

11 β -Acetoxykhivorin, a New Limonoid

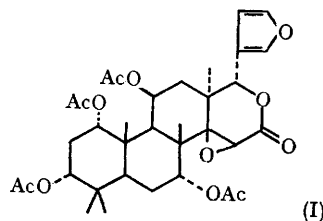
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THE timber of a specimen of *Khaya madagascariensis* Jumelle et Perrier collected near Majunga was rich in limonoids. The main constituent (ca. 0.1%) was obtained as crystals, m.p. 268°, $[\alpha]_D^{27} -27^\circ$, (methanolate, m.p. 165° and 218°). The spectra have the characteristic features of the khivorin group of limonoids, the n.m.r. shows four acetate groups, and the mass spectrum gave M 644, corresponding to an acetoxykhivorin isomer. The four protons adjacent to acetate groups show up in the n.m.r. spectrum as three resolved ABX peaks at δ 4.56 (J^* 5), 4.65 (J^* 6), and 4.74 (J^* 5 c./sec.) and a quintet at δ 51.0 (band width 18 c./sec.). Decoupling experiments showed that this signal was coupled with J 4 c./sec. to a doublet at δ 2.94, and with J 5 c./sec. to a pair of doublets at δ 1.45. After decoupling this appeared as a doublet (J 15 c./sec.), which we think is half an AB pair, the other half of which is concealed under the acetate bands. The only protons in a khivorin nucleus which could show this coupling are those at C-6 or C-11,¹ and since the presence of a 7 α -acetoxy-group is demonstrated by the normal position of H-15 at δ 3.57, we conclude that the

quintet is due to a proton at H-11. The coupling of 4 c./sec. to the H-9 proton shows that the H-11 proton is equatorial, that is the acetate is 11 β . The protons responsible for the ABX signals must now be at positions 1, 3, and 7; ond. and the coupling constants all equatorial, so that the compound is 11 β -acetoxykhivorin (I).

We have also found this compound in *Khaya nyasica* but not in any other species as yet. This may suggest a relation between these two botanically distinctive species.



(Received, July 22nd, 1968; Com. 993.)

¹ J. W. Powell, *J. Chem. Soc. (C)*, 1966, 1794.