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NEOLIGNANS FROM AN *ANIBA* SPECIES*

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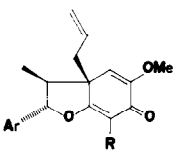
Key Word Index—*Aniba* sp.; Lauraceae; neolignans; allyl-aryl-methyl-tetrahydrooxobenzofuran neolignans; aryl-methyl-propenyl-dihydrobenzofuran neolignans; allyl-aryl-methyl-bicyclo[3,2,1]octenone neolignans; burchellin; guianin.

Abstract—A benzene extract of the trunk of an *Aniba* species (Lauraceae) contained benzyl benzoate, benzyl salicylate, sitosterol and the neolignans (2*S*,3*S*,3a*R*)-3a-allyl-5-methoxy-3-methyl-2-piperonyl-2,3,3a,6-tetrahydro-6-oxobenzofuran (burchellin); (2*S*,3*S*,3a*R*)-3a-allyl-5-methoxy-3-methyl-2-veratryl-2,3,3a,6-tetrahydro-6-oxobenzofuran; (2*S*,3*S*,3a*R*)-3a-allyl-5,7-dimethoxy-3-methyl-2-veratryl-2,3,3a,6-tetrahydro-6-oxobenzofuran; (2*S*,3*S*,5*S*)-5-allyl-5-methoxy-3-methyl-2-veratryl-2,3,5,6-tetrahydro-6-oxobenzofuran; (2*R*,3*R*)-7-methoxy-3-methyl-5-propenyl-2-veratryl-2,3-dihydrobenzofuran; *rel*-(1*R*,5*R*,6*R*,7*R*,8*S*)-1-allyl-8-hydroxy-3-methoxy-7-methyl-4-oxo-6-piperonylbicyclo[3,2,1]oct-2-ene (guianin); *rel*-(1*S*,5*S*,6*S*,7*R*,8*R*)-1-allyl-8-hydroxy-3,5-dimethoxy-7-methyl-4-oxo-6-piperonylbicyclo[3,2,1]oct-2-ene; *rel*-(1*S*,5*S*,6*S*,7*R*,8*R*)-8-acetoxy-1-allyl-3-hydroxy-5-methoxy-7-methyl-4-oxo-6-piperonylbicyclo[3,2,1]oct-2-ene; *rel*-1*S*,5*S*,6*S*,7*R*,8*R*)-8-acetoxy-3,5-dimethoxy-7-methyl-4-oxo-6-piperonylbicyclo[3,2,1]oct-2-ene; *rel*-(1*R*,5*S*,6*R*,7*R*)-1-allyl-3-methoxy-7-methyl-4,8-dioxo-6-piperonylbicyclo[3,2,1]oct-2-ene.

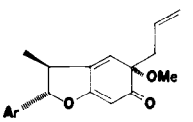
The classification of *Aniba* sp., provisional ref. 60, from the vicinity of Manaus, Amazonas, will be possible upon completion of the revision of Lauraceae by Dr. K. Kubitzki, Hamburg. Fractionation of a C_6H_6-extract of its trunk wood gave benzyl benzoate and benzyl salicylate, esters which occur in many species of this genus [2], and sitosterol, besides two known (**1a**, **5a**) and eight previously unknown (**1b**,**c**; **2b**; **4**; **5b**,**c**,**d**; **6a**) neolignans.

Burchellin (**1a**) [3,4] and its Cope rearrangement product **2a** were reported to co-occur in *A. terminalis* Ducke [5]. In *A.* sp. 60 burchellin was accompanied by three compounds, **1b**, **c** and **2b**, shown by spectral (Table 1) and ORD (**1**: pk 383 ± 5, tr 290 ± 5, pk 255 ± 5. **2**: pk 290 ± 5, tr 280 ± 2, pk 274 ± 5) data to differ only in substitution from, respectively, **1a** and **2a**. Double PMR irradiation at τ 6.42 (OMe-5) of **1a** resulted in NOE intensity enhancement of the singlet at τ 4.67, which thus must correspond to H-4. This requires allocation of the additional methoxyl of **1c** to C-7 and assignment of the τ 4.41 ± 0.01 signals of **1a** and **b** to H-7. The PMR frequencies for H-4 and H-7 given in previous papers [3–5] must, consequently, be interchanged.

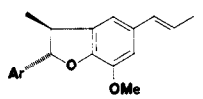
Licarin-A (**3a**) was reported to occur in *Licaria aritu* Ducke [6]. Its methyl ether **3b** is identical in all respects,



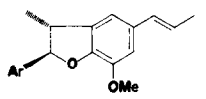
(1a) Ar = pi, R = H
(1b) Ar = ve, R = H
(1c) Ar = ve, R = OMe



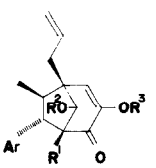
(2a) Ar = pi
(2b) Ar = ve



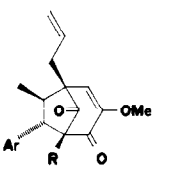
(3a) Ar = gu
(3b) Ar = ve



(4) Ar = ve



(5a) Ar = pi, R' = R² = H, R³ = Me
(5b) Ar = pi, R' = OMe, R² = H, R³ = Me
(5c) Ar = pi, R' = OMe, R² = Ac, R³ = H
(5d) Ar = pi, R' = OMe, R² = Ac, R³ = Me
(5e) Ar = pi, R' = OMe, R² = R³ = Ac



(6a) Ar = pi, R = H
(6b) Ar = pi, R = OMe

pi ... piperonyl, ve ... veratryl, gu ... guaiacyl

* Part 34 in the series "The Chemistry of Brazilian Lauraceae". For Part 33 see ref. [1]. Taken from part of the Doctorate thesis presented by J.B.F. to the Universidade de São Paulo (1976). Sponsored by Ministério do Planejamento (Financiadora de Estudos e Projetos S.A.) through Academia Brasileira de Ciências and by Fundação de Amparo à Pesquisa do Estado de São Paulo.

Table 1. PMR spectra (60 MHz, τ) of compounds of types **1** and **2**

Protons	**1a*** (CCl_4)	**1b** (CCl_4)	**1c** (CCl_4)	**2a** ($CDCl_3$)	**2b** (CCl_4)
Me-3	8.87, *d*, 7.0 Hz	8.89 *d*, 7.0 Hz	8.89, *d*, 7.0 Hz	8.75, *d*, 7.2 Hz	8.68, *d*, 7.0 Hz
$C\underline{H}_2CH$	7.5–8.0, *m*	7.5–8.0, *m*	7.5–8.0, *m*	7.58, *d*, 6.6 Hz	7.62, *d*, 7.0 Hz
H-3	7.5–8.0, *m*	7.5–8.0, *m*	7.5–8.0, *m*	6.9–7.2, *m*	6.8–7.2, *m*
OMe-5	6.42, *s*	6.42, *s*	6.42, *s*	7.00, *s*	6.94, *s*
OMe-7	—	—	6.30, *s*	—	—
ArOMe	—	6.20, *s*	6.20, *s*	—	6.20, *s*
$CH{=}C\underline{H}_2$	4.7–5.0, *m*	4.8–5.1, *m*	4.7–5.0, *m*	4.9–5.1, *m*	4.8–5.1, *m*
H-4	4.67, *s*	4.74, *s*	4.70, *s*	4.91, *s*	4.94, *s*
H-7	4.40, *s*	4.42, *s*	—	4.54, *s*	4.50, *s*
$C\underline{H}{=}CH_2$	4.0–4.7, *m*	4.0–4.7, *m*	4.3–4.6, *m*	4.2–4.6, *m*	4.0–4.8, *m*
H-2	4.82, *d*, 9.0 Hz	4.97, *d*, 9.0 Hz	4.94, *d*, 9.0 Hz	3.94, *d*, 3.0 Hz	3.94, *d*, 3.0 Hz
O_2CH_2	4.05 *s*	—	—	4.03 *s*	—
3ArH	3.29, *s*	3.29, *s*	3.25, *s*	3.30 *s*	3.25 *s*

* For a completely resolved 220 MHz spectrum see Ref. [3].

with the exception of the antipodal ORD curve, to a further constituent of *A.* sp. 60, which thus must possess structure **4**.

Guianin (**5a**) (ν_{max} 1681 cm^{-1}) was reported to occur in *A. guianensis* Aubl. [7]. In *A.* sp. 60 guianin is accompanied by its oxidation product **6a** (ν_{max} 1748, 1683 cm^{-1}), and three additional compounds, **5b**, **c** and **d**. The PMR spectra (Table 2) of guinanin (**5a**), **5b** (ν_{max} 1689 cm^{-1}), **5c** (ν_{max} 1683 cm^{-1}) and **5d** (ν_{max} 1700 cm^{-1}) are very similar, except for the replacement of the CH.C=O signal of **5a** by OMe signals in **5b**, **c** and **d**. Oxidation of **5b** with Jones reagent leads to a diketone (**6b**) (ν_{max} 1758, 1696 cm^{-1}), confirming the existence of a secondary carbinol in a 5-membered ring. Methylation of the enol (reversible UV shift upon successive addition of NaOH and HCl) **5c** leads to **5d**, while acetylation to the enolic acetate **5e** (ν_{max} 1786 cm^{-1}) causes a paramagnetic shift of 0.6 ppm of the signal due to the olefinic proton at C-2. The secondary carbinol of **5a** (H-8, τ 6.02) and **5b** (H-8, τ 6.14) is acetylated in **5c** (H-8, τ 4.74 and **5d** (H-8, τ 4.77). The ORD curves of the compounds of series **5** (Fig. 1), are sufficiently similar to warrant

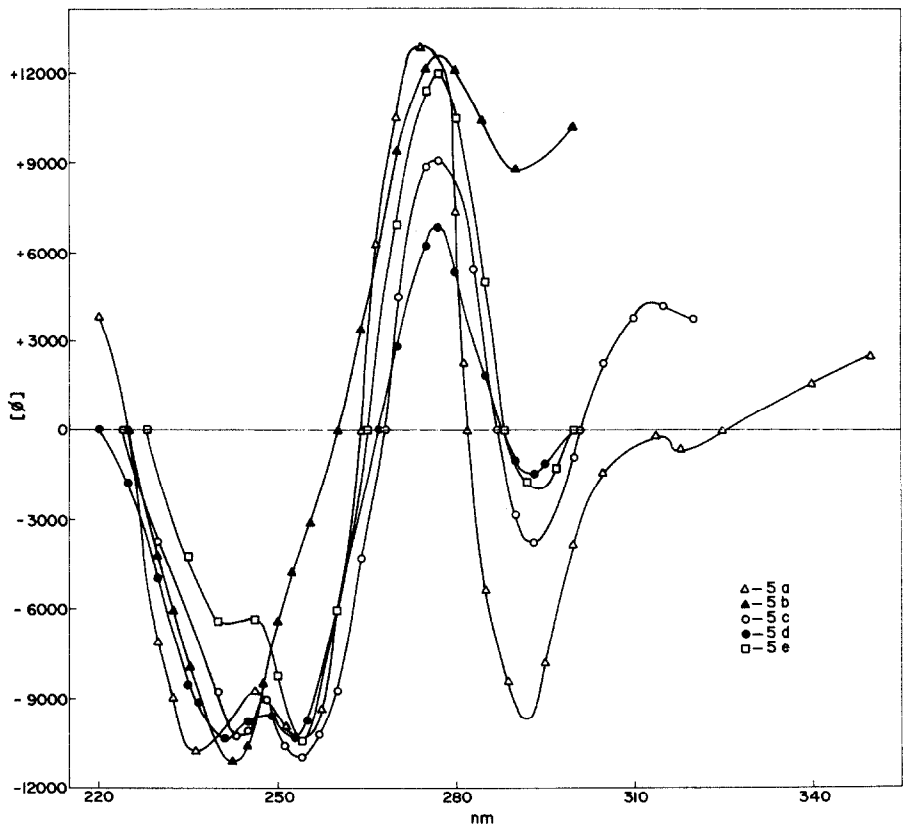


Fig. 1. ORD curves of compounds 5a–e in MeOH.

Table 2. PMR spectra (60 MHz, τ) of compounds of types **5** and **6**

Protons	**5a*** ($CDCl_3$)	**5b** (CCl_4)	**5c** (CCl_4)	**5d** (CCl_4)	**6a** (CCl_4)
Me-7	8.77, *d*, 7.0 Hz	9.14, *d*, 6.0 Hz	8.77, *d*, 7.0 Hz	8.80, *d*, 7.0 Hz	8.89, *d*, 7.0 Hz
$C\underline{H}_2CH$	7.3–7.9, *m*	7.3–7.8, *m*	7.5–7.9, *m*	7.5–7.9, *m*	7.4–7.7, *m*
H-7	7.3–7.9, *m*	7.3–7.8, *m*	7.5–7.9, *m*	7.5–7.9, *m*	7.4–7.7, *m*
H-5	6.3–6.9, *m*	—	—	—	6.2–6.5, *m*
OH	8.12, *s*	7.3–7.8, *m*	4.32, *s*	—	—
H-6	6.3–6.9, *m*	6.3–6.7, *m*	6.7–7.0, *m*	6.7–7.0, *m*	6.7–7.3, *m*
H-8	5.97, *s*	6.14, *s*	4.74, *s*	4.77, *s*	—
OAc-8	—	—	7.80, *s*	7.82, *s*	—
OMe-3	6.35, *s*	6.36, *s*	—	6.40, *s*	6.39, *s*
OMe-5	—	6.97, *s*	6.75, *s*	6.82, *s*	—
$CH=C\underline{H}_2$	4.6–4.9, *m*	4.6–5.0, *m*	4.6–5.0, *m*	4.6–5.1, *m*	4.6–5.0, *m*
$C\underline{H}=CH_2$	4.0–4.5, *m*	4.1–4.5, *m*	4.1–4.5, *m*	4.0–4.6, *m*	3.9–4.4, *m*
$O_2C\underline{H}_2$	4.10, *s*	4.05, *s*	4.09, *s*	4.14, *s*	4.07, *s*
H-2	3.87, *s*	4.47, *s*	3.70, *s*	4.04, *s*	3.85, *s*
H-5′	3.2–3.6, *m*	3.10, *s*	3.44, *s*	3.47, *s*	3.2–3.6, *m*
H-2′,6′		3.34, *s*	3.49, *s*	3.54, *s*	

* For a completely resolved 220 MHz spectrum see ref. [7].

the conclusion that all possess the relative stereochemistry previously assigned to guianin (**5a**). The slight ORD differences shown by **5b** are tentatively attributed to preferred orientation of the aryl group, a proposal which derives support upon comparison of the Me-7, OMe-5 and H-2 PMR data recorded in Table 2.

EXPERIMENTAL

Isolation of the constituents. Complete botanical material pertaining to an *Aniba* sp. from the Ducke Forest Reserve, Manaus, Amazonas, was deposited at INPA, Manaus, Herbaria Bot. 43452, Chem. 60/74. A description is available from the botanist W. Rodrigues. Trunk wood (9.0 kg) gave a C_6H_6-ext. (10 g) which was chromatographed on a dry Si gel (290 g) column with C_6H_6–EtOH (95:5) into 7 successive fractions. TLC (Si gel) with aid of the indicated solvents for development was used to separate fr. A (0.26 g, $CHCl_3$–EtOH) into **1c** and **1b**; fr. B (1.5 g, C_6H_6–EtOH 95:5) into **1c**, **1b** and **1a**; fr. D (0.7 g, Et_2O) into **5a** and **1a**; fr. F (0.98 g, C_6H_6–AcOEt 8:2) into **6a**, **4** and **5d**; fr. G (0.40 g, C_6H_6) into benzyl salicylate (150 mg) and benzyl benzoate (50 mg). Rechromatography on a dry Si gel (80 g) column with C_6H_6–EtOH (95:5) was used to separate fr. C (2.4 g) into 3 subfractions. TLC applied to subfr. C.1 (Et_2O) gave **1c**, **1b**, **5b** and **5a**; to subfr. C.2 ($CHCl_3$–EtOH 9:1) gave **1b** and **1a**; to subfr. C.3 (Et_2O) gave **1a** and **2b**. Crystallization from MeOH was used to separate fr. E (0.7 g) into sitosterol (150 mg) and a soln separated by TLC (C_6H_6–AcOEt 8:2) into **5c** and **6a**. Total quantities of neolignans obtained in mg: **1a** 70, **1b** 287, **1c** 165, **2b** 53, **4** 41, **5a** 12, **5b** 17, **5c** 32, **5d** 18.

Burchellin (**1a**) [3–5]. NOE (60 MHz, CCl_4): Irrad. at τ 6.42 (OMe-5) resulted in signal enhancements of 11% (H-4), 0% (H-7), −2% (H-2, $=CH_2$), 0% (O_2CH_2).

(2*S*,3*S*,3*aR*)-3a-*Allyl*-5-*methoxy*-3-*methyl*-2-*veratryl*-2,3,3a,6-*tetrahydro*-6-*oxobenzofuran* (**1b**). Viscous oil (Found: M^+ 356.1614, $C_{21}H_{24}O_5$ requires: M^+ 356.1624). λ_{max}^{MeOH} nm (log ε): 235 (4.18), 260 (4.29), 285 (4.03) inf. ν_{max}^{film} cm^{-1}: 1658, 1613, 1515, 1266, 1151, 1031, 924. MS *m/e* (rel int.): 357 (33) $M^+ + 1$, 356 (100) M^+, 326 (40), 316 (71), 315 (59), 191 (23), 182 (23), 181 (21), 180 (23), 179 (35), 178 (100), 177 (27), 167 (48), 166 (48), 165 (60), 163 (36), 151 (42), 149 (26), 120 (22). ORD (*c* 1.1 mg/100 ml, MeOH, 225–350 nm): $[\phi]_{225}$ −31870, $[\phi]_{250}^{pk}$ −5420, $[\phi]_{287}^{tr}$ −46790, $[\phi]_{302}$ 0, $[\phi]_{318}^{pk}$ +40000, $[\phi]_{350}$ +2710.

(2*S*,3*S*,3a*R*)-3a-*Allyl*-5,7-*dimethoxy*-3-*methyl*-2-*veratryl*-2,3,3a,6-*tetrahydro*-6-*oxobenzofuran* (**1c**). Viscous oil (Found: M^+ 386.1718, $C_{22}H_{26}O_6$ requires; M^+ 386.1730). λ_{max}^{MeOH} nm (log ε): 229 (4.30), 271 (4.32), 303 (3.86). ν_{max}^{film} cm^{-1}: 1647, 1608, 1511, 1036, 922, MS *m/e* (rel. int.): 386 (3) M^+, 356 (8), 195 (100), 178 (30), 167(30), 166(30), 165 (30). ORD (*c* 1.2 mg/100 ml, MeOH, 240–400 nm): $[\phi]_{240}^{tr}$ −33270, $[\phi]_{260}^{pk}$ −3990, $[\phi]_{295}^{tr}$ − 74540, $[\phi]_{312}$ 0, $[\phi]_{329}^{pk}$ + 38600, $[\phi]_{351}$ 0, $[\phi]_{365}^{tr}$ − 13310, $[\phi]_{400}$ − 8650.

(2*S*,3*S*,5*S*)-5-*Allyl*-5-*methoxy*-3-*methyl*-2-*veratryl*-2,3,5,6-*tetrahydro*-6-*oxobenzofuran* (**2b**). Viscous oil (Found: M^+ 356.1610, $C_{21}H_{24}O_5$ requires: M^+ 356.1624). λ_{max}^{MeOH} nm (log ε): 230 (4.38), 278 (4.36), 313 (4.28). ν_{max}^{film} cm^{-1}: 1680, 1645, 1613, 1517, 1381, 1192, 1031, 930. MS (*m/e*): 357 (33) $M^+ + 1$, 356 (100) M, 342 (62), 326 (33), 210 (21), 205 (21), 182 (46), 181 (33), 180 (21), 179 (29), 178 (100), 177 (38), 167 (38), 166 (42), 165 (42), 163 (29), 151 (25), 149 (38). ORD (*c* 5.2 mg/100 ml, MeOH, 212–295 nm): $[\phi]_{212}$ 70, $[\phi]_{239}^{tr}$ −7730, $[\phi]_{251}$ 0, $[\phi]_{277}^{pk}$ +11730, $[\phi]_{282}^{tr}$ +11530, $[\phi]_{295}^{pk}$ +13240.

(2*R*,3*R*)-7-*Methoxy*-3-*methyl*-5-*propenyl*-2-*veratryl*-2,3-*dihydrobenzofuran* (**4**). Viscous oil (Found: M^+: 340.1670, $C_{21}H_{24}O_4$ requires M^+ 340.1675). λ_{max}^{MeOH} nm (log ε): 275 (3.99). ν_{max}^{film} cm^{-1}: 2997, 1601, 1521, 1262, 1137, 1906, 960. PMR (CCl_4, τ): 3.0–3.4 (*m*, ArH), 3.4–3.6 (*m*, $\underline{H}C=CHMe$), 3.8–4.2 (*m*, $HC=C\underline{H}Me$), 4.99 (*d*, *J* 9.0 Hz, H-2), 6.14 (*s*, OMe), 6.19 (*s*, OMe), 6.3–7.0 (*m*, H-3), 8.15 (*dd*, *J* 5.0 Hz e indet., $HC=CHC\underline{H}_3$), 8.64 (*d*, *J* 7.0 Hz, Me-3). MS *m/e* (rel. int.): 341 (19) $M^+ + 1$, 340 (63) M^+, 325 (5), 165 (37), 151 (100). ORD (*c*, 3.4 mg/100 ml, MeOH, 225–320 nm): $[\phi]_{225}$ 0, $[\phi]_{245}^{tr}$ −12070, $[\phi]_{280}$ 0, $[\phi]_{307}^{pk}$ +8040, $[\phi]_{320}$ +6540.

rel-(1*S*,5*S*,6*S*,7*R*,8*R*)-1-*Allyl*-8-*hydroxy*-3,5-*dimethoxy*-7-*methyl*-4-*oxo*-6-*piperonylbicyclo*[3,2,1]*oct*-2-*ene* (**5b**), viscous oil (Found: M^+ 372.1567, $C_{21}H_{24}O_6$ requires: M^+ 372.1571). λ_{max}^{MeOH} nm (log ε): 234 (3.96), 263 (3.82). ν_{max}^{film} cm^{-1}: 3412, 1689, 1486, 1249, 1103, 1048, 941, 814. MS *m/e* (rel. int.): 373 (7) $M^+ + 1$, 372 (22) M^+, 343 (12), 192 (23), 179 (90), 167 (34), 160 (35), 149 (20), 147 (23), 83 (62), 81 (100). ORD (*c*, 4.0 mg/100 ml, MeOH, 225–300 nm): $[\phi]_{225}$ 0, $[\phi]_{243}^{tr}$ −11160, $[\phi]_{260}$ 0, $[\phi]_{277}^{pk}$ +12560, $[\phi]_{290}^{tr}$ +8840, $[\phi]_{300}$ +10230.

rel-(1*S*,5*S*,6*S*,7*R*,8*R*)-8-*Acetoxy*-1-*allyl*-3-*hydroxy*-5-*methoxy*-7-*methyl*-4-*oxo*-6-*piperonylbicyclo*[3,2,1]*oct*-2-*ene* (**5c**). Viscous oil (Found: M^+ 400.1523, $C_{22}H_{24}O_7$ requires: M^+ 400.1522). λ_{max}^{MeOH} nm (log ε): 233 (3.75), 274 (3.81), $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 233 (3.75), 294 (3.81), 319 (3.79), $\lambda_{max}^{MeOH+NaOH+HCl}$ nm (log ε): 233 (3.75), 274 (3.81), $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε) 235 (3.69), 280 (3.64), 324 (3.38). ν_{max}^{film} cm^{-1}: 3445, 1746, 1683, 1484, 1220, 1033, 928. MS *m/e* (rel. int.): 401 (20) $M^+ + 1$, 400 (100) M^+, 266 (20), 196 (45), 195 (50), 162 (70), 161 (75), 160 (32), 149 (19), 147 (85), 133 (36), 129 (24), 102 (29). ORD (*c* 4.2 mg/100 ml, MeOH, 224–320 nm): $[\phi]_{224}$ 0, $[\phi]_{243}^{tr}$ −10240, $[\phi]_{248}^{pk}$ −10050, $[\phi]_{254}^{tr}$ −11000, $[\phi]_{268}$ 0, $[\phi]_{277}^{pk}$ + 9100, $[\phi]_{287}$ 0, $[\phi]_{293}^{tr}$ −3790, $[\phi]_{301}$ 0, $[\phi]_{313}^{pk}$ +4360, $[\phi]_{320}$ +3790.

rel-(1*S*,5*S*,6*S*,7*R*,8*R*)-8-*Acetoxy*-3,5-*dimethoxy*-7-*methyl*-4-*oxo*-6-*piperonylbicyclo*[3,2,1]*oct*-2-*ene* (**5d**). mp 133–136° (Found: M^+ 414.1683, $C_{23}H_{26}O_7$ requires M^+ 414.1678). λ_{max}^{MeOH} nm (log ϵ): 234 (3.50), 268 (3.48), λ_{max}^{KBr} cm^{-1}: 1745, 1700, 1614, 1486, 1221, 1096, 930. MS *m/e* (rel. int.): 415 (44) $M^+ + 1$, 414 (95) M^+, 399 (16), 384 (51), 372 (30), 355 (25), 354 (26), 322 (64), 179 (47), 162 (100), 161 (47), 151 (52), 150 (58), 149 (56), 135 (70). ORD (*c* 4.64 mg/100 ml, MeOH, 220–300 nm): $[\phi]_{220}$ 0, $[\phi]_{241}^{tr}$ −10350, $[\phi]_{249}^{pk}$ −9630, $[\phi]_{253}^{tr}$ −10350, $[\phi]_{267}$ 0, $[\phi]_{277}^{pk}$ +6780, $[\phi]_{288}$ 0, $[\phi]_{293}^{tr}$ −1500, $[\phi]_{300}$ 0.

rel-(1*R*,5*S*,6*R*,7*R*)-1-*Allyl*-3-*methoxy*-7-*methyl*-4,8-*dioxo*-6-*piperonylbicyclo*[3,2,1]*oct*-2-*ene* (**6a**). Viscous oil (Found: M^+ 340.1318, $C_{20}H_{20}O_5$ requires M^+ 340.1311). λ_{max}^{MeOH} nm (log ϵ): 230 (3.72), 276 (3.68). ν_{max}^{film} cm^{-1}: 1748, 1683, 1601, 1484, 1434, 1223, 1148, 1032, 924. MS *m/e* (rel. int.): 341 (8) $M^+ + 1$, 340 (39) M^+, 310 (81), 300 (28), 242 (31), 179 (100), 151 (37), 149 (27), 135 (96), 121 (39), 106 (36). ORD (*c* 5.6 mg/100 ml, MeOH, 224–320 nm): $[\phi]_{224}$ 0, $[\phi]_{256}^{tr}$ −12140, $[\phi]_{278}$ 0, $[\phi]_{286}^{pk}$ +2730, $[\phi]_{295}^{tr}$ +1520, $[\phi]_{320}$ +6680.

Oxidations. The cmpd. in Me_2CO was treated with Jones reagent (2.7 g CrO_3, 10 ml H_2O, 2.3 ml conc. H_2SO_4) drop by drop at 25° until persistance of a yellow brown colour. The mixture was pured into H_2O and extd. with $CHCl_3$. Evap. of the solvent gave a residue which was purified by filtration through Si gel ($CHCl_3$). Thus guianin (**5a**)[7] gave **6a**; **5b** gave 1-*allyl*-3,5-*dimethoxy*-7-*methyl*-4,8-*dioxo*-6-*piperonylbicyclo*[3,2,1]*oct*-2-*ene* (**6b**), viscous oil (Found: M^+ 370.1413, $C_{21}H_{22}O_6$ requires: M^+ 370.1416). ν_{max}^{film} cm^{-1}: 1758, 1696, 1612, 1490, 1248, 1042, 930.

Acetylation (Ac_2O, C_5H_5N, room temp.) of **5c** gave 3,8-*diacetoxy*-1-*allyl*-5-*methoxy*-7-*methyl*-4-*oxo*-6-*piperonylbicyclo*-[3,2,1]*oct*-2-*ene* (**5e**), viscous oil (Found: 442.1624, $C_{24}H_{26}O_8$ requires 442.1627). λ_{max}^{MeOH} nm (log ϵ): 235 (3.54), 279 (3.28), 311 (2.28). ν_{max}^{film} cm^{-1}:1786, 1752, 1706, 1644, 1490, 1218, 1038, 954. PMR (CCl_4, τ): 3.24 (*s*, H-2), 3.44 (*s*, ArH), 3.6–4.5 (*m*, C<u>H</u>=CH_2), 4.12 (*s*, O_2CH_2), 4.6–5.1 (*m*, CH=C<u>H</u>$_2$), 4.72 (*s*, H-8), 6.3–6.5 (*m*, H-6), 6.72 (*s*, OMe-5), 7.3–8.0 (*m*, H-7 and C<u>H</u>$_2$CH), 7.82 (*s*, OAc-8), 8.78 (*d*, *J* 7.0 Hz, Me-7). MS *m/e* (rel. int.): 442 (52) M^+, 411 (20), 401 (35), 367 (25), 366 (35), 365 (20), 340 (42), 328 (33), 308 (34), 299 (32), 281 (33), 264 (60), 252 (56), 208 (65), 180 (80), 179 (70), 178 (52), 162 (100), 161 (100), 160 (80), 150 (75), 149 (80), 135 (80). ORD (*c*, 1.78 mg/100 ml, MeOH, 228–300 nm): $[\phi]_{228}$ 0, $[\phi]_{240}^{tr}$ −6460, $[\phi]_{246}^{pk}$ −6350, $[\phi]_{254}^{tr}$ −10430, $[\phi]_{265}$ 0, $[\phi]_{277}^{pk}$ +12020, $[\phi]_{288}$ 0, $[\phi]_{294}^{tr}$ −1990, $[\phi]_{300}$ 0.

Methylation (Me_2SO_4, K_2CO_3, Me_2CO, 5 hr. reflux) of **5c** gave **5d**.

REFERENCES

1. Franca, N. C., Gottlieb, O. R., Magalhães, M. T., Mendes, P. H., Maia, J. G. S., Silva, M. L. da and Gottlieb, H. E. (1976) *Phytochemistry* **15**, 572.
2. Gottlieb, O. R. (1972) *Phytochemistry* **11**, 1537.
3. Araújo Lima, O., Gottlieb, O. R. and Taveira Magalhães, M. (1972) *Phytochemistry* **11**, 2031.
4. Aiba, C. J., Fernandes, J. B., Gottlieb, O. R. and Maia, J. G. S. (1975) *Phytochemistry* **14**, 1597.
5. Gottlieb, O. R., Leão da Silva, M. and Scattone Ferreira, Z. (1975) *Phytochemistry* **14**, 1825.
6. Aiba, C. J., Campos Corrêa, R. G. and Gottlieb, O. R. (1973) *Phytochemistry* **12**, 1163.
7. Bülow, M. V. von, Franca, N. C., Gottlieb, O. R. and Puentes Suarez, A. M. (1973) *Phytochemistry* **12**, 1805.