Extractives from West African Timbers. Part XV. The Structure of the Low-melting Compound from *Khaya senegalensis*

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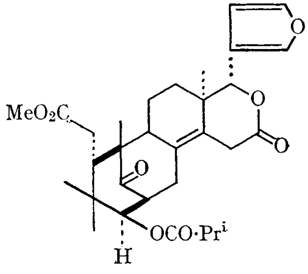
IN Part VI of this Series[1] we reported the isolation of a substance m.p. 88—100° $[\alpha]^{21}_{D} = -139°$, from the timber of *Khaya senegalensis*. The substance is a mixture, which we have been unable to purify further, but we now report that the main constituent (*ca.* 85%) is (I) the isobutyryl ester of the 3β-alcohol to which the corresponding ketone is *Cedrela odorata* Substance B[2] (=mexicanolide[3]). The remainder is probably largely the acetate of the same alcohol.

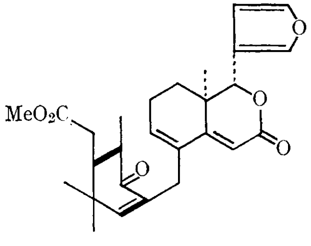
The mass spectrum indicates a molecular weight of 540, corresponding to a formula of $C_{31}H_{40}O_8$. The n.m.r. spectrum shows peaks attributable to a β-substituted furan (δ 7·4 and 7·6, α-protons; and δ 6·5, β-proton) a singlet at δ 5·7 (the H-17 proton of the meliacin series), and a three-proton singlet at δ 3·75 (CO_2Me group).

Treatment of (I) with methanolic sulphuric acid gave a trimethoxy-compound m.p. 154—155°, the isobutyrate of the alcohol (IIIa), analogous to the *Cedrela odorata* Substance C (IIId), obtained in a similar way from Substance B.[2] The structure of this isobutyrate has been proved by its partial synthesis from the alcohol (IIIa),[2] of which the structure and stereochemistry are definitely known from the *X*-ray-crystallographic analysis of Adeoye and Bekoe.[4]

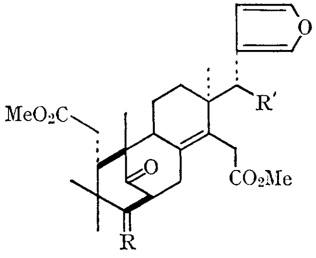
Hydrolysis of the isobutyrate of (IIIa) with alkali, followed by remethylation with diazomethane, gives not the expected alcohol (IIIa), but the stereoisomer (IIIb), which is obtained in small yield together with (IIIa) by the borohydride reduction of *Cedrela odorata* Substance C. The inversion must involve alkyl–oxygen fission of the isobutyrate ester at C-3, and is almost certainly due to a neighbouring-group effect in which an unstable intermediate lactone is formed between C-3 and the carboxyl group at C-6. The iodoacetate of (IIIc), which would be expected to undergo hydrolysis by acyl–oxygen fission much more readily than an isobutyrate, is hydrolysed as expected, without inversion at C-3.



(I)



(II)



(III) a; R=H, β-OH; R'=OMe
b; R=H, α-OH; R'=OMe
c; R=H, β-OH; R'=Cl
d; R=O, R'=OMe

Alkaline hydrolysis followed by acidification and steam distillation, gives in 92% yield a mixture of volatile acids. The n.m.r. spectrum of the sodium salts of these showed them to consist of about 85% of isobutyric acid and 15% of acetic acid. The non-volatile part from the hydrolysis gave a poorly crystalline substance, which on the basis of spectral evidence we consider to be (II), a substance obtained from mexicanolide by borohydride reduction, acetylation, and hydrolysis.[3]

(*Received, November* 30*th*, 1965; *Com.* 748.)

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[1] C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, **1963**, 980.

[2] C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *Chem. Comm.*, 1965, 281.

[3] J. D. Connolly, R. McCrindle, and K. H. Overton, *Chem. Comm.*, 1965, 162.

[4] S. A. Adeoye and D. A. Bekoe, *Chem. Comm.*, 1965, 301.