West African Timbers. Part XIV. The Structure of Turraeanthin, a Triterpene Monoacetate from *Turraeanthus africanus*

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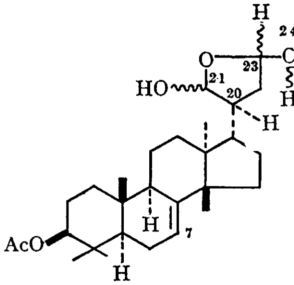
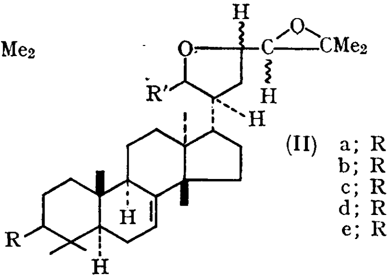
EXTRACTION of the heartwood of *Turraeanthus africanus* (Meliaceae)[1] (*cf.* Ref. 1) has afforded a new compound, turraeanthin (I), m.p. 218—220°, $[\alpha]_D + 3°$. Analyses and mass spectrometry indicate the formula $C_{32}H_{50}O_5$ and ions corresponding to the loss of acetic acid and water appear in the mass spectrum. The infrared spectrum has bands at 3590 (OH), 1724, and 1245 (OAc), 822 (C=CH), and 1030 cm.$^{-1}$. There is no band indicative of a β-substituted furan. Bands are found in the n.m.r. (60 Mc./sec.) spectrum at τ 4·65 (2H at C-7 and C-21), 5·45 (1H at C-3), 6·05 (1H at C-23), 6·50 (1H in OH), 7·15 (doublet) (1H at C-24), 7·95 (–O–CO–CH_3), 8·68 (2Me) and 8·98—9·19 (5Me). The methyl bands are singlets. In the presence of D_2O the band at τ 6·50 disappeared indicating the presence of only one OH group while the broad band at τ 4·65 sharpened. At 100 Mc./sec. the methyl region was resolved into four peaks at τ 8·94 (1Me), 9·00 (1Me), 9·07 (2Me), and 9·15 (1Me) and the band at τ 4·65 was resolved into two peaks at τ 4·63 (1H at C-21) and 4·73 (1H at C-7).

Oxidation with chromic acid–pyridine gave a γ-lactone (IIa) $C_{32}H_{48}O_5$, $\nu_{\max}$ 1780 cm.$^{-1}$ (no OH band at 3590 cm.$^{-1}$). The n.m.r. spectrum had no band at τ 6·50 and the band at τ 4·64 was due to only one proton so a 5-membered cyclic hemiacetal structure must be present in turraeanthin. The other proton absorbing at τ 4·65 is a vinyl proton indicating the presence of a trisubstituted double bond. It is not hydrogenated under mild conditions and ozonolysis does not afford any volatile fragment. The double bond is therefore in a ring. Alkaline hydrolysis of turraeanthin affords the hydroxy-compound (IIb), $C_{30}H_{48}O_4$, m.p. 182—184°, $[\alpha]_D - 35°$, oxidation of which gives a keto-lactone (IIe) and the ketone (IIc). Acetylation of turraeanthin affords an acetate, $C_{33}H_{52}O_6$ (IId), also obtained by acetylation of the hydroxy-compound (IIb). Turraeanthin is therefore a monoacetate. The band at τ 5·45 is due to the proton on the acetoxy-carbon. Its band-width and shape is typical of that of the 3α-proton of triterpene 3β-acetates.

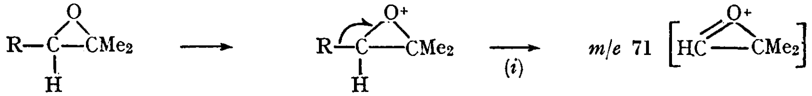
The fifth oxygen atom of turraeanthin is present as an epoxy-group. Both turraeanthin and its lactone (IIa) show a doublet at τ 7·15 (*J*, 8 c./sec.) due to a proton on an epoxy-ring. This together with the absorption of two methyl groups at τ 8·75 suggests the presence of the group (III). This accounts for a strong peak at *m/e* 71 in the



(I)



(II) a; R = H, β-OAc; R′ = O
b; R = H, β-OH; R′ = H, ξ-OH
c; R = O; R′ = H, ξ-OH
d; R = H, β-OAc; R′ = H,ξ-OAcOAc
e; R = O; R′ = O



(III)

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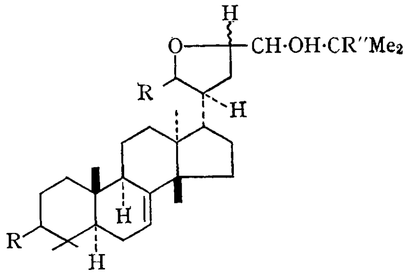
mass spectrum of the lactone (IIa) resulting from the fragmentation mechanism (i) indicated. Treatment of turraeanthin with methanolic hydrogen chloride converted the hemiacetal grouping into an acetal and opened the epoxide ring to give the chlorohydrin (IVa) and the methoxyhydrin (IVb). The former had bands at τ 8·35 and 8·40 (2Me of $CClMe_2$). A similar reaction with methanolic sulphuric acid also caused hydrolysis of the acetate group affording compound (IVc) which with chromic acid–pyridine afforded the ketone (IVd) the negative Cotton curve of which was almost superimposable upon that of flindissone lactone (Va).[2] The relationship of the epoxide group to the hemiacetal group was demonstrated by a spin decoupling experiment on the lactone (IIa). Irradiation of the proton at C-23 absorbing at τ 5·85 caused collapse of the doublet at τ 7·15 due to the epoxide proton at C-24.

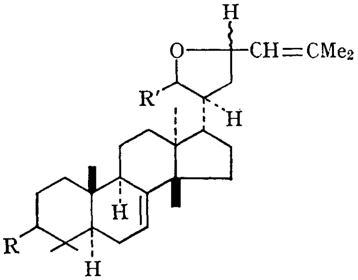
The presence in Meliaceae and the related Rutaceae and Simarubaceae species of a number of degraded triterpenes such as limonin,[3,4] gedunin,[5,6] and simarolide,[7,8] all of which can be formally derived by oxidative degradation of tirucalla-7,24-dien-3β-ol (≡ 20αH-butyrospermol) together with the evidence described suggested that turraeanthin was (I) and closely related to flindissol (Vb)[2,9] isolated from *Flindersia dissosperma* Domin and *F. maculosa* Lindl, species related to the Meliaceae species. The keto-lactone (IIe) with sulphuric acid in ether gave the glycol (IVe). This was converted (*cf.* ref. 10) into the cyclic thionocarbonate and hence to a product which after several recrystallisations to remove traces of trimethyl phosphite afforded flindissone lactone (Va), m.p. 190—194°, $[\alpha]_D$ − 81°. No depression of melting point was observed on admixture with flindissone lactone, m.p. 191—193°, $[\alpha]_D$ − 83°. Infrared, mass, and n.m.r. spectra were identical.

It is hoped that the remaining stereochemical features of (I), *i.e.* at C-21, C-23, and C-24 will be determined by *X*-ray-crystallographic examination of the *p*-bromobenzoate derivative (IVf).

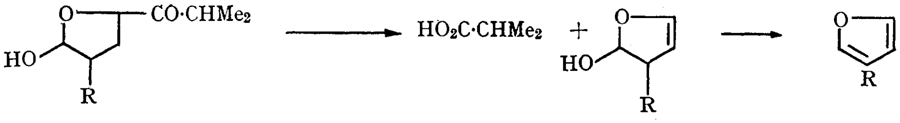
The side-chain of turraeanthin represents a further stage beyond that found in flindissol in



(IV) a; R = H, β-OAc; R′ = H, ξ-OMe; R″ = Cl
b; R = H, β-OAc; R′ = H, ξ-OMe; R″ = OMe
c; R = H, β-OH; R′ = H, ξ-OMe, R″ = OMe
d; R = O; R′ = H, ξ-OMe; R″ = OMe
e; R = O; R′ = H, ξ-OH; R″ = OH
f; R = H, β-OAc; R′ = H,-*p*-bromobenzoate; R″=Cl



(V) a; R = O; R′ = O
b; R = H, α-OH; R′ = H, α-OH



(VI) (VII) (VIII)

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the degradation of the tirucallol side-chain to a β-substituted furan. One possible route to the furan structure is the isomerisation of the epoxide to the ketone (VI) followed by the oxidation of this to give (VII). Analogies for this oxidation are to be found in the biogenesis of nyctanthic acid,[11,12] limonin,[3] and methyl angolensate.[13] Finally, dehydration of (VII) leads to the furan (VIII).

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