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BICYCLO[3,2,1]OCTANOID NEOLIGNANS FROM *ANIBA SIMULANS**

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Key Word Index—*Aniba simulans*; Lauraceae; benzofuranoid neolignans; bicyclo[3,2,1]octanoid neolignans, benzofuranoid/bicyclo[3,2,1]octanoid interconversion.

Abstract—Six bicyclo[3,2,1]octanoid neolignans, isolated from the benzene extract of *Aniba simulans* Allen (Lauraceae) trunk wood, are shown to derive from two basic structures: 1-allyl-8-hydroxy-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-7-methyl-3-oxobicyclo[3,2,1]octane, substituted by 4-hydroxy, 4-hydroxy-5-methoxy, 4-methoxy or 4,5-dimethoxy groups; and 1-allyl-8-hydroxy-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-7-methyl-4-oxobicyclo[3,2,1]oct-2-ene, substituted by 3-hydroxy or 3-hydroxy-5-methoxy groups. The structural proposals are based on spectral data, interconversions and synthesis of a derivative from the known (2*R*,3*S*,3a*S*)-3a-allyl-5-methoxy-2-(3′-methoxy,4′,5′-methylenedioxyphenyl)-3-methyl-2,3,3a,6-tetrahydro-6-oxobenzofuran.

INTRODUCTION

In previous papers on an *Aniba* sp. (Lauraceae), now tentatively classified by Dr. K. Kubitzki, Hamburg, as *Aniba simulans* Allen, the occurrence of 15 neolignans, 14 benzofuranoids belonging to structural types designated **1**–**5** [2] and one bicyclo[3,2,1]octanoid [3], was described. Only a minute quantity of the latter compound having been obtained, the determination of its constitution had to rely solely on spectral data. On such grounds, **6a** had been preferred to **6b**. Specifically, the benzylic proton was represented by a PMR doublet, which seemed to preclude the presence of protonated carbons at the two vicinal positions. Construction of models, however, showed that in several stereoisomers, such as, e.g. in **7c**, the benzylic proton could also be represented by a doublet because of a dihedral angle HC(6)- C(5)H of *ca* 90°. A reexamination of the compound thus seemed desirable.

RESULTS

In order to prepare an additional quantity of the compound, a fresh benzene extract of *A. simulans* trunk wood was fractionated on florisil and silica. Besides benzofuranoid neolignans, including **2d**, **3a** and **3b** [2], two compounds were obtained and characterized as bicyclo[3,2,1]octanoid neolignans by molecular formulae, $C_{21}H_{26}O_6$ and $C_{22}H_{28}O_7$, and PMR in $CDCl_3$. The solutions darkened considerably overnight. The decomposition products, purified by silica TLC, were identified, again by HRMS and PMR, as the respective de-*O*-Me derivatives $C_{20}H_{24}O_6$ and $C_{21}H_{26}O_7$, the former being identical with the bicyclooctanoid neolignan (**6**) described in the previous paper [3].

Indeed, when another portion of the benzene extract was fractionated on silica as described previously [3], i.e. employing $CHCl_3$ as a developing solvent, this α-ketol was obtained directly, together with the additional de-*O*-Me derivative $C_{21}H_{26}O_7$, and two diosphenols $C_{20}H_{22}O_6$ and $C_{21}H_{24}O_7$. The structural relation of these pairs of α-ketols/diosphenols was demonstrated by transformation of the former into the latter with Bi_2O_3, a specific agent for such transformations [4]. Methylation of the diosphenols gave ethers, $C_{21}H_{24}O_6$ and $C_{22}H_{26}O_7$, whose oxidation led to $C_{21}H_{22}O_6$ and $C_{22}H_{24}O_7$, characterized as diketones (ν_{max} 1755 and 1690 cm^{-1}). Both have superimposable ORD curves and UV spectra. The PMR spectra again express the structural analogy of the compounds. The sole significant difference stems from the substitutive presence on a sp^3-C either of a H or a OMe. Thus, both α-ketols must have analogous structures and, should the initial structural hypothesis be sound, allow the described reaction sequences to be formulated **7a** → **7c** → **8a** → **8c** → **9a** and **7b** → **7d** → **8b** → **8d** → **9b**.

The correctness of these formulations was shown by the fact that **9a** can also be obtained by acid catalyzed isomerization of **1f**, a compound with known absolute configuration [2, 3, 5]. Clearly, this reaction proceeds by opening of the benzylic C–O bond to **10** and thus all chiral centres except the benzylic one have identical absolute configurations in precursor (**1f**) and product (**9a**). Nevertheless, since the PMR spectrum gives evidence for the *trans*-arrangement of the Me and aryl substituents in **9a** (and **9b**), the absolute configuration of C-6 can also be considered established.

DISCUSSION

The ease of the reactions **7a** → **7c** and **7b** → **7d** initiated presumably by a trace of acid in the chloroform solvent,

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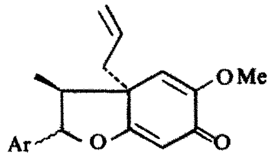
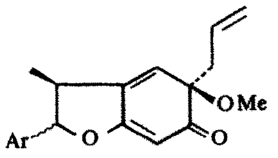
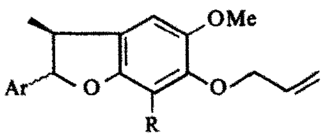
* Part 45 in the series 'The Chemistry of Brazilian Lauraceae'. For Part 44 see ref. [1]. Taken from part of the Doctorate thesis presented by O.C.C. (Organization of American States graduate fellow, on leave of absence from Universidade de Costa Rica) to the Universidade de São Paulo (1977). Sponsored by Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Pesquisas, Manaus, and by Fundação de Amparo à Pesquisa do Estado de São Paulo.



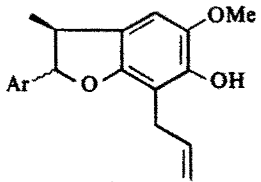
1
1f Ar = β-Mp



2
2d Ar = α-Mp
2f Ar = β-Mp



3
3a Ar = α-Tp, R = H
3b Ar = α-Tp, R = OMe



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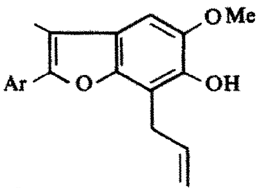

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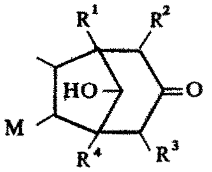
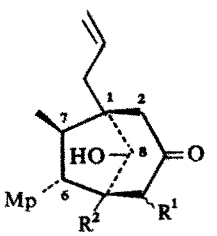
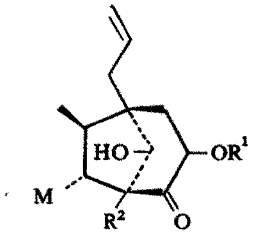


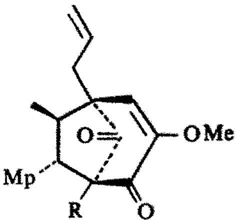
6a $R^1 = R^3 = H$, $R^2 = OH$, R^4 = allyl
6b R^1 = allyl, $R^2 = R^4 = H$, $R^3 = OH$



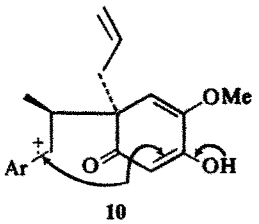
7a $R^1 = OMe$, $R^2 = H$
7b $R^1 = R^2 = OMe$
7c $R^1 = OH$, $R^2 = H$
7d $R^1 = OH$, $R^2 = OMe$



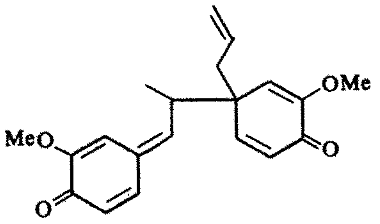
8a $R^1 = R^2 = H$
8b $R^1 = H$, $R^2 = OMe$
8c $R^1 = Me$, $R^2 = H$
8d $R' = Me$, $R^2 = OMe$



9a R = H
9b R = OMe



10



11

Tp . . . 3,4,5-trimethoxphenyl
Mp . . . 3-methoxy-4,5-methylenedioxyphenyl

leads to the complicated question of the actual existence of many of the neolignan types in Lauraceae species. With respect to the benzofuranoid types **1–3**, we demonstrated their stability under conditions of extraction from the plant and separation on silica [3]. Confirmation that structures of types **2–5** are not artificial rearrangement products of benzofuranoids of type **1** is seen in the isolation of **2d**, **3a** and **3b** now also by separation on florisil (Experimental, Procedure 1). Such products, however, could be produced non-enzymatically, *post-mortem*, in the plant, and a final answer to this question will have to await analysis of wood samples immediately after collection.

The acid catalysed transformation **1f**→**9a**, described in the present paper, opens an additional line of thought. Do benzofuranoid and bicyclooctanoid neolignans arise by bifurcation of the biosynthetic route from a common precursor (**11**) subject to different cyclization modes, as we have advocated so far [6], or are initially formed benzofuranoids of type **1** rearranged to bicyclooctanoids? In the latter alternative, does the rearrangement occur *in vivo*, *post-mortem* or *in vitro*? The ease of the observed benzofuranoid–bicyclooctanoid transformation depends on the particular stereochemistry of **1f**, being less facile with 2,3-*trans* compounds of type **1** [7]. Even if bicyclooctanoids should indeed be formed directly from bicyclic precursors (**11**), considering the observed reactions **7a**→**7c** and **7b**→**7d**, how can one be sure about the metabolic or artificial nature of particular representatives of the bicyclooctanoid group of neolignans?

EXPERIMENTAL

Isolation of compounds. Procedure 1. A trunk wood sample (5 kg) of *A. simulans* (voucher Herbarium INPA 46800) was percolated with C_6H_6. A portion (15 g) of the extract (20 g) was chromatographed on a dry column (200 g florisil, petrol –Et2O 2:3). The column was cut into 12 equal portions, which on elution gave 12 fractions. Fractions 1–4 (2.9 g) contained terpenes, camphor, benzyl benzoate and sitosterol. Fractions 5–7 (2.5 g) were rechromatographed on florisil (120 g), giving with petrol–Et_2O in the indicated proportions terpenes (1 g, 17:3), **3a** (50 mg, 4:1) [2], **3b** (30 mg, 4:1 to 7:3) [2], a mixture (200 mg, 7:3) and **2d** (500 mg, 1:1) [2]. The mixture was separated into **7a** (70 mg) and **7b** (95 mg) by Si gel TLC (petrol–Et_2O, 3:7). Fractions 8–10 (6.5 g) contained known benzofuranoid neolignans [2, 3]. Fractions 11 and 12 contained resins. Procedure 2. In the isolation procedure described in ref. [2], applied to a sample derived from the specimen represented by voucher Herbarium INPA 46798, a fraction designated E was separated by Si gel TLC ($CHCl_3$ – MeOH, 24:1) into a mixture of slower moving **1f**, **2d** and **2f** and a mixture of faster moving 6,7-dimethoxycoumarin and bicyclo[3,2,1] octanoid neolignans. The latter mixture was separated by Si gel TLC (Et_2O) into **7d** (80 mg, R_f 0.37), the coumarin (30 mg, R_f 0.23), **7c** (250 mg, R_f 0.50), **8b** (70 mg, R_f 0.57) and **8a** (150 mg, R_f 0.82).

Reactions. The Me ethers (**7a**, **7b**, 30 mg) in $CHCl_3$ were kept at room temp. (12 hr). The solns were evapd. The residues, purified by Si gel TLC (petrol–Ft_2O, 3:7), gave resp **7c** (17 mg) and **7d** (24 mg). The α-ketols (**7c** 30 mg, **7d** 30 mg) and Bi_2O_3 (30 mg) in HOAc (3 ml) were heated under reflux (**7c** 0.5 hr, **7d** 1.5 hr). The mixtures were cooled to room temp., diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ solns were washed, dried and evapd. The residues, purified by Si gel TLC (Et_2O) gave resp **8a** (29 mg) and **8b** (25 mg). The diosphenols (**8a** 30 mg, **8b** 30 mg), K_2CO_3 (1 g), Me_2SO_4 (0.2 ml) in Me_2CO (10 ml) were refluxed (**8a** 1 hr, **8b** 2 hr). Work-up of the reaction mixtures, including Si gel TLC (Et_2O), gave resp **8c** (25 mg) and **8d** (20 mg). The *O*-methyldiosphenols (**8c** 30 mg, **8d** 4 mg) in Me_2CO were treated dropwise with Jones reagent [8] until the solns had a persistent brown-yellow colour. Work-up of the reaction mixtures, including Si gel TLC (Et_2O) gave resp **9a** (22 mg) and **9b** (2 mg).

(1R, 5S, 6R, 7R, 8S)-*Allyl-8-hydroxy-4-methoxy-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-7-methyl-3-oxobicyclo*[3, 2, 1]*octane* (**7a**). Viscous oil (found: M^+ 374.1735. $C_{21}H_{26}O_6$ requires: M^+ 374.1729). λ_{max}^{MeOH} (nm): 235 inf., 277, 305 inf. (ε 6900, 2400, 1200). ν_{max}^{film} (cm^{-1}): 3311, 1718, 1620, 1515, 1450, 1053, 934. PMR (CCl_4, 60 MHz, τ): 9.18 (*d*, *J*=7 Hz, Me-7), 7.18–7.95 (*m*, $C\underline{H}_2-CH=$, 2H-2, H-5, H-6, H-7), 6.48 (*s*, OMe-4), 6.2 (*s*, OMe-3′), 5.7 (*s*, H-8), 5.66 (*d*, *J*=5 Hz, H-4), 4.76–5.18 (*s*, $=CH_2$), 4.2 (*s*, O_2CH_2), 3.85–4.52 (*m*, $C\underline{H}=CH_2$), 3.47 (*d*, *J*=2 Hz, H-2′), 3.4 (*d*, *J*=2 Hz, H-6). ORD (*c* 5 mg/10 ml, MeOH, 400–255 nm): $[\phi]_{400}$ – 350, $[\phi]^{tr}_{345}$ – 1800, $[\phi]_{303}$ 0, $[\phi]^{pk}_{290}$ + 350. $[\phi]_{282}$, 0, $[\phi]^{tr}_{255}$ – 2600.

(1R,5R,6S,7R,8R)-1-*Allyl-8-hydroxy-4,5-dimethoxy-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-7-methyl-3-oxobicyclo*-[3,2,1]*octane* (**7b**). Viscous oil (found: M^+ 404.1829, $C_{22}H_{28}O_7$ requires: M^+ 404.1835). λ_{max}^{MeOH} (nm): 236 inf., 275, 300 inf. (ε 6800, 1760, 480). ν_{max}^{film} (cm^{-1}): 3436, 1704, 1624, 1506, 1445, 926, 835, 815. PMR (CCl_4, 60 MHz, τ): 9.22 (*d*, *J*=7 Hz, Me-7), 7.2–7.9 (*m*, $CH_2-CH=$, 2H-2, H-7, OH), *ca* 7 (*d*, *J* indet., H-6), 6.92 (*s*, OMe-5), 6.42 (*s*, OMe-4), 6.14 (*s*, OMe-3′), 5.6 (*s*, H-8), 5.43 (*s*, H-4), 4.7–5.12 (*m*, $=CH_2$), 4.12 (*s*, O_2CH_2), 3.80–4.50 (*m*, $C\underline{H}=CH_2$), 3·49 (*d*, *J* = 2 Hz, H-2′), 3.42 (*d*, *J* = 2 Hz, H-6′). MS (*m/e*): 405 (26), 404 (100) M^+, 237 (20), 209 (12), 207 (10), 205 (10), 195 (28), 194 (10), 193 (15), 192 (26), 181 (12), 180 (12), 179 (28), 166 (14), 165 (55), 163 (15), 154 (18), 151 (18), 149 (10), 135 (10), 91 (18), 85 (15), 83 (28). ORD (*c* 5.05 mg/10 ml, MeOH, 400–225 nm): $[\phi]_{400}$ –250, $[\phi]^{tr}_{335}$ –1450, $[\phi]_{305}$ 0, $[\phi]^{pk}_{292}$ +550, $[\phi]_{285}$ 0, $[\phi]^{tr}_{257}$ –3200, $[\phi]_{253}$ 0.

(1R,5S,6R,7R,8S)-1-*Allyl-4,8-dihydroxy-6-(3′-*methoxy-*4′,5′-methylenedioxyphenyl)-7-methyl-3-oxobicyclo*[3,2,1] *octane* (**7c**). Mp 93–94° (Et_2O) (found: M^+ 360.1567. $C_{20}H_{24}O_6$ requires: M^+ 360.1673). λ_{max}^{MeOH} (nm): 239 inf., 275, 281 *sh* (ε 4900, 1250, 1050). ν_{max}^{KBr} (cm^{-1}): 3388, 1704, 1630, 1610, 1500, 1455, 1044, 930. PMR ($CDCl_3$, 60 MHz, τ): 9.12 (*d*, *J* = 7 *Hz*, Me-7), 7.63–8.23 (*m*, $CH_2CH=$, H-7), 7.75 (*d*, *J*=8 Hz, H-6; det. by $Eu(fod)_3$-shift), 7.62 (*s*, H-2), 7.46 (*d*, *J* = 4 Hz, H-5), 6.14 (*s*, OMe-3′), 5.82 (*d*, *J*=4 Hz, H-4; *s* upon double irrad. at τ 7.46), 5.76 (*s*, H-8), 4.63–5.08 (*m*, $CH=C\underline{H}_2$), 3.77–4.43 (*m*, $C\underline{H}=CH_2$), 4.1 (*s*, O_2CH_2), 3.43 (*d*, *J*=2 Hz, H-2′), 3.28 (*d*, *J*=2 Hz, H-6′). MS (*m/e*): 360 (100) M^+, 361 (24), 270 (68), 271 (15), 229 (22), 192 (11), 165 (16). ORD (*c* 4.84 mg/10 ml, MeOH, 220–400 nm): $[\phi]^{tr}_{317}$ – 2750, $[\phi]_{294}$ 0, $[\phi]^{pk}_{285}$ + 150, $[\phi]_{277}$ 0, $[\phi]^{tr}_{255}$ –2900, $[\phi[_{247}$ 0, $[\phi]^{pk}_{245}$ +800. Acetylation (Ac_2O, C_5H_5N, room temp., 20 hr) followed by the usual work-up gave a mixture which was separated by Si gel TLC (Et_2O) into **7c** (R_f 0.5, 22%), *monoacetate* (R_f 0.57, 8%) and diacetate (R_f 0.64, 70%). Diacetate; viscous oil, λ_{max}^{MeOH} (nm): 239 inf., 275, 281 *sh* (ε 4950, 3900, 3600). ν_{max}^{film} (cm^{-1}): 1730, 1626, 1504, 1449, 1236, 936, 842. PMR (60 MHz, $CDCl_3$, τ): 9.04 (*d*, J=7 Hz, Me-7), 7.36–8.2 (*m*, $C\underline{H}_2CH=$, H-6, H-7), 7.82 (*s*, OAc), 7.8 (*s*, OAc), 7.52 (*s*, H-2), 7.55 (*d*, *J*=4 Hz, H-5), 6.06 (*s*, OMe-3′), 4.53 (*d*, J=4 Hz; *s* upon double irrad. at τ 7.55; H-4), 4.67 (*s*, H-8), 4.73–5.16 (*m*, $CH=CH_2$), 3.76–4.43 (*m*, $C\underline{H}=CH_2$), 4.03 (*s*, O_2CH_2), 3.56 (*d*, *J*=2 Hz, H-2′), 3.46 (*d*, *J* = 2 Hz, H-6′). MS (*m/e*): 444 (34) M^+, 445 (10), 384 (17), 296 (19), 283 (18), 282 (23), 270 (21), 192 (11), 165 (10), 85 (10), 83 (11), 55 (12), 43 (100), 41 (17).

(1R,5R,6S,7R,8R)-1-*Allyl-4,8-dihydroxy-5-methoxy-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-6-methyl-3-oxobicyclo*-[3,2,1]*octane* (**7d**). Viscous oil (found: M^+ 390. 1686, $C_{21}H_{26}O_7$ requires: M^+ 390.1679). λ_{max}^{MeOH} (nm): 237 *sh*, 274 (ε 6000, 2050). ν_{max}^{film} (cm^{-1}): 3472, 1718, 1637, 1515, 1456, 1437, 934, 841. PMR (60 MHz, $CDCl_3$, τ): 9.18 (*d*, *J*=7 Hz, Me-7), 7.60–8.16 (*m*, $C\underline{H}_2CH=$, H-7), 7.58 (*d*, *J*=8 Hz, H-6), 7.56 (*s*, H-2), 6.67 (*s*, OMe-5), 6.13 (*s*, OMe-3′), 5.89 (*s*, H-8), 5.61 (*s*, H-4), 4.65–5.05 (*m*, $CH=C\underline{H}_2$), 3.73–4.4 (*m*, $C\underline{H}=CH_2$), 4.07 (*s*, O_2CH_2), 3.53 (*d*, *J* = 2 Hz, H-2′), 3.38 (*d*, *J* = 2 Hz, H-6′). MS (*m/e*): 390 (60), M^+, 391 (15), 349 (13), 317 (94), 318 (21), 300 (29), 259 (12), 192 (20), 181 (17), 167 (20), 165 (28), 149 (56), 137 (12), 123

(10), 91 (15), 86 (18), 84 (29), 77 (16), 59 (40), 57 (36), 55 (28), 43 (100), 41 (48).

(1S,5S,6R,7R,8S)-1-*Allyl*-3,8-*dihydroxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4-*oxobicyclo*[3,2,1]*oct*-2-*ene* (**8a**). Mp 186–187° (Et_2O) (found: M^+ 358.1410, $C_{20}H_{22}O_6$ requires: M^+ 358.1416). λ_{max}^{MeOH} (nm): 245, 258 inf. (ε 9150, 8500). $\lambda_{max}^{MeOH+NaOH}$ (nm): 243, 285, 306 (ε 6850, 4900, 5500). ν_{max}^{KBr} (cm^{-1}): 3400, 1665, 1628, 1500, 1447, 925, 860, 830. PMR (60 MHz, $CDCl_3$, τ): 9.01 (*d*, *J*=7 Hz, Me-7), 7.40–7.86 (*m*, $C\underline{H}_2CH=$, H-6, H-7), 6.97 (*s*, H-5), 6.1 (*s*, OMe-3′), 6 (*s*, H-8), 4.6–5.05 (*m*, $CH=C\underline{H}_2$), 3.87–4.43 (*m*, $CH=C\underline{H}_2$), 4.06 (*s*, O_2CH_2), 3.98 (*s*, H-2), 3.42 (*d*, *J*=2 Hz, H-2′), 3.28 (*d*, *J*=2 Hz, H-6′). MS (*m/e*): 358 (100) M^+ 359 (25), 287 (20), 209 (56), 193 (17), 192 (79), 179 (17), 165 (19), 137 (21), 91 (12), 77 (10), 42(12). ORD (*c*2 mg/10 ml, MeOH, 220–400 nm): $[\phi]^{tr}_{350}$ −1800, $[\phi]_{328}$ 0, $[\phi]^{pk}_{303}$ +5250, $[\phi]_{284}$ 0, $[\phi]^{tr}_{262}$ −4900, $[\phi]^{pk}_{245}$ −1100.

(1S,5R,6S,7R,8R)-1-*Allyl*-3,8-*dihydroxy*-5-*methoxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4-*oxobicyclo*-[3,2,1]*oct*-2-*ene* (**8b**). Mp 164–165° (Et_2O) (found: M^+ 388.1519, $C_{21}H_{24}O_7$ requires: M^+ 388.1522). λ_{max}^{MeOH} (nm): 244, 262 (ε 8250, 7400). $\lambda_{max}^{MeOH+NaOH}$ (nm): 242 inf., 285 inf., 285 inf., 306 (ε 6150, 3900, 4850). ν_{max}^{KBr} (cm^{-1}): 3492, 1680, 1630, 1500, 1450, 1430, 922, 853. PMR (60 MHz, $CDCl_3$, τ): 9.08 (*d*, *J*=7 Hz, Me-7), 7.30–7.86 (*m*, $C\underline{H}_2CH=$, H-6, H-7), 6.66 (*s*, OMe-5), 6.1 (*s*, OMe-3′), 5.99 (*s*, H-8), 4.57–4.97 (*m*, $CH=C\underline{H}_2$), 3.93 (*s*, H-2), 3.77–4.43 (*m*, $C\underline{H}=CH_2$), 4 (*s*, O_2CH_2), 3.5 (*d*, *J*=2 Hz, H-2′), 3.3 (*d*, *J*=2 Hz, H-6′). MS (*m/e*): 388 (8) M^+, 358 (3), 329 (4), 315 (3), 279 (11), 256 (6), 213 (4), 209 (4), 192 (28), 179 (7), 167 (38), 149 (92), 129 (9), 112 (14), 95 (21), 91 (9), 85 (54), 77 (12), 73 (38), 71 (47), 69 (47), 67 (42), 57 (76), 55 (85), 43 (84), 41 (100). ORD (*c* 2.2 mg/10 ml, MeOH, 220–400 nm): $[\phi]^{tr}_{350}$ −1300, $[\phi]_{330}$ 0, $[\phi]^{pk}_{305}$ +2150, $[\phi]_{282}$ 0, $[\phi]^{tr}_{260}$ −3850, $[\phi]^{pk}_{243}$ −2100.

(1S,5S,6R,7R,8S)-1-*Allyl*-8-*hydroxy*-3-*methoxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4-*oxobicyclo*-[3,2,1]*oct*-2-*ene* (**8c**). Viscous oil (found: M^+ 372.1565, $C_{21}H_{24}O_6$ requires: M^+ 372.1573). λ_{max}^{MeOH} (nm): 243, 258 inf. (ε 10900, 8850). ν_{max}^{film} (cm^{-1}): 3356, 1695, 1637, 1616, 1515, 1453, 935, 833. PMR (60 MHz, $CDCl_3$, τ): 9.05 (*d*, *J*=7 Hz, Me-7), 7.37–7.86 (*m*, $C\underline{H}_2CH=$, H-6, H-7), 7.02 (*s*, H-5), 6.37 (*s*, OMe-3), 6.13 (*s*, OMe-3′), 6 (*s*, H-8), 4.56–5.03 (*m*, $CH=C\underline{H}_2$), 3.43–4.1 (*m*, $C\underline{H}=CH_2$), 4.08 (*s*, O_2CH_2), 4.33 (*s*, H-2), 3.38 (*d*, *J*=2 Hz, H-2′), 3.28 (*d*, *J*=2 Hz, H-6′). MS (*m/e*): 372 (9) M^+, 354 (2), 301 (2), 279 (3), 209 (6), 192 (9), 179 (5), 165 (6), 149 (18), 101 (18), 83 (21), 77 (7), 59 (61), 55 (28), 43 (100), 41 (29). ORD (*c* 3.2 mg/ 25 ml, MeOH, 220–400 nm): $[\phi]^{tr}_{355}$ −4000, $[\phi]_{325}$ 0, $[\phi]^{pk}_{300}$ +7250, $[\phi]_{280}$ 0, $[\phi]^{tr}_{260}$ −9100, $[\phi]^{pk}_{245}$ −3400.

(1S,5R,6S,7R,8R)-1-*Allyl*-8-*hydroxy*-3,5-*dimethoxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4-*oxobicyclo*-[3,2,1]*oct*-2-*ene* (**8d**). Viscous oil (found: M^+ 402.1685, $C_{22}H_{26}O_7$ requires: M^+ 402.1679). λ_{max}^{MeOH} (nm): 243, 258 inf. (ε 7100, 7250). ν_{max}^{film} (cm^{-1}): 3356, 1692, 1629, 1506, 1449, 934. PMR (60 MHz, $CDCl_3$, τ): 9.1 (*d*, *J*=7 Hz, Me-7), 7.2–7.7 (*m*, $C\underline{H}_2CH=$, H-6, H-7), 6.7 (*s*, OMe-5), 6.33 (*s*, OMe-3), 6.13 (*s*, OMe-3′), 6 (*s*, H-8), 4.58–4.98 (*m*, $CH=C\underline{H}_2$), 4.3 (*s*, H-2), 3.37–4.03 (*m*, $C\underline{H}=CH_2$), 4.05 (*s*, O_2CH_2), 3.51 (*d*, *J*=2 Hz, H-2′), 3.32 (*d*, *J*=2 Hz, H-6′). MS (*m/e*): 402 (3) M^+, 372 (7), 360 (3), 354 (3), 317 (3), 279 (2), 243 (4), 223 (3), 181 (13), 149 (3), 113 (11), 91 (9), 83 (35), 77 (15), 71 (17), 57 (89), 55 (72), 43 (100), 41(75). ORD (*c* 2 mg/25 ml, MeOH, 220–400 nm): $[\phi]^{tr}_{345}$ −3150, $[\phi]_{330}$ 0, $[\phi]^{pk}_{304}$ +3950, $[\phi]_{277}$ 0, $[\phi]_{257}$ −9650, $[\phi]^{pk}_{240}$ −6500.

(1S,5S,6R,7R)-1-*Allyl*-3-*methoxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4,8-*dioxobicyclo*[3,2,1]*oct*-2-*ene* (**9a**). Mp 147–148° (Et_2O) (found: M^+ 370.1422, $C_{21}H_{22}O_6$ requires: M^+ 370.1416). λ_{max}^{MeOH} (nm): 248 inf., 269 (ε 8650, 9000). ν_{max}^{film} (cm^{-1}): 1754, 1689, 1631, 1608, 1506, 1453, 1433, 936, 853. PMR (60 MHz, $CDCl_3$, τ): 8.93 (*d*, *J*=7 Hz, Me-7), 7.33–7.57 (*m*, $C\underline{H}_2CH=$), 7.63–8.13 (*m*, H-7), 7.43 (*d*, *J*=8 Hz, H-6), 6.45 (*s*, H-5), 6.26 (*s*, OMe-3), 6.12 (*s*, OMe-3′), 4.58–5.05 (*m*, $CH=C\underline{H}_2$), 4.73–4.4 (*m*, $C\underline{H}=CH_2$), 4.04 (*s*, O_2CH_2), 4.15 (*s*, H-2), 3.73 (*s*, H-2′,6′). MS (*m/e*): 370 (100) M^+, 371 (26), 329 (20), 301 (15), 205 (38), 192 (50), 191 (29), 179 (12), 177 (16), 166 (33), 165 (21), 125 (23), 119 (12), 91 (16), 77 (16), 65 (12), 53 (13), 39 (16). ORD (*c* 2.82 mg/25 ml, MeOH, 220–400 nm): $[\phi]^{tr}$[illegible] −11300, $[\phi]_{335}$ 0, $[\phi]^{pk}_{313}$ +20000, $[\phi]_{295}$ 0, $[\phi]^{tr}_{280}$ −[illegible], $[\phi]$[illegible] 0, $[\phi]^{pk}_{258}$ +8600, $[\phi]_{242}$ 0.

(1S,5R,6S,7R)-1-*Allyl*-3,5-*dimethoxy*-6-(3′-*methoxy*-4′,5′-*methylenedioxyphenyl*)-7-*methyl*-4,8-*dioxobicyclo*[3,2,1]*oct*-2-*ene* (**9b**). ν_{max}^{film} (cm^{-1}): 1754, 1689.

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