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LAURACEAE

CONSTITUENTS OF *ANIBA HOSTMANNIANA**

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Aniba hostmanniana (Nees) Mez is an arboreous species of Lauraceae which grows in the Amazon region. The bark contains an essential oil (0·8 %) which was separated by GLC into terpenes (1·2%), sesquiterpenes (4·0%), 3,4-dimethoxyallylbenzene (0·3%) and 2,4,5-trimethoxyallylbenzene (94·5%). The wood contains, besides a similar essential oil (1·3%) composed of terpenes (0·5%), sesquiterpenes (0·9%) and 2,4,5-trimethoxyallylbenzene (98·6%), also sitosterol and *N*-[β-(4-methoxyphenyl)-ethyl]-3,4,5-trimethoxycinnamamide.

Volatile constituents were classified as terpenes and sesquiterpenes according to GLC retention times. 3,4-Dimethoxyallylbenzene and sitosterol were identified by direct comparison with authentic samples. The trimethoxyallylbenzene was identified through its PMR spectrum. This contains, besides signals due to three methoxyl and one allyl group, two singlets at τ 3·25 and 3·42. The corresponding pair of aromatic protons occupy, consequently, nonequivalent *para* positions. These data define the compound unequivocally as 2,4,5-trimethoxyallylbenzene, one of the rarer natural allylbenzenes, which was isolated previously from *Caesulia axillaries* and named γ-asarone.[2]

The remaining constituent, $C_{21}H_{25}NO_5$, was recognized as an amide: In spite of a N–H band in the IR spectrum (3300 cm^{-1}), it did not form an acetate. The presence of a sole hydrogen linked to nitrogen was ascertained by NMR spectrometry. Although the corresponding proton signal was broadened due to H–N interaction, it is clearly a 1:2:1 triplet (J 5·6 Hz), indicating linkage of the nitrogen to a methylene group. This is represented by a double triplet (τ 6·38, J 5·6 and 6·5 Hz), and thus flanked additionally by another CH_2 group. The chemical shift of the corresponding signal (τ 7·18, t, J 6·5 Hz) defines the benzylic nature of this group, concluding the evidence for a β-phenylethyl substituent on the nitrogen. Since the compound is an amide, the nitrogen must, of course, sustain also a carbonyl. This, in turn, participates in a *trans*-cinnamoyl unit, identified by two doublets (τ 3·72 and 2·46, J 15·8 Hz).

At this stage only the substitution pattern of the aryl units in the cinnamoyl and the phenylethyl moieties had to be defined. Both are symmetric: One forming a 4-methoxyphenyl unit represented by an AA'BB' system of four aromatic protons which, in view of the chemical shift of its two doublets (τ 2·86 and 3·16, J 8·4 Hz), is probably part of the β-phenylethyl moiety [cf. β-(4-methoxyphenyl)-ethylamine τ 2·94 and 3·24, J 8·4 Hz];[3] and the other forming a trimethoxyphenyl unit which, in view of the chemical shift of its two-proton

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singlet (τ 3·31), is probably part of a 3,4,5-trimethoxycinnamoyl moiety [cf. 3,4,5-trimethoxycinnamic acid τ 3·21].[3] PMR data thus defined the compound as *N*-[β-(4-methoxyphenyl)-ethyl]-3,4,5-trimethoxycinnamamide, a deduction which is consistent with the mass spectrum (Table 1). The identity of the compound was, finally, confirmed also through identification of the products of hydrolysis: β-(4-methoxyphenyl)-ethylamine and 3,4,5-trimethoxybenzoic acid.

The derivation from a cinnamic acid type precursor is apparent in numerous constituents of *Aniba* species and, indeed, the entire Lauraceae family. In contradistinction, alkaloids based on the $C_6C_2NC_2C_6$-skeleton, though extremely widespread in the Lauraceae, have not yet been located in the genus *Aniba*.[4] Metabolization of phenylalanine and tyrosine here seems to lead preferentially to such exceptional products as β-nitrophenylethane[5] and the amide described in this paper.

TABLE 1. INTERPRETED MASS SPECTRUM OF *N*-[β-(4-METHOXYPHENYL)-ETHYL]-3,4,5-TRIMETHOXYCINNAMAMIDE

	m/e	%
$Ar.CH{=}CH{=}C(\overset{+}{=}O)NH.CH_2.CH_2.Ar'$	371	21
$Ar.CH{=}CH.C({=}NH).\overset{+}{O}H$	237	51
$Ar.CH{=}CH{-}C(NH_2\overset{+}{)}.O$ (a)	236	100
$Ar{-}CH{=}CH{-}C{\equiv}O^+$ (b)	221	81
$[(a) - CH_2O]^+$ and/or $[(b) - CH_3]^+$	206	27
$Ar'{-}CH_2{-}CH_2{}^+$	135	24
$Ar'{-}CH_2{}^+$	121	30

Ar—3,4,5-trimethoxyphenyl; Ar′—4-methoxyphenyl.
All peaks of more than 15% relative intensity are quoted.

EXPERIMENTAL

M.ps were taken on a Kofler hot stage and are uncorrected. PMR spectra were determined on Varian instruments, in $CDCl_3$ solutions containing TMS as internal standard; s—singlet, d—doublet, t—triplet, m—multiplet. The MS were determined on a Perkin–Elmer model 200 spectrometer.

The essential oils of Aniba hostmanniana. These were obtained by vapour entrainment of the powdered plant material. Analytical GLC employed a 2 m × 4·5 mm column filled with 20% Carbowax 20M on Chromosorb P. Column temp 200°; inlet temp 240°, detector (catharometer) temp 280°, H_2 flow rate 80 ml/min.

The constituents of Aniba hostmanniana. The powdered wood (6 kg) was extracted with benzene. The benzene solution was evaporated and the residue (100 g) was chromatographed on Merck Kieselgel 0·05–0·20 mm (1 kg), yielding the following useful fractions with the indicated eluants: F_1 (benzene), F_2 (benzene–$CHCl_3$, 9:1), F_3 ($CHCl_3$). F_1 was evaporated. The oily residue (80 g) was distilled under vacuum, giving 2,4,5-trimethoxyallylbenzene (60 g) at 138–139·5°/8 mm Hg. F_2 was evaporated. The residue was recrystallized from benzene–light petroleum, giving sitosterol (600 mg). F_3 was evaporated. The residue was recrystallized from benzene, giving *N*-[β-(4-methoxyphenyl)-ethyl]-3,4,5-trimethoxycinnamamide (350 mg).

2,4,5-*Trimethoxyallylbenzene.* Colourless oil, b.p. 138–140°/8 mm Hg, $n_D^{25°}$ 1·532, $d_D^{25°}$ 1·0795. (M found: 208, $C_{12}H_{16}O_3$ requires: 208.) IR identical to spectrum given in lit.[2] PMR (60 MHz, τ): 3·25 (s, H-6), 3·42 (s, H-3), 3·8–4·4 (m, $=C\underline{H}$), 4·92 and 5·12 (m, $=C\underline{H}_2$), 6·15 (s, $OC\underline{H}_3$), 6·21 (s, $OC\underline{H}_3$), 6·24 (s, $OC\underline{H}_3$), 6·67 (d, J 6·5 Hz, $-C\underline{H}_2-$).

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[4] O. R. GOTTLIEB, *Phytochem.* **11,** 1537 (1972).

[5] O. R. GOTTLIEB and M. TAVEIRA MAGALHÃES, *J. Org. Chem.* **24,** 2070 (1959).

N-[β-(4-*Methoxyphenyl*)-*ethyl*]-3,4,5-*trimethoxycinnamamide*. Fine white needles, m.p. 144·5–146° (benzene). (Found: C, 67·48; H, 6·90; N, 3·77. $C_{21}H_{25}NO_5$ requires: C, 67·91; H, 6·78; N, 3·77%.) $\lambda_{\max}^{\text{EtOH}}$ (nm): 233, 302 (ϵ 18 200, 14 650), no alteration in presence of NaOH or HCl. $\nu_{\max}^{\text{KCl}}$ (cm^{-1}): 3300, 1658, 1610, 1580, 1510, 1455, 1420, 1325, 1245, 1220, 1135, 975. PMR (220 MHz, τ): 2·46 and 3·72 (doublets, *J* 15·8 Hz, Ar—C$\underline{\text{H}}$=C$\underline{\text{H}}$—CO). 2·86 and 3·16 (doublets, *J* 8·4 Hz, aromatic AA′BB′ system), 3·31 (s, 2 aromatic Hs), 4·15 (broad, t, *J* 5·6 Hz, N$\underline{\text{H}}$), 6·19 and 6·23 (singlets, respectively one OC$\underline{\text{H}}_3$ at C-4 and two OC$\underline{\text{H}}_3$ at C-3 and C-5 of the cinnamoyl moiety), 6·28 (s, one OC$\underline{\text{H}}_3$ at C-4 of the β-phenylethyl moiety), 6·38 (double t, *J* 5·6 and 6·5 Hz, N–C$\underline{\text{H}}_2$), 7·18 (t, *J* 6·5 Hz, Ar–C$\underline{\text{H}}_2$). MS (peaks of less than 5% relative intensity are not quoted): M 371 (21%), *m/e* (%) 238 (7), 237 (51), 236 (100), 221 (81), 207 (5), 206 (27), 193 (8), 192 (12), 191 (8), 190 (13), 178 (5), 177 (5), 163 (10), 162 (7), 161 (5), 149 (5), 148 (5), 147 (7), 135 (24), 134 (8), 133 (7), 122 (6), 121 (30), 120 (8), 119 (10), 118 (5), 105 (6), 103 (6), 102 (5).

The compound (50 mg) and aq. conc. HCl (3 ml) were heated under reflux (1 hr). After cooling to room temp, H_2O (10 ml) was added and the mixture extracted with Et_2O. The Et_2O was evaporated and the residue (15 mg) identified with 3,4,5-trimethoxy-*trans*-cinnamic acid by comparison of m.p. and IR spectrum with literature data.[3] The aqueous solution was turned alkaline by addition of aq. NaOH and again extracted with Et_2O. The solution was evaporated and the residue (12 mg) identified with β-(4-methoxyphenylethyl)-amine by comparison of the IR spectrum with literature data.[3]

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Key Word Index—Aniba hostmanniana; Lauraceae; 3,4-dimethoxyallylbenzene; 2,4,5-trimethoxyallylbenzene; *N*-[β-(4-methoxyphenyl)-ethyl]-3,4,5-trimethoxycinnamamide.

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LEGUMINOSAE

INDOLE BASES OF *DESMODIUM GYRANS*

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Plant. *Desmodium gyrans* DC. (tribe: Lotoideae). *Occurrence*. In northern parts of Bengal, N. Circars, Deccan and Hills of Carnatic and also W. Ghats, up to 3000 ft, in grass lands and forest undergrowth widespread but nowhere very common.[1] *Uses*. The leaves exhibit tonic, diuretic, febrifuge and aphrodisiac properties; the roots find use in the Indian system of medicine as emollient, laxative, antidysenteric and remedy for coughs and asthma. *Previous work*. On *D. pulchellum* Benth. ex Baker,[2] *D. gangeticum* DC.,[3] *D. triflorum* DC.,[4] *D. tiliafolium* G. Don.[5]

Present work. Dried and finely ground plant materials (leaves, 2 kg; roots, 0·5 kg) were continuously extracted with light petroleum (60–80°), petroleum extract triturated with aqueous citric acid (12%), liberated bases (marked 'weak' base fraction) from the clarified acidic solution chromatographed over Brockmann neutral alumina. Defatted plant material

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