 1625, 1605. PMR (τ): 2.09 (*s*, H-2). (h) *Formation of* 7,3'-*diethoxy*-2',4'-*dimethoxyisoflavan* (**1d**). Hydrogenation (room temp., 1 atm., 20 hr) of **4a** (90 mg) over 10% Pd/C (50 mg) in AcOH (15 ml) gave **1d**, identical (mp, IR, PMR) with the diethyl ether of natural (±)-mucronulatol.

Synthesis of (±)-*mucronulatol* (**1c**). (a) *Formation of* 2,3,4-*trimethoxyacetophenone*. BF_3–AcOH (200 ml) was added to pyrogallol (85 g). The mixture was heated (100°, 30 min) and 2N HCl (200 ml) was added. The ppt. was collected and cryst. to 2,3,4-trihydroxyacetophenone (65 g), pale yellow plates, mp 171° (lit. [27] mp 173°). MeI-methylation gave the title cmpd. (77%), oil, bp 175°, 20 mm (lit. [28] bp 174°, 19 mm). (b) *Formation of* 2,3,4-*trimethoxyphenylacetic acid* (**6d**). A mix-

ture of 2,3,4-trimethoxyacetophenone (42 g), S (12.8 g) and morpholine (35 ml) was heated under reflux (2 hr), dissolved in $CHCl_3$ and extracted with 2 N HCl. Evapn of the $CHCl_3$ gave a residue which was boiled with 10% aq. NaOH (200 ml, 16 hr). The soln was extracted with Et_2O, acidified and re-extracted with $CHCl_3$. This extract was shaken with aq. $NaHCO_3$. Acidification of the aq. soln, extraction with $CHCl_3$, purification by chromatography (Si gel, $CHCl_3$) gave **6d** (17.7 g) mp 102° (C_6H_6) (lit. [29] mp 103°) (c) *Formation of 3-hydroxy-2,4-dimethoxyphenylacetic acid* (**6c**). **6d** [30] (12 g) was heated (100°, 3 hr) with conc HCl (150 ml). The mixture was evapd and the residue heated under reflux (12 hr) with 1% HCl in EtOH (500 ml). Evapn of the solvent and chromatography of the residue (Si gel, C_6H_6–$CHCl_3$) gave ethyl 3-hydroxy-2,4-dimethoxyphenylacetate (4.2 g). Hydrolysis of the ester with 2 N aq. NaOH have **6c** (3.5 g), mp 86°. (d) *Formation of 3-hydroxy-2,4-dimethoxybenzyl 2,4-dihydroxyphenyl ketone* (**3c**). **6c** (200 mg), resorcinol (150 mg) and BF_3–Et_2O (3 ml) as in ref. [1], gave **3c** (170 mg), prisms, mp 153° (AcOEt–petrol). [Found: C, 63.30; H, 5.39. $C_{16}H_{16}O_6$ requires: C, 63.15; H, 5.30%]. ν_{max} (cm^{-1}): 3500, 1625. (e) *Formation of 7,3'-dihydroxy-2',4'-dimethoxyisoflavone* (**4c**). **3c** (140 mg) and $HC(OEt)_3$ (10 ml) as in ref. [1], gave **4c** (81 mg), plates, mp 260° (EtOH–petrol). [Found: C, 64.79; H, 4.60. $C_{17}H_{14}O_6$ requires: C, 64.97; H, 4.49%]. ν_{max} (KBr, cm^{-1}): 1640, 1620, 1585. PMR ($F_3C.CO_2H$, τ): 1.16 (*s*, H-2). (f) *Formation of (±)-7,3'-dihydroxy-2',4'-dimethoxyisoflavan* (**1c**). Hydrogenation of **4c** (100 mg), as described above for **4a**, gave **1c**, identical (mp, IR, PMR) with natural (±)-mucronulatol.

Synthesis of (±)-mucroquinone (**9**). (a) *Formation of 3-hydroxy-4-methoxybenzylidene rhodanine* (**5b**). Isovaniline (10 g), treated as described above for the formation of **5a**, gave **5b** (11 g), yellow crystals, mp 226° (MeOH). [Found: C, 49.37; H, 3.41; N, 4.94; S, 23.77 $C_{11}H_9NO_3S_2$ requires: C, 49.44, H, 3.39; N, 5.24, S, 23.95%]. (b) *Formation of 3-(3-hydroxy-4-methoxyphenyl)-2-thionopropionic acid* (**6e**). **5b** (11 g), treated as described above for the formation of **6a**, gave **6e** (3.88 g), pale yellow microcrystals, mp 165° (AcOEt). [Found: C, 53.35; H, 4.74; S, 14.40. $C_{10}H_{10}O_4S$ requires: C, 53.18; H, 4.46; S, 14.15%]. (c) *Formation of 3-(3-hydroxy-4-methoxyphenyl)-2-oximinopropionic acid.* **6e** (3.8 g), treated as above for the formation of an oximinopropionic acid, gave the title cmpd. (2.1 g), crystals, mp 158° ($CHCl_3$). [Found: C, 53.35; H, 4.84; N, 6.23. $C_{10}H_{11}NO_5$ requires: C, 53.33; H, 4.92; N, 6.22%]. (d) *Formation of 3-hydroxy-4-methoxybenzylcyanide* (**6f**). The preceding oximino acid (23 g) in C_5H_5N (100 ml) was heated under reflux (1 hr). Fractional dist. (134–138°, 0.2 mm) gave **6f** (9 g), needles, mp 59° (C_6H_6–petrol). [Found: C, 66.43; H, 5.76; N, 8.73. $C_9H_9NO_2$ requires: C, 66.25; H, 5.56; N, 8.58%]. (e) *Formation of 3-hydroxy-4-methoxyphenylacetic acid* (**6g**). **6f** (1 g) was heated (100°, 45 min) with 2N aq. NaOH. Acidification and $CHCl_3$ extraction gave **6g** (960 mg), needles, mp 129° ($CHCl_3$–petrol). (Lit. mp 130° [31], 131° [32]). (f) *Formation of 3-hydroxy-4-methoxybenzyl 2,4-dihydroxy-3-methoxyphenyl ketone* (**3d**). **6g** (200 mg), pyrogallol-2-methyl ether [33] (200 mg) and BF_3–Et_2O (3 ml) as in ref. [1], gave **3d** (120 mg), plates, mp 126° (C_6H_6). [Found: C, 63.33; H, 5.41. $C_{16}H_{16}O_6$ requires: C, 63.15; H, 5.30%]. ν_{max} (cm^{-1}): 3500, 1620. (g) *Formation of 7,3'-dihydroxy-8,4'-dimethoxyisoflavone* (**4d**). **3d** (1.0 g) and $HC(OEt)_3$ (40 ml) as in ref. [1], gave **4d** (690 mg), fine needles, mp 209° (EtOH–petrol). [Found: C, 65.16; H, 4.65. $C_{17}H_{14}O_5$ requires: C, 64.97; H, 4.46%]. ν_{max} (cm^{-1}): 3500, 1640, 1620, 1600. (h) *Formation of (±)-7,3'-dihydroxy-8,4'-dimethoxyisoflavan* (**1e**). Hydrogenation of **4d** (760 mg), as described above for **4a**, gave **1e** (580 mg), needles, mp 160° (C_6H_6). [Found: C, 67.63; H, 5.80. $C_{17}H_{18}O_5$ requires: C, 67.54; H, 6.00%]. ν_{max} (cm^{-1}): 3500, 1600. (i) *Formation of (±)-2-methoxy-5-(7-hydroxy-8-methoxychroman-3-yl)-1,4-benzoquinone* (**9**). Fremy's salt [$ON(SO_3K)_2$, 450 mg] in H_2O (15 ml) was added to **1e** (100 mg) in MeOH (25 ml). The mixture was stirred (24 hr), diluted with H_2O and extracted with $CHCl_3$. Evapn of the $CHCl_3$ gave an oil which was fractionated by TLC. Cryst. of the appropriate fraction gave **9** (14 mg), fine, dark yellow needles, mp 181° (EtOH). [Found: C, 64.64; H, 5.05. $C_{17}H_{16}O_6$ requires: C, 64.55, H, 5.10%], identical (UV, IR, PMR) with natural (−)-mucroquinone.

Synthesis of (±)-dihydroxymucronucarpan trimethyl ether (**1f**). (a) *Formation of 2,3,4-trimethoxybenzyl 2-hydroxy-4,5-dimethoxyphenyl ketone* (**3e**). **6d** (450 mg), 3,4-dimethoxyphenol [34] (320 mg) and BF_3–Et_2O (7 ml) as in ref. [1], gave **3e** (410 mg), rhombs, mp 121° (C_6H_6–petrol). [Found: C, 63.23; H, 6.18. $C_{19}H_{22}O_7$ requires: C, 62.98; H, 6.12%]. ν_{max} (cm^{-1}): 1620 (b) *Formation of 6,7,2',3',4'-pentamethoxyisoflavone* (**4e**). **3e** (470 mg) and $HC(OEt)_3$ (30 ml) as in ref. [1], gave **4e** (359 mg), plates, mp 169° ($CHCl_3$–AcOEt). [Found: C, 64.64; H, 5.42. $C_{20}H_{20}O_7$ requires: C, 64.51; H, 5.41%]. ν_{max} (cm^{-1}): 1640, 1600. (c) *Formation of (±)-6,7,2',3',4'-pentamethoxyisoflavan* (**1f**). Hydrogenation of **4e**, as described above for **4a**, gave **1f** (190 mg), plates, mp 123° (EtOH–petrol). [Found: C, 66.60; H, 6.39 $C_{20}H_{24}O_6$ requires: C, 66.65; H, 6.71%], identical (UV, IR, PMR) with the trimethyl ether of the dihydro-derivative of natural (+)-mucronucarpan.

Synthesis of (±)-mucronucarpan (**12a**). (a) *Formation of 3-hydroxy-2,4-dimethoxybenzyl 2,5-dihydroxy-4-methoxyphenyl ketone* (**3f**). **6c** (650 mg), 4-hydroxy-3-methoxyphenol [35] (500 mg) and BF_3–Et_2O (10 ml) as in ref. [1], gave **3f** (370 mg), needles, mp 164° (EtOH–petrol). [Found: C, 61.25; H, 5.67. $C_{17}H_{18}O_7$ requires: C, 61.07; H, 5.43%]. ν_{max} (cm^{-1}): 3500, 1620. (b) *Formation of 6,3'-dihydroxy-7,2',4'-trimethoxyisoflavone* (**4f**). **3f** (408 mg) and $HC(OEt)_3$ (30 ml) as in ref. [1], gave **4f** (222 mg), microcrystals, mp 208° (EtOH). [Found: C, 62.91; H, 4.73. $C_{18}H_{16}O_7$ requires: C, 62.79; H, 4.68%]. ν_{max} (cm^{-1}): 3500, 1630. (c) *Formation of 6,2',3'-trihydroxy-7,4'-dimethoxyisoflavone* (**4g**). **4f** (1.56 g) was heated under reflux with $AlCl_3$ (1.69 g) in MeCN (20 ml). The solvent was evapd, the residue warmed with 2 N HCl, the ppt. collected and recryst. to **4g** (800 mg), microcrystals, mp 266° (EtOH). [Found: C, 61.87; H, 4.12. $C_{17}H_{14}O_7$ requires: C, 61.82; H, 4.27%]. ν_{max} (KBr, cm^{-1}) 1640, 1620. *Triacetate* (**4h**), needles, mp 138° (MeOH). [Found: C, 60.64; H, 4.38. $C_{23}H_{20}O_{10}$ requires: C, 60.53; H, 4.42%]. ν_{max} (cm^{-1}): 1760, 1640, 1615. PMR (τ): 2.15 (*s*, H-2). (d) *Formation of (±)-2,10-dihydroxy-3,9-dimethoxypterocarpan* (**12a**). Hydrogenation (room temp., 1 atm.) of **4g** (490 mg) over 10% Pd/C (300 mg) in HOAc was allowed to proceed until 4.3 molecular equivalents of H_2 had been absorved. The mixture was filtered, the AcOH evapd and the residue dissolved in EtOH from which **4g** crystallised and was removed. Evapn of the mother liquor gave a residue which was fractionated by TLC (Si gel, Et_2O) to (±)-mucronucarpan (56 mg) (**12a**), needles, mp 173° (EtOH). [Found: C, 64.10; H, 5.07. $C_{17}H_{16}O_6$ requires: C, 64.55; H, 5.09%], identical (IR, PMR) with natural (+)-mucronucarpan. (e) *Formation of (±)-6,2',3'-trihydroxy-7,4'-dimethoxyisoflavan* (**1g**). Hydrogenation (room temp., 1 atm., 3.5 hr) of **4g** (112 mg) over 10% Pd/C (112 mg) in HOAc (10 ml) gave, after the usual work up, **1g** (73 mg), rhombs, mp 168° (MeOH). [Found: C, 64.37; H, 5.86. $C_{17}H_{18}O_6$ requires: C, 64.14, H, 5.70%], identical (UV, IR) with the dihydro-derivative of natural (+)-mucronucarpan

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