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NATURAL OCCURRENCE OF ERDTMAN'S DEHYDRODIISOEUGENOL*

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Key Word Index—*Licaria aritu*; Lauraceae; neolignans; dehydrodiisoeugenol; licarin-A; licarin-B; (2*S*,3*S*)-2,3-dihydro-2-(4′-hydroxy-3′-methoxyphenyl)-7-methoxy-3-methyl-5-*trans*-propenylbenzofuran; (2*S*,3*S*)-2,3-dihydro-7-methoxy-3-methyl-2-piperonyl-5-*trans*-propenylbenzofuran.

Abstract—The wood of *Licaria aritu* Ducke (Lauraceae) contains the neolignans licarin-A, (2*S*,3*S*)-2,3-dihydro-2-(4′-hydroxy-3′-methoxyphenyl)-7-methoxy-3-methyl-5-*trans*-propenylbenzofuran and licarin-B, (2*S*, 3*S*)-2,3-dihydro-7-methoxy-3-methyl-2-piperonyl-5-*trans*-propenylbenzofuran.

Licaria aritu Ducke is an arboreous Lauraceae species which occurs along the Manaus–Itacoatiara road, Amazonas State. Its trunk wood contains two related neolignans,[2] licarin-A, $C_{18}H_{15}O.OH\ (OMe)_2$, and licarin-B, $C_{18}H_{15}O.OMe.O_2CH_2$. The hydroxyl, methoxyl and methylenedioxy functions in these formulae were assigned after inspection of the PMR spectra; no additional features were noticeable in these spectra. Both revealed the association of the, by now, easily recognizable[1,3–5] *trans*-2-aryl-3-methyl-2,3-dihydrobenzofuran unit (τ 4·9, *d*, *J* 9 Hz, H-2; τ 6·5, *dq*, *J* 9 and 7 Hz, H-3; τ 8·7, *d*, *J* 7 Hz, $C\underline{H}_3$-3) with a *trans*-propenyl group. In the dihydro derivatives, the PMR-signals due to the propenyl groups give way to Ar-propyl signals. The 60 MHz spectra show that the aromatic substitution patterns of both licarins are identical. These are defined as shown in Ia for licarin-A and in Ib for licarin-B through analysis of the 220 MHz spectrum obtained for the latter compound. The absolute stereochemistry shown in the formulae was deduced from the ORD curves, which are both comparable to the analogous curves[5] of (2*S*,3*S*)-2-aryl-3-methyl-2,3-dihydrobenzofurans, rather than to the antipodal curves of (2*R*,3*R*)-derivatives. The MS of the licarins are compatible with the proposed constitutions if, as in previous cases,[1,5] 1,4-hydrogen shifts are evoked to rationalize the fragmentation pathways.

Except for its optical activity, licarin-A is identical with dehydrodiisoeugenol,[6] a fact which was ascertained by direct comparison of PMR-spectra and co-TLC. The constitution

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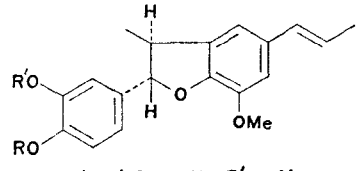
of dehydrodiisoeugenol was elucidated in 1933 by Erdtman,[7,8] who immediately grasped that one 'könnte die Möglichkeit ins Auge fassen, dass das Lignin durch oxydative Polymerisation eines in der Seitenkette oxydierten Propylguajakols entsteht'. This view is, of course, today widely accepted, and although, as far as we know, dehydrodiisoeugenol has not previously been found in nature, it has been considered a lignin model compound[9] ever since.



(I a) R = H ; R' = Me
(I b) R-R' = CH_2

EXPERIMENTAL

For experimental techniques see Ref. 5.

Isolation of the constituents of Licaria aritu. Ground trunk wood (2·3 kg) was extracted with benzene in a Soxhlet. The concentrated C_6H_6 solution deposited crystals of Ib (5 g) which were separated by filtration. The residual extract (93 g) was chromatographed on silica yielding an additional quantity of Ib (3 g) upon elution with C_6H_6 and Ia (2 g) upon elution with C_6H_6–$CHCl_3$ (1:1).

Licarin-A (Ia). Colourless crystals, m.p. 114–116° (hexane) [lit.[7] m.p. for (±)-dehydrodiisoeugenol 133–134° (EtOH)]. (Found: C, 73·9; H, 6·6. $C_{20}H_{22}O_4$ requires: C, 73·6; H, 6·7%.) λ_{max}^{MeOH} (nm): 220, 273 (ε 33 500, 26 700). ν_{max}^{KBr} (cm^{-1}): 3375, 1600, 1450, 1335, 1275, 1200, 1150, 1130, 1030, 960, 900, 860, 815. ORD (*c* 1·16, MeOH, 400–230 nm): $[\phi]_{400}$ −3950, $[\phi]_{350}$ −5100, $[\phi]_{330}$ −6200, $[\phi]_{310}$ −7900, $[\phi]_{294}$ −11 400, $[\phi]_{280}$ −6200, $[\phi]_{268}$ 0, $[\phi]_{260}$ +5650, $[\phi]_{248}$ +14 600, $[\phi]_{240}$ +10 100, $[\phi]_{230}$ ~0. PMR ($CDCl_3$, 60 MHz, τ): 3·00–3·25 (*m*, five ArH), 3·60 (*d*, *J* 15·5 Hz, propenyl α-CH), 3·89 (*dq*, *J* 15·5, 5·2 Hz, propenyl β-CH), 4·31 (*s*, OH), 4·86 (*d*, *J* 9·2 Hz, H-2), 6·07 (*s*, OCH_3), 6·10 (*s*, OCH_3), 6·52 (*dq*, *J* 9·2, 6·7 Hz, H-3), 8·08 (*d*, *J* 5·2 Hz, propenyl CH_3), 8·57 (*d*, *J* 6·7 Hz, CH_3-3). MS: M 326 (100%), *m/e* (%) 311 (10), 283 (5), 202 (15), 189 (7), 174 (5), 165 (6), 164 (5), 163 (11), 161 (5), 151 (9), 150 (5), 149 (12), 137 (19), 131 (8), 129 (5), 128 (8), 117 (5), 115 (10), 103 (8).

Licarin-B (Ib). Colourless needles, m.p. 91–92° (MeOH). (Found: C, 74·6; H, 6·3. $C_{20}H_{20}O_4$ requires: C, 74·4; H, 6·2%). λ_{max}^{EtOH} (nm): 220, 272 (ε 35 300, 20 100). ν_{max}^{KBr} (cm^{-1}): 1600, 1490, 1450, 1330, 1250, 1220, 1210, 1140, 1035, 970, 960, 930. ORD (*c* 1·04, MeOH, 400–220 nm): $[\phi]_{400}$ −1250, $[\phi]_{380}$ −1900, $[\phi]_{340}$ −2500, $[\phi]_{320}$ −6400, $[\phi]_{300}$ −12 400, $[\phi]_{290}$ −6250, $[\phi]_{280}$ 0, $[\phi]_{270}$ +5000, $[\phi]_{260}$ +13 700, $[\phi]_{250}$ +22 400, $[\phi]_{235}$ +12 000, $[\phi]_{220}$ ~0. PMR ($CDCl_3$, 220 MHz, τ): 3·08 (*d*, *J* 1·5 Hz, H-5), 3·14 (*dd*, *J* 8·0, 1·5 Hz, H-6'), 3·23 (*d*, indet., H-7), 3·24 (*dd*, *J* 8·0, indet., H-5'), 3·25 (*d*, *J* indet., H-2'), 3·66 (*dq*, *J* 16·0, ~1 Hz, propenyl α-CH), 3·91 (*dq*, *J* 16·0, 6·5 Hz, propenyl β-CH), 4·10 (*s*, O_2CH_2), 4·96 (*d*, *J* 8·9 Hz, H-2), 6·15 (*s*, OCH_3), 6·61 (approx. quint., *J ca.* 8, H-3), 8·16 (*d*, *J* 6·5, ~1 Hz, propenyl CH_3), 8·65 (*d*, *J* 7·0 Hz, CH_3-3). MS: M 324 (100%), *m/e* (%) 309 (10), 295 (6), 281 (5), 202 (5), 189 (8), 174 (6), 165 (5), 162 (5), 149 (9), 148 (5), 147 (10), 135 (14), 117 (5), 115 (5), 103 (5).

Dihydrolicarin-B. Obtained from licarin-B (100 mg) by catalytic hydrogenation [Pd–C (20 mg), EtOH (10 ml)]. M found: 326, $C_{20}H_{22}O_4$ requires: 326. PMR (CCl_4, τ): 3·08–3·56 (*m*, five ArH), 4·07 (*s*, O_2CH_2), 4·98 (*d*, *J* 9·0 Hz, H-2), 6·13 (*s*, OCH_3), 6·66 (*dq*, *J* 9·0, 6·5 Hz, H-3), 7·44 (app. *t*, *J* ~7 Hz, propyl α-CH_2), 8·15–8·75 (*m*, propyl β-CH_2), 8·60 (*d*, *J* 6·5 Hz, CH_3-3), 8·99 (*t*, *J* 7·0 Hz, propyl CH_3).

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