Chromatography. The following solvent systems were used: BAW, *n*-BuOH–HOAc–H_2O (4:1:5 and 6:2:2); BuHCl, *n*-BuOH–2N HCl (1:1); HOAc–HCl, HOAc–conc. HCl–H_2O (3:1:8 and 15:3:82); dil. HOAc (85:15); dil. HCl (97:3); Bu-HCl–W, *n*-BuOH–HCl–H_2O (5:1:2).

Purification of anthocyanins. A concentrated extract was streaked on paper MN 218 (Machery and Nagel) and separated with BAW for 24–36 hr. Bands were further purified by successive chromatography in dil. HOAc and BAW on paper 2043b and 2945b (Schleicher and Schüll), pigments being eluted from the paper with MAW (MeOH–HOAc–H_2O, 70:5:25).

Spectral analysis. Purified pigments in MeOH containing 0.1% HCl were used to give absorptivities of 0.60–0.90 at the visible maximum.

Acid hydrolysis. Total hydrolysis of crude extracts or the purified pigments was in 10% HCl at 100°C for 1 hr. The aglycones were extracted with amyl alcohol and chromatographed, along with appropriate markers, on 0.1 mm cellulose TLC plates (Schleicher and Schüll) using HOAc–HCl. The aqueous hydrolysate was vacuum concentrated and chromatographed, with authentic sugars, with BAW (6:2:2) on 0.5mm cellulose TLC plates. Controlled hydrolysis of the purified pigments was in 10% HCl at 60–70° for at least 1 hr. Aliquots were examined on 0.1mm cellulose TLC plates using HOAc–HCl and Bu–HCl–W.

Alkaline hydrolysis. Alkaline hydrolysis was in 10% KOH under N_2 in the dark at 25° for 1 hr [14]. After acidification, the reaction mixture was evaporated to dryness under vacuum and the solid residue extracted with *n*-PrOH (3 × 1ml). The PrOH extract was evaporated to dryness and the residue redissolved in MeOH. Portions of this solution were chromatographed, with samples of the crude extract and authentic samples from *Matthiola incana*, on paper 2043b (Schleicher and Schüll) using BAW. An additional portion of each MeOH extract was evaporated to dryness, extracted with Et_2O (3 × 1ml) which was evaporated to dryness, and the residue redissolved in MeOH. This solution was spectrally examined and chromatographed along with hydroxycinnamic acid markers on 0.1mm cellulose TLC plates using BAW.

Acknowledgment—These investigations were supported by a grant from the Deutsche Forschungsgemeinschaft.

REFERENCES

1. Wit, F. (1937) *Genetica* **19**, 1.
2. Beale, G. H. (1941) *J. Genetics* **42**, 197.
3. Alston, R. E. (1964) In *Biochemistry of Phenolic Compounds* (Harborne J. B. ed.), p. 171. Academic Press, London.
4. Harborne, J. B. (1967) *Comparative Biochemistry of the Flavonoids*. Academic Press, New York.
5. Timberlake, C. F., Bridle, P. and Tanchev, S. S. (1971) *Phytochemistry* **10**. 165.
6. Hess, D. and Meyer, C. (1962) *Z. Naturforsch* **176**, 853.
7. Harborne, J. B. and Gavazzi, G. (1969) *Phytochemistry* **8**, 999.
8. Lowry, J. B. (1972) *Phytochemistry* **11**, 725.
9. Anderson, D. W., Gueffroy, D. E., Webb, A. D. and Kepner, R. E. (1970) *Phytochemistry* **9**, 1579.
10. Fong, R. A., Webb, A. D. and Kepner, R. E. (1974) *Phytochemistry* **13**, 1001.
11. Bloom, M. and Geissman, T. A. (1973) *Phytochemistry* **12** 2005.
12. Stafford, H. A. (1965) *Plant Physiol.* **40**, 130.
13. Fong, R. A., Kepner, R. E. and Webb, A. D. (1971) *Am. J. Enol. Vit.* **22**, 150.
14. Anderson, D. W., Julian, E. A., Kepner, R. E. and Webb, A. D. (1970) *Phytochemistry*, **9**, 1569.
15. Seyffert, W. private communication (1976).

Phytochemistry, 1977, Vol. 16, pp. 301–302, Pergamon Press, Printed in England.

STRUCTURE OF ANIBA-DIMER-A ISOLATED FROM *ANIBA GARDNERI**

YVONNE P. MASCARENHAS† and OTTO R. GOTTLIEB‡

†Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560 São Carlos, São Paulo;
‡Instituto de Química, Universidade de São Paulo, c.p. 20780, São Paulo, Brasil

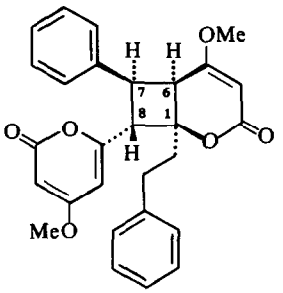
(*Received* 12 *July* 1976)

Key Word Index—*Aniba gardneri*; Lauraceae; aniba-dimer-A; *rel*-(1*R*,6*S*,7*S*,8*S*)-5-methoxy-7-phenyl-8-[6-(4-methoxy-2-pyronyl)]-1-(*E*)-styryl-2-oxabicyclo[4,2,0]octa-4-en-3-one.

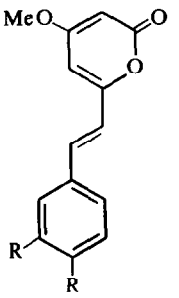
Abstract—Aniba-dimer-A from *Aniba gardneri* (Lauraceae) is shown by X-ray crystallography to be *rel*-(1*R*,6*S*,7*S*,8*S*)-5-methoxy-7-phenyl-8-[6-(4-methoxy-2-pyronyl]-1-(*E*)-styryl-2-oxabicyclo[4,2,0]octa-4-en-3-one.

Aniba-dimer-A (**1**), a constituent of *Aniba gardneri* (Meissn.) Mez (Lauraceae), was synthesized by exposure of the co-occurring monomer 5,6-dehydrocavain (**2a**) to sunlight. The structure proposed for aniba-dimer-A (**1**) relied on a consideration of NMR and MS data [2,3]. As already noted with respect to the analogous photodimer of tri-*O*-methylhispidin (**2b**) [4], it is not possible to distinguish between the four possible stereoisomers by consideration of vicinal coupling constants for the cyclobutane protons. The sole configurational detail

* Part 38 in the series 'The Chemistry of Brazilian Lauraceae'. For Part 37 see ref [1]. Sponsored by Conselho Nacional de Desenvolvimento Científico e Tecnológico, Fundação de Amparo à Pesquisa do Estado de São Paulo, Banco Interamericano de Desenvolvimento and Banco Nacional de Desenvolvimento Econômico.



(1)



(2a) R = H
(2b) R = OMe

advanced previously for aniba-dimer-A concerned the ring juncture, which was assumed to be *cis*. Treatment with base under equilibrating conditions should effect the isomerization of the 1,6-*trans* derivative to the 1,6-*cis* form and, indeed, an isomer of **1**, equally produced by photoirradiation of **2**, gave aniba-dimer-A (**1**) by percolation through alumina [5].

Unequivocal proof of the structure and the elucidation of the missing configurational details was achieved by direct X-ray crystallographic analysis. Crystals are orthorhombic, space group $Pna2_1$. Cell dimensions: $a = 11.058$ (1), $b = 20.616$ (1), $c = 10.345$ (1) Å; $V = 2358.4$ (5) Å^3. Observed density = 1.28 (2) g/cm^3; calculated density = 1.284 g/cm^3; $Z = 4$. The intensities of 1554 independent reflections measured by diffractometry with monochromatic CuKα radiation was used in the structure analysis. The phase problem was solved by the multisolution tangent refinement method [5], and the atomic parameters of carbons and oxygens were refined by the block-diagonal least-squares method to give $R = 0.122$. Anisotropic thermal parameters were assumed for all the atoms. Details of the X-ray structural analysis will be published in Anais da Academia Brasileira de Ciências.

The molecular structure found in the crystal is shown in Fig. 1.

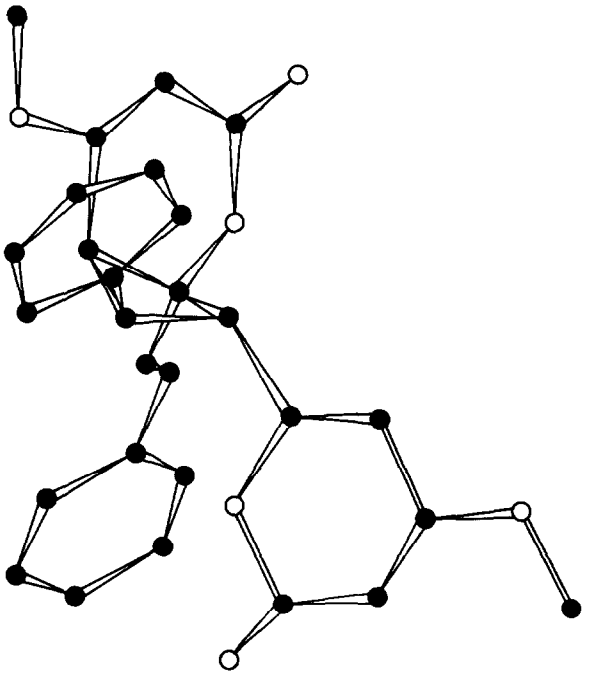


Fig. 1. X-ray structure of aniba-dimer-A (**1**) (● = carbon atoms, O = oxygen atoms).

REFERENCES

1. Aiba, C. J., Gottlieb, O. R., Pagliosa, F. M., Yoshida, M. and Magalhães, M. T. (1977) *Phytochemistry* **16**, in press.
2. Bülow, M. V. von and Gottlieb, O. R. (1968) *An. Acad. Brasil. Ciênc.* **40**, 299.
3. Rezende, C. M. A. da M., Bülow, M. V. von, Gottlieb, O. R., Pinho, S. L. V. and Rocha, A. I. da (1971) *Phytochemistry* **10**, 3167.
4. Bartle, K. D., Edwards, R. L., Jones, D. W. and Mir, I. (1967) *J. Chem. Soc. C*, 413.
5. Gottlieb, O. R., Veloso, D. P. and Pereira, M. O. da S. (1975) *Rev. Latinoamer. Quím*, **6**, 188.
6. Germain, G., Mein, P. and Woolfson, M. M. (1970) *Acta Cryst. B* **26**, 274.