The possibility of physoxanthin being a mono-*cis* isomer of β-cryptoxanthin (**2**) [6, 7] is inconsistent with its electronic spectrum and chiroptical properties. Mono-*cis*-**2** is predicted to show opposite Cotton effect of all-*trans*-**2** [4].

In conclusion, the CD data of physoxanthin evaluated in relation to accumulated knowledge on CD properties of carotenoids is taken to disprove a mono-*cis* form of **2** and 3′ (or 2′) hydroxylation of the ε-ring, and is compatible with physoxanthin being identical with α-cryptoxanthin (**5**) [8]. The occurrence in *Physalis alkekengi* of other carotenoids with end group **c**, namely cryptoxanthin (**2**), zeaxanthin (**7**) and lutein (**3**) supports the preference for a 3-hydroxy-β-ring in physoxanthin. Although the reported melting points for α-cryptoxanthin (**5**) [9] from *Capsicum annuum* and physoxanthin [10], differed, this is not uncommon, and failure to separate them chromatographically also favours the assignment of identical structures.

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BENZOFURANOID NEOLIGNANS FROM *LICARIA ARMENIACA**

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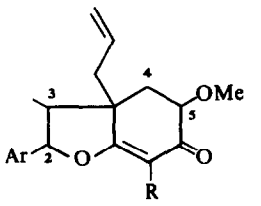
Key Word Index—*Licaria armeniaca*; Lauraceae: hexahydro-6-oxobenzofuran neolignans: structural determination.

Abstract—The trunkwood of *Licaria armeniaca* (Nees) Kosterm. (Lauraceae) contains sitosterol, 6,7-dimethoxycoumarin and two novel benzofuranoid neolignans: (2*S*, 3*S*, 3a*R*, 5*R*)-3a-allyl-5-methoxy- and 5,7-dimethoxy-2-(3′, 4′-methylenedioxyphenyl)-3-methyl-2,3,3a,4,5,6-hexahydro-6-oxobenzofurans.

Wood of the Amazonian Lauraceae species *Licaria armeniaca* (Nees) Kosterm. contains, besides sitosterol and 6,7-dimethoxycoumarin, two novel compounds, $C_{18}H_{17}O_2 \cdot OMe$ (**1a**) and $C_{18}H_{16}O_2 \cdot O_2CH_2(OMe)_2$ (**1b**). Spectral data indicate both to belong to the small group of hexahydro-6-oxobenzofuran neolignans, represented so far only by canellin-B (**1c**) [1] and porosin (**1d**) [2].

Concerning the aliphatic C_6C_3-moiety, **1d** is a useful model for **1a**, both showing the H-7 PMR singlet at



	Ar	Me	Al	OMe	R
1a	α-Pi	β	α	β	H
1b	α-Pi	B	α	β	OMe
1c	α-Pi	β	β	α	OMe
1d	α-Ve	α	β	α	H
1e	β-Pi	β	α	β	H

Ar = aryl, Me = methyl, Al = allyl, Pi = piperonyl, Ve = veratryl.

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τ 4.4, while **1c** is a model for **1b**, both showing an additional OMe singlet instead of the H-7 signal. Concerning the aromatic C_6C_3-moiety, **1c** is a better model for **1a** and **1b** than **1d**, not only on account of the O_2CH_2 substitution, all 3 compounds (**1a**, **1b**, **1c**) leading to diagnostic MS fragments of *m/e* 162 $[PiCHCHMe]^{+\cdot}$ and 149 $[PiCO]^+$, but also to the *trans* relation of the substituents at C-2 and 3, all 3 compounds showing Me resonances at lower field (τ 8.8) than porosin (τ 9.5). Although configurationally identical, the 2,3-substituents of **1a**, **1b** vs **1c** show different conformations, as expressed by $J_{H\text{-}2,H\text{-}3}$ respectively 2 vs 10 Hz. Canellin-B (**1c**) and **1b** being isomeric, this can be due to difference in chirality at C-3a. Indeed, the α-aryl at C-2 confers relative protection upon the α-CH_2 at C-3a of **1a** and **1b** (τ 7.65, 7.84) and the axial α-H at C-4 of **1c** (τ 8.24), as compared to the β-CH_2 at C-3a of **1c** and **1d** (τ 7.4, 7.5) and the axial β-H at C-4 of **1a** (τ 8.16).

The relative configuration shown in **1a** and **1b** also represents the absolute configurations of the compounds, on the assumption that the correlation between a positive Cotton effect at 285 nm and (2*S*)-chirality, deduced for 2,3,3*a*,6-tetrahydro-6-oxobenzofurans [3], is valid in the present case. Partial epimerization at C-2 of **1a** reduced the intensity of the corresponding ORD band, evidence for the correctness of the assignment of the wavelength to the benzenoid chromophore.

Hexahydro-6-oxobenzofuran neolignans such as **1a**, **1b**, **1c** and **1d** are putative biogenetic precursors of the seemingly much more numerous class of tetrahydro-6-oxobenzofurans [4]. It may, therefore, be anticipated that many further hexahydro-derivatives exist in nature.

EXPERIMENTAL

Isolation of the constituents. Licaria armeniaca (Nees) Kosterm. was collected at the Ducke Forest Reserve, Manaus (Amazonas). Voucher Herbarium INPA 47251. Dry powdered trunkwood (8 kg) was percolated with C_6H_6 at room temp. The extract (5.5 g) was chromatographed on a dry column (SiO_2 150 g, C_6H_6–EtOAc, 1:1). This was extruded and divided into 12 equal parts which gave, from bottom to top, 12 fractions. Frs. 1–3 were composed of fatty material (1.7 g). Frs. 4–7 were recrystallized from MeOH to sitosterol (1 g). Frs. 8–10 gave by perparative-TLC (SiO_2, Et_2O) **1a** (170 mg), **1b** (92 mg) and 6,7-dimethoxycoumarin (200 mg).

(2S,3S,3aR,5R)-3a-*Allyl*-5-*methoxy*-2-(3′,4′-*methylenedioxyphenyl*)-3-*methyl*-2,3,3a,4,5,6-*hexahydro*-6-*oxobenzofuran* (**1a**), chromatographically pure viscous oil (Found: M, 342.1461. $C_{20}H_{22}O_5$ requires: M, 342.1490). λ_{max} (MeOH, nm): 255, 285 (ε12500, 3800). ν_{max} (film, cm^{-1}): 1663, 1630, 1500, 1490, 1440, 1230, 1180. PMR (100 MHz, $CDCl_3$, τ): 3.2 (*br s*, 3 ArH), 4.04 (*s*, O_2CH_2), 4.2–4.6 (*m*, CH=), 4.44 (*s*, H-7), 4.78 (*d*, J = 2 Hz, H-2), 4.9 (*dd*, J = 2, 10 Hz) and 5.2 (*dd*, J = 2, 16 Hz), (CH_2=), 6.08 (*dd*, J = 5, 12 Hz, H-5*ax*), 6.42 (*s*, OMe-5), 7.36 (*dq*, J = 2, 8 Hz, H-3), 7.68 (*dd*, J = 7, 14 Hz) and 7.84 (*dd*, J = 7, 14 Hz), (CH_2-3a), 7.7 (*dd*, J = 5, 12 Hz, H-4*eq*), 8.16 (*t*, J = 12, 12 Hz, H-4*ax*), 8.8 (*d*, J = 8 Hz, Me-3). MS *m/e* (%): 342 (45) M, 311 (48), 284 (48), 269 (25), 257 (58), 241 (14), 214 (25), 181 (85), 175 (100), 162 (64), 149 (10), 135 (22), 115 (20), 103 (20), 91 (14), 77 (22). ORD (*c*, 3.2 mg/100 ml, MeOH): $[\phi]_{400}$ + 11800, $[\phi]^{pk}_{340}$ +27950, $[\phi]_{312}$ 0, $[\phi]^{tr}_{285}$ −38700, $[\phi]_{265}$ 0.

(2S,3S,3aR,5R)-3a-*Allyl*-5,7-*dimethoxy*-2-(3′,4′-*methylenedioxyphenyl*)-3-*methyl*-2,3,3*a*,4,5,6-*hexahydro*-6-*oxobenzofuran* (**1b**), crystals, mp 122–125° (Me_2CO) (Found: M, 372.1623. $C_{21}H_{24}O_6$ requires: M, 372.1641). λ_{max} (MeOH, nm): 239 infl., 268, 285 infl. (ε4400, 14000, 10300). ν_{max} (KBr, cm^{-1}): 1670, 1640, 1500, 1490, 1440, 1230, 1185. PMR (60 MHz, $CDCl_3$, τ): 3.18 (*br s*, 3 ArH), 3.98 (*s*, O_2CH_2), 4.2–4.5 (*m*, CH=), 4.73 (*d*, J = 2 Hz, H-2), 4.9 (*dd*, J = 2, 10 Hz) and 5.2 (*dd*, J = 2, 16 Hz), (CH_2=), 6.07 (*dd*, J = 5, 12 Hz, H-5*ax*), 6.17 (*s*, OMe-7), 6.38 (*s*, OMe-5), 7.35 (*dq*, J = 2, 8 Hz, H-3), 7.62 (*dd*, J = 7, 14 Hz) and 7.83 (*dd*, J = 7, 14 Hz), (CH_2-3a), 7.67 (*dd*, J = 5, 12 Hz, H-4*eq*), 8.17 (*t*, J = 12, 12 Hz, H-4*ax*), 8.8 (*d*, J = 8 Hz, Me-3). MS *m/e* (%): 372 (30) M, 342 (45), 331 (87), 303 (100), 271 (30), 190 (32), 181 (28), 175 (12), 162 (86), 149 (26), 135 (96), 115 (62), 104 (82), 103 (52), 91 (60), 77 (87). ORD (*c*, 4.8 mg/100 ml, MeOH): $[\phi]_{400}$ +2150, $[\phi]^{pk}_{355}$ +6200, $[\phi]_{327}$ 0, $[\phi]^{tr}_{288}$ −19400, $[\phi]_{267}$ 0, $[\phi]^{pk}_{262}$ +1950, $[\phi]_{255}$ 0.

Epimerization of **1a** *to* **1e**. A soln of **1a** (70 mg) and TsOH (1 mg) in MeOH (15 ml) was stirred (50°, 2 hr). The soln was cooled, neutralized with dil $NaHCO_3$, filtered and evapd. The residue was separated by preparative-TLC (SiO_2, C_6H_6–EtOAc 1:1) into a complex mixture (20 mg) and a mixture of **1a** + **1e** (40 mg), as indicated by TLC and PMR (60 MHz, $CDCl_3$, τ). Integration of the doublets at 8.83 and 9.5 indicated a **1a**–**1e** ratio of 3:1. ORD (*c*, 4.0 mg/100 ml, MeOH): $[\phi]_{400}$ +6000, $[\phi]^{pk}_{340}$ +15400, $[\phi]_{312}$ 0, $[\phi]^{tr}_{285}$ −23950, $[\phi]_{265}$ 0.

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