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FURAN DITERPENES OF THE *PLATHYMENIA* GENUS

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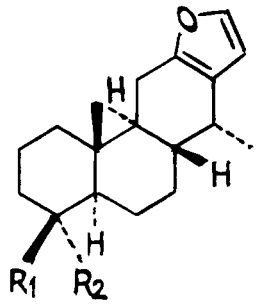
ABSTRACT.—Wood samples of *Plathymenia foliolosa* and *Plathymenia reticulata* were analyzed. Methyl vinhaticoate (**1**) and vinhaticyl acetate (**2**) were shown to be the major constituents in each species, respectively. The structure of the diterpene ester **2** was established as (4R, 7R, 11bR)-1,2,3,4,4a,5,6,6a,7,11,11a,11b-dodecahydro-4, 7, 11b-trimethylphenantro [3,2-*b*] furan-4-methanol acetate from the spectroscopic data, chemical reactions, and X-ray diffraction studies. Stereochemistries of the secondary methyl group at C-7 and the B/C ring junction in **1** were determined by chemical transformations of **1** and **2** to the alcohol **4**.

The "Vinhático" wood from Brazil was studied by King and co-workers in 1953 and attributed to the species *Plathymenia reticulata* Benth (1,2). The major constituent, easily isolated by crystallization from the heartwood hexane extract, was named methyl vinhaticoate (**1**) and shown to be a solid ester of a new diterpenic acid. Its stereochemistry, with the exceptions of the B/C ring junction and the secondary methyl group in the position C-7, was reported in 1955 (3). Later, Gottlieb and others (4), making reference to the unpublished work of Mors and Monteiro, reported the presence of **1** and vinhaticyl acetate (**2**) in *P. reticulata* and *Plathymenia foliolosa* Benth. However, for the latter substance, there were no details on the structural determination or stereochemical assignments. In the present work, we report the chemical investigation of wood samples of *P. reticulata* and *P. foliolosa* and discuss the structural determination of **1** and **2**, with the final stereochemistry of both substances determined by X-ray diffraction studied and chemical conversion.



1 $R_1=CH_3$ $R_2=COOMe$
2 $R_1=CH_3$ $R_2=CH_2OAc$
3 $R_1=CH_2OAc$ $R_2=CH_3$
4 $R_1=CH_3$ $R_2=CH_2OH$

DISCUSSION

Vinhaticyl acetate (**2**) and methyl vinhaticoate (**1**) were detected in both species, with **2** the major constituent in *P. reticulata* and **1** in *P. foliolosa*. The mass spectrum of the acetate has the molecular ion at 344 daltons. The furan ring was indicated by ir absorptions at 3180, 1650, 1510, 1450, and 895 cm^{-1}. The pmr spectrum revealed the presence of two unshielded protons, δ 7.00 (d, $J=2$ Hz) and 5.93 (d, $J=2$ Hz), characteristic of protons located in a furan system. The base peak at 108 daltons in the mass spectrum also indicated the presence of this moiety in the molecule.

The absorption at 1725 cm^{-1} in the ir, as well as the presence of a singlet (3H) at $\delta=1.91$ in the pmr spectrum, confirmed the presence of an acetate group. The presence of an AB system in the pmr ($\delta=3.76$, 1H, d, $J=10$ Hz and $\delta=3.49$, 1H, d, $J=10$ Hz) is indicative of an equatorial CH_2 group bonded to an heteroatom.

This assignment is supported by the peak at M^+ 73 daltons (loss of CH_2OCOCH_3). The presence of three additional methyl groups is detected by further analysis of the pmr spectrum ($\delta=0.96$, 3H, s; $\delta=0.80$, 3H, s and $\delta=0.90$, d, 3H, $J=7$ Hz).

From the above observations, as well as analysis of analogous substances isolated from this genus (1), it is possible to suggest the structure **2** for vinhaticyl acetate.

This structure is similar to vouacapenyl acetate (**3**) (5). However, the difference in melting points (80-81° for **2** and 112° for **3**) suggest that **2** is diastereomeric with **3** and, as such, was not previously reported in the literature. The stereochemistry was confirmed by X-ray analysis (Figure 1), and by the reduction of **1** with $LiAlH_4$ giving the alcohol **4** (mp 130-131°), which was identical with the saponification product of vinhaticyl acetate (**2**).

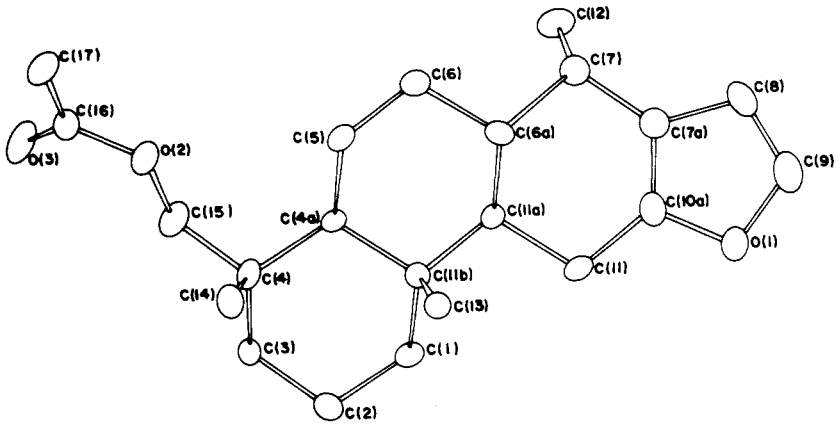


FIGURE 1. Spatial structure of vinhaticyl acetate (**2**).

Mmp of these two alcohols produced no depression. These results support the assignment of the structure of **2** as (4R,7R,11bR)-1,2,3,4,4a,5,6,6a,7,11,11a,11b-dodecahydro-4,7,11b-trimethylphenanthro[3,2-b] furan-4-methanol acetate.

There has been disagreement among botanists concerning these two studies originally described by Benthan (5) when he established the genus *Plathymenia*. Later, Ducke (6) considered the genus to be monospecific, with *P. reticulata* as a unique species. Heringer (7) and Mattos Filho (8) later proposed to designate the two species on the basis of the morphology of fruits, trunk bark, leaves, and wood anatomy. These data, and the analytical findings reported here, support the need for further chemical study to assess the value of **1** and **2** as taxonomic markers for this genus.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were taken on a Mettler hot stage apparatus model FP-5/52 and are uncorrected. The ir spectra were recorded on Perkin-Elmer 1320 spectrometer. The nmr spectra were taken on a Varian EM-360 with TMS as an internal standard. The mass spectra were run on a HP-5995 instrument. Specific rotations were taken on an automatic polarimeter Autopol III.

SOURCE OF PLANT MATERIAL.—The two authentic wood samples analyzed (*P. reticulata* and *P. foliolosa*) were kindly supplied by Prof. Armando Filho, Laboratory of Vegetal Anatomy, Botanical Garden, Rio de Janeiro, Brazil. Additional wood samples and voucher material were collected in the Minas Gerais Stater (*P. foliolosa*), in the Araripe National Forest, Ceará, and in the Piauí State (*P. reticulata*).

The final botanical classifications were done by Profs. P. Bezerra and A.G. Fernandes, Universidade Federal do Ceará, Brazil, and confirmed by Prof. Mattos Filho by anatomical examination.

Samples were finely ground and extracted with hexane in a soxhlet giving an oily residue for both species. These residues, when dissolved in MeOH and kept at 0° for 24 h, gave two different crystalline substances described below:

P. foliolosa afforded crystals, very soluble in $CHCl_3$ and Me_2CO, recrystallized from MeOH: mp 106°, $[\alpha]^{25}D$ +66.0 c=1, $CHCl_3$; ir ν max (KBr) 2992, 2937, 1712, 1650, 1510, 1450, 1240, 1002, 895 cm^{-1}; ms *m/z* M^+ 330, 271, 161, 133, 131, 109, 108, 81, 59, 55; pmr (CCL_4, 60 MHz) δ=6.99 (1H, d, J=2 Hz), 3.54 (3H, s, H_3 C-0), 1.07 (3H, s, Ch_3), 0.85 (3H, d, J=7 Hz), 0.82 (3H, s, CH_3).

All spectral data and physical constants are in agreement with the structure of methyl vinhaticoate (**1**) (Figure 2) and were comparable with the literature data (1).

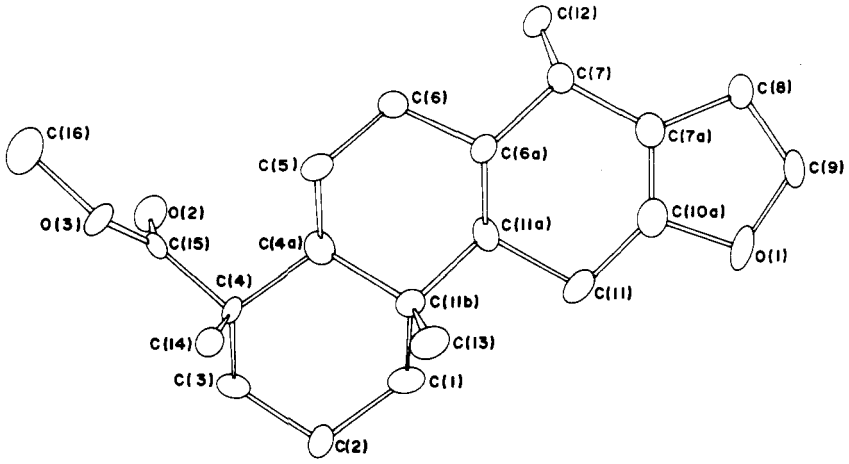


FIGURE 2. Spatial structure of methyl vinhaticoate (**1**).

P. reticulata gave large orthorombic crystals, very soluble in $CHCl_3$ and Me_2CO, mp 80-81°, $[\alpha]^{25}D$ +80.0 (c=1, $CHCl_3$); ir ν max (KBr) 3180, 2997, 2922, 1720, 1650, 1510, 1450, 1240, 1220, 1020, 895 cm^{-1}; ms *m/z* M^+ 344, 271, 175, 147, 145, 133, 131, 109, 108, 81, 43; pmr (CCl_4, 60 MHz) δ=7.00 (1H, d, J= 2 Hz), 5.93 (1H, d, J= 2 Hz), 3.76 (1H, d, J= 10 Hz), 3.49 (1H, d, J= 10 Hz): 1.91 (3H, s, H_3 C-0=0), 0.90 (3H, d, J=7 Hz), 0.86 (3H, s, CH_3), 0.80 (3H, s, CH_3).

SAPONIFICATION OF **2**.—Compound **2** (200 mg) was treated with KOH (200 mg) in MeOH (50 ml) and refluxed for 3 h. To this reaction mixture was added H_2O (50 ml), followed by extraction with $CHCl_3$ (3×15 ml). The $CHCl_3$ extract was dried and the solvent evaporated to afford a white solid that was crystallized from MeOH, mp 131-133°, $[\alpha]^{25}D$ +81 (c=1, CCL_3); ir ν max (KBr) 3450, 2950, 2900, 1650, 1510, 1450, 1390, 1200, 1050, 1035, 910 cm^{-1}; ms *m/z* M^+ 302, 271, 133, 131, 109, 108, 81, 79, 69, 67, 55, 41; pmr (CCl_4, 60 MHz) δ 7.10 (1H, d, J=2 Hz), 6.02 (1H, d, J=2 Hz), 3.60 (1H, d, J=10 Hz), 3.02 (1H, d, J=10 Hz), 0.95 (3H, d, J=7 Hz), 0.93 (3H, s, CH_3), 0.80 (3H, s, CH_3).

REDUCTION OF **1**.—To an ethereal solution (5 ml) of lithium aluminum hydride (80 mg), a solution of **1** (500 mg) in Et_2O (10 ml) was slowly added. After the vigorous initial reaction, the mixture was refluxed for an additional 1.3 h. Dilute HCl was carefully added, and the product isolated from the ethereal phase and recrystallized from MeOH as white crystals, mp 131-133° $[\alpha]^{25}D$ (c=1, $CHCl_3$), with identical spectral data as the product obtained by the saponification of **2**. Mmp (equimolecular mixture) of these two substance does not show any significative depression (mp 130-133°).

X-RAY DIFFRACTION ANALYSIS OF **1** AND **2**.—The cell dimensions and the intensity data were obtained using a CAD-4 automated diffractometer using CuK α radiation, θ-2θ scan mode (2θ up to 70°), variable scan rate. The intensities were corrected for Lorentz-polarization effects but not for absorption. The crystal structure was solved by direct method and refined by least square method using the SHELX-76 programs. The final disagreement index was 0.038. The intermolecular distances are all above 3.0 Å.

Analysis of **2** yielded cell constants as follows: a=8.035(1) Å, b=14.399(3) Å, c=16.758(2) Å, and indicated the space group P $2_12_12_1$, which with Z=4 (p calcd=1.18 g cm^{-3}) demanded 4 molecules by unitary cell. The final disagreement index was 0.038.

Analysis of **1** yielded cell constants are follows: a=6.851(2) Å, b=8.396(1) Å, c=32.033(3) Å, and

indicated the space group P $2_12_12_1$ which with Z=4 demanded 4 molecules by unitary cell. The final disagreement index was 0.071.

The complete crystal structures will be published elsewhere.

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