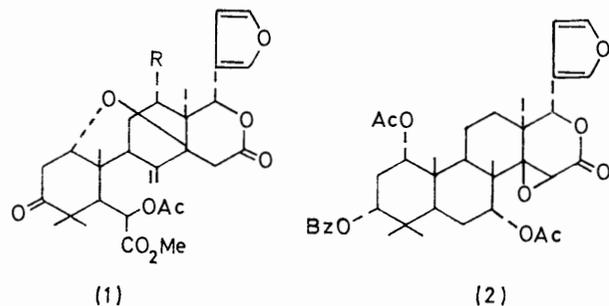


## Limonoid Extractives from Species of *Guarea*. An Unusual Shielding Effect on an Acetyl Group

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The bark of *Guarea* species has been found to be a rich source of limonoids. One has been identified as methyl 6,12 $\alpha$ -diacetoxyangolensate (1; R = OAc); the 12-acetyl group in this is strongly shielded by the furan ring.

THE genus *Guarea* (Meliaceae) contains a large number of species, mostly little known South American trees. Two, *G. cedrata* and *G. thompsonii*, are large African timber trees. The timber of the latter yields dihydrogedunin;<sup>1</sup> that of the former gives considerable amounts of glycerides and sesquiterpenes, but we have been unable to isolate any limonoids. We have now found that the bark of both species contains limonoids. The main constituent is dregeanin,<sup>2,3</sup> a complex limonoid which is still of unknown structure. However, the bark of *G. thompsonii* gave also two simpler compounds: methyl 6-acetoxyangolensate (1; R = H) and a new compound, m.p. 249–251°,  $[\alpha]_D^{26}$  –59.5°. The n.m.r. spectrum of the latter was strikingly similar to that of methyl 6-acetoxyangolensate, except that it showed an extra three-proton singlet at  $\delta$  1.50 and an extra one-proton multiplet at  $\delta$  5.16 p.p.m., partly concealed by the methylene resonances. The molecular weight was 586 (C<sub>31</sub>H<sub>38</sub>O<sub>11</sub>), and hydrolysis gave two molecules of acetic acid. It seemed probable that the compound was an acetoxy-derivative of methyl 6-acetoxyangolensate. Two problems remained, to locate the acetoxy-group, and to account for the very high-field resonance of the acetate methyl group ( $\delta$  1.50).



At 100 MHz, three bands were visible of the multiplet at  $\delta$  5.16 (splitting 6 Hz) but additional bands might have been hidden under the methylene signals at  $\delta$  5.07 and 5.30 or under the H-6 signal ( $\delta$  5.30, not resolved from the methylene signal). Irradiation at  $\delta$  2.50 caused the three visible bands at  $\delta$  5.07, 5.13, and 5.19 to collapse to a singlet at  $\delta$  5.16. This suggested strongly that we were observing three bands of a quartet, of which the fourth was concealed. In methyl 6-

acetoxyangolensate there are only two places an acetoxy-group can be introduced to give a multiplet: C-11 and C-12. Substitution at C-12 should give rise to a quartet, as observed; substitution at C-11 should give rise to a more complex multiplet. It therefore seemed probable the compound was a 12-acetate. In fact the 220 MHz spectrum of a solution in hexadeuteriobenzene showed the quartet clearly resolved from the neighbouring resonances.

A model shows that a 12 $\alpha$ -acetyl group in this structure is close to the furan ring, and we consider that it is the shielding effect of this ring that is responsible for the unusual chemical shift of the acetate methyl group. For comparison we prepared the benzoate (2) by benzoylation of 3-deacetylkhivorin. In the n.m.r. spectrum of this compound, in which the relative positions of the 1 $\alpha$ -acetate group and aromatic ring are similar to those in structure (1; R = OAc), one of the acetate methyl resonances was shifted upfield to  $\delta$  1.55, a position similar to that observed in our natural product. We consider that the evidence cited justifies the proposal of structure (1; R = OAc) for the *Guarea* compound.

### EXPERIMENTAL

**Extraction of *Guarea* bark.**—The bark was extracted with refluxing light petroleum (b.p. 60–80°) by our usual procedure.<sup>4</sup> Chromatography of the extract over alumina gave numerous fractions which we hope to describe later, methyl 6 $\alpha$ -acetoxyangolensate (ca. 0.001%), and methyl 6 $\alpha$ ,12 $\alpha$ -diacetoxyangolensate (ca. 0.01%) as prisms, m.p. 249–251° (from methanol),  $[\alpha]_D^{26}$  –59.5° (Found: C, 63.2; H, 6.6. C<sub>31</sub>H<sub>38</sub>O<sub>11</sub> requires C, 63.5; H, 6.5%). Quantitative hydrolysis gave 2 mol. equiv. of volatile acid, identified as acetic acid by the n.m.r. spectrum of the sodium salt.

**Benzoylation of 3-Deacetylkhivorin.**—Benzoylation of 3-deacetylkhivorin with benzoyl chloride in pyridine gave the benzoate, m.p. 268–270° (Found: C, 68.5; H, 7.0. C<sub>37</sub>H<sub>44</sub>O<sub>10</sub> requires C, 68.5; H, 6.8%),  $\delta$  1.55 (3H, s, OAc), 2.18 (3H, s, OAc), and 4.88 p.p.m. (1H, m,  $W_{\frac{1}{2}}$  5 Hz, H-3) (otherwise similar to khivorin).

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<sup>1</sup> J. R. Housely, F. E. King, T. J. King, and P. R. Taylor, *J. Chem. Soc.*, 1962, 5095.

<sup>2</sup> D. A. H. Taylor, *J. Chem. Soc.*, 1965, 3495.

<sup>3</sup> D. A. Okorie and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1968, 1328.

<sup>4</sup> E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1968, 1974.