Nyasin, an Extractive from *Khaya nyasica* Stapf.

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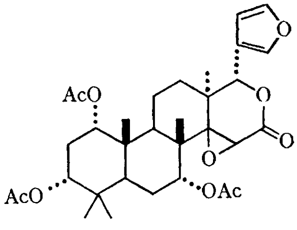
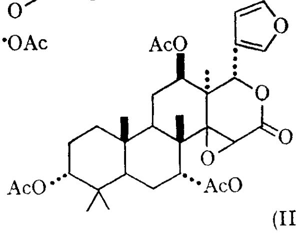
WE have examined a number of specimens of the timber of *Khaya ivorensis*. All except one (from Angola, which is not authenticated), have given khivorin (I) as the main extractive (*ca.* 0·1%);[1] and on thin-layer chromatography show a characteristic pattern of three spots, identified by isolation[2] as due to khivorin, methyl angolensate (*ca.* 0·002%), and mainly the noncrystalline 7-deacetylkhivorin. A seed sample has given methyl angolensate, *Cedrela odorata* substance B, and 6-deoxyswietenolide.[3] This last has not been isolated before as a natural product; but its acetate has been described as fissinolide[4] and as grandifoliolin.[5]

We now report the examination of *Khaya nyasica*, supplied by the Forest Department of Tanzania; the Forest Products Research Laboratory, Princes Risborough; and the Musée Royale de l'Afrique Centrale, Tervuren. All samples gave thin-layer chromatograms indistinguishable from those of *Khaya ivorensis*, and one (herbarium reference Semsei 1025) gave similar yields of extractives. Another sample (herbarium reference Semsei 943) gave as the major product a crystalline mixture (66 mg.), m.p. 280°. Chromatography of this over alumina gave khivorin and a new compound which we name nyasin, m.p. 302°, $[\alpha]_D^{22} = -42°$. Nyasin is very similar to khivorin in its infrared spectrum, and the mass spectrum shows it is an isomer of khivorin. The n.m.r. spectrum is also similar to that of khivorin, but two of the methyl groups are shifted (from δ 1·02, and 1·08 to δ 1·35 and 1·45) and the protons at the base of the acetates, instead of forming one unresolved band, show as three clearly resolved ABX triplets at δ 4·55, 4·60, 5·00 ($J_{AX} + J_{BX}$ = 5·2, 5·6, 5·4 c./sec.). These coupling constants are very similar to those recently determined for 3-deacetylkhivorin[6] and show that nyasin contains three quasi-axial acetoxyl groups; in each of which the base proton is coupled to two other protons. On biogenetic grounds it is most probable that two of these are at 3 and 7; a 7α-acetate is also indicated by the normal position of H-15 at δ 3·60,[7] and by the appearance of one of the acetoxy-methyls at δ 2·13, characteristically downfield of the other two at δ 2·02, 2·03. The third acetate can only be at C-12. Examination of Dreiding models suggests that the



(I)



(II)

observed coupling constants correspond to a 12α-acetate; but this does not account for the downfield shift of two methyl groups. Examination of Courtauld models shows that in the 12β-acetate there is a considerable degree of steric hindrance between the acetate and the furan ring, and that the molecule is more stable with ring c in the boat form in which the 12β-acetate is bent forward and contacts the C-10 and C-8 methyl groups. This steric effect is reinforced by the necessity of having the lactone group planar.[8] In this form the 12α-proton bisects the angle between the two C-11 protons, giving rise to the observed coupling constants. We therefore consider that nyasin is the 3α,7α,12β-triacetate (II).

In 11β-acetoxygedunin[9] there is a very similar shift of two methyl groups, and also in the 11β,12α-diacyloxy-compound, hirtin.[10] In anthothecol on the other hand, none of the methyl groups are significantly shifted from their positions in cedrelone; whereas H-1 is shifted downfield from δ 6·90 to δ 7·44. Although conformational analysis of anthothecol is complex, we consider this supports the original assignment as 11α-acetoxycedrelone.[11] The C-11 proton in anthothecol gives rise to a pair of overlapping ABX triplets (each $w/2 = 16$ c./sec.; separation 9 c./sec.) centred at δ 5·4.

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