

Extractives from *Khaya senegalensis* A. Juss

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CONTINUING our chemical survey of the genus *Khaya*, we have now examined extractives from a specimen of *Khaya senegalensis* which we collected at mile 170, south of Ilorin on the Lagos road. (Herbarium specimens are preserved as F.H.I. 060689). This was quite distinct from previous specimens that we have examined.¹⁻³ The timber gave methyl angolensate and minor amounts of other substances, the bark gave a crystalline mixture of methyl angolensate (20%) and a new

compound, $C_{27}H_{34}O_7$ (M^+ , 486), m.p. 252°, $[\alpha]_D^{20} -83^\circ$. The i.r. spectrum showed this to be a hydroxy-compound, and it gave an acetate, m.p. 170—174° (methanolate), $[\alpha]_D^{20} -84^\circ$. The n.m.r. spectrum was very similar to that of methyl angolensate, except for the appearance of a new doublet at δ 4.5 ($J = 3$ c./sec. $CHOH$, broad singlet after the addition of D_2O), and the downfield shift of two methyl groups from δ 1.2, 0.96 to δ 1.46, 1.40. This suggested that the compound

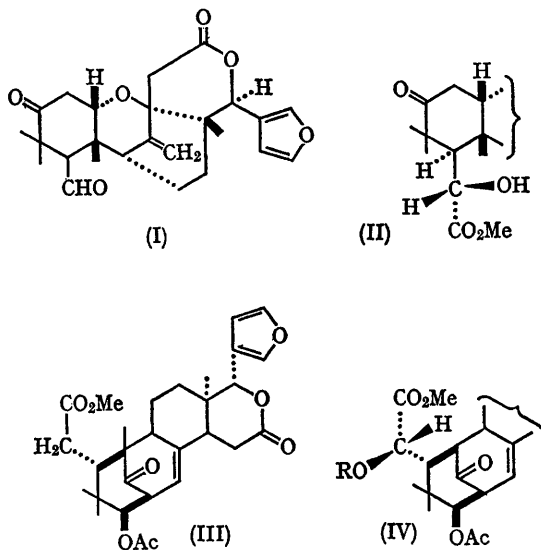
was a hydroxy-derivative of methyl angolensate. The pK_a of the derived acid (m.p. 275°) was 4.85, suggesting that the hydroxyl group was in position 6, α to the methoxycarbonyl group. This was confirmed by lead tetra-acetate oxidation of the acid, which gave a non-crystalline substance showing the expected spectral properties for the nor-aldehyde (I), in particular a doublet due to the aldehydic proton at δ 10.0, ($J = 2$ c./sec.). We therefore consider that the compound is methyl 6-hydroxyangolensate (II). This compound has been reported, but not described, by Overton and his colleagues⁴ as a constituent of *Khaya grandifoliola*.

Extraction of the seed, obtained from a group of trees in the same area, gave the known compounds khivorin, 3-deacetylkhivorin, methyl angolensate, and 7-deacetyl-7-oxokhivorin, and two new compounds. One of these, obtained in small quantity, was an alcohol, m.p. 260 – 265° (M^+ , 470), the other was an acetate, $C_{29}H_{36}O_8$, (M^+ , 512), m.p. 223 – 226° , $[\alpha]_D^{20} = -150^\circ$, isomeric with grandifoliolin.⁵ The n.m.r. spectrum of the two compounds were very similar, suggesting that one was the acetate of the other. The n.m.r. spectrum of the acetate was largely similar to that of grandifoliolin, indicating the presence of the same structural elements. Hydrolysis of the acetate, followed by esterification with diazomethane, gave a new alcohol, m.p. 193 – 195° , $[\alpha]_D^{20} = -89^\circ$, which on acetylation gave an isomeric acetate, m.p. 209 – 212° , $[\alpha]_D^{20} = -86^\circ$, apparently an epimer of the first since the base proton of the acetate, present in the spectrum of the natural isomer as a doublet at δ 4.75 ($J = 9$ c./sec.), was replaced by a broad singlet ($w/2 = 2$ c./sec.) at δ 4.68.

This change in the spectrum is characteristic of the epimerisation which occurs at C-3 on alkaline hydrolysis of swietenine,⁶ and we consider that our compound is 6-deoxydestigloylswietenine acetate (III). The assignment is fully supported by the detail of the n.m.r. spectrum, which in particular shows a one proton signal at δ 5.4 (pair of triplets, $w/2 = 3$ c./sec., separation 7 c./sec.) shifted downfield in the epimer to δ 5.9, with the same structure. This position, structure, and downfield shift on epimerisation at C-3 are all shown by the vinyl proton at C-30 in swietenine.⁶ The structural assignment is further supported by the isolation

from the bark of a small quantity of a new compound $C_{31}H_{38}O_{10}$, (M^+ , 570), m.p. 250 – 252° , $[\alpha]_D^{20} = -131^\circ$, which gave a very similar n.m.r. spectrum, except that it contained two acetate groups. On alkaline hydrolysis and re-esterification with diazomethane, this gave a compound, m.p. 223 – 226° , $[\alpha]_D^{20} = -88^\circ$, differing from the expected destigloylswietenine⁶ in m.p., and in that the n.m.r. spectrum showed four separate methyl groups at δ 0.7, 0.88, 1.10, 1.38; whereas in destigloylswietenine three of these are coincident at δ 1.0.⁶ It seemed probable that our natural diacetate was 6-epidestigloylswietenine diacetate (IV), and this is supported by the result of chromic acid oxidation of the diol, which gave a compound, not obtained pure or crystalline, but which showed in the n.m.r. spectrum four methyl groups absorbing in the places recorded for dehydrodestigloylswietenine.

From the recorded rotation increments, it seems probable but not certain⁷ that methyl 6-hydroxyangolensate is also epimeric at C-6 with swietenine; as shown in the formula (II).



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⁵ E. K. Adesogan and D. A. H. Taylor, *Chem. Comm.*, 1967, 225.

⁶ J. D. Conolly, R. Henderson, R. McCrindle, K. H. Overton, and N. S. Bhacca, *J. Chem. Soc.*, 1965, 6935.

⁷ cf., L. F. Fieser and M. Fieser, "Steroids", Reinhold, New York, 1959, p. 612.