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NEOLIGNANS FROM AN *ANIBA* SPECIES*

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Key Word Index—*Aniba* sp.; Lauraceae; neolignans; 3a-allyl-2-aryl-5-methoxy-3-methyl-2,3,3a,6-tetrahydro-6-oxobenzofurans; 5-allyl-2-aryl-5-methoxy-3-methyl-2,3,5,6-tetrahydro-6-oxobenzofurans; 6-*O*-allyl-2-aryl-5-methoxy-3-methyl-2,3-dihydrobenzofurans; 7-allyl-2-aryl-6-hydroxy-5-methoxy-3-methyl-2,3-dihydrobenzofurans; 1-allyl-4,8-dihydroxy-7-(3-methoxy-4,5-methylenedioxyphenyl)-6-methyl-3-oxobicyclo[3,2,1]octane.

Abstract—A benzene extract of the trunk wood of an *Aniba* species contained 3a-allyl-2-aryl-5-methoxy-3-methyl-2,3,3a,6-tetrahydro-6-oxobenzofurans which may be responsible, through sequential Cope, retro-Claisen and Claisen rearrangements respectively for the formation of the co-occurring 5-allyl-2-aryl-5-methoxy-3-methyl-2,3,5,6-tetrahydro-6-oxobenzofurans; the 6-*O*-allyl-2-aryl-5-methoxy-3-methyl-2,3-dihydrobenzofurans and the 7-allyl-2-aryl-6-hydroxy-5-methoxy-3-methyl-2,3-dihydrobenzofurans. The examination of the stereochemistry of these products led to the formulation of burchellin, previously isolated from *Aniba burchellii* Kostermans, as (2S,3S,3aR)-3a-allyl-5-methoxy-2-piperonyl-3-methyl-2,3,3a,6-tetrahydro-6-oxobenzofuran. The structure 1-allyl-4,8-dihydroxy-7-(3-methoxy-4,5-methylenedioxyphenyl)-6-methyl-3-oxobicyclo[3,2,1]octane is tentatively proposed for an additional neolignan.

Aniba burchellii Kosterm. contains the neolignan burchellin (**1a**) [2] whose biosynthesis probably involves oxidative coupling of isoeugenol and eugenol units [3]. Fractionation of a C_6H_6-extract of an *Aniba* sp. akin to the *gigantifolia* O. C. Schmidt [4]—*guianensis* Aubl. [5]—*hostmanniana* (Nees) Mez [6]—group, whose classification will be possible upon completion of the revision of Lauraceae by Dr. K. Kubitzki, Hamburg, gave 3 additional burchellin analogues (**1c**, **1d**, **1e**), also 2 α-allylcyclohexadienones (**2b**, **2c**), 2 *O*-allylphenols (**3c**, **7**), 2 *C*-allylphenols (**4b**, **4d**) and a bicyclo[3,2,1]octane derivative (**9**). The formation of the compounds belonging to structural types **2**, **3** (=**7**) and **4** can best be explained by sequential Cope, retro-Claisen and Claisen rearrangements of compounds belonging to type **1**. Thus, although **1b** and **8** were not isolated during the present work, their natural occurrence is highly probable. In the laboratory, these reactions require high temperatures (Table 1). The instability of burchellin (**1a**) upon treatment with 4 N KOH in MeOH at reflux temp. is known [2] and slight decomposition of **1e** and **2c** in boiling EtOH–$C_6H_5NEt_2$ 19:1 was observed. Under plant extraction conditions, however, i.e. in refluxing neutral or acid treated C_6H_6 or EtOH, **1e** and **2c** are completely stable. Compounds belonging to all 4 structural types, including the missing links **2a**, **2d**, **2e**, **3a**, **3b**, **3d**, **3e**, **4a**, **4c** and **4e**, may thus occur naturally.

Structural assignments of type **1** compounds were based on comparison of data with published data for **1a**. With the exception of signals due to differential substitution, significant PMR-spectral similarities and dissimilarities (Table 2) showed **1c**, like burchellin (**1a**), to be a 2,3-*trans* derivative (Me-3 τ 8·8) and **1d** and **1e** to be 2,3-*cis*

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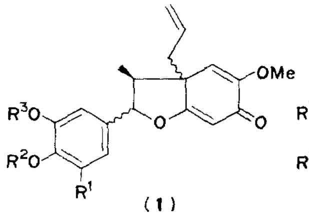

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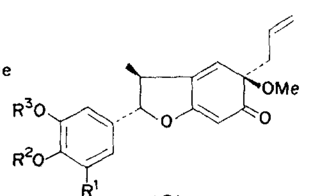

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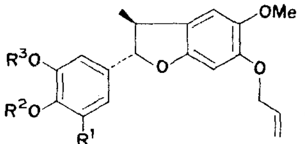

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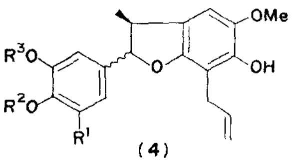

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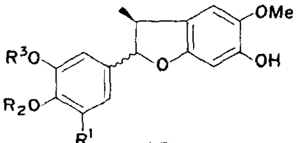

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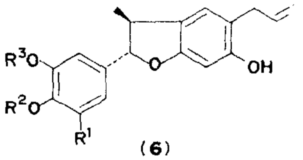


(6)

Obtained by isolation	Obtained by pyrolysis		Aryl-2	Allyl-3a*	R^1	R^2 R^3
1†	4, 5	a	α	β	H	$-CH_2-$
2, 4	4, 5	b	α		OMe	$-CH_2-$
1, 2, 3	3, 4, 5, 6	c	α	α	OMe	Me Me
1, 4	4, 5	d	β	α	OMe	$-CH_2-$
1	4, 5	e	β	α	OMe	Me Me

* Only for type (1) cmpds.
† From *Aniba burchellii*

derivatives (Me-3 τ 9·5). The compounds of type **2** (Table 2) were clearly again 2,3-*trans* derivatives (Me-3 τ 8·6) supporting the allyl group on a sp^3-C (CH_2 τ 7·6). Since one of their methoxyls (τ 7·0), however, had also to be placed on a sp^3-C, and only one fully substituted sp^3-C can exist in these molecules, an α,β-γ,δ rather than an α,β-α′,β′ unsaturated cyclohexadienone system characterizes these compounds and determined, as expected [2], the appearance of UV maxima at relatively higher wavelenth (315 nm, against 260 nm in all compounds of type **1**). IR carbonyl maxima present at 1640 cm^{-1} in compounds of type **1** and 1685 cm^{-1} in compounds of type **2**, are absent from the spectra of compounds belonging to types **3**, **4**, **5** and **6**. These are, indeed, either 2,3-*trans* (**3c**; **4a**, **4b**, **4c**; **5a**, **5b**, **5c**; **6**: Me-3 τ 8·6) or 2,3-*cis* (**4d**, **4e**; **5d**, **5e**: Me-3 τ 9·2) dihydrobenzofurans with the allyl groups either on oxygen (**3c**, **7**: CH_2 τ 5·5), carbon (**4a**–**e**; **6c**: CH_2 τ 6·6) or absent (**5a**–**e**).

Interpretation of the MS (Scheme 1) relied upon previously formulated rearrangement and fragmentation paths [2] and were fully consistent with the proposed structures. These were further checked by PMR double irradiation experiments involving H-3. In each of the cases studied (**1c**, **1d**, **1e**; **2b**, **2c**; **4d**) the doublets attributed to Me-3 and H-2 collapsed to singlets. Additionally, irradiation at the allyl methine proton frequency of

Table 1. Pyrolysis of compounds (see Experimental)

Cmpd. 100 mg	Solvent 10 ml	Temp. (°)	Time (hr)	SiO_2-TLC developing solv.	Products proportion
(1a)	$C_6H_5NEt_2$	225	2·5	$CHCl_3$-AcOEt (99:1)	4a-5a 2·3:1·0
(1d)	$C_6H_5NEt_2$	225	2		4d-5d 2·7:1·0
(1e)	$C_6H_5NEt_2$	225	2	$CHCl_3$	4e-5e 6·5:1·0
	EtOH	78	5		recovered 1e
	EtOH-AcOH 19:1	78	5		id.
	EtOH-$C_6H_5NEt_2$ 19:1	78	5		id. + trace 4e
(2b)	$C_6H_5NEt_2$	225	2		4b-5b 2·7:1·0
(2c)	$C_6H_5NEt_2$	225	2	C_6H_6-Me_2CO (4:1)	4c-5c 4·3:1·0
	$C_6H_5NEt_2$	155	5		3c-4c 18·7:1·0
	C_6H_6	80	10		recovered 2c
	C_6H_6-AcOH 19:1	80	10		id.
	C_6H_6-$C_6H_5NEt_2$ 19:1	80	10		id. + trace 3a, 4a
	EtOH	78	10		recovered 2c
	EtOH-AcOH 19:1	78	10		id.
	EtOH-$C_6H_5NEt_2$ 19:1	78	10		2c-(3a + 4a)-other 8:1:1
(3c)	$C_6H_5NEt_2$	225	2		4c-5c-6c 11·7:1·0:2·3

Table 2. PMR Data of neolignans of structural types **1** and **2**

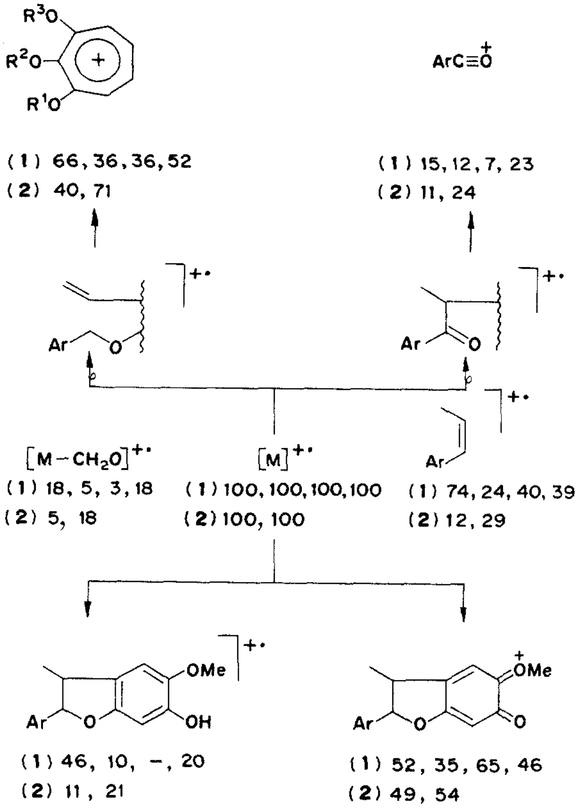
Protons	**1a** 220 MHz ($CDCl_3$)	**1c** 220 MHz ($CDCl_3$)	**1d** 60 MHz ($CDCl_3$)	**1e** 220 MHz (CCl_4)	**2b** 60 MHz (CCl_4)	**2c** 220 MHz (CCl_4)
Me-3	8·84 *d* 6·9 Hz	8·82 *d* 7·0 Hz	9·50 *d* 7·0 Hz	9·53 *d* 7·0 Hz	8·65 *d* 7·0 Hz	8·64 *d* 7·0 Hz
C$\underline{H}_2$CH=CH$_2$	·45 7·66 *dd* *dd* 13·0 Hz 13·0 Hz 6·8 Hz 6·8 Hz	7·72 7·83 *dd* *dd* 12·5 Hz 12·5 Hz 6·3 Hz 6·3 Hz	7·07–7·60 *m*	7·46–7·69 *m*	7·62 *d* 7·0 Hz	7·62 *d* 7·0 Hz
H-3	7·72 *dq* 9·5, 6·9 Hz	7·30 *dq* 7·0 Hz, indet.		7·28–7·46 *m*	6·96–7·16 *m*	6·96–7·16 *m*
OMe-5	6·32 *s*	6·38 *s*	6·34 *s*	6·48 *s*	7·00 *s*	7·00 *s*
ArOMe		6·16 6·16 6·20 *s* *s*	6·10 *s*	6·25 6·25 6·32 *s* *s*	6·10 *s*	6·19 6·19 6·28 *s* *s*
CH$_2$CH=C$\underline{H}_2$	4·92 4·99 *dd* *dd* 9·5 Hz 16·5 Hz 1·5 Hz 1·5 Hz	4·96–5·08 *m*	4·69–5·09 *m*	4·87–5·03 *m*	4·84–5·17 *m*	4·98–5·12 *m*
H-7	4·57 *s*	4·62 *s*	4·50 *s*	4·64 *s*	4·94 *s*	5·10 *s*
H-4	4·21 *s*	4·21 *s*	4·19 *s*	4·41 *s*	4·54 *s*	4·53 *s*
CH$_2$C$\underline{H}$=CH$_2$	4·45 *ct* 6·8 Hz 6·8 Hz 9·5 Hz 16·5 Hz	4·32–4·96 *m*	4·00–4·50 *m*	4·25–4·48 *m*	4·20–4·67 *m*	4·32–4·55 *m*
H-2	4·83 *d* 9·5 Hz	4·71 *d* indet.	4·00–4·50 *m*	4·16 *d* 5·0 Hz	3·94 *d* 3·0 Hz	3·96 *d* 3·0 Hz
O_2CH_2	4·03 *s*		4·00 *s*		4·05 *s*	
ArH-2,6	3·17–3·25 *m*	3·50 *s*	3·57 *s*	3·69 *s*	3·57 *s*	3·60 *s*
ArH-5	3·17–3·25 *m*					

s Singlet, *d* doublet, *dd* double doublet, *dq* double quartet, *qt* quadruple triplet, *m* multiplet.

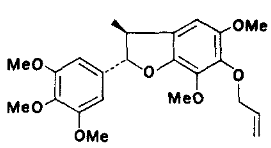
2b and **2c** lessened considerably the resolution of the CH$_2$-bands.

Pyrolysis of the compounds of type **1**, **2** and **3**, leading to expected products (Table 1), confirmed the proposed structures and solved some of the stereochemical problems. Initially, since all the derived, natural and synthetic, *trans*-2,3-dihydrobenzofurans (types **3**–**7**, series a–c) give ORD curves [λ(nm) of extrema: tr (315 ± 7), 0 (301 ± 4), pk (287 ± 3), tr (267 ± 3), pk 248 (±7)] of (2S,3S)-compounds [2], the absolute configuration at C-2 and 3 must be as shown in **1**–**7**, series a–c, and only the stereochemistries of C-3a in **1a** and **1c**, and of C-5 in **2b** and **2c** remain to be determined. The ORD curves of **1a** and **1c** are different and the compounds must be epimeric at C-3a. Indeed, the PMR signals due to the CH$_2$-groups at this chiral centre occur at significantly higher field in the spectrum of **1c** than of **1a** (Δ 0·27 and 0·17 ppm). The allyl group of **1c** must thus possess the 3aS-configuration, protruding into the relatively protected zone above the aromatic ring. In contrast, the *trans*-arrangement (2S,3aR-configuration) must exist between the allyl group and the aromatic ring of burchellin (**1a**). Since it is highly probable that **2c** is the Cope rearrangement product of **1c**, it must show the 5R-configuration. Although **1b**, the putative precursor of **2b**, was not isolated, the (2S,3S,5R)-stereochemistry can nevertheless also be assumed for **2b**, due to the similarity of its ORD curve and the curve of **2c**.

To our knowledge no correlations of stereochemistry and ORD curves of 2,3-*cis*-dihydrobenzofurans have yet been published. Thus, at this time, it can only be stated that all the natural and synthetic *cis*-2,3-dihydrobenzofurans (types **4**, **5**; series d, e), giving similar ORD curves [λ(nm) of extrema: p*K* (314 ± 7), 0 (295 ± 10), tr (282 ± 6), 0 (265 ± 6), pk (245 ± 0)], have identical absolute stereochemistry. The parent compounds, whose relative configuration is shown in **1d** and **1e**, have of course not only this same stereochemistry at C-2,3, but also identical configuration



Scheme 1. Interpreted MS of compounds of structural types **1** and **2**. Relative peak intensities given in order **1a**, **1c**, **1d**, **1e** and **2b**, **2c**.



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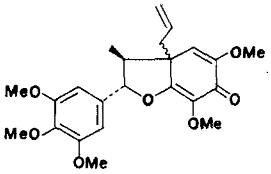

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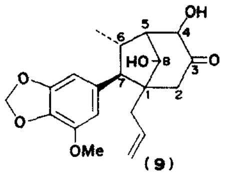

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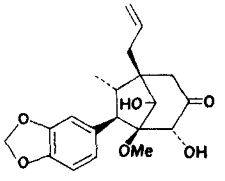

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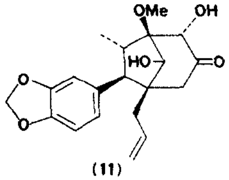


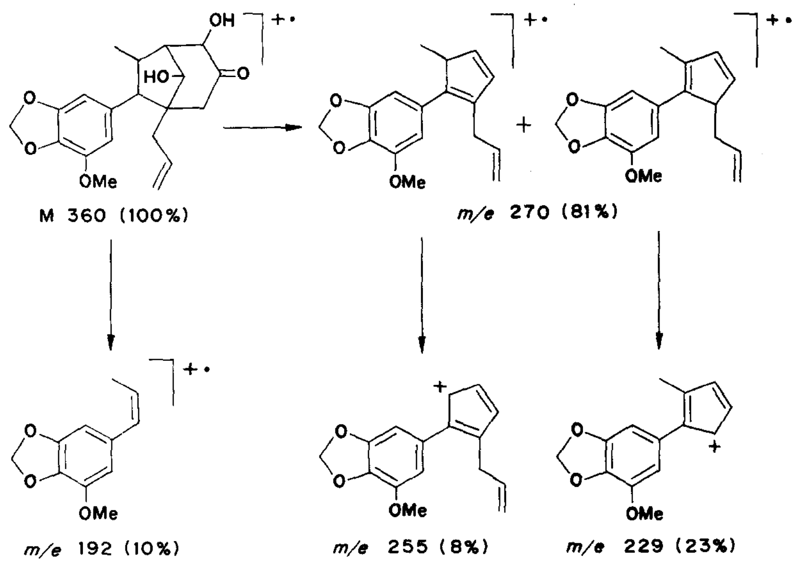
(11)

Table 3. PMR Data of Bicyclo[3,2,1]octane neolignans

Protons	**9** 220 MHz ($CDCl_3$)	(**10** or) **11** 220 MHz ($CDCl_3$)
Me-6	9·12 *d* 7·0 Hz	9·23 *d* 7·0 Hz
$C\underline{H}CH{=}CH_2$	8·00 *dd* 8·5 Hz 14·2 Hz	7·93 *dd* 9·0 Hz 13·5 Hz
H-5 2H-2 H-6 $C\underline{H}CH{=}CH_2$	7·55–7·93 *m*	7·37–7·60 *m*
OH-4	8·22 *s*	7·58 *s*
H-7	7·49 *d* 3·4 Hz	7·37–7·60 *m*
OMe-5		6·72 *s*
OH-8	6·39 *s*	6·23 *s*
ArOMe	6·20 *s*	
H-4	5·87 *d* 2·8 Hz	5·90 *s*
H-8	5·80 *s*	5·63 *s*
$CH_2CH{=}C\underline{H}_2$	4·81–4·94 *m*	4·83–4·95 *m*
$CH_2C\underline{H}{=}CH_2$	4·06–4·23 *m*	4·02–4·22 *m*
O_2CH_2	4·15 *s*	4·14 4·15 AB syst. J indet.
ArH-6	3·38 *d* 1·4 Hz	3·37 *s*
ArH-2	3·53 *d* 1·4 Hz	3·12 *s*
ArH-5		3·37 *s*

at C-3a, in view of the similarity of their ORD curves. Close correspondence of CH_2-chemical shifts exists for **1a** on one hand, and **1d** and **1e** on the other. A *trans*-relationship between the allyl groups and the aromatic rings of **1d** and **1e** is thus tentatively considered.

The formula of compound **9**, $C_{20}H_{24}O_6$, established by high resolution MS, was expanded to $C_{18}H_{17}O.2OH.OMe.O_2CH_2$ after inspection of the 220 MHz PMR spectrum. The compound is thus an isomer of canellin-C for which, tentatively, structures **10** or **11** [7] were proposed. The IR spectrum of **9** again indicated the presence of



Scheme 2. Interpreted MS of compound **9**.

a carbonyl in saturated environment (ν_{max} 1705 cm^{-1}) and the PMR spectra of **9** and canellin-C were also very similar (Table 3). The significant differences concern the methoxyl which, situated on the aliphatic portion of canellin-C (τ 6·72), substitutes the aryl group of **9** (τ 6·20). The oxymethine proton at C-2 of **9** is thus not adjacent to a fully substituted bridgehead carbon, as in canellin C (τ 5·90, *s*), and represented by a doublet (τ 5·87). The H-8 signal continues as a singlet (canellin-C τ 5·63, **9** τ 5·80). The dihedral angle HC(8)-C(5)H must, thus, measure around 82°, a fact which requires the hydroxyl at C-8 to be directed towards the 5-membered ring (cf. [5]). Since the benzylic C$\underline{H}$ is represented by a clean doublet, this group cannot be adjacent to C-5 and structure **9** results. The *trans*-arrangement of the aryl and methyl substituents is compatible with the C$\underline{H}_3$-frequency which occurs at relatively high field (τ 9·12). All prominent mass spectral peaks are easily rationalized on grounds of structure **9** (Scheme 2).

EXPERIMENTAL

Isolation of the constituents. Plant material of an *Aniba* sp. from the Ducke Forest Reserve, Manaus, Amazonas, was deposited at INPA, Manaus, Herbaria Bot. 42237, Chem. 31/73. A description is available from the botanist W. Rodrigues. Trunk wood (5 kg) gave a C_6H_6 ext. (14·4 g) which was chromatographed on a silica (300 g) column, giving the following fractions with the indicated eluants: $A_1(C_6H_6)$, A_2 (C_6H_6–EtOH 99·8:0·2), A_3 and A_4 (C_6H_6–EtOH 99·5:0·5). A_1 was crystallized from MeOH giving sitosterol (158 mg). The mother liquor was purified by TLC (SiO_2, $CHCl_3$–MeOH 95:5) to give **2b** (152 mg). A_2 was fractionated by TLC (SiO_2, $CHCl_3$–MeOH 99:1) into **2b** (35 mg), **9** (12 mg), **3c** (25 mg) and **1c** (29 mg). A_3 was fractionated by TLC (SiO_2, Et_2O) into **3c** (145 mg), **1c** (27 mg), a mixt. of **4d** + **4b** (37 mg), **7** (22 mg) and **1d** (59 mg). Similarly, A_4 gave **1d** (347 mg), **2c** (776 mg) and **1e** (387 mg).

Pyrolysis of the constituents (Table 1). A soln of the cmpd. in the indicated solvent under N_2 was maintained at the indic. temp. for the indic. time. The cooled reaction mixture was ext. with Et_2O. The Et_2O-soln. was washed with 10% aq. HCl, H_2O and dried. The solvent was evaporated and the residue fractionated by TLC (conditions indic.) into products which were eluted with solvents and weighed. TLC-spots indicated quantitative conversion into the indic. products. The elution technique, however, resulted in losses of *ca* 40%.

(2S,3S,3aS)-3a-*Allyl*-5-*methoxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3,3a,6-*tetrahydro*-6-*oxobenzofuran* (**1c**), viscous oil (Found: M 386·1720. $C_{22}H_{26}O_6$ requires: M 386·1729). λ_{max}^{MeOH} (nm): 257, 285 (ε 16120, 2800). ν_{max}^{film} (cm^{-1}): 1646, 1601, 1504, 1449, 1405, 1343, 1229, 1147, 840, 751. PMR: Table 2. MS: Scheme 1. ORD (c 3·72 mg/100 ml, MeOH, 225–400 nm): $[\phi]_{355}^{pK}$ +7900, $[\phi]_{366}$ 0, $[\phi]_{310}^{tr}$ −17100, $[\phi]_{290}^{pK}$ −12450, $[\phi]_{276}^{tr}$ −15550, $[\phi]_{262}$ 0, $[\phi]_{238}$ +17100.

rel-(2R,3S,3aS)-3a-*Allyl*-5-*methoxy*-2-(3-*methoxy*-4,5-*methylenedioxyphenyl*)-3-*methyl*-2,3,3a,6-*tetrahydro*-6-*oxobenzofuran*. (**1d**), crystals, mp 161–163° (found: C, 68·43; H, 6·10; $C_{21}H_{22}O_6$ requires: C, 68·09; H, 5·98%). λ_{max}^{MeOH} (nm): 256, 285 (ε 16020, 4940). ν_{max}^{film} (cm^{-1}): 1645, 1605, 1506, 1453, 1431, 1383, 1236, 1159, 1049, 942. PMR: Table 2. MS: Scheme 1. ORD (c 1·75 mg/100 ml, MeOH, 215–350 nm): $[\phi]_{320}^{tr}$ −55000, $[\phi]_{302}$ 0, $[\phi]_{290}^{pK}$ +59100, $[\phi]_{260}^{tr}$ +56100.

rel-(2R, 3S, 3aS)-3a-*Allyl*-5-*methoxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3,3a,6-*tetrahydro*-6-*oxobenzofuran*. (**1e**), viscous oil (found: M 386·1738. $C_{22}H_{26}O_6$ requires: M 386·1729). λ_{max}^{MeOH} (nm): 235 inf., 259, 295 (ϵ 21470, 15950, 7670). ν_{max}^{film} (cm^{-1}): 1645, 1608, 1506, 1460, 1364, 1241, 1166, 1131, 1010, 945, 791. **PMR**: Table 2. **MS**: Scheme 1. **ORD** (c 1·62 mg/100 ml, MeOH, 225–350 nm): $[\phi]_{320}^{tr}$ −54000, $[\phi]_{299}$ 0, $[\phi]_{275}^{pK}$ +52100, $[\phi]_{250}^{tr}$ 44700, $[\phi]_{230}$ +51200.

(2S,3S,5R)-5-*Allyl-5-methoxy-2-(3-methoxy-4,5-methylenedioxyphenyl)-3-methyl-2,3,5,6-tetrahydro-6-oxobenzofuran*. (**2**b), viscous oil (found: M 370·1410. $C_{21}H_{22}O_6$ requires: 370·1416). λ_{max}^{MeOH} (nm): 248, 287 inf., 316 (ϵ 17280, 6310, 9720). ν_{max}^{film} (cm^{-1}): 1685, 1612, 1517, 1455, 1435, 1378, 1194, 1097, 939, 760. **PMR**: Table 2. **MS**: Scheme 1. **ORD** (c 5·03 mg/100 ml, MeOH, 225–380 nm): $[\phi]_{376}$ 0, $[\phi]_{342}^{tr}$ −94100, $[\phi]_{313}$ 0, $[\phi]_{270}^{pK}$ +62650, $[\phi]_{242}$ 0.

2S,3S,5R)-5-*Allyl-5-methoxy-2-(3,4,5-trimethoxyphenyl)-3-methyl-2,3,5,6-tetrahydro-6-oxobenzofuran*. (**2**c), viscous oil (found: M 386·1735. $C_{22}H_{26}O_6$ requires: M 386·1729). λ_{max}^{MeOH} (nm): 235 inf., 314 (ϵ 21200, 10070). ν_{max}^{film} (cm^{-1}): 1686, 1608, 1506, 1458, 1377, 1242, 1190, 1131, 899, 831. **PMR**: Table 2. **MS**: Scheme 1. **ORD** (c 3·20 mg/100 ml, MeOH, 230–380 nm): $[\phi]_{372}$ 0, $[\phi]_{342}^{tr}$ −32500, $[\phi]_{317}$ 0, $[\phi]_{280}^{pK}$ +36350, $[\phi]_{247}$ 0, $[\phi]_{240}$ −4700, $[\phi]_{238}^{tr}$ −6950, $[\phi]_{234}$ 0.

(2S,3S)-6-0-*Allyl-5-methoxy-2-(3,4,5-trimethoxyphenyl)-3-methyl-2,3-dihydrobenzofuran* (**3**c), viscous oil (found: M 386·1724. $C_{22}H_{26}O_6$ requires: M 386·1729). λ_{max}^{MeOH} (nm): 230 inf., 298, 330 inf. (ϵ 28200, 12790, 680). ν_{max}^{film} (cm^{-1}): 1591, 1494, 1457, 1416, 1359, 1239, 1130, 1014, 851, 762. **PMR** (CCl_4, τ): 3·42 (*s*, H-4), 3·50 (*s* ArH-2,6), 3·60 (*s*, H-7), 3·74–4·30 (*m*, $CH_2C\underline{H}=CH_2$), 4·44–4·94 (*m*, $CH_2CH=C\underline{H}_2$), 5·12 (*d*, *J* 8·0 Hz, H-2), 6·19 (*s*, 2) ArOMe), 6·27 (*s*, ArOMe), 6·29 (*s*, ArOMe), 5·45–5·63 (*m*, $C\underline{H}_2CH=CH_2$), 6·57–7·00 (*m*, H-3), 8·66 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 387 (20) M + 1, 386 (100) M, 345 (23), 177 (62), 149 (21), 41 (10). **ORD** (c 3·38 mg/100 ml, MeOH, 235–350 nm): $[\phi]_{320}^{tr}$ −11400, $[\phi]_{305}$ 0, $[\phi]_{288}^{pK}$ 16700, $[\phi]_{265}^{tr}$ 9050, $[\phi]_{250}^{pK}$ +17050.

(2S,3S)-6-0-*Allyl-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)-3-methyl-2,3-dihydrobenzofuran*. (**7**), viscous oil (found: M 416·1840. $C_{23}H_{28}O_7$ requires: 416·1835). λ_{max}^{MeOH} (nm): 230 inf., 292, 340 inf. (ϵ 57980, 12550, 1310). ν_{max}^{film} (cm^{-1}): 1590, 1503, 1464, 1422, 1359, 1239, 1130, 1042, 837. **PMR** (CCl_4, τ): 3·54 (*s*, ArH-2,6), 3·67 (*s*, H-4), 3·89–4·34 (*m*, $CH_2C\underline{H}=CH_2$), 4·44–5·00 (*m*, $CH_2CH=C\underline{H}_2$), 5·05 (*d*, *J* 8·0 Hz, H-2), 6·07 (*s*, ArOMe), 6·17 (*s*, 2 ArOMe), 6·25 (*s*, ArOMe), 6·27 (*s*, ArOMe), 5·44–5·64 (*m*, $C\underline{H}_2CH=CH_2$), 6·54–7·00 (*m*, H-3), 8·64 (*d*, *J* 7·0 Hz. Me-3). **MS** (*m/e*): 417 (3%) M + 1, 416 (10) M, 386 (10), 279 (25), 208 (10), 207 (16), 167 (37), 150 (11), 149 (100), 113 (21), 71 (39), 57 (52), 43 (35), 41 (25). **ORD** (c 4·99 mg/100 ml MeOH, 250–360 nm): $[\phi]_{312}^{tr}$ −10000, $[\phi]_{300}$ 0, $[\phi]_{287}^{pK}$ +14100, $[\phi]_{265}^{tr}$ +4900, $[\phi]_{248}$ +11600.

(2S,3S)-7-*Allyl-6-hydroxy-5-methoxy-2-(3,4-methylenedioxyphenyl)-3-methyl-2,3-dihydrobenzofuran*. (**4**a), viscous oil (found: M 340·1269. $C_{20}H_{20}O_5$ requires 340·1272). λ_{max}^{MeOH} (nm): 221, 236 inf., 296 (ϵ 19200, 12520, 10350). ν_{max}^{film} (cm^{-1}) 3510, 1610, 1480, 1440, 1380, 1340, 1240, 1150, 1030, 930, 830. **PMR** (CCl_4, τ): 3·12–3·25 (*m*, ArH-2,5,6), 3·38 (*s*, H-4), 4·05–4·42 (*m*, $CH_2C\underline{H}=CH_2$), 4·06 (*s*, O_2CH_2), 4·34 (*s*, ArOH), 4·70–5·10 (*m*, $CH_2CH=C\underline{H}_2$), 4·95 (*d*, *J* 9·0 Hz, H-2), 6·20 (*s*, ArOMe), 6·40–6·90 (*m*, H-3), 6·80 (*d*, *J* 7·0 Hz, $C\underline{H}_2CH=CH_2$), 8·63 (*d*, *J* 6·7 Hz, Me-3).

(2S,3S)-7-*Allyl-6-hydroxy-5-methoxy-2-(3-methoxy-4,5-methylenedioxyphenyl)-3-methyl-2,3-dihydrobenzofuran*. (**4**b), Viscous oil (found: 370·1400. $C_{21}H_{22}O_6$ requires: M 370·1416). λ_{max}^{MeOH} (nm): 240 inf., 297, 330 inf. (ϵ 17510, 12590, 1600); $\lambda_{max}^{MeOH+NaOH}$ (nm): 307, 360 (ϵ 14520, 1620). ν_{max}^{film} (cm^{-1}): 3498, 1635, 1507, 1465, 1430, 1326, 1194, 1139, 1094, 841. **PMR** (CCl_4, τ): 3·54 (*s*, ArH-2,6), 3·57 (*s*, H-4), 3·80–4·27 (*m*, $CH_2C\underline{H}=CH_2$), 4·10 (*s*, O_2CH_2), 4·54 (*s*, ArOH), 4·75–5·22 (*m*, $CH_2CH=C\underline{H}_2$), 5·09 (*d*, *J* 8·0 Hz, H-2), 6·17 (*s*, ArOMe), 6·20 (*s*, ArOMe), 6·55–6·92 (*m*, H-3 and $C\underline{H}_2CH=CH_2$), 8·67 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 371 (23%) M + 1, 370 (100) M, 205 (15), 167 (24), 165 (11), 149 (66), 57 (21), 43 (10). **ORD** (c 3·3 mg/100 ml, MeOH, 235–360 nm): $[\phi]_{314}^{tr}$ −13450, $[\phi]_{301}$ 0, $[\phi]_{290}$ +17900, $[\phi]_{250}$ 0. *Acetate*, viscous oil (Found: M 412·1538. $C_{23}H_{24}O_7$ requires: M 412·1546). λ_{max}^{MeOH} (nm): 240 inf., 297, 330 inf. (ϵ 20280, 12940, 1290). ν_{max}^{film} (cm^{-1}): 1762, 1632, 1506, 1469, 1433, 1370, 1226, 1197, 767. **PMR** (CCl_4, τ): 3·47 (*s*, H-4), 3·52 (*s*, ArH-2,6), 3·95–4·50 (*m*, $CH_2C\underline{H}=CH_2$), 4·09 (*s*, O_2CH_2), 4·80–5·19 (*m*, $CH_2CH=C\underline{H}_2$), 5·07 (*d*, *J* 8·0 Hz, H-2), 6·15 (*s*, ArOMe), 6·29 (*s*, ArOMe), 6·55–6·87 (*m*, H-3, $C\underline{H}_2CH=CH_2$), 7·79 (*s*, COMe), 8·62 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 412 (8%) M, 370 (22), 222 (21), 207 (30), 179 (65), 149 (38), 71 (28), 57 (23), 43 (100), 42 (10), 41 (27). **ORD** (c 5·75 mg/100 ml, MeOH, 240–340 nm): $[\phi]_{316}^{tr}$ −26600, $[\phi]_{298}$ 0, $[\phi]_{260}^{pK}$ +16550, $[\phi]_{244}$ 0, $[\phi]_{243}$ −12950.

(2S,3S)-7-*Allyl-6-hydroxy-5-methoxy-2-(3,4,5-trimethoxyphenyl)-3-methyl-2,3-dihydrobenzofuran*. (**4**c), viscous oil (Found: 386·1724. $C_{22}H_{26}O_6$ requires: M 386·1729). λ_{max}^{MeOH} (nm): 230 inf., 298, 330 inf. (ϵ 42600, 12600, 680); $\lambda_{max}^{MeOH+NaOH}$ (nm): 305, 360 (ϵ 13000, 300). ν_{max}^{film} (cm^{-1}): 3498, 1591, 1505, 1465, 1419, 1360, 1322, 1234, 1131, 843. **PMR** (CCl_4, τ): 3·50 (*s*, ArH-2,6), 3·57 (*s*, H-4), 3·65–4·34 (*m*, $CH_2C\underline{H}=CH_2$), 4·50 (*s*, ArOH), 4·77–5·19 (*m*, $CH_2CH=C\underline{H}_2$), 5·07 (*d*, *J* 8·0 Hz, H-2), 6·20 (*s*, ArOMe), 6·22 (*s*, 2ArOMe), 6·30 (*s*, ArOMe), 6·55–6·92 (*m*, H-3 and $C\underline{H}_2CH=CH_2$), 8·65 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 387 (26%) M + 1, 386 (100) M, 371 (29), 279 (10) 177 (17), 167 (21), 149 (41), 57 (16), 43 (10). **ORD** (c 3·61 mg/100 ml, MeOH, 245–360 nm): $[\phi]_{315}^{tr}$ −24050, $[\phi]_{298}$ 0, $[\phi]_{288}^{pK}$ +11850, $[\phi]_{275}$ 0. *Acetate* viscous oil (Found) M 428·1828. $C_{24}H_{28}O_7$ requires: M 428·1835). λ_{max}^{MeOH} (nm): 230, 298, 330 (ϵ 40000, 12380, 1860). ν_{max}^{film} (cm^{-1}): 1758, 1591, 1503, 1464, 1366, 1225, 1129, 762. **PMR** (CCl_4, τ): 3·47 (*s*, H-4), 3·52 (*s*, ArH-2,6), 3·90–4·50 (*m*, $CH_2C\underline{H}=CH_2$), 4·80–5·17 (*m*, $CH_2CH=C\underline{H}_2$), 5·02 (*d*, *J* 8·0 Hz, H-2), 6·22 (*s*, 2ArOMe), 6·29 (*s*, ArOMe), 6·67–6·85 (*m*, H-3, $C\underline{H}_2CH=CH_2$), 7·79 (*s*, COMe), 8·62 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 428 (14%) M, 386 (35), 222 (13), 195 (10), 181 (10), 149 (36), 57 (24), 55 (20), 44 (45), 43 (100), 41 (31).

rel-(2R,3S)-7-*Allyl-6-hydroxy-5-methoxy-2-(3-methoxy-4,5-methylenedioxyphenyl)-3-methyl-2,3-dihydrobenzofuran*. (**4**d), viscous oil (Found: M 370·1411. $C_{21}H_{22}O_6$ requires: M 370·1416). λ_{max}^{MeOH} (nm): 240 inf., 298, 325 (ϵ 16620, 12670, 4360); $\lambda_{max}^{MeOH+NaOH}$ (nm): 308, 348 (ϵ 13650, 5100). ν_{max}^{film} (cm^{-1}) 3305, 1627, 1504, 1456, 1423, 1322, 1218, 1134, 827, 758. **PMR** (CCl_4, τ): 3·55 (*s*, H-4), 3·64 (*s*, ArH-2,6), 3·75–4·27 (*m*, $CH_2C\underline{H}=CH_2$), 4·10 (*s*, O_2CH_2), 4·44 (*d*, *J* 8·0 Hz, H-2), 4·57 (*s*, ArOH), 4·79–5·22 (*m*, $CH_2CH=C\underline{H}_2$), 6·15 (*s*, ArOMe), 6·20 (*s*, ArOMe), 6·20–6·83 (*m*, H-3 and $C\underline{H}_2CH=CH_2$), 9·24 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 371 (23%) M + 1, 370 (100) M, 222 (39), 207 (25), 205 (13), 179 (25), 167 (21), 165 (12), 149 (59), 85 (27), 83 (46), 57 (20), 43 (39), 41 (10). **ORD** (c 5·36 mg/100 ml, MeOH, 255–400 nm): $[\phi]_{316}^{pK}$ +20950, $[\phi]_{294}$ 0, $[\phi]_{287}^{tr}$ −5500, $[\phi]_{271}$ 0, $[\phi]_{256}^{pK}$ +34500. *Acetate*, viscous oil (Found: M 412·1529. $C_{23}H_{24}O_7$ requires: M 412·1546). λ_{max}^{MeOH} (nm): 230 inf., 298, 325 inf. (ϵ 25890, 12430, 5360). ν_{max}^{film} (cm^{-1}): 1766, 1643, 1511, 1469, 1436, 1375, 1241, 1034, 853, 772. **PMR** (CCl_4, τ): 3·44 (*s*, H-4), 3·62 (*s*, ArH-2,6), 3·70–4·29 (*m*, $CH_2C\underline{H}=CH_2$), 4·10 (*s*, O_2CH_2), 4·39 (*d*, *J* 8·0 Hz, H-2), 4·80–5·20 (*m*, $CH_2CH=C\underline{H}_2$), 6·17 (*s*, ArOMe), 6·30 (*s*, ArOMe), 6·07–6·85 (*m*, H-3, $CH_2CH=CH_2$), 7·80 (*s*, COMe), 9·17 (*d*, *J* 7·0 Hz, Me-3). **MS** (*m/e*): 413 (9) M + 1, 412 (39) M, 371 (24), 370 (100), 369 (17), 368 (50), 208 (17), 207 (73), 179 (19), 165 (15), 149 (10), 104 (56), 76 (64), 57 (21), 43 (100), 42 (100), 41 (92). **ORD** (c 4·61 mg/100 ml, MeOH, 225–360 nm): $[\phi]_{335}$ 0, $[\phi]^{pK}_{317}$ + 16050, $[\phi]_{308}$ 0, $[\phi]^{tr}_{265}$ −37 500, $[\phi]_{255}$ 0, $[\phi]^{pK}_{240}$ +58 950.

rel-(2R,3S)-7-*Allyl*-6-*hydroxy*-5-*methoxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**4**e), Viscous oil (found: M 386·1733. $C_{22}H_{26}O_6$ requires: 386·1729). λ_{max}^{MeOH} (nm) 230 in., 298, 324 (ϵ 25850, 12780, 8000); $\lambda_{max}^{MeOH+NaOH}$ (nm) 308, 351 (ϵ 14138, 10950). ν_{max}^{film} (cm^{-1}): 3510, 1588, 1506, 1461, 1415, 1324, 1231, 1125, 1013, 841. PMR (CCl_4, τ): 3·57 (*s*, H-4), 3·60 (*s*, ArH-2,6), 3·74–4·24 (*m*, $CH_2C\underline{H}{=}CH_2$), 4·39 (*d*, *J* 8·0 Hz, H-2), 4·44 (*s*, ArOH), 4·77–5·19 (*m*, $CH_2CH{=}C\underline{H}_2$), 6·20 (*s*, ArOMe), 6·24 (*s*, ArOMe), 6·25 (*s*, ArOMe), 6·30 (*s*, ArOMe), 6·47–6·70 (*m*, H-3 and $C\underline{H}_2CH{=}CH_2$), 9·24 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 387 (23%) M + 1, 386 (100) M, 371 (29), 279 (12), 181 (10), 149 (38), 57 (18), 43 (17), ORD (c 3·90 mg/100 ml, MeOH, 225–380 nm): $[\phi]^{pK}_{307}$ +10 900, $[\phi]_{285}$ 0, $[\phi]^{tr}_{276}$ −2950, $[\phi]_{269}$ 0, $[\phi]_{235}$ +47 500. *Acetate*, viscous oil (found: M 428·1819. $C_{24}H_{28}O_7$ requires 428·1835). λ_{max}^{MeOH} (nm): 230, 298, 330 (ϵ 29 840, 12 250, 2740). ν_{max}^{film} (cm^{-1}): 1762, 1596, 1507, 1463, 1365, 1231, 1034, 929, 772. PMR (CCl_4, τ): 3·44 (*s*, H-4), 3·62 (*s*, ArH-2,6), 3·95–4·49 (*m*, $CH_2C\underline{H}{=}CH_2$), 4·37 (*d*, *J* 8·0 Hz, H-2), 4·79–5·17 (*m*, $CH_2CH{=}C\underline{H}_2$), 6·22 (*s*, ArOMe), 6·24 (*s*, ArOMe), 6·29 (*s*, 2ArOMe), 6·42–6·84 (*m*, H-3, $C\underline{H}_2CH{=}CH_2$), 7·77 (*s*, COMe), 9·15 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 428 (3) M, 222 (56), 207 (31), 196 (56), 181 (18), 149 (11), 125 (12), 110 (10), 79 (10), 55 (20), 43 (100), 41 (18). ORD (c 5·31 mg/100 ml, MeOH 230–340 nm): $[\phi]_{340}$ 0, $[\phi]^{pK}_{318}$ +12 100, $[\phi]_{305}$ 0, $[\phi]^{tr}_{288}$ −19 350, $[\phi]_{254}$ 0, $[\phi]^{pK}_{241}$ +56 450, $[\phi]_{236}$ 0.

(2S,3S)-6-*Hydroxy*-5-*methoxy*-2-(3-*methoxy*-4,5-*methylenedioxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**5**b), Viscous oil (found: M 330·1399. $C_{18}H_{18}O_6$ requires: M 330·1403). λ_{max}^{MeOH} (nm): 240 inf., 299, 330 inf. (ϵ 16830, 12 720, 2530); $\lambda_{max}^{MeOH+NaOH}$ (nm): 240, 309, 350 (ϵ 21 570, 12 320, 1890); ν_{max}^{film} (cm^{-1}): 3445, 1630, 1499, 1458, 1438, 1323, 1215, 1157, 842. PMR (CCl_4, τ): 3·47 (*s*, H-4), 3·52 (*s*, ArH-2,6), 3·60 (*s*, H-7), 4·09 (*s*, O_2CH_2), 4·64 (*s*, ArOH), 5·10 (*d*, *J* 8·0 Hz, H-2), 6·14 (*s*, ArOMe), 6·19 (*s*, ArOMe), 6·54–6·94 (*m*, H-3), 8·67 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 331 (5%) M + 1, 330 (29) M, 279 (29), 167 (42), 165 (10), 150 (12), 149 (100), 57 (29), 43 (16), 41 (10). ORD (c 3·10 mg/100 ml, MeOH, 230–240 nm): $[\phi]^{tr}_{320}$ −9550, $[\phi]_{305}$ 0, $[\phi]^{pK}_{285}$ +10650, $[\phi]^{tr}_{270}$ +7400, $[\phi]^{pK}_{255}$ +11 700.

(2S,3S)-6-*Hydroxy*-5-*methoxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**5**c), Viscous oil (found: M 346·1431. $C_{19}H_{22}O_6$ requires: 346·1416). λ_{max}^{MeOH} (nm): 230 inf., 299, 330 inf. (ϵ 27910, 12 580, 2760); $\lambda_{max}^{MeOH+NaOH}$ (nm): 309, 355 (ϵ 15 640, 3220). ν_{max}^{film} (cm^{-1}): 3439, 1583, 1486, 1451, 1418, 1359, 1227, 1122, 1000. PMR (CCl_4, τ): 3·47 (*s*, H-4), 3·50 (*s*, ArH-2,6), 3·59 (*s*, H-7), 4·62 (*s*, ArOH), 5·25 (*d*, *J* 8·0 Hz; H-2), 6·19 (*s*, ArOMe), 6·20 (*s*, 2ArOMe), 6·30 (*s*, ArOMe), 6·54–6·94 (*m*, H-3), 8·64 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 347 (11%) M + 1, 346 (46) M, 331 (21), 279 (35), 167 (47), 150 (13), 149 (100), 71 (23), 57 (25), 55 (10). 43 (14), 41 (10). ORD (*c* 6·52 mg/100 ml. MeOH, 240–360 nm): $[\phi]^{tr}_{323}$ −9200, $[\phi]_{305}$ 0, $[\phi]^{pK}_{288}$ +15 350, $[\phi]^{tr}_{265}$ +6150, $[\phi]_{247}$ +26 700. *Acetate*, viscous oil. λ_{max}^{MeOH} (nm): 230, 297, 330 (ϵ 32 260, 12 400, 2190). ν_{max}^{film} (cm^{-1}): 1763, 1594, 1497, 1460, 1419, 1217, 1134, 1020, 911, 767. PMR (CCl_4, τ): 3·37 (*s*, H-4), 3·50 (*s*, ArH-2,6), 3·54 (*s*, H-7), 5·24 (*d*, *J* 8·0 Hz, H-2), 6·20 (*s*, 2ArOMe), 6·29 (*s*, ArOMe), 6·30 (*s*, ArOMe), 6·53–6·95 (*m*, H-3), 7·80 (*s*, COMe), 8·62 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 388 (1%) M, 279 (23), 196 (28), 182 (28), 181 (18), 167 (100), 150 (15), 149 (100), 71 (88), 57 (80), 55 (12), 43 (15).

rel-(2R,3S)-6-*Hydroxy*-5-*methoxy*-2-(3-*methoxy*-4,5-*methylenedioxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**5**d) viscous oil (found: M 330·3998. $C_{18}H_{18}O_6$ requires: M 330·1403). λ_{max}^{MeOH} (nm): 240 inf., 299, 330 inf. (ϵ 15680, 12850, 2110); $\lambda_{max}^{MeOH+NaOH}$ (nm): 240, 309, 350 (ϵ 22630, 14790, 2110). ν_{max}^{film} (cm^{-1}): 3493, 1627, 1500, 1425, 1329, 1201, 1145, 1043, 823, 754. PMR (CCl_4, τ): 3·45 (*s*, H-4), 3·59 (*s*, H-7), 3·60 (ArH-2,6), 4·10 (*s*, O_2CH_2), 4·47 (*d*, *J* 8·0 Hz, H-2), 4·62 (*s*, ArOH), 6·14 (*s*, ArOMe), 6·19 (*s*, ArOMe), 6·37–6·74 (*m*, H-3), 9·24 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 331 (7%) M + 1, 330 (35) M, 328 (19), 279 (13), 182 (61), 180 (72), 179 (67), 167 (100), 165 (11), 151 (12), 149 (47), 57 (28). 43 (40). ORD (c 2·15 mg/100 ml, MeOH, 230–400 nm): $[\phi]^{pK}_{320}$ +17450, $[\phi]_{301}$ 0, $[\phi]^{tr}_{283}$ −12250, $[\phi]_{259}$ 0, $[\phi]_{249}$ +23280. *Acetate*, viscous oil (Found: M 372·1197. $C_{20}H_{20}O_7$ requires: M 372·1209). λ_{max}^{MeOH} (nm): 230, 298, 330 (ϵ 22960, 12670, 4830). ν_{max}^{film} (cm^{-1}): 1758, 1632, 1491, 1419, 1369, 1213, 1137, 1048, 946, 756. PMR (CCl_4, τ): 3·17 (*s*, H-4), 3·50 (*s*, H-7), 3·60 (*s*, ArH-2,6), 4·10 (*s*, O_2CH_2), 4·40 (*d*, *J* 8·0 Hz, H-2), 6·15 (*s*, ArOMe), 6·29 (*s*, ArOMe), 6·34–6·74 (*m*, H-3), 7·77 (*s*, COMe), 9·17 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 373 (4%) M + 1), 372 (28) M, 331 (17), 330 (80), 182 (30), 180 (11), 179 (15), 167 (43), 165 (32), 149 (49), 71 (24), 57 (46), 43 (100), 41 (26). ORD (*c* 1·55 mg/100 ml, MeOH, 225–360 nm): $[\phi]_{344}$ 0, $[\phi]^{pK}_{318}$ +12 500, $[\phi]_{308}$ 0, $[\phi]^{tr}_{265}$ −29 750, $[\phi]_{253}$ 0, $[\phi]^{pK}_{243}$ +15 350, $[\phi]_{230}$ 0, $[\phi]_{223}$ −21 100.

rel-(2R,3S)-6-*Hydroxy*-5-*methoxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**5**e), Viscous oil (found: M 346·1408. $C_{19}H_{22}O_6$ requires: M 346·1416). λ_{max}^{MeOH} (nm): 230 inf., 299, 330 inf. (ϵ 26 300, 12650, 1040); $\lambda_{max}^{MeOH+NaOH}$ (nm): 309, 365 (ϵ 12400, 290). ν_{max}^{film} (cm^{-1}): 3389, 1596, 1501, 1462, 1421, 1362, 1243, 1133, 1016, 767. PMR (CCl_4, τ): 3·39 (*s*, H-4), 3·54 (*s*, ArOH-2,6), 3·55 (*s*, H-7), 4·42 (*d*, *J* 8·0 Hz, H-2), 4·64 (*s*, ArOH), 6·17 (*s*, ArOMe), 6·19 (*s*, 2ArOMe), 6·30 (*s*, ArOMe), 6·42–6·82 (*m*, H-3). 9·22 (*d*, *J* 7·0 Hz, Me-3). MS (*m/e*): 347 (20%) M + 1, 346 (100) M, 332 (10), 331 (44), 279 (21), 196 (27), 181 (15), 167 (37), 150 (10), 149 (55), 57 (27), 43 (13), 41 (10). ORD (*c* 3·06 mg/100 ml, MeOH, 230–360 nm): $[\phi]^{pK}_{320}$ +16850, $[\phi]_{304}$ 0, $[\phi]^{tr}_{288}$ −14700, $[\phi]_{267}$ 0, $[\phi]_{245}$ +47 100.

(2S,3S)-5-*Allyl*-6-*hydroxy*-2-(3,4,5-*trimethoxyphenyl*)-3-*methyl*-2,3-*dihydrobenzofuran*. (**6**c), Viscous oil (found: M 356·1625. $C_{21}H_{24}O_5$ requires: M 356·1609). λ_{max}^{MeOH} (nm): 230 inf., 291 (ϵ 31 790, 12 720); λ_{max}^{MeOH} (nm): 305 (ϵ 11 100). ν_{max}^{film} (cm^{-1}): 3345, 1591, 1491, 1450, 1411, 1349, 1240, 1131, 996, 848. PMR (CCl_4, τ): 3·17 (*s*, H-4), 3·40 (*s*, ArH-2,6), 3·60 (*s*, H-7), 3·87–4·50 (*m*, $CH_2C\underline{H}{=}CH_2$), 4·57–5·05 (*m*, $CH_2CH{=}C\underline{H}_2$ and H-2), 5·00 (*s*, ArOH), 6·15 (*s*, 3 ArOMe), 6·12–6·75 (*m*, H-3 and $C\underline{H}_2CH{=}CH_2$), 8·62 (*d*, 7·0 Hz, Me-3). MS (*m/e*): 357 (22%) M + 1, 356 (100) M, 341 (44), 149 (11), 85 (26), 83 (43). ORD (2·76 mg/100 ml, MeOH, 250–360 nm): $[\phi]_{308}$ −36 900, $[\phi]_{297}$ 0, $[\phi]^{pK}_{285}$ +49 550, $[\phi]^{tr}_{265}$ +25950, $[\phi]^{pK}_{251}$ +55 500.

1-*Allyl*-4,8-*dihydroxy*-7-(3-*methoxy*-4,5-*methylenedioxyphenyl*)-6-*methyl*-3-*oxobicyclo*[3,2,1]*octane*. (**9**), Viscous oil (found: M 360·1614. $C_{20}H_{24}O_6$ requires: M 360·1597). λ_{max}^{MeOH} (nm): 239 inf., 275 (ϵ 20 580, 4490); $\lambda_{max}^{MeOH+NaOH}$ (nm): 239, 275, 310 (ϵ 22 770, 7190, 4490). ν_{max}^{film} (cm^{-1}): 3446, 1704, 1629, 1504, 1447, 1133, 1087, 928, 756. PMR: Table 3. MS: Scheme 2. ORD (*c* 1·92 mg/100 ml, MeOH, 245–350 nm): $[\phi]^{tr}_{317}$ −9300, $[\phi]_{294}$ 0, $[\phi]^{pK}_{285}$ +1600, $[\phi]_{277}$ 0, $[\phi]^{tr}_{235}$ −5600, $[\phi]_{247}$ 0, $[\phi]^{pK}_{245}$ +1700.

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