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PELTOGYNOIDS OF *GONIORRHACHIS MARGINATA**

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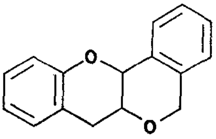
Key Word Index—*Goniorrhachis marginata*; Leguminosae; peltogynoids.

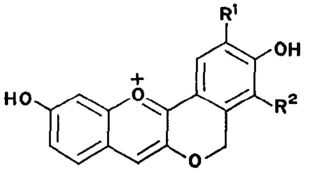
Abstract—Two novel types of natural peltogynoids represented by the flavanones (Vb), (Ve) and (Vg) and the chalcone (VIc) were encountered during the examination of the heartwood constituents of *Goniorrhachis marginata* Taub.

INTRODUCTION

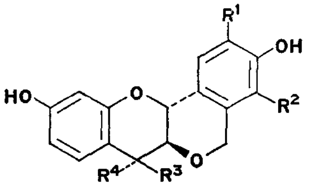
Goniorrhachis marginata Taub., known in Brasil by the trivial name guarabú, belongs to a monotypic genus of the Leguminosae–Caesalpinioideae which is closely akin to *Peltogyne*.[2] In the present paper we wish to report on the structure of four crystalline constituents of its heartwood. As had been anticipated, they are peltogynoids. The types of known natural products associated with the peltogynane skeleton (I)[3] are represented by compounds which can be formally related to anthocyanidin (II),[4a] flavan-3,4-diol (III),[4] flavonol (IV)[4a,5] and dihydroflavonol (V).[6,7] In a similar way, the new compounds contain either flavanone (Vb, Ve, Vg) or chalcone (VIc) nuclei.



(I) Peltogynane



	R¹	R²	
(IIa)	H	OH	Peltogynidin[4a]
(IIb)	H	OH	Mopaidin[4a]



	R¹	R²	R³	R⁴
(IIIa)	OH	H	H	OH
	(+)-Peltogynol[4]			
(IIIb)	OH	H	OH	H
	(+)-Peltogynol-B[4]			
(IIIc)	H	OH	H	OH
	(+)-Mopanol[4]			
(IIId)	H	OH	OH	H
	(+)-Mopanol-B[4]			

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[2] A. DE MATTOS FILHO, *Arq. Jardim Botânico Rio de Janeiro* **18**, 215 (1961).

[3] A. C. JAIN, P. D. SARPAL and T. R. SESHADRI, *Tetrahedron Letters* 4381 (1966).

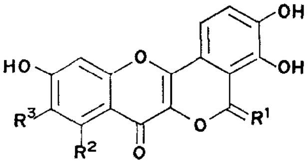
[4] S. E. DREWES and D. G. ROUX, (a) *J. Chem. Soc.* **C**, 1407 (1967); (b) *J. Chem. Soc.* **C**, 1644 (1966).

[5] F. E. KING, T. J. KING and P. J. STONES, *J. Chem. Soc.* 4594 (1954).

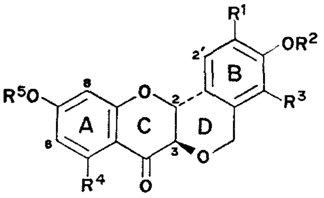
[6] O. R. GOTTLIEB and J. RÊGO DE SOUSA, *Anais Acad. Brasil. Ciênc.* **42** (Suppl.), 65 (1970).

[7] E. V. BRANDT, D. FERREIRA and D. G. ROUX, *Chem. Commun.* 116 (1971).

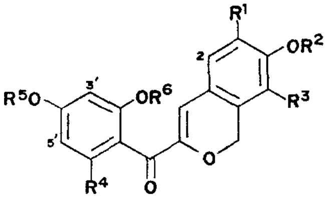
The first compound, $C_{16}H_8O_3(OH)_3OMe$, showed spectral characteristics (λ_{max} 286 nm, ϵ 20 500) suggestive of a flavanone or a 3-hydroxyflavanone constitution.[8,9] Indeed, upon addition of base, the intense absorption maximum (λ_{max} 330 nm, ϵ 30 400) typical of the chalcone chromophore appeared. No hydroxyl being present at C-5 (absence of a UV-shift upon addition of $AlCl_3$–HCl), such a group must be located at C-7; acetylation of the compound resulted in the shift of the IR-carbonyl absorption from 1675 to 1700 cm^{-1}. The PMR spectrum of the acetate (Vd, Table 1) lacked a signal at characteristically low field, precluding the existence also of hydrogen on C-5. It became imperative, therefore, to locate the methoxyl at this position. The analysis of the ring A of the flavanone was thus complete, since the PMR-spectrum indicated the presence of a pair of *meta*-related aromatic protons (τ 3·46 and 3·62, doublets, J 2·0 Hz) which cannot be located on ring C (see below).



	R^1	R^2	R^3
(IVa)	H,H	H	H
	Mopanin[4a]		
(IVb)	O	OH	OMe
	Distemonanthin[5]		



	R^1	R^2	R^3	R^4	R^5
(Va)	OH	H	H	OH	H
	Crombeone[7]				
(Vb)	OH	H	H	OMe	H
(Vc)	OMe	Me	H	OMe	Me
(Vd)	OAc	Ac	H	OMe	Ac
(Ve)	H	H	OH	OMe	H
(Vf)	H	OAc	OAc	OMe	Ac
(Vg)	OH	H	H	H	H
(Vh)	OMe	Me	H	H	Me
	Tri-*O*-methylpeltogynone[4b]				
(Vi)	OAc	Ac	H	H	Ac
(Vj)	H	H	OH	H	H
(Vk)	H	Me	OMe	H	Me
	Tri-*O*-methylmopanone[4b]				



	R^1	R^2	R^3	R^4	R^5	R^6
(VIa)	OMe	Me	H	OMe	Me	H
(VIb)	OMe	Me	H	OMe	Me	Me
(VIc)	H	H	OH	H	H	H
(VId)	H	Ac	OAc	H	Ac	Ac

The spectrum of the tri-*O*-acetyl derivative contained, furthermore, signals assignable to a methylene group (τ 5·02, s; c.f. the ring-D $C\underline{H}_2$ signal of peltogynol tetraacetate: τ 5·19, s),[4b] and to a pair of vicinal protons (τ 4·70, dd, J 12·0 and 0·5 Hz, τ 5·66, d, J 12·0 Hz; cf. the *trans* 2H,3H signals of 3-hydroxyflavanones: τ 4·4 and 5·6, doublets, J 12 Hz).[10] The secondary splitting of the 2-H signal revealed benzylic coupling with a 2'-proton on the ring C. The PMR signals due to this and the remaining benzenoid proton are substantially singlets, a fact which defines their *para*-relationship.

The constitutional proposal (Vb), which thus emerged for this compound, was confirmed, if only with respect to skeleton and oxygenation pattern, by transformation of its trimethyl ether (Vc) into the chalcone VIa. This was fully characterized by analysis of its PMR spectrum (Table 2), $KMnO_4$ oxidation to 2-hydroxy-4,6-dimethoxybenzoic acid, and Me_2SO_4–K_2CO_3 methylation to a monomethyl ether (VIb).

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[8] T. A. GEISSMAN (editor) *The Chemistry of Flavonoid Compounds*, Pergamon Press, Oxford (1962).

[9] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer, Berlin (1970).

[10] L. M. JACKMAN, in *Progress in the Chemistry of Organic Natural Products* (edited by L. ZECHMEISTER), Vol. XXIII, p. 315, Springer, Wien (1965).

Comparison of the spectral data of Vb with those of the second and third *Goniorrhachis* compounds led to constitutional proposals also for them. Indeed the only significant difference in the spectra of the triacetates of Vb and Ve, i.e. Vd and $C_{16}H_8O_3(OAc)_3OMe$ (Vf, Table 1), refers to the PMR-signals due to the two aromatic protons on ring-C. Benzylic coupling of the proton at C-2 to the proton at the 2′-position is still observed in the derivative of Ve. The 2′-H signal is here, however, substantially a doublet (*J* 8·5 Hz), indicating the vicinal relationship of the two protons on ring C, and leading to the constitution Ve for the second flavanone.

TABLE 1. PMR SPECTRA OF *Goniorrachis* FLAVANONES

		Vd	Vf	Vi	Vh	Vk^{4b}
H-2	τ	4·70	4·73	4·62	4·74	4·78
	M	dd	dd	dd	bd	d
	J	12·5, 0·5	12·0, 0·5	12·0 ,0·5	12·2	12·2
H-3	τ	5·66	5·70	5·50	5·65	5·76
	M	d	d	d	d	d
	J	12·0	12·0	12·0	12·2	12·2
H-5	τ	—	—	1·95	2·11	2·14
	M	—	—	dd	d	
	J	—	—	8.5, 2.0	8·5	
H-6	τ	3·46	3·46	3·04	3·37	3·40
	M	d	d		dd	
	J	2·0	2·0		8·5, 2·0	
H-8	τ	3·62	3·62	3·04	3·48	3·50
	M	d	d		d	
	J	2·0	2·0		2·0	
H-2′	τ	2·49	2·41	2·40	2·88	2·64
	M	bs	dd	s	s	d
	J	—	8·5, 0·5	—	—	8·5
H-3′	τ	—	2·76	—	—	3·11
	M	—	d	—	—	d
	J	—	8·5	—	—	8·5
H-5′	τ	3·06	—	3·05	3·44	—
CH$_2$	τ	5·02	5·10 5·15	4·97	5·05	5·03
	M	s	d. ,d	s	s	d, d
	J	—	15·0	—	—	16·0
O*CH*$_3$	τ	6·10	6·10	—	6·05	6·16
		—	—	—	6·14	6·19
		—	—	—	6·14	6·19
OCO*CH*$_3$	τ	7·66	7·70	7·66	—	—
		7·66	7·70	7·66	—	—
		7·68	7·73	7·68	—	—

TABLE 2. PMR SPECTRA OF *Goniorrhachis* CHALCONES

		VIa	VIc	VId
H-β	τ	3·16	3·19	3·28
H-2	τ	3·46	3·18	+
	M	s	d	
	J	—	8·0	
H-3	τ	—	3·31	+
	M	—	d	
	J	—	8·0	
H-5	τ	3·46	—	—
H-3′	τ	3·87	3·66	+
	M	d	d	
	J	2·5	2·5	
H-5′	τ	3·89	3·58	+
	M	d	dd	
	J	2·5	9·0, 2·5	
H-6′	τ	—	1·80	2·45
	M	—	d	d
	J	—	9·0	9·0
CH$_2$	τ	4·70	4·70	4·88
O*CH*$_3$	τ	6.10	—	—
		6·14	—	—
		6·14	—	—
		6·17	—	—
O*H*	τ	indet.	−2·83	—
		—	6·53	—
		—	6·53	—
		—	6·53	—
OCO*CH*$_3$	τ	—	—	7·68
		—	—	7·68
		—	—	7·72
		—	—	7·94

Notes to Tables 1 and 2. The spectra were registered in $CDCl_3$ solution at 60 MHz (Vd,f,i; VIa,d), 100 MHz (Vk) and 220 MHz (Vh), or in $(CD_3)_2CO$ solution at 220 MHz (VIc). TMS was used as internal reference. + Signal included in an unresolved multiplet τ 2·8–3·0, representing four protons. Multiplicity (M) of bands, if omitted, refers to singlets. s singlet, d doublet, dd double doublet, b broad.

In contradistinction, the only significant difference in the PMR spectra of the triacetates of Vb and Vg, i.e. Vd and $C_{16}H_9O_3(OAc)_3$ (Vi, Table 1), refers to the signals due to the substituents of ring A. In the derivative of the third flavanone, the methoxyl of Vb is clearly replaced by an additional aromatic proton. The chemical shift and multiplicity (τ 1·95, dd, *J* 8·5 and 2·0 Hz) of its PMR signal places it at the deprotected 5-position, *ortho* and *para* related with the two other protons of ring A, leading to the constitution Vg for the third flavanone. In confirmation of this, Me_2SO_4–K_2CO_3 methylation gave a trimethyl ether which proved to be identical, by direct comparison, with the oxidation product of tri-*O*-methylpeltogynol Vh.

TABLE 3. INTERPRETED MS OF THE FLAVANONES Vb, e, g, h, k AND THE CHALCONE VIc

	m/e	Vh[11] %	Vk[11] %	*m/e*	Vb %	Ve %	*m/e*	Vg %	VIc %
M	342	35	31	330	22	56	300	100	26
M-H_2O	324	4	4	312	3	6	282	3	6
RDA/A + H	151	6	4	167	100	100	137	40	100
RDA/A	150	40	48	166	14	7	136	10	6
RDA/B	192	100	100	164	13	60	164	18	5
RDA/B − H	191	27	10	163	10	9	163	9	4

RDA/A or B. Fragment generated through the retro-Diels–Alder cleavage of ring C of the flavanones,[11] encompassing either ring A or B.

The MS of compounds Vb, Ve and Vg were consistent with the proposed constitutions, and are interpretable according to the fragmentation paths proposed for the synthetic trimethyl ethers of peltogynone (Vh) and mopanone (Vk)[11] (Table 3). (+)-Tri-*O*-methylpeltogynone (Vh) and (+)-tri-*O*-methylmopanone (Vk) were also helpful in the assignment of the absolute configurations (2*R*,3*R*) to the new flavanones. Indeed, the published ORD curves for the synthetic derivatives[4b] are very similar among themselves and to the curves obtained for our natural isolates (Table 4). The similarity of the curves of Vh and Vk indicates that the differences in substitution pattern do not invalidate stereochemical assignments based on the comparison of ORD-curves in this field.

TABLE 4. ORD MAXIMA OF (+)-FLAVANONES (SOLVENT MeOH)

Vb		Ve		Vg		Vh[4b]*		Vk[4b]	
λ(nm)	$10^{-3}[\phi]$	λ(nm)	$10^{-3}[\phi]$	λ(nm)	$10^{-3}[\phi]$	λ(nm)	$10^{-3}[\phi]$	λ(nm)	$10^{-3}[\phi]$
239	+45·0	239	+50·3	242	+47·5	240	+46·5	240	Pos.
278sh	−3·8	278sh	+6·0	278	+25·6	272	+16·0	276	Pos.
						280	+17·5		
292	−17·1	313	−1·1	310	−33·5	312	−21·5	310	Neg.
337	+17·1	344	+7·2	333	+23·8	336	+14·5	335	Pos.

* These data were taken from a small graph and are subject to error of λ ± 2 nm, $10^{-3}[\phi]$ ±0·5.

The intense yellow colour and typical UV spectrum (λ_{max} 395 nm, ϵ 16 500) characterized the fourth compound, $C_{16}H_8O_2(OH)_4$, as a chalcone. The complete structure VIc was easily deduced from the PMR (Table 2) and MS (Table 3). In confirmation, treatment with acid yielded a flavanone (Vj, disregard indication of stereochemistry), whose trimethyl ether was indistinguishable from tri-*O*-methylmopanone (Vk)[3b] by TLC and IR spectrometry.

Harborne[12] correlates structural modifications of flavonoids with phylogeny. Chalcones

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[11] S. E. DREWES and H. BUDZIKIEWICZ, *J. Chem. Soc.* C, 63 (1969).

[12] J. B. HARBORNE, in *Comparative Phytochemistry* (edited by T. SWAIN) p. 271, Academic Press, London (1966).

and flavanones are considered primitive characters, while absence of the 5-hydroxyl group constitutes an advanced character. Both these criteria point to *Goniorrhachis* as a remnant of the previously possibly widespread ancestors to *Peltogyne* and related genera.

EXPERIMENTAL

M.ps were determined using a Kofler hot stage microscope and are uncorrected. Separations were carried out using either Merck Kieselgel 0·05–0·20 mm (column chromatography) or Merck Kieselgel G (TLC) PMR spectra were determined using Varian instruments. For symbols see notes to Tables 1 and 2. MS were determined with an AEI, model MS9, spectrometer. Only peaks of *m/e* > 100 and intensity $> 5\%$ are quoted. The ORD curves were registered on a Bendix Polarmatic 62 instrument. The methyl ethers were prepared by reflux in Me_2CO with Me_2SO_4–K_2CO_3. The acetates were prepared with Ac_2O–pyridine at room temp.

Isolation of the constituents of Goniorrhachis marginata. The powdered heartwood (4·6 kg) was successively extracted with benzene and EtOH. The EtOH solution was evaporated and the residue (400 g) was chromatographed on silica, yielding the following useful fractions with the indicated eluants: F_1 ($CHCl_3$–MeOH 98:2), F_2 ($CHCl_3$–MeOH 98:3), F_3 ($CHCl_3$–MeOH 98:6), F_4 ($CHCl_3$–MeOH 98:7). Upon slow evaporation of the solvent, F_1 gave crystals which were filtered and rechromatographed on silica. Upon slow evaporation of the fraction eluted with $CHCl_3$–MeOH 98:2, crystals appeared. These were collected by filtration and washed with $CHCl_3$, giving VIc (300 mg). F_2 was evaporated and the residue was rechromatographed on silica, using $CHCl_3$–MeOH 97:3 as eluant. Evaporation of the solvent produced Vg (500 mg). F_3 and F_4 were evaporated. The residues were washed with MeOH and recrystallized from MeOH, giving respectively Vb (400 mg) and Ve (100 mg).

(6aR,12aR)-2,3,10-*Trihydroxy*-8-*methoxy*-6,12-*dioxabenz*(*a*)*anthracen*-7(5H,6aH,12aH)-*one* (Vb). Crystals, m.p. 260–262°. (Found: C, 61·70; H, 4·21. Calc. for $C_{17}H_{14}O_7$: C, 61·82; H, 4·27%.) λ_{max}^{EtOH} (nm): 286, 320 (ϵ 20 500, 9200), no shift with $AlCl_3$/HCl, $\lambda_{max}^{EtOH+NaOH}$ (nm): 250, 330 (ϵ 14 500, 30 400), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 247, 325 (ϵ 7900, 29 400). ν_{max}^{KBr} (cm^{-1}): 1675, 1620, 1580, 1525, 1475, 1430, 1285, 1110, 1055, 880, 830, 780. MS: M 330 (22%), *m/e* (%) 312 (3), 168 (13), 167 (100), 166 (14), 164 (13), 163 (10), 152 (6), 136 (8), 135 (6), 124 (6), 123 (5), 107 (5). ORD (MeOH, c, 0·4, 455–222 nm): $[\phi]_{455}$ +2370, $[\phi]_{357}$ +8910, $[\phi]_{337}$ +17 050, $[\phi]_{320}$ 0, $[\phi]_{312}$ −6150, $[\phi]_{292}$ −17 050, $[\phi]_{278}$ −3780, $[\phi]_{272}$ 0, $[\phi]_{250}$ +21 300, $[\phi]_{239}$ +45 000, $[\phi]_{235}$ +28 880, $[\phi]_{232}$ +26 000, $[\phi]_{229}$ 0, $[\phi]_{227}$ −8050, $[\phi]_{222}$ −24 150.

Trimethyl ether (Vc). Needles, m.p. 248–251° ($CHCl_3$–MeOH). ν_{max}^{KBr} (cm^{-1}): 1695, 1610, 1575, 1500, 1455 1210, 1100, 1010, 795.

Triacetate (Vd). Needles, m.p. 219–221° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1750, 1700, 1600, 1580, 1500, 1375, 1200 885.

(6aR,12aR)-3,4,10-*Trihydroxy*-8-*methoxy*-6,12-*dioxabenz*(*a*)*anthracen*-7(5H,6aH,12aH)-*one* (Ve). Crystals, m.p. 280–282° (MeOH). (Found: C, 61·59; H, 4·25. Calc. for $C_{17}H_{14}O_7$: C, 61·82; H, 4·27%.) λ_{max}^{EtOH} (nm): 286, 320 (ϵ 26 400, 5000), no shift with $AlCl_3$–HCl, $\lambda_{max}^{EtOH+NaOH}$ (nm): 254, 330 (ϵ 23 100, 45 200), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 250, 325 (ϵ 9900, 33 000). ν_{max}^{KBr} (cm^{-1}): 3450, 3400, 3330, 1675, 1600, 1500, 1470, 1455, 1300, 1210, 1100, 970, 925, 920. MS: M 330 (56%), *m/e* (%) 312 (6), 169 (5), 168 (33), 167 (100), 166 (7), 165 (6), 164 (60), 163 (9), 162 (6), 152 (9), 151 (6), 137 (6), 136 (18), 135 (6), 124 (9), 107 (6). ORD (MeOH; *c*, 0·22, 625–303 nm; *c*, 0·022, 303–233 nm): $[\phi]_{625}$ +860, $[\phi]_{500}$ +1280, $[\phi]_{400}$ +310,, $[\phi]_{344}$ +7230, $[\phi]_{333}$ +5900, $[\phi]_{316}$ 0, $[\phi]_{313}$ −1100, $[\phi]_{303}$ 0, $[\phi]_{294}$ +2650, $[\phi]_{278}$ +6000, $[\phi]_{256}$ +12 300, $[\phi]_{254}$ +12 300, $[\phi]_{239}$ +50 290, $[\phi]_{233}$ +28 220.

Triacetate (Vf). Needles, m.p. 238–240°, ν_{max}^{KBr} (cm^{-1}): 1755, 1700, 1600, 1580, 1480, 1460, 1360, 1200, 1150, 1025, 820. PMR: Table 1.

(6*aR*,12*aR*)-2,3,10-*Trihydroxy*-6,12-*dioxabenz*(*a*)*anthracen*-7(5*H*,6*aH*,12*aH*)-*one* (Vg). Rods, m.p. 259–261° ($CHCl_3$–MeOH). (Found: C, 63·81; H, 3·97. Calc. for $C_{16}H_{12}O_6$: C, 64·00; H, 4·03%.) λ_{max}^{EtOH} (nm): 281, 315 (ϵ 15 600, 9000), no shift with $AlCl_3$–HCl, $\lambda_{max}^{EtOH+NaOH}$ (nm): 251, 341 (ϵ 22 800, 33 600), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 282, 335 (ϵ 13 200, 12 000). ν_{max}^{KBr} (cm^{-1}): 3350, 1675, 1640, 1610, 1560, 1515, 1460, 1275, 1200, 1080, 970, 850, 790. MS: M 300 (100%), *m/e* (%) 282 (3), 164 (18), 163 (9), 151 (14), 150 (7), 137 (40), 136 (10), 135 (7), 108 (8), 107 (8). ORD (MeOH, *c*, 0·14, 455–222 nm): $[\phi]_{455}$ +2810, $[\phi]_{385}$ +5630, $[\phi]_{357}$ +10 570, $[\phi]_{333}$ +23 810, $[\phi]_{324}$ 0, $[\phi]_{319}$ −22 050, $[\phi]_{310}$ −33 540, $[\phi]_{303}$ −25 460, $[\phi]_{292}$ 0, $[\phi]_{286}$ +14 990, $[\phi]_{278}$ +25 560, $[\phi]_{263}$ +15 000, $[\phi]_{250}$ +28 230, $[\phi]_{242}$ +47 460, $[\phi]_{233}$ +15 000, $[\phi]_{229}$ 0, $[\phi]_{227}$ −7050, $[\phi]_{222}$ −13 860.

Trimethyl ether (Vh). Needles ($CHCl_3$–MeOH), m.p. and m. m.p. with an authentic specimen, 211–213°. ν_{max}^{KBr} (cm^{-1}): 1690, 1612, 1510, 1440, 1375, 1340, 1260, 1230, 1200, 1120, 1090, 1025, 850, 825, 805, 725. PMR: Table 1.

Triacetate (Vi). Needles, m.p. 197–200° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1760, 1700, 1610, 1580, 1500, 1440, 1360. 1200, 900. PMR: Table 1.

Conversion to chalcone (VIa). Vb (200 mg) in 10% KOH aq. (50 ml) was maintained under reflux until complete dissolution of the material (4 hr). After cooling to room temp., the solution was filtered and extracted exhaustively with AcOEt. The AcOEt-solution was washed with water, dried and evaporated. The residue, after washings with MeOH, was composed of light yellow needles of VIa (100 mg), m.p. 144–146° (MeOH). λ_{max}^{EtOH} (nm): 360 (ϵ 48 700), $\lambda_{max}^{EtOH+NaOH}$ (nm): 350 (ϵ 48 700). ν_{max}^{KBr} (cm^{-1}): 1630, 1575, 1485, 1375, 1270, 1220, 1150, 1075, 1020, 830, 800. PMR: Table 2.

Methyl ether (VIb). Very light yellow needles, m.p. 152–153° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1660, 1600, 1450, 1275, 1220, 1150, 1125, 1010, 810.

Oxidation of VIa. To an acetone soln of VIa (50 mg) solid $KMnO_4$ was added in small portions until persistence of the violet colour. Excess $KMnO_4$ was destroyed with $NaHSO_3$. The acetone was evaporated and the residue taken up with 5% Na_2CO_3 aq. The filtered aqueous solution was acidified with HCl and extracted with $CHCl_3$. The $CHCl_3$-solution, washed with water, dried and evaporated, gave 2-hydroxy-4,6-dimethoxybenzoic acid (8 mg), needles, m.p. 153–155° (MeOH) [lit.[13] m.p. 152–154°]. ν_{max}^{KBr} 3200, 1675, 1625, 1600, 1440, 1350, 1280, 1210, 1110, 1040, 925, 840, 820, 780, 750, 690. PMR ($CDCl_3$, τ): 3·82 (d, *J* 2·5 Hz, H-3), 3·95 (d, *J* 2·5 Hz, H-5), 5·80 (s, $OC\underline{H}_3$), 6·18 (s, $OC\underline{H}_3$). MS: 198 (33%), *m/e* (%), 182 (13), 181 (100), 155 (8), 153 (37), 152 (5), 139 (5), 138 (52). 126 (5), 110 (12).

2,4-*Dihydroxyphenyl* 1-*hydro*-7,8-*dihydroxy*-2-*oxa*-3-*naphthyl ketone* (VIc). Intensely yellow needles, m.p. 246–248° ($CHCl_3$–MeOH). (Found: C, 63·78; H, 4·00. Calc. for $C_{16}H_{12}O_6$: C, 64·00; H, 4·03%.) UV (immediately after preparation of solution) λ_{max}^{EtOH} (nm): 250, 305, 395 (ϵ 9300, 8700, 16 500), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 284, 320, 416 (ϵ 14 100, 9300, 11 100), $\lambda_{max}^{EtOH+NaOH}$ (nm): 257, 346 (ϵ 14 600, 31 300), $\lambda_{max}^{EtOH+NaOH+HCl}$ (nm): 235, 282, 322 (ϵ 13 200, 14 400, 9300), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 247, 354, 400 (ϵ 9900, 12 900, 15 000). UV (1 hr after preparation of solution) λ_{max}^{EtOH} (nm): 256, 285, 345 (ϵ 10 800, 8100, 26 100). UV (3 days after preparation of solution) λ_{max}^{EtOH} (nm): 240, 282, 325 (ϵ 13 500, 14 500, 9500). ν_{max}^{KBr} (cm^{-1}): 3475, 3300, 3150, 1630, 1620, 1590, 1500, 1460, 1340, 1275, 1160, 975, 940, 790. PMR: Table 2. MS: M 300 (26%), *m/e* (%) 282 (6), 164 (5), 138 (12), 137 (100), 136 (6), 135 (13).

Tetraacetate (VId). Very light yellow crystals, m.p. 136–138° (MeOH). λ_{max}^{EtOH} (nm): 240, 345 (ϵ 13 100, 14 000). ν_{max}^{KBr} (cm^{-1}): 1770, 1755, 1675, 1575, 1470, 1370, 1260, 1200, 1005, 910, 880, 825.

(±)-*Mopanone*. The chalcone VIc (100 mg) was dissolved in EtOH–H_2O 1:1 (400 ml). HCl conc. (20 ml) was added and the solution maintained under reflux until the yellow colour had been nearly discharged. The EtOH was evaporated. After cooling to room temp. and saturation with NaCl, was the solution extracted with AcOEt. The organic layer was separated and dried. Evaporation of the solvent gave a residue which was chromatographed on silica. Elution with $CHCl_3$–MeOH 24:1 and slow evaporation of the fractions yielded needles (40 mg), m.p. 265–270°. λ_{max}^{EtOH} (nm): 235, 282, 325 (ϵ 13 400, 14 500, 9600), no modification in presence of $AlCl_3$–HCl, $\lambda_{max}^{EtOH+NaOH}$ (nm): 257, 346 (ϵ 14 400, 31 800), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 238, 284, 328 (ϵ 18 000, 21 000, 13 800). ν_{max}^{KBr} (cm^{-1}): 3500, 3400, 3100, 1680, 1615, 1585, 1460, 1380, 1170, 1120, 1090, 970.
(±)-*Trimethylmopanone*. Crystals, m.p. 220–222° [lit.[4b] m.p. for (+)-tri-*O*-methylmopanone 210°]. Indistinguishable by TLC and IR spectrometry from (+)-trimethylmopanone.

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