DUCKEIN, AN ALKALOID FROM *ANIBA DUCKEI**

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Abstract—A re-investigation of the trunk wood of *Aniba duckei* Kosterm. (Lauraceae) revealed the presence of two new natural compounds, 2,6-dihydroxy-4-methoxyphenyl 3-pyridyl ketone (duckein) and 2,6,4'-trihydroxy-4-methoxybenzophenone.

Aniba duckei Kosterm., the source of commercial rosewood oil [2], is an Amazonian Lauraceae species. Previous investigations revealed the presence in its trunk wood of the 2-pyrones anibine (1a) [3], 4-methoxyphenylcoumalin (1b) [4] and 4-methoxyparacotoin (1c) [3] and of the benzophenone cotoin (2b) [5].

		(a)	3 – pyridyl
(1)		(b)	phenyl
		(c)	piperonyl
		(d)	4 –hydroxyphenyl

(2)
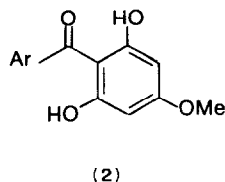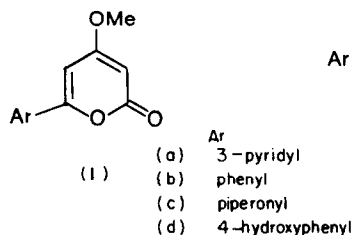
Chromatographic fractionation of the material contained in the mother liquor, resulting from the crystallization of crude anibine [3], yielded, besides an additional quantity of anibine, two new compounds, $C_{12}H_6NO(OH)_2OMe$ and $C_{13}H_6O(OH)_3OMe$. Their colour, UV and IR spectra were compatible with cotoin type 2-hydroxybenzophenone structures. The PMR spectra each contained at the high field limit of the aro-

matic region, a two-proton singlet, which can be associated with *meta*-hydrogens on phloroglucinol derived rings. The PMR spectra of the respective acetates again showed the *meta*-hydrogens represented by a singlet. These rings must, therefore, be symmetrically substituted. In the case of the dihydroxy compound this imposes, of course, partial structure (2) as the only possibility. The same structure must also represent the trihydroxy compound, since the most prominent peaks in the MS of both appear at *m/e* 167. Fragment ions, respectively at *m/e* 78 and 93, define Ar in the case of the former as pyridyl and in the case of the latter as hydroxyphenyl. Indeed, the PMR signals due to the 3-pyridyl part of anibine (1a) are all reproduced in the spectrum of the former for which, consequently, structure (2a) must be reserved. And again, the PMR signals due to an AA'BB'-system are registered in the spectrum of the other one and this must, consequently, be formulated as (2d).

Isolation of (2a), for which the name duckein is proposed, provides additional evidence for the biosynthetic connection of 2-pyrones and benzophenones in Lauraceae [6]. Chain extension of a nicotinoyl precursor by 2 acetate units would lead to anibine (1a) and by 3 acetate units would lead to duckein (2a), whereas chain extension of a benzoyl unit by 2 acetate units would lead to 4-methoxyphenylcoumalin (1b) and by 3 acetate units

would lead to cotoin (**2b**). The availability of aroyl precursor units in lauraceous plants is considered plausible on the one-hand because of the widespread natural occurrence of nicotinic acid, compared with the absence of β-3-pyridylacrylic acid, and on the other because of the presence of the benzoyl group, in the benzyl [7] and phenylethyl [8] benzoates of *Aniba* species.

EXPERIMENTAL

Isolation of anibine (**1a**), *duckein* (**2a**) *and* 2,6,4′-*trihydroxy*-4-*methoxybenzophenone* (**2d**). The mother liquor resulting from the crystallization of crude anibine (10 g)[3] was evaporated. The residue (3·5 g) was chromatographed on a silica column. Elution with the indicated solvents yielded in order fractions A (CHCl₃), B (CHCl₃–MeOH, 99:1) and C (CHCl₃–MeOH, 19:1). Each of these fractions was recrystallized from EtOH yielding respectively **1a** (10 mg), **2a** (15 mg) and **2d** (100 mg).

Duckein (**2a**). Yellow crystals, m.p. 243–245°. (Found: C, 63·58; H, 4·47; N, 5·80. $C_{13}H_{11}NO_4$ requires: C, 63·67; H, 4·52; N, 5·71%). λ_{max}^{EtOH} (nm): 210, 235 inf., 310 (ϵ 19350, 6850, 8550); $\lambda_{max}^{EtOH + NaOH}$ (nm): 230, 275 inf., 316 (ϵ 14200, 3450, 4650); $\lambda_{max}^{EtOH + NaOAc}$ (nm): 221, 275 inf., 313 (ϵ 17150, 2950 inf., 7350); $\lambda_{max}^{EtOH + HCl}$ (nm): 215, 265, 315 (ϵ 17950, 3650, 8100). ν_{max}^{KBr} (cm⁻¹): 1635, 1600, 1570, 1530, 1425, 1385, 1325, 1260, 1200, 1160, 1087, 1035, 930, 805, 710. PMR (TFA, τ): 3·76 (*s*, H-3, H-5), 6·07 (*s*, OMe). MS (*m/e*): 245 (50%) M, 244 (90), 167 (100), 106 (13), 95 (12), 79 (11), 78 (37), 69 (24), 51 (32) and 39 (15). *Diacetate*, PMR (CDCl₃, τ): 1·0 (*b*, H-2′), 1·3 (*b*, H-6′), 1·95 (*dt*, *J* 8·0, 2·0 Hz, H-4′), 2·65 (partially covered by solv. peak, *dd*, *J* ~6·5, ~5·0 Hz, H-5′), 3·31 (*s*, H-3, H-5), 6·12 (*s*, OMe), 8·07 (*s*, 2 COMe).

2,6,4′-*Trihydroxy*-4-*methoxybenzophenone* (**2d**). Yellow crystals, m.p. 179–181°. (Found: C, 64·81; H, 4·78. $C_{14}H_{12}O_5$ requires: C, 64·61; H, 4·65%). λ_{max}^{EtOH} (nm): 211, 235 inf., 290 inf., 308, 320 inf. (ϵ 30700, 19500, 15850, 16400, 15850); no shift in presence of HCl; $\lambda_{max}^{EtOH + NaOH}$ (nm): 235, 328 (ϵ 24450, 27800); $\lambda_{max}^{EtOH + NaOAc}$ (nm): 211, 223 inf., 304, 340 (ϵ 28350, 19500 inf., 14800, 14800); $\lambda_{max}^{EtOH + AlCl_3}$ (nm): 224, 287 inf., 325 (ϵ 24950, 13000, 14800). ν_{max}^{KBr} (cm⁻¹): 3225, 1640, 1605, 1580, 1545, 1505, 1420, 1375, 1310, 1245, 1210, 1150, 1075, 1040, 965, 918, 842, 823, 800, 760, 693. PMR [(CD₃)₂CO, τ]: 2·33 (~*d*, *J* 8·5 Hz, H-2′, H-6′), 3·13 (~*d*, *J* 8·5 Hz, H-3′, H-5′), 3·92 (*s*, H-3, H-5), 6·20 (*s*, OMe). MS (*m/e*): 261 (13%) M + 1, 260 (89) M, 259 (89) M − 1, 167 (75), 166 (100), 138 (37), 121 (41), 93 (22). *Triacetate*. Colourless crystals, m.p. 134–135°. ν_{max}^{KBr} (cm⁻¹): 1770, 1760, 1660, 1630, 1580, 1565, 1500, 1465, 1430, 1370, 1325, 1270, 1200, 1155, 1130, 1050, 890 and 855. PMR (CDCl₃, τ): 2·19 (~*d*, *J* 8·5 Hz, H-2′, H-6′), 2·85 (~*d*, *J* 8·5 Hz, H-3′, H-5′), 3·33 (*s*, H-3, H-5), 6·14 (*s*, OMe). 7·67 (*s*, OCOMe-4′), 8·09 (*s*, OCOMe-2 and -6). *Monomethyl ether* was obtained by methylation with CH_2N_2/Et₂O and purification by TLC (SiO₂). C_6H_6–AcOEt–EtOH, 50:43:7). PMR [(CD₃)₂CO, τ]: 2·40 (~*d*, *J* 8·5 Hz, H-2′, H-6′), 3·10 (~*d*, *J* 8·5 Hz, H-3′–H-5′), 3·83 (*s*, H-3, H-5), 6·13 (*s*, OMe-4), 6·38 (*s*, OMe-4′).

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