The Meliacins (Limonoids): Minor Constituents of *Khaya anthotheca*: Reduction of the Meliacins with Zinc–Copper Couple

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The residues collected after isolation of anthothecol from *Khaya anthotheca* have afforded a new meliacin for which the structure (2b) (11β-acetoxyazadirone) is proposed. In addition, deacetylanthothecol and a sterol mixture shown by g.l.c. to consist of stigmasterol, β-sitosterol, campesterol, cycloeucalenol, and 24-methylenecycloartanol, were isolated. In the course of model experiments with anthothecol aimed at structural correlation with the new compound, zinc–copper couple was found to be a convenient and superior reagent for reduction of epoxides to olefins, αβ-unsaturated ketones to saturated ketones, and ketols and their acetates to ketones, in the meliacin series. By using this reagent new reduction products of anthothecol have been prepared and characterised.

FROM samples of the timber of the mahogany, *Khaya anthotheca*, obtained from Ghana, Nigeria, and Cameroun, anthothecol (1) has been isolated as the principal meliacin.[1] We have now investigated the residues accumulated over the years after the isolation of anthothecol from specimens of the timber collected from the Nigeria–Cameroun border. After removal of a small acidic fraction the neutral residue was chromatographed on alumina and three groups of compounds were identified as methylsterols, phytosterols, and meliacins. G.l.c. showed the methylsterol fraction to consist of cycloeucalenol and 24-methylenecycloartanol, and the phytosterol fraction to contain stigmasterol, β-sitosterol, and campesterol. By column and preparative layer chromatography the meliacin fraction was separated into two compounds, one of which was identified as deacetylanthothecol. The other was a new meliacin of molecular formula $C_{30}H_{38}O_6$ (elemental analysis and mass spectrum). Its i.r. spectrum showed the absence of a hydroxy-function but the presence of ester (1 712 cm^{-1}), αβ-unsaturated carbonyl (1 670 cm^{-1}) and β-substituted furan (1 500 and 875 cm^{-1}) groups. The n.m.r. spectrum was very similar to that of azadirone (2a) and in particular showed peaks attributable to H-1 and H-2 (δ 5.88 and 7.15), H-7 (5.5), and H-15 (5.21), besides a β-substituted furan and five tertiary *C*-methyl groups. There were however two acetate peaks at δ 1.92 and 2.08 and an additional low-field multiplet at δ 5.7 attributed to C*H*·OAc. This suggested that the compound was an acetoxyazadirone.[2] From the multiplicity of the C*H*·OAc signal (quintuplet, $W_{\frac{1}{2}}$ 20 Hz) the most likely position of the acetoxy-group is C-11β *cf.* δ 5.73 (quintuplet, $W_{\frac{1}{2}}$ 21 Hz) and 5.77 (quintuplet, $W_{\frac{1}{2}}$ 21 Hz) for the 11-H of 11β-acetoxygedunin and 6α,11β-diacetoxygedunin, respectively.[3] We therefore propose structure (2b) for the new meliacin.

The quantity of the compound available being inadequate for degradative studies, confirmation of the structure was sought from partial synthesis. Anthothecol appeared a suitable starting material for model studies since it possesses a cyclopentane ring D and an oxygen function at C-11, and was available in adequate quantity. Our first step involved reduction of the 14,15-epoxide. This has been achieved in low yield with chromium(II) chloride.[1] Kupchan *et al.*[4] have used zinc-copper couple to reduce epoxides in the sesquiterpene series. When anthothecol was treated with the latter reagent in boiling methanol, two compounds, A and B, were obtained. Their spectra indicated that in both the epoxy-group had been reduced to a double bond (H-15 absorptions at δ 5.70 and 5.90, respectively) and the 1,2-bond was saturated. In addition the diosphenol grouping was reduced [negative iron(III) chloride test]. Compound A has a hydroxy-function and is therefore formulated as (3a) whereas compound B is without a hydroxy-function and is formulated as (3b). The C*H*·OH proton in compound A gave an n.m.r. signal at δ 4.56 which was a singlet, although rather broad. Because of this, compounds A and B were initially formulated as (4a) and (4b) respectively. Structure (3) was however preferred for the following reasons. In the 14,15-deoxy-series with partial structure (5), H-15 absorbs at δ 5.65 for 7α-hydroxy- and at about 6.48—6.63 for 7-oxo-compounds.[5] Halsall *et al.*[6] observed that in (6a) the H-15 signal is at δ 5.26 whereas in (6b) it is at δ 5.60, and on oxidation of the hydroxy-group to the ketone (6c) there is a further downfield shift of the H-15 signal to δ 5.98. Thus there is a progressive downfield shift of the H-15 signal on going from 7-acetoxy through hydroxy to 7-oxo. However when compound A was acetylated there was no significant change in the position of the H-15 peak. It is therefore unlikely that the hydroxy-group is at C-7. Structure (4b) would imply the formation of compound B through reduction of the 7-oxo-group in anthothecol to a hydroxy-group. On the other hand (3b) could have arisen from reduction of the ketol (3a). The latter appeared more probable. In support of this, reduction of the acetate of compound A with the reagent gave compound B, which was also obtained by reduction of anthothecol acetate. Finally when compound B was reduced with aluminium isopropoxide in propan-2-ol (see later) a monohydroxy-compound was formed in the n.m.r. spectrum of which the H-15 signal had moved slightly upfield from δ 5.9

[1] C. W. L. Bevan, A. H. Rees, and D. A. H. Taylor, *J. Chem. Soc.*, 1963, 983; E. K. Adesogan, D. A. Okorie, and D. A. H. Taylor; *J. Chem. Soc.* (*C*), 1970, 205.

[2] D. Lavie and M. K. Jain, *Chem. Comm.*, 1967, 278; D. Lavie, E. C. Levy, and M. K. Jain, *Tetrahedron*, 1971, **27**, 3927.

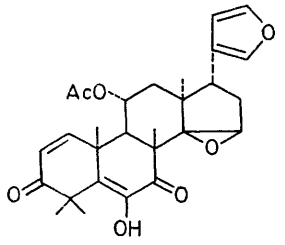
[3] J. D. Connolly, R. McCrindle, K. H. Overton, and J. Feeny, *Tetrahedron*, 1966, **22**, 891.

[4] S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, 1971, **36**, 1187.

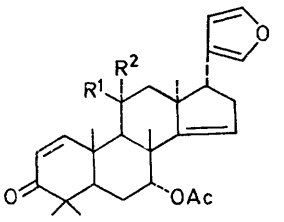
[5] S. N. Ohochuku, Ph.D. Thesis, Ibadan, 1970, p. 69.

[6] J. G. Buchanan and T. G. Halsall, *J. Chem. Soc.* (*C*), 1970, 2280.

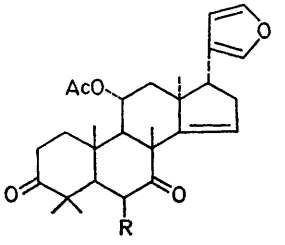
to 5.75, lending support to the presence of a 7-oxo-group in (3b). In view of the small coupling constant of the



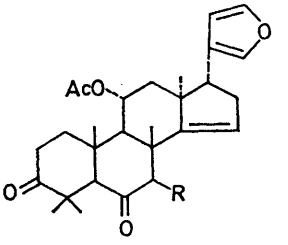
(1)



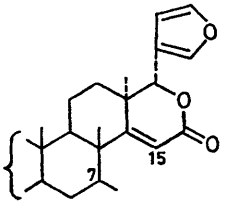
(2) a; $R^1 = R^2 = H$
b; $R^1 = OAc, R^2 = H$
c; $R = H, R^2 = OAc$



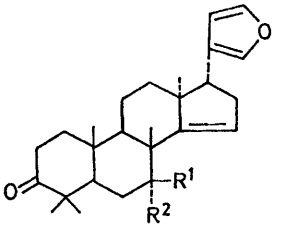
(3) a; R = OH
b; R = H



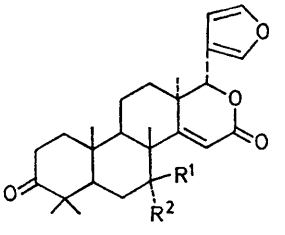
(4) a; R = OH
b; R = H



(5)



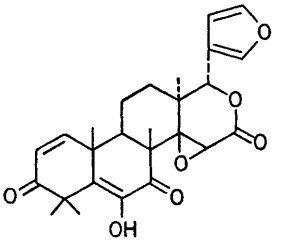
(6) a; $R^1 = H, R^2 = OAc$
b; $R^1 = H, R^2 = OH$
c; $R^1 R^2 = O$



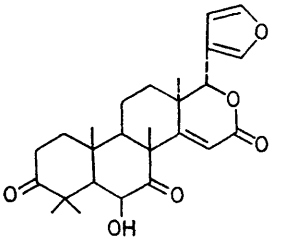
(7) a; $R^1 = H, R^2 = OAc$
b; $R^1 = H, R^2 = OH$
c; $R^1 R^2 = O$

C*H*·OH proton in compound A the 6-OH was assigned the β-configuration.

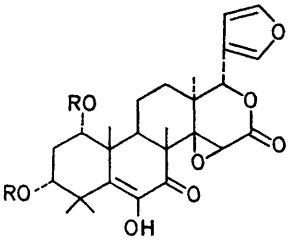
To examine the scope of its reaction the reagent was used to reduce other meliacins. Thus the 14,15-epoxy-group was smoothly reduced in khivorin and in dihydrogedunin, this therefore being a more convenient method for the preparation of the deoxy-compounds than reduction with chromium(II) chloride. The 1,2-double bond in gedunin was also readily reduced, thus enabling the preparation of the deoxy-dihydro-compounds (7a—c) in good yield and in one step from gedunin and the corresponding derivatives. The diosphenol (8) was prepared from 7-deacetoxy-7-oxogedunin with oxygen in potassium t-butoxide.[7] On reduction with zinc–copper couple it gave the ketol (9). The diosphenols (10a and b) were also prepared and characterised but the quantities obtained were insufficient to study their reduction. In the reduction of the diosphenols it is thought that the 5,6-double bond is reduced first to form a ketol, which is then more slowly



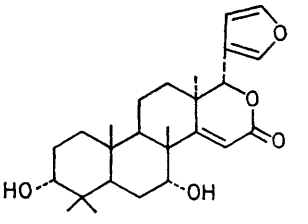
(8)



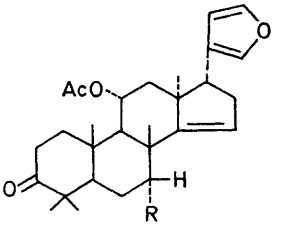
(9)



(10) a; R = Ac
b; R = H



(11)



(12) a; R = OH
b; R = OAc

reduced to the ketone. Thus in the higher boiling solvent ethanol, anthothecol gave mainly compound B (3b). The ketol acetate would be expected to be reduced more readily than the ketol, and in agreement with this anthothecol acetate gave only compound B.

[7] D. H. R. Barton, S. K. Pradhan, S. Sternhell, and J. F. Templeton, *J. Chem. Soc.*, 1961, 255; J. R. Housley, F. E. King, T. J. King, and P. R. Taylor, *ibid.*, 1962, 5095.

With regard to the model studies related to the partial synthesis of (2b), the diketone (3b) thus appeared a satisfactory intermediate. It was expected that its reduction with aluminium isopropoxide would give a diol which would have to be selectively oxidised to the 3-oxo-7-ol. To investigate this step the diol (11) was prepared from 7-deacetoxy-14,15-deoxy-1,2-dihydro-7-oxogedunin, and its selective oxidation to the 3-oxo-7-ol was successfully carried out with silver carbonate on Celite.[8] However with (3b) the reduction with aluminium isopropoxide was very slow and gave only a monohydroxy-derivative (12a). In the n.m.r. spectrum of the product the H-15 signal had moved upfield from δ 5.90 to 5.75, indicating that it was the 7-oxo-group that was reduced. The relative unreactivity of the 3-oxo-group towards reduction in similar compounds has been observed.[9] Acetylation of (12a) afforded the acetate (12b). By using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), deoxydihydrogedunin was oxidised back to deoxygedunin. It might be expected that with the same reagent (12b) would afford (2c), *i.e.* the 11-epimer of the natural product; and that with the corresponding 11β-acetate as starting material, it would be possible to obtain the natural product by the same procedure.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. (in Nujol) and u.v. (in methanol) spectra were taken with Perkin-Elmer 137 instruments. ^{1}H N.m.r. spectra were obtained for solutions in deuteriochloroform with Me_4Si as internal standard (Varian A56/60 spectrophotometer). Mass spectra were obtained with a Perkin-Elmer–Hitachi RMU 6E spectrometer. Silica gel refers to Merck silica gel (0.05—0.2 mm) and alumina refers to Spence activated alumina type H. T.l.c. plates were made with Merck silica gel PF 254 + 366 or PF 254 and were eluted with benzene–ethyl acetate (3 : 1). Light petroleum refers to the fraction of b.p. 60—80°. Gas chromatograms were run with glass columns (2 m × 2 mm) packed with 3% OV-17 on GasChrom Q with N_2 as carrier gas at 260 °C oven temperature. Optical rotations were measured for solutions in chloroform with a Perkin-Elmer 141 polarimeter at 20 °C.

Preparation of Zinc–Copper Couple (*ZCC*).—Zinc dust (50 g) was stirred for 1 min with dilute hydrochloric acid (3%; 40 cm^3). The resulting mixture was immediately washed by decantation; thrice with 3% hydrochloric acid, five times with distilled water, twice with copper sulphate solution (2%; 75 cm^3 each time), five times with distilled water, and finally five times with the solvent to be used for the reaction.

Extraction of Khaya anthotheca.—Timber samples of *Khaya anthotheca* were collected in Kumba Forest Reserve in Cameroun, as well as in Ghana and at the Nigeria–Cameroun border. The chopped wood was extracted as usual overnight with light petroleum. Anthothecol [1] was isolated from the extract in the usual way and by column chromatography on activated alumina. The residue (89 g) left after removal of most of the anthothecol from the extract was chromatographed on a column of activated alumina (1 500 g). Elution was carried out with light petroleum and mixtures of light petroleum and ether. 50% Ether in light petroleum eluted a mixture (A) of triterpenes (8 g), 60% ether–petroleum eluted a mixture (B) of methylsterols (10 g), and 70% ether–petroleum eluted a mixture (C) of sterols (30 g).

Mixture A. The mixture A (8 g) was chromatographed on a column of silica gel. 10% Ether–petroleum first eluted deacetylanthothecol, which gave crystals (from methanol) (3 g), m.p. 218°, $[\alpha]_D$ −67°, $\nu_{max.}$ 3 350, 1 680, 1 495, and 873 cm^{-1}, identical (^{1}H n.m.r. and mass spectra and g.l.c.) with an authentic sample [1] (Found: C, 71.1; H, 6.6. Calc. for $C_{26}H_{30}O_6$: C, 71.2; H, 6.0%). It readily formed an acetate, m.p. 233° (from methanol), $[\alpha]_D$ −79°, on treatment with acetic anhydride in pyridine, identical with authentic anthothecol acetate.

Further elution of the column with 50% ether–petroleum gave 11β-*acetoxyazadirone* (2b) as a gum (0.2 g), purified by preparative t.l.c. to afford crystals (120 mg), m.p. 230°, (from ether), $[\alpha]_D$ +35°, $\nu_{max.}$ 1 712, 1 670, 1 500, and 875 cm^{-1}; $\lambda_{max.}$ 213 nm (ε 10 000); δ 0.78 (3 H, s), 1.07 (6 H, s), 1.44 (3 H, s), 1.48 (3 H, s), 1.92 (3 H, s, OAc), 2.08 (3 H, s, OAc), 5.21 (1 H, unresolved t, H-15), 5.5 (1 H, d, *J* 10 Hz, H-2), 6.26 (1 H, m, furan β-H), 7.15 (1 H, d, *J* 10 Hz, H-1), 7.25 (1 H, m, furan α-H), and 7.4 (1 H, m, furan α-H), M^+ 494 (Found: C, 72.1; H, 7.9. $C_{30}H_{38}O_6$ requires C, 72.8; H, 7.7%).

Mixture B. This was homogenous on t.l.c., but g.l.c. and the mass spectrum showed it to be a mixture of cycloeucalenol and 24-methylenecycloartanol. Their acetates could not be separated on a silver nitrate–silica gel column.

Mixture C. This mixture, which was homogenous on t.l.c., could not be separated. G.l.c. and the mass spectrum showed it to contain three compounds, identified by co-injection on g.l.c. as β-sitosterol, stigmasterol, and campesterol.

Reduction of Anthothecol (1) *with Zinc–Copper Couple*.—Anthothecol (10 g) in methanol (1 l) was heated at reflux for 24 h with zinc–copper couple, prepared as described from zinc dust (200 g). The reaction mixture was cooled and filtered. The solvent was removed by distillation to give a crude product (9 g), which was chromatographed on silica gel. Chloroform–petroleum (1 : 3) eluted crude (3b) (1 g) and (3a) (6.5 g) in that order. Each product was further purified separately by rechromatography on silica gel and elution with petroleum–ether mixtures.

11α-*Acetoxy*-7-*deacetoxy*-1,2-*dihydro*-6-*hydroxy*-7-*oxo*-*azadirone* (3a) on rechromatography was eluted with petroleum–ether (1 : 4) and crystallised from methanol, m.p. 230°, $[\alpha]_D$ −45°; $\nu_{max.}$ 3 600, 1 715, 1 690, 1 500, and 871 cm^{-1}; δ 0.75 (3 H, s), 0.95 (3 H, s), 1.21 (6 H, s), 1.45 (3 H, s), 2.03 (3 H, s, OAc), 3.40br (1 H, s, exchanged with D_2O, 6-OH), 4.56br (1 H, s, H-6), 5.25 (1 H, m, H-11), 5.7 (1 H, t, *J ca.* 2 Hz, H-15), 6.26 (1 H, m, furan β-H), 7.25 (1 H, m, furan α-H), and 7.33 (1 H, m, furan α-H), M^+ 468, (Found C, 71.5; H, 7.5. $C_{28}H_{36}O_6$ requires C, 71.8; H, 7.6%).

11α-*Acetoxy*-7-*deacetoxy*-1,2-*dihydro*-7-*oxoazadirone* (3b) was eluted with petroleum–ether (1 : 1) and crystallised from methanol, m.p. 205—206, $[\alpha]_D$ +40°; $\nu_{max.}$ 1 712, 1 495, and 850 cm^{-1}; δ 0.75 (3 H, s), 0.90 (3 H, s), 1.08 (3 H, s), 1.10 (3 H, s), 1.35 (3 H, s), 5.3 (1 H, m, H-11), 5.9 (1 H, t, *J ca.* 2 Hz, H-15), 6.26 (1 H, m, furan β-H), 7.25 (1 H, m, furan α-H), and 7.35 (1 H, m, furan α-H); M^+ 452

[8] V. Balogh, M. Fetizon, and M. Golfier, *J. Org. Chem.*, 1971, **36**, 1339; M. Fetizon, M. Golfier, and J. M. Louis, *Chem. Comm.*, 1969, 1102.

[9] R. Hodges, S. G. McGeachin, and R. A. Raphael, *J. Chem. Soc.*, 1963, 2515.

(Found: C, 74.2; H, 7.7. $C_{28}H_{36}O_5$ requires C, 74.3; H, 8.0%).

Conversion of (3a) *into* (3b). Compound (3a) (1 g) was acetylated overnight with acetic anhydride–pyridine. The product, which was not obtained crystalline, was reduced in methanol with zinc–copper couple as for (1) to afford (3b) as crystals (400 mg), m.p. 205° (from methanol), identical (mixed m.p. and spectra) with the compound described above.

Zinc–Copper Couple Reduction of Gedunin and Derivatives.—*14,15-Deoxy-1,2-dihydrogedunin* (7a). Gedunin (1 g) in dry methanol (200 cm³) was treated as for anthothecol with zinc–copper couple (prepared from 20 g of zinc dust) to give 14,15-deoxy-1,2-dihydrogedunin, m.p. 222°, identical with a sample [10] obtained from gedunin by reduction with chromium(II) chloride followed by hydrogenation over Adams catalyst.

7-Deacetyl-14,15-deoxy-1,2-dihydrogedunin, (7b). 7-Deacetylgedunin (2 g) in dry methanol (300 cm³) was treated as usual with zinc-copper couple (from 40 g of zinc dust). Work-up and purification by preparative t.l.c. gave (7b) as crystals (1 g) from methanol, m.p. 242—244°, $[\alpha]_D$ + 117°, identical with a sample obtained by the chromium(II) chloride reduction procedure.[10]

7-Deacetoxy-14,15-deoxy-1,2-dihydro-7-oxogedunin (7c). 7-Deacetoxy-7-oxogedunin (2 g) in dry methanol (250 cm³) was treated as above with zinc–copper couple (from 40 g of zinc dust). Work-up and purification by preparative t.l.c. gave (7c) as crystals (1 g) from methanol–chloroform, m.p. 268—272°, $[\alpha]_D$ +2°, identical with a sample obtained by the chromium(II) chloride reduction procedure.[10]

7-Deacetoxy-14,15-deoxy-7-oxokhivorin.— 7-Deacetoxy-7-oxokhivorin (1 g) in dry methanol (150 ml) was reduced as above with zinc–copper couple (from 20 g of zinc dust). Work-up and chromatography on silica gel [elution with petroleum–ether (1 : 1)] gave the product as crystals (500 mg) from methanol, m.p. 263°. Its spectra were identical with published data.[11]

Conversion of 7-Deacetoxy-7-oxogedunin into the Diosphenol (8).—Finely powdered 7-deacetoxy-7-oxogedunin (2.5 g) in a solution of potassium t-butoxide in t-butyl alcohol (1M; 500 cm³) was shaken with oxygen until absorption had virtually stopped (*ca.* 10 min). The mixture was diluted with water (300 ml), acidified (dilute HCl), and extracted with chloroform. The extract was extracted in turn with sodium hydroxide (4M). The alkaline extract was acidified (dilute HCl) and the precipitate taken up in chloroform. This solution was washed with distilled water, dried (Na_2SO_4), filtered, and distilled to leave a residue (2 g), which gave a positive enol test with iron(III) chloride. The residue was chromatographed on silica gel. Elution with petroleum–ether (1 : 1) gave the crude *7-deacetoxy-5,6-didehydro-6-hydroxy-7-oxogedunin* (1 g) which after re-chromatography on silica gel gave crystals from petroleum–ether; m.p. 208°, $[\alpha]_D$ +26°; $\nu_{max.}$ 3 450 (OH), 1 750 (lactone), 1 670 (C=O of diosphenol), and 1 494 and 874 cm⁻¹ (β-substituted furan); δ 1.10 (6 H, s, 2 CH_3), 1.31 (3 H, s, CH_3), 1.50 (3 H, s, CH_3), 1.55 (3 H, s, CH_3), 4.10 (1 H, s, H-15), 5.50 (1 H, s, H-17), 6.10 (1 H, d, *J* 10 Hz H-2), 6.30 (1 H, m, furan β-H), 6.60 (1 H, s, exchanged with D_2O, 6-OH), 6.88 (1 H, d, *J* 10 Hz, H-1), and 7.45 (2 H, m, furan α-protons) (Found: C, 68.7; H, 6.5. $C_{28}H_{28}O_7$ requires C, 69.0; H, 6.2%).

Reduction by Zinc–Copper Couple of the Diosphenol (8.)—The diosphenol (8) in dry methanol (150 cm³) was reduced as above with zinc–copper couple (from 25 g of zinc dust). The product (1 g) isolated by normal work-up was chromatographed on silica gel and gave *7-deacetoxy-14,15-deoxy-1,2-dihydro-6-hydroxy-7-oxogedunin* as crystals (from methanol), m.p. 243°, $[\alpha]_D$ +92°; $\nu_{max.}$ 3 400 (OH), 1 725 (lactone), 1 680 (C=O), and 1 495 and 874 cm⁻¹ (β-substituted furan); δ 1.00 (3 H, s, CH_3), 1.10 (3 H, s, CH_3), 1.23 (6 H, s, two CH_3), 1.60 (3 H, s, CH_3), 4.7 (1 H, m, H-6), 5.10 (1 H, s, H-17), 6.0 (1 H, s, H-15), 6.51 (1 H, m, furan β-H), and 7.53 (2 H, m, furan α-protons) (Found: C, 70.8; H, 7.25. $C_{26}H_{32}O_6$ requires C, 70.9; H, 7.3%).

Conversion of 7-Deacetoxy-7-oxokhivorin into the Diosphenols (10a *and* b).—7-Deacetoxy-7-oxokhivorin (2.0 g) in a solution of potassium butoxide in t-butyl alcohol (1M; 450 cm³) was shaken with oxygen until absorption had virtually terminated (*ca.* 10 min). The products were isolated with 7-deacetoxy-7-oxogedunin. The material (2 g) was chromatographed on silica gel. Two diosphenols were eluted with n-hexane–ether (3 : 2 and 1 : 1). The less polar was purified by preparative t.l.c. and gave crystals of *7-deacetoxy-1,3-di-O-acetyl-5,6-didehydro-6-hydroxy-7-oxokhivorin* (10a) (from hexane–ether), m.p. 250°, $\nu_{max.}$ 3 450 (OH), 1 750 (lactone), 1 715 (acetate), 1 675 (C=O of diosphenol), and 1 500 and 875 cm⁻¹ (β-substituted furan); δ 0.96 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 1.33 (6 H, two Me), 1.41 (3 H, s, CH_3), 1.95 (3 H, s, Ac), 2.06 (3 H, s, Ac), 4.0 (1 H, s, H-15), 5.45 (1 H, s, H-17), 6.35 (1 H, m, furan β-H), 6.60 (1 H, s, exchanged with D_2O, 6-OH), and 7.45 (2 H, m, furan α-hydrogens) (Found: C, 64.2; H, 7.3. $C_{30}H_{36}O_{10}$ requires C, 64.7; H, 6.5%).

The second product was further purified by chromatography on silica gel and gave crystals of *7-deacetoxy-5,6-didehydro-6-hydroxy-7-oxokhivorin* (10b) (from hexane–ether), m.p. 245°, $[\alpha]_D$ −95°; $\nu_{max.}$ 3 400 (OH), 1 730 (lactone), 1 655 (C=O of diosphenol), and 1 500 and 875 cm⁻¹ (β substituted furan); δ 1.05 (6 H, s, two Me), 1.20 (3 H, s, CH_3), 1.33 (3 H, s, CH_3), 1.5 (3 H, s, CH_3), 4.08 (1 H, s, H-15), 5.50 (1 H, s, H-17), 6.43 (1 H, m, furan β-H), and 7.50 (2 H, m, furan α-hydrogens) (Found: C, 65.9; H, 6.9. $C_{26}H_{32}O_8$ requires C, 66.1; H, 6.8%).

7-Deacetyl-3;14,15-dideoxy-1,2-dihydro-3-hydroxygedunin, (11) *and its Conversion into the Ketol* (7b).—7-Deacetoxy-14,15-deoxy-1,2-dihydro-7-oxogedunin (7c) (2 g) and aluminium isopropoxide (5 g) in dry propan-2-ol (200 cm³) were heated with slow removal by distillation of acetone and propan-2-ol for 3 h. The reaction was stopped when no more acetone was detected (2,4-dinitrophenylhydrazine test) in the distillate. The reaction mixture was further concentrated by distillation to a small volume. It was cooled, poured with stirring into dilute hydrochloric acid, and extracted with chloroform. The extract was dried, filtered, and distilled to leave a residue (1.4 g). The unpurified diol (11) (t.l.c., i.r., and ^1H n.m.r. data agreed with its structure) in dry benzene (250 cm³) and silver carbonate on Celite (40 g) were heated at reflux (heating mantle) for 20 h, after which the starting material had all reacted (t.l.c.). The mixture was cooled and filtered, and the solvent removed by distillation. The residue (800 mg) crystallised from methanol and was identical (m.p., mixed m.p, i.r. and ^1H n.m.r. spectra) with (7b) obtained from zinc–copper couple reduction of 7-deacetylgedunin.

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[11] M. E. Obasi, Ph.D. Thesis, Ibadan, 1971, p. 42.

Reduction of the Ketone (3b) *with Aluminium Isopropoxide*.—The ketone (3b) (2.0 g) and aluminium isopropoxide (5 g) in dry propan-2-ol (200 ml) were heated as above with slow removal of acetone. The reaction did not go to completion even after several hours heating with occasional addition of further dry propan-2-ol and aluminium isopropoxide. The product was however worked up as above, and chromatographed on silica gel. Ether–petroleum (1 : 9) eluted starting material (3b) (450 mg), m.p. 205°, and the reduction product, 11α-*acetoxy*-7-*deacetyl*-1,2-*dihydroazadirone* (12a) (500 mg), was eluted with ether–petroleum (1 : 4) and crystallised from methanol, m.p. 214°, $[\alpha]_D$ −75°; $\nu_{max.}$ 3 400 (OH), 1 725 (acetate), 1 700 (C=O), and 1 500 and 875 cm^{-1} (β-substituted furan); δ 0.80 (3 H, s, CH_3), 0.83 (3 H, s, CH_3), 1.03 (3 H, s, CH_3), 1.06 (3 H, s, CH_3), 1.12 (3 H, s, CH_3), 2.33br (1 H, s, exchanged with D_2O, 7-OH), 3.25 (1 H, m, H-7), 5.12 (1 H, m, H-11), 5.75 (1 H, t, *J* 3 Hz, H-15), 6.25 (1 H, m, furan β-H), and 7.25 and 7.35 (each 1 H, m, furan α-H) (Found: C, 74.3; H, 8.3. $C_{28}H_{38}O_5$ requires C, 74.0; H, 8.4%). Treatment with acetic anhydride in acetic acid in the presence of toluene-*p*-sulphonic acid gave the *acetate* (12b), m.p. 226° (from methanol), $[\alpha]_D$ −30°; δ 4.7 (1 H, m, H-7), 5.66 (1 H, t, *J ca.* 3 Hz, H-15), 6.30 (1 H, m, furan β-H), 7.26 and 7.40 (each 1 H, m, furan α-H), and 2.03 and 2.09 (each 3 H, s, AcO) (Found: C, 72.4; H, 8.3. $C_{30}H_{40}O_6$ requires C, 72.6; H, 8.1%).

Oxidation of Deoxydihydrogedunin by DDQ.—Deoxydihydrogedunin (7a) (400 mg) and dichlorodicyanoquinone (900 mg) in dry dioxan (30 cm^3) were heated at reflux for 32 h. The cooled mixture was filtered and diluted with water. The product was extracted with dichloromethane (3 × 100 cm^3); the extract was washed with water, dried, and filtered and evaporated and the residue was purified by preparative t.l.c. and crystallised from methanol to give deoxygedunin (150 mg).

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