The chemistry of Brazilian Lauraceae

XLVI. Notes on **Aniba** species

Aura M. P. de Diaz (*)
Otto R. Gottlieb (**)
Aderbal F. Magalhães (***)
Eva G. Magalhães (***)
José G. S. Maia (*)
Celira C. Santos (***)

Abstract

Aniba affinis, A. cylindriflora and **A. mas** (Lauraceae) were found to contain respectively benzofuranoid (and a previously unknown bicyclo [3, 2, 1] octanoid) neolignans, 6-styryl-2-pyrones and 6-styryl-4-methoxy-2-pyrones.

In continuation of a series of reports on the chemical composition of Lauraceae, belonging predominantly to the genus *Aniba* [Alvarenga *et al.*, 1977b and previous papers of the series] we examined the following species.

Aniba affinis (Meissn.) Mez

The specimen, from the confluence of the rivers Negro and Maipendi, Amazonas, voucher Herbarium INPA, Manaus, 58520, was collected and identified by Dr. K. Kubitzki, Hamburg.

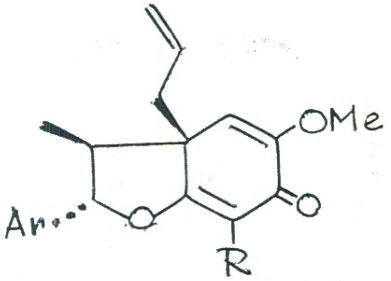
A trunk wood sample (370 g) was extracted with ethanol. The chloroform soluble part (6 g) of the extract (25.5 g) was chromatographed on a silica column. Elution with benzene gave, in order, terpenes (54 mg), benzyl salicylate (40 mg), benzyl benzoate (600 mg), (2S,3S) - 7 - allyl - 6 - hydroxy - 5 - methoxy - 3 - methyl - 2 - piperonyl - 2,3 - dihydrobenzofuran (*4* [Gottlieb *et al.*, 1975] 30 mg), (2S,3S) - 6 - 0 - allyl - 5 - methoxy - 3 - methyl - 2 - piperonyl - 2,3 - dihydrobenzofuran (*3* [Gottlieb *et al.*, 1975; Alvarenga *et al.*, 1977a] 32 mg), sitosterol (85 mg), 2 - guaiacyl - 7 - methoxy - 3 - methyl - 5 - propenyl - 2,3 - dihydrobenzofuran (*5* [Aiba *et al.*, 1973] +*6a*, 60 mg), (1S, 5S, 6S, 7R, 8R) - 1 - allyl - 3,8 - dihydroxy - 5 - methoxy - 7 - methyl - 4 - oxo - 6 - piperonylbicyclo [3,2,1] oct-2-ene (*7e*, 18 mg). Elution with benzene-chloroform 7:3 gave (2S, 3S, 5S) - 5 - allyl - 5 - methoxy - 3 - methyl - 2 - piperonyl - 2, 3, 5, 6 - tetrahydro - 6 - oxobenzofuran (*2a* [Alvarenga *et al.*, 1977a] 150 mg) and (2S, 3S, 3aR) — 3a - allyl - 5 - methoxy - 3 - methyl - 2 - piperonyl - 2, 3, 3a, 6 - tetrahydro - 6-oxobenzofuran (*1a* [Lima *et al.*, 1972] 1.19 g). The compounds were purified either by recrystallization (*1a*, burchellin), or by preparative TLC (silica, *2a*: C_6H_6-AcOEt 8:2, all other C_6H_6). The presence of benzaldehyde in benzyl benzoate + benzyl salicylate fractions was ascertained by the characteristic ^1H NMR peaks [Bhacca *et al.*, 1962]. The identity of all other compounds, with exception of *7e* which has not been described previously, was confirmed by direct comparison with authentic samples.

Dehydrodiisoeugenol was previously obtained from Lauraceae in crystalline form (*5* [Alba *et al.*, 1973]). The fact that it was isolated form *A. affinis* as an oil may indicate the simultaneous presence of the enantiomers *5* + *6a* (for an analogous case see Aiba and Gottlieb, 1975). In this connection it is significant to recall that a previously examined specimen of an *A.* species, provisional ref. 60, voucher INPA 43452, was shown to contain *6b* [Fernandes *et al.*, 1976]. This specimen, now also identified with *A. affinis* by Dr. Kubitzki, contains additionally 1a, 1b, 1c, 2b and four bicyclo [3,2,1] octanoid neolignans *7a, 7b, 7c*

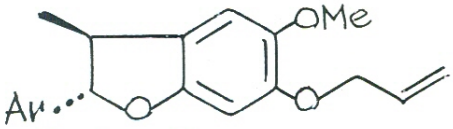
(*) — Instituto Nacional de Pesquisas da Amazônia, Manaus.
(**) — Instituto de Química, Universidade de São Paulo, SP.
(***) — Instituto de Química, Universidade Estadual de Campinas, SP.

and *7d*. The ^{1}H NMR spectrum of *7b* is closely comparable with the analogous spectrum of *7e* isolated during the present study (Table 1). The only significant difference refers to the substitution of OMe/OH signals, consistent with the fact that the novel compound *7e* is a 3-de-O-methyl derivative of *7b*.

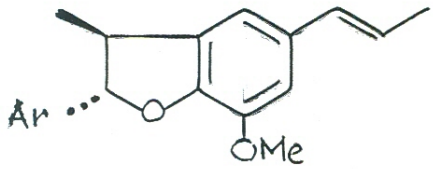
The chemical composition of both specimens is, thus, closely akin. Indeed, compounds *3* and *4*, which were isolated only during the present study, are rearrangement products belonging to the reactional sequence *1a* —> *2a* —> *3* —> *4*; and *8* which was isolated only during the previous study, is an oxidation



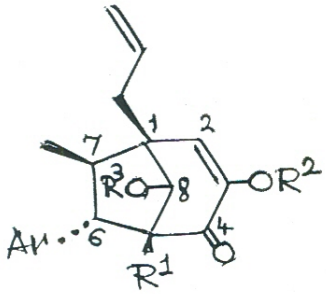
1a/*** Ar = Pi, R = H
*1b** Ar = Ve, R = H
*1c** Ar = Ve, R = OMe



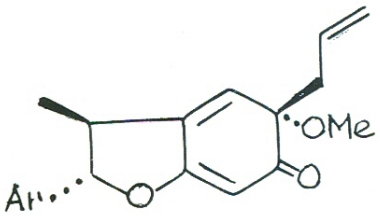
*3*** Ar = Pi



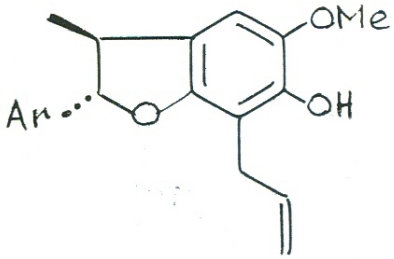
*5*** Ar = Gu



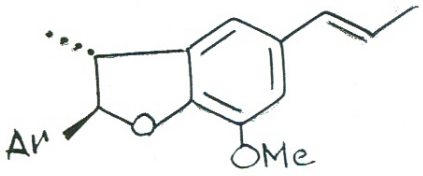
*7a** Ar = Pi, R^1 = H, R^2 = Me, R^3 = H
*7b** Ar = Pi, R^1 = OMe, R^2 = Me, R^3 = H
*7c** Ar = Pi, R^1 = OMe, R^2 = Me, R^3 = Ac
*7d** Ar = Pi, R^1 = OMe, R^2 = H, R^3 = Ac
*7e*** Ar = Pi, R^1 = OMe, R^2 = R^3 = H



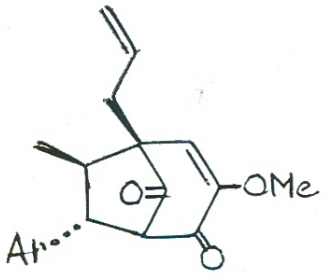
*2a*** Ar = Pi
*2b** Ar = Ve



*4*** Ar = Pi



*6a*** Ar = Gu
*6b** Ar = Ve



*8** Ar = Pi

Constituents of two specimens of *A. affinis*:
* [Fernandes *et al.*, 1976], ** present study.
Gu ... guaiacyl, Ve ... verattryl, Pi ... piperonyl

product of *7a*. It may be, however, of some significance that piperonyl derivatives were found accompanied by guaiacyl derivatives in the present study and veratryl derivatives in the previous study.

7e, viscous oil, ν_{max}^{film} (cm^{-1}): 1670, 1629, 1498, 1265, 1190, 955. M+. 358, $C_{20}H_{22}O_6$ requires: 358. Me_2SO_4 - methylation gives *7b*.

TABLE 1. ^1H NMR spectra of 7b (Fernandes et al., 1976) and 7e in CCl_4

	multiplicity	7b τ	7e τ
Me-7	d, J 6.0 Hz	9.14	8.90
CH_2-1, H-7	m	7.3-7.8	7.6-8.2
H-6	m	6.3-6.7	6.8-7.1
OMe-5	s	6.97	6.90
OMe-3	s	6.36	—
H-8	s	6.14	6.29
CH = CH_2	m	4.6-5.0	4.7-5.2
CH = CH_2	m	4.1-4.5	3.9-4.3
H-2	s	4.47	4.37
O_2CH_2	s	4.05	4.08
H-2', 5', 6'	m	3.1-3.3	3.3

Aniba cylindriflora Kosterm.

The specimen, from Paraná do Tautú, affluent of Rio Negro, Amazonas, voucher Herbarium INPA, Manaus, 47352, was identified by Dr. K. Kubitzki, Hamburg. A trunk wood sample was treated as described for *Aniba parviflora* (Meissn.) Mez [Rezende *et al.*, 1971] and yielded three of its constituentes: 6 - styryl - 2 pyrone, 6 - (4' - hydroxy - 3' - methoxystyryl) - 2 - pyrone, 6 - (3',4' - methylenedioxystyryl - 2 - pyrone, besides 6- (3',4' - dimethoxystyryl) - 2 - pyrone, so far known only by synthesis [Bittencourt *et al.*, 1971].

Aniba mas Kosterm.

The specimen, from the Ducke Forest Reserve, Manaus, Amazonas, voucher Herbarium INPA, Manaus, 42207, was identified by Dr. K. Kubitzki, Hamburg. A trunk wood sample was treated as described for *Aniba permollis* (Nees) Mez [Rezende *et al.*, 1971] and yielded the same constituents: 6 - (3',4' - methylenedioxyphenyl) - 4 - methoxy - 2 - pyrone, 6 - styryl - 4 - methoxy - 2 - pyrone, 6 - (3',4' - dimethoxystyryl) - 4 - methoxy - 2 - pyrone and 6 - (3',4' - methylenedioxystyryl) - 4 - methoxy - 2 - Pyrone. It is indeed probable that the samble thought to be derived from *A. permollis* [Rezende *et al.*, 1971] might have been derived from *A. mas* since Dr. Kubitzki is doubtful concerning the correctness of the identification of the specimen used in the previous study.

Resumo

A madeira do tronco das espécies amazônicas **Aniba affinis, A. cylindriflora** e **A. mas** contém respectivamente neolignanas benzofuranoídicas (e uma biciclo [3, 2, 1] octanoídica previamente desconhecida), 6-estiril-2-pironas e 6-estiril-4-metoxi-2-pironas.

Literature cited

Aiba, C.J.; Corrêa, R.G.C. & Gottlieb, O.R.
1973 — The natural occurrence of Erdtman's dehydrodiisoeugenol. **Phytochemistry**, 12 : 1163-1164.

Aiba, C.J. & Gottlieb, O.R.
1975 — Synthesis of (±)-licarin-B. **Phytochemistry**, 14 : 253-255.

Alvarenga, M.A. de; Brocksom, U.; Castro, C.O.; Gottlieb, O.R. & Magalhães, M.T.
1977a — Neolignans from **Aniba burchellii**. **Phytochemistry**, 16 : in print.

Alvarenga, M.A.; Castro, C.O.; Giesbrecht, A.M. & Gottlieb, O.R.
1977b — Bicyclo [3, 2, 1] octanoid neolignans from **Aniba simulans**. **Phytochemistry**, 16 : in print.

Bhacca, N.S.; Hollis, D.P.; Johnson, L.F.; Pier, E.A. & Shoolery, J.N.
1962 — **NMR Spectra Catalog.**, Palo Alto, Calif. Varian Associates.

Bittencourt, A.M.; Gottlieb, O.R.; Mors, W.B.; Magalhães, M.T.; Mageswaran, S.; Ollis, W.D. & Sutherland, I.O.
1971 — The natural occurrence of 6-styryl-2-pyrones and their synthesis. **Tetrahedron**, 27 : 1043-1048.

Fernandes, J.B.; Gottlieb, O.R. & Maia, J.G.S.
1976 — Neolignans from an **Aniba** species. **Phytochemistry**, 15 : 1033-1036.

Gottlieb, O.R.; Silva, M.L. da & Ferreira, Z.S.
1975 — Neolignans from **Aniba terminalis**. **Phytochemistry**, 14 : 1825-1827.

Lima, O.A.; Gottlieb, O.R. & Magalhães, M.T.
1972 — Burchellin, a neolignan from **Aniba burchellii**. **Phytochemistry**, 11:2031-2037.

Rezende, C.M.A. da M.; Bülow, M.V. von; Gottlieb, O.R.; Pinho, S.L.V. & Rocha, A.I. da
1971 — The 2-pyrones of Aniba species. **Phytochemistry**, 10 : 3167-3172.