Pergamon

PII: S0031-9422(97)00172-6

Phytochemistry, Vol. 45, No. 7, pp. 1527–1528, 1997

0031-9422/97 $17.00+0.00

THE NATURAL OCCURRENCE OF MAGNOSALICIN DIASTEREOMERS*

MARIA DE FÁTIMA DA SILVA, FRANCISCA S. N. TAVEIRA, JOSÉ GUILHERME SOARES MAIA,† LUCIA M. CONSERVA,‡ MASSAYOSHI YOSHIDA and OTTO R. GOTTLIEB§

Departamento de Química, Universidade Federal do Pará, 66060-060, Belém; ‡ Departamento de Química, Universidade Federal de Alagoas, 50072-970, Maceió; § Instituto de Química, Universidade de São Paulo, 05508-900, São Paulo, Brazil

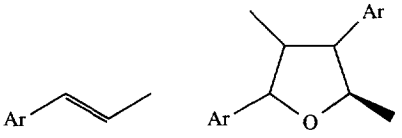
(*Received* 10 *December* 1996)

Key Word Index—*Aniba puchury-minor*; Lauraceae; arylpropanoids; tetrahydrofuran neolignans; essential oils.

Abstract—*Aniba puchury-minor* contains besides common mono- and chiefly sesquiterpenes, asaraldehyde and a series of monomeric arylpropanoids including *E*-asarone, magnosalicin and two of its diastereomers. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Co-occurrence and biogenetic considerations suggested *E*-asarone (**1**) to be the precursor of the structurally unique [2] antiallergic neolignan magnosalicin (**2a**) of *Magnolia salicifolia* [3]. Indeed, peracid oxidation of **1** led to **2a**, albeit in modest yield and, as expected, accompanied by the three diastereomers **2b**, **c** and **d** [4]. It remained to be verified if the *in vivo* transformation of **1** proceeds via some stereochemical control exclusively into **2a**, or if, as *in vitro*, this compound is also accompanied by its diastereomers. The present report shows the latter of these alternatives to be the correct one.



2a 7 βAr, 8 αMe, 7' βAr
2b 7 αAr, 8 βMe, 7' αAr
2c 7 βAr, 8 βMe, 7' αAr
2d 7 αAr, 8 αMe, 7' βAr

Ar -= 2,4,5=trimethoxyphenyl

RESULTS AND DISCUSSION

Aniba puchury-minor (Mart.) Mez is a lauraceous tree, in Amazonia popularly known as 'casca preciosa arana'. The investigation of a hexane extract of its trunk wood led to the isolation of asaraldehyde, *O*-methyleugenol, *O*-methylisoeugenol, isoasarone and *E*-asarone (**1**), in addition to magnosalicin (**2a**) and the corresponding diastereomers **2b** and **c** here reported for the first time as natural products. The identification of all these compounds relied on full spectral interpretations and comparisons with published data.

The analyses of an essential oil from leaves (yield 0.5%) revealed the percental composition in terpenoids (limonene 1.59, α-copaene 6.58, α-cubebene 2.01, β-cubebene 0.43, cyperene 2.04, α-bergamotene 7.27, β-caryophyllene 5.08, germacrene B 13.42, α-humulene 0.98, β-farnesene 2.30, germacrene D 4.02, β-bisabolene 3.94 and spathulenol 6.11). Besides 3,4-dioxygenated and 3,4,5-trioxygenated phenylpropanoids (myristicin 8.43, *O*-methyleugenol 2.28, elemicin 23.46 and isoelemicin 8.33) predominated strongly over 2,4,5-trioxygenated derivatives (*E*-asarone and isoasarone 1.83). In contrast, in the oils from stems (yield 0.4%) and barks (yield 0.7%) terpenoids were not detected and among the phenylpropanoids 2,4,5-trioxygenated derivatives appeared very conspicuously, as indicated by the percental compositions, respective, to stem and bark oils (myristicin 7.96, 1.26; *O*-methylisoeugenol 6.45, 43.10; *O*-methyl-

* Part 106 in the series 'The Chemistry of Brazilian Lauraceae'. For Part 105 see ref. [1]. Taken from parts of the M.Sc. theses submitted by F.S.N.T. and M.F.S. to Universidade Federal do Pará (1991 and 1995).

† Author to whom correspondence should be addressed.

eugenol 17.62, 4.37; isodillapiol 0, 7.88; elemicin 1.30, 1.42, isoelemicin 13.91, 11.87; versus *E*-asarone and isoasarone 52.75, 29.95).

EXPERIMENTAL

Trunk wood, leaves, stems and barks were collected on Serra de Carajás, Municipality of Marabá, Pará State, June 1988. Voucher specimens (no. 131.479) were deposited at the Herbarium of Museu Paraense Emílio Goeldi, Belém, Brazil.

Isolation of extractives. Ground trunk wood (6.0 kg) was extracted with hexane under reflux. A portion (17 g) of the total extract (42 g) was submitted to silica CC. Elution with hexane–EtOAc mixts gave frs A (8:2), B and C (7:3), D and E (1:1). Fr. A (7.2 g) was further purified by silica CC. Elution with hexane–EtOAc mixts of gradually increasing polarities gave *O*-methyleugenol (49 mg) and *O*-methylisoeugenol (20 mg). By the same procedure fr. B gave isoasarone and **1** (35 mg). Fr. C was recrystallized from MeOH to sitosterol (53 mg). Fr. D (0.7 g) was purified by silica CC. The fr. eluted with CH_2Cl_2–Me_2CO 9:1 was recrystallized from hexane–EtOAc to asaraldehyde (22 mg) and **2a** (90 mg). Fr. E (2.1 g) was submitted to repeated silica CC. Elution with CH_2Cl_2–Me_2CO mixts of increasing polarities and purification by silica TLC via development with cyclohexane–Me_2CO 7:3 gave **2a** (17 mg), **2b** (17 mg), and **2c** (impurified by **2b**, 28 mg).

Analysis of essential oils. Air dried leaves, stems and barks were submitted to vapour entrainment, yielding respectively 0.5, 0.4 and 0.7% of essential oil. The oils were analysed in a quadrupole GC/MS at 70 eV in the EI mode, using a 30 m (0.25 mm) fused silica capillary column containing a 0.25 μm film of AW-54. Helium was used as carrier gas, adjusted to a linear velocity of 33 cm sec^{-1} (measured at 150°). Split flow was adjusted to a 20:1 ratio. Split-splitless injection of 2 μl of a 1:1000 *n*-hexane soln was done at 50°. The temp. was programmed at 4° min^{-1} up to 180° and then at 20° min^{-1} up to 250°.

Acknowledgements—The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico for financial support and to Prof. A. A. Craveiro, Universidade Federal do Ceará, for GC/MS analyses.

REFERENCES

1. Garcez, W. S., Yoshida, M. and Gottlieb, O. R., *Phytochemistry*, 1995, **39**, 815.
2. Gottlieb, O. R. and Yoshida, M., in *Natural Products of Woody Plants: Chemicals Extraneous to the Lignocellulosic Cell Wall*, ed. J. W. Rowe. Springer, Heidelberg, 1989, p. 439.
3. Tsuruga, T., Ebizuka, Y., Nakajima, J., Chun, Y.-T., Noguchi, H., Jitaka, Y. and Sankawa, U., *Tetrahedron Letters*, 1984, **25**, 4129.
4. Mori, K., Komatsu, M., Kido, M. and Nakagawa, K., *Tetrahedron*, 1966, **42**, 523.