The Meliacins (Limonoids). Acid-catalysed Reactions of Meliacin Epoxides

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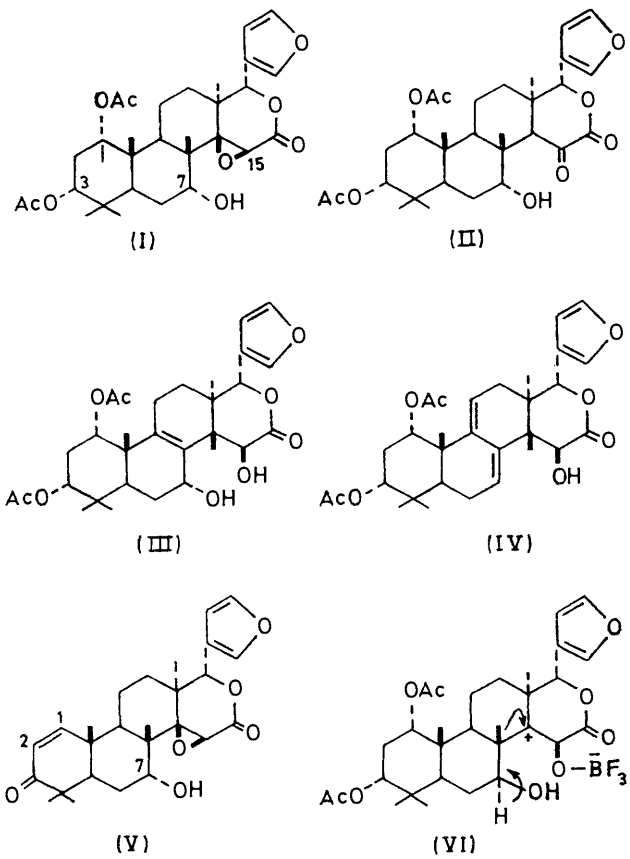
Meliacin 14,15-epoxides in which ring D is a δ-lactone are stable to acid if C-7 carries an oxo- or an acetoxy-function. However, such compounds having a 7α- or 7β-hydroxy-group undergo ready acid-catalysed rearrangements not hitherto observed. The 1,2-epoxy-3-oxo-system, in the absence of the 14,15-epoxide function, is slowly hydrolysed by acid to a diol. Structures have been assigned to the products of the rearrangement reactions.

THE acid-catalysed reactions of meliacin 14,15-epoxides in which ring D is a cyclopentane system have been studied.[1] In contrast, the meliacin 14,15-epoxides with a δ-lactone system in ring D are generally considered to be stable to acid. We recently published a preliminary report [2] of some acid-catalysed epoxide rearrangements not hitherto observed which are undergone by the latter class of meliacins. We now give further details of this work as well as an account of the reactions of 1,2-epoxygedunin derivatives. The rearrangements were generally carried out by treatment of a solution of the epoxide in dry benzene with a few drops of boron trifluoride–ether complex for 6—12 h. Under these conditions the 14,15-epoxy-δ-lactone systems were stable in compounds having a 7-acetoxy- or 7-oxo-group, whereas the 7-hydroxy-derivatives gave a variety of rearrangement products.

7-Deacetylkhivorin (I) was made by Meerwein–Ponndorf reduction of 7-oxokhivorin. Contrary to earlier reports,[3] it was obtained as a crystalline product. 7β-Hydroxykhivorin was prepared by reduction of 7-oxokhivorin with sodium borohydride. In its n.m.r. spectrum the 7-proton gave rise to a broad signal at τ 6·16 ($W_{\frac{1}{2}}$ 10 Hz) and the 15-proton signal had suffered a paramagnetic shift to τ 5·45 (from τ 6·12 in the 7α-OH isomer) due to interaction between the 7β-OH and 15-H. 7β-Hydroxygedunin (V; 7β-OH) was obtained in good yield from 7-oxogedunin by partial reduction at low temperature with sodium borohydride.

The initial step in the reactions of the 7-hydroxy-compounds is most probably the opening of the epoxide system to form an intermediate with a carbonium ion at C-14. In this intermediate the 15-proton is axial and α-oriented. It could therefore be readily eliminated as a proton or migrate as a hydride ion, leading to a 15-oxo-



system such as in (II). Alternatively the C-8 methyl

[1] W. R. Chan, J. A. Gibbs, and D. R. Taylor, *Chem. Comm.*, 1967, 720; E. K. Adesogan, D. A. Okorie, and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1970, 205.

[2] D. E. U. Ekong and M. D. Selema, *Chem. Comm.*, 1970, 783.

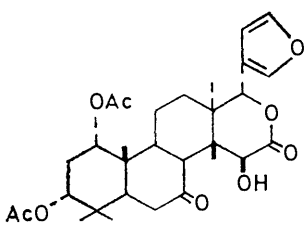
[3] N. S. Ohochuku and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1969, 864.

group, which is also axial but β-oriented could migrate, leading to the formation of an allyl alcohol [*e.g.* (III)] which is dehydrated in the acidic medium to form a heteroannular diene [*e.g.* (IV)]. Both types of product deacetylkhivorin as well as compounds of corresponding structures from 7-deacetylgedunin (V) and 1,2-dihydro-7-deacetylgedunin. Elimination of the 15-proton is probably assisted by the axial 7α-OH, because with

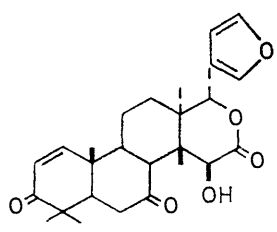
N.m.r. signals (τ values)

Compound	7-H	15-H	17-H	C-Me	OAc	Furans	Miscellaneous
(II)	5·47(m)		4·96	8·73, 8·82, 9·02, 9·08(6-H)	7·98, 8·00	2·57(m, 2H, 3·60(m)	5·25(m, 2H, 1-H and 3-H)
(IV)	3·60(m)	5·50	4·64	8·84, 8·95(6H), 9·02, 9·05	8·00, 8·10	2·57(m, 2H), 3·61m	4·90(m, 11-H), 4·86(m, 1-H), 5·20(m, 3-H)
15-*O*-Acetyl- (IV)	4·45(m)	4·22	4·68	8·75, 8·96, 8·99(6H), 9·10	7·76, 8·00, 8·12	2·58(m, 2H), 3·64(m)	4·90(m, 2H, 1-H and 11-H), 5·21(m, 3-H)
(VII)		4·15	4·70	8·72, 8·80, 8·85, 9·00, 9·10	7·98, 8·02	2·54(m, 2H), 3·61(m)	7·20(d, *J* 12 Hz, 8-H), 5·20(m, 2H, 1-H and 3-H)
(VII) with C(7)H·OH	6·00(m)	5·25	4·71	8·66, 8·78, 9·10(9H)	7·99, 8·04	2·57(m, 2H), 3·65(m)	5·26(m, 2H, 1-H and 3-H)
15-*O*-Acetyl- (VII)		3·22	4·78	8·66, 8·73, 8·83, 9·01, 9·13	7·92, 8·00, 8·04	2·60(m, 2H), 3·65(m)	7·28(d, *J* 12 Hz, 8-H), 5·22(m, 2H, 1-H and 3-H)
(VIII)		5·82	4·56	8·37, 8·85(9H), 9·04		2·56(m, 2H), 3·62(m)	6·98(d, *J* 12 Hz, 8-H), 3·26(d, 1-H, 4·05(d, 2-H) (*J* 10 Hz)
15-*O*-Acetyl- (VIII)		4·48	4·48	8·18, 8·76, 8·84, 8·90, 9·08	7·86	2·56(m, 2H), 3·61(m)	3·30(d, 1-H), 4·10(d, 2-H) (*J* 10 Hz)
(X)	4·80(m)	4·27	5·03	8·74, 8·78, 8·85(6H), 9·31	7·98	2·56(m, 2H), 3·58(m)	6·53(d, 1-H), 5·63(d, 2-H) (*J* 3 Hz)
(XI)	4·74(m)	4·32	5·02	8·66, 8·70, 8·83, 8·87(6H)	7·80, 8·02	2·53(m, 2H), 3·66(m)	3·30(s, 1-H)

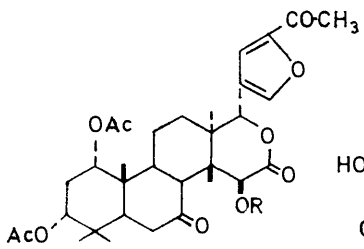
are indeed formed in about equal amounts from the 7α-hydroxy-compounds; *i.e.* (II) and (IV) from 7-



(VII)

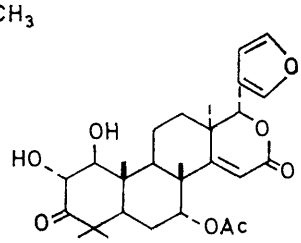


(VIII)

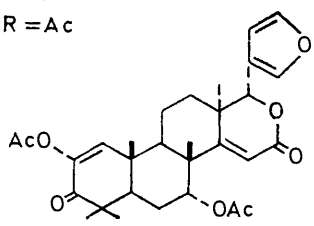


(IX)

a; R=H
b; R=Ac



(X)



(XI)

7β-hydroxy-compounds no 15-oxo-products were obtained. In the 7β-hydroxy-compounds the 7-proton is axial and α-oriented. Methyl migration from C-8 therefore, besides affording the heteroannular diene, could, as shown in (VI), also lead to a C-7 ketone, possibly *via* its enolate. This last is the major product from the 7β-hydroxy-compounds, *i.e.* (VII) from 7β-hydroxykhivorin and (VIII) from 7β-hydroxygedunin as well as the corresponding 1,2-dihydro-compound from 1,2-dihydro-7β-hydroxygedunin.

The n.m.r. spectra of the rearrangement products are summarised in the Table. They show striking differences between the two corresponding compounds (VII) and (VIII). In (VIII) the 15-proton gives an unexceptional singlet at τ 5·82 although one of the tertiary methyl signals appears further downfield than usual at τ 8·37. On the other hand in (VII) the 15-proton signal is at the abnormal downfield position of τ 4·15 whereas the methyl signals are at their normal position. That the signals at τ 5·82 and 4·15 each represent an *H*C·OH system has already been demonstrated.[2] The unusual absorptions are probably due to the magnetic anisotropy of the C-7 carbonyl group. This view is supported by the fact that when the C-7 ketone systems in both compounds were reduced with borohydride the 15-H and C-14 methyl signals moved to their normal positions. The difference between the two compounds (VII) and (VIII) could arise from differences in the configuration of the 8-proton. If the C-7 enolate intermediate is protonated on the α-face an all-chair conformation is possible but would produce severe steric strain between the methyl groups at C-10 and C-14. Consequently, a flexible conformation with chair forms for rings A and D and boats or twist-boats for rings B and C could be preferred, which would result in deshielding of the C-14 methyl group by the C-7 ketone system. On the other

hand the most probable conformation when the 8-proton is β-oriented would have a boat for ring c and chairs for the other rings, and lead to the deshielding of H-15 as in (VII). Protonation of the β-surface might be preferred in (VII) because of the steric effect of the 1α- and 3α-acetoxy-groups.

The iodoacetate and the *p*-iodobenzoate of (VII) were prepared for a possible *X*-ray structural determination but unfortunately no single crystals were obtained. However, single crystals could be grown from (VII) itself. Attempted Baeyer–Villiger oxidation of (VII) in acetic acid–acetic anhydride was unsuccessful, but the reaction gave a product (IXa) of *C*-acetylation of the furan ring. This was characterised as its *O*-acetate, obtained by acetylation with acetic anhydride in pyridine. *C*-Acetylation of the furan ring of khivorin has also been achieved.[4]

That the αβ-epoxy-δ-lactones undergo ready rearrangement only when the molecule has a 7-hydroxy-group suggests the participation of the 7-OH in the opening of the epoxide ring. When 1,2-epoxy-7-deacetylgedunin was treated with acid, only the 14,15-epoxide system reacted, giving the 1,2-epoxy-derivatives of the products obtained from 7-deacetylgedunin. On the other hand 1,2-epoxy-14,15-deoxygedunin reacted only very slowly with acid and gave a small yield of a diol which we formulate as (X). Its n.m.r. spectrum, which was better resolved after addition of D_2O, contained two one-proton doublets at τ 6·53 and 5·63 (*J* 3 Hz). We assign these to 1-H and 2-H, respectively. One of the methyl peaks (τ 9·31) is further upfield than the rest. In view of the method of preparation (see Experimental section) the configuration of the 1,2-epoxide is most probably α. The formation of the diol may have occurred during the work-up by nucleophilic attack of a water molecule on the epoxide–boron trifluoride complex. The product should therefore be *trans*. Because of the polarity of the carbonyl group at C-3, the direction in which the epoxide opens is likely to be that which places the positive charge on C-1. Since the nucleophilic attack is *trans* this would lead to a 1β-OH,2α-OH configuration for the diol. The observed coupling constant would then be consistent if ring A is in a boat conformation. In this conformation the C-10 methyl group is in the diamagnetic shielding cone of the C-3 carbonyl group and would therefore resonate, as observed, at higher field than the other tertiary methyl groups. When this carbonyl group is reduced with borohydride all the methyl signals appear in their normal position, between τ 8·70 and 9·08.

When acetylated, the diol gave a monoacetate (XI) which is an enol acetate ($\nu_{max.}$ 1760 cm^{-1}) showing a singlet vinyl proton resonance at τ 3·30 (1-H) in the n.m.r. spectrum. This could have been formed by β-elimination of water during the acetylation.

The stability of the αβ-epoxy-δ-lactones is further enhanced if the furan ring at C-17 is oxidised to a carboxylic acid system. Such compounds are stable to dilute acid even when they possess a 7-OH group. On the other hand khivorin (with 7-OAc) when treated under more vigorous acidic conditions (*e.g.* heating with 10% toluene-*p*-sulphonic acid in benzene) was largely destroyed, but a small amount of compound (IV) could be isolated.

EXPERIMENTAL

General procedures are as described in ref. 5.

7β-Hydroxykhivorin.—7-Oxokhivorin (6·0 g) dissolved in chloroform (40 ml) and methanol (80 ml) and cooled in an ice-bath was reduced with sodium borohydride (1·0 g). The product, *7β-hydroxykhivorin* (3 g) had m.p. 258—260° (from methanol), $[\alpha]_D$ +31° (Found: C, 66·1; H, 7·4%; *m/e* 544. $C_{30}H_{40}O_9$ requires C, 66·2; H, 7·4%; *M*, 544), $\nu_{max.}$ 3450 (OH), 1740, 1725 (δ-lactone and acetate), 1500, and 875 cm^{-1} (β-substituted furan), τ 6·16 (m, 7-H), and 5·45 (s, 15-H).

7β-Acetoxykhivorin.—Acetylation of 7β-hydroxykhivorin with pyridine–acetic anhydride gave *7β-acetoxykhivorin*, m.p. 295—300° (from methanol), τ 4·92 (m, 7-H) and 6·31 (s, 15-H).

General Procedure for the Rearrangement Reactions.—A 4% (w/v) solution of the epoxide in dry benzene was treated with boron trifluoride–ether complex (10 drops per g of compound) for 6—12 h at room temperature. The solution was then poured into 6% sodium hydrogen carbonate solution and the mixture was extracted with chloroform. The extract was washed with water, dried, and evaporated.

Rearrangement of 7-Deacetylkhivorin.—The product from 7-deacetylkhivorin (2·0 g) showed four spots on t.l.c. corresponding to three new compounds and the starting material. It was chromatographed on a silica gel column (2·5 × 40 cm), and fractions were eluted with ether–light petroleum mixtures. 40% Ether eluted *compound* (IV) (0·6 g), m.p. 264—268° (from methanol), $[\alpha]_D$ −53·3° (Found: C, 68·2; H, 7·1%; *m/e* 526. $C_{30}H_{38}O_8$ requires C, 68·4; H, 7·3%; *M*, 526), $\nu_{max.}$ 3400 (OH), 1750, 1720, 1500, and 875 cm^{-1}, $\lambda_{max.}$ 247 nm (ε 12,000); *acetate*, m.p. 302—304°. 45% Ether eluted unchanged starting material (0·2 g).

Elution with 60% ether gave *compound* (II) (0·7 g), m.p. 232—234° (from methanol), $[\alpha]_D$ +35·6° (Found: C, 66·1; H, 7·4%; *m/e* 544. $C_{30}H_{40}O_9$ requires C, 66·2; H, 7·4%; *M*, 544), $\nu_{max.}$ 3350 (OH), 1715, 1710, 1500, and 875 cm^{-1}, $\lambda_{max.}$ (MeOH) 215 (5000) and 262 nm (5400), $\lambda_{max.}$ (MeOH–NaOH) 216 and 300 nm. Only traces of the fourth compound were isolated.

Rearrangement of 7β-Hydroxykhivorin.—7β-Hydroxykhivorin (2·0 g) dissolved in dry benzene (50 ml) was rearranged with boron trifluoride–ether (12—15 drops). The products were chromatographed on a silica gel column (2·5 × 30 cm) and eluted with ether–light petroleum mixtures. 40% Ether eluted compound (IV) (0·3 g), identical with that obtained from 7-deacetylkhivorin. 50% Ether eluted unchanged starting material (0·4 g). 80% Ether eluted *compound* (VII) (0·9 g), m.p. 270—271° (from methanol), $[\alpha]_D$ −32° (Found: C, 66·3; H, 7·4%; *m/e* 544. $C_{30}H_{40}O_9$ requires C, 66·2; H, 7·4%; *M*, 544), $\nu_{max.}$ 3400 (OH), 1740, 1710, 1500, and 875 cm^{-1}; 15-O-*acetate*, m.p. >350°, $\nu_{max.}$ 1760, 1715, 1500, and 875 cm^{-1} (Found: C, 65·5; H, 7·2. $C_{32}H_{42}O_{10}$ requires C, 65·5;

[4] M. D. Selema. Ph.D. Thesis, Ibadan University, 1971.
[5] C. W. L. Bevan, D. E. U. Ekong, and J. I. Okogun, *J. Chem. Soc.* (*C*), 1968, 1067.

H, 7·2%); 15-*oxo-analogue*, m.p. 268—269°, $\nu_{max.}$ 1750, 1725, 1500, and 875 cm^{-1} (Found: C, 66·6; H, 7·1%; *m/e* 542. $C_{30}H_{38}O_9$ requires C, 66·4; H, 7·1%; *M*, 542), τ (no peak for 15-H) 4·33 (17-H), and 8·53, 8·77, 8·82, 9·00, and 9·11 (all CMe). Sodium borohydride reduction of compound (VII) gave a product which did not crystallise, $\nu_{max.}$ 3300 (OH), 1730 (δ-lactone and ester), 1500, and 875 cm^{-1} (furan), τ 5·25 (15-H).

Attempted Buffered Baeyer–Villiger Oxidation of Compound (VII).—To the ketone (VII) (100 mg) dissolved in chloroform–methylene dichloride (10 ml) was added disodium hydrogen orthophosphate (200 mg) and a cold mixture of hydrogen peroxide (30%; 5 ml), methylene chloride (10 ml), and acetic anhydride (4 ml) containing a drop of sulphuric acid. The mixture was set aside overnight at room temperature. On work-up it afforded *compound* (IXa) (70 mg), m.p. 283—285°, insoluble in chloroform (Found: C, 65·6; H, 7·1%; *m/e* 586. $C_{32}H_{42}O_{10}$ requires C, 65·5; H, 7·2%; *M*, 586), $\nu_{max.}$ 3350 (OH), 1760, 1720, and 1710 cm^{-1} [no peaks at 1500 and 875 cm^{-1} (for β-substituted furan); instead a peak at $\nu_{max.}$ 865 (medium) indicated a disubstituted furan]; 15-O-*acetate*, m.p. 310—311° (Found: C, 64·9; H, 7·1. $C_{34}H_{44}O_{11}$ requires C, 65·0; H, 7·1%), $\nu_{max.}$ 1780, 1750, and 1710 cm^{-1}, τ 7·80, 7·90, and 7·97 (6H) (4 × Ac), 8·63, 8·67, 8·82, 9·01, and 9·12 (5 × CMe), 5·20 (m, 1-H and 3-H), 3·26 (15-H), 5·02 (17-H), and 3·62 and 3·10 (β- and α-proton of furan).

Iodoacetate of Compound (VII).—Compound (VII) (0·5 g) was dissolved in dry chloroform (10 ml), and chloroacetyl chloride (25 ml) and a drop of pyridine were added. The mixture was set aside at room temperature for 4 days; the solution had then turned yellow. On work-up it gave the *chloroacetate* (0·2 g), m.p. 340—341° (from methanol) (Found: C, 64·2; H, 6·8; Cl, 5·6. $C_{32}H_{41}ClO_{10}$ requires C, 64·1; H, 6·9; Cl, 5·7%), τ 5·90 (CH_2Cl). The chloroacetate (100 mg) in acetone (1 ml) was heated under reflux with a solution of sodium iodide (0·5 g) in acetone (3 ml) for 4 h to give the *iodoacetate*, which formed tiny needles (40 mg), m.p. 315—316° (from methanol), τ 6·22 (dd, *J* 8·5 Hz, ICH_2·CO).

7β-*Hydroxygedunin*.—7-Oxogedunin (2·0 g) dissolved in chloroform (50 ml) and methanol (100 ml) was cooled in an ice-bath. Sodium borohydride (200 mg) in methanol was added in small portions to the cooled stirred solution. The mixture was cooled and stirred for a further 10—15 min and then worked up. Crystallisation of the product from methanol gave 7β-hydroxygedunin (1·3 g), m.p. 263—265°, $[\alpha]_D$ +100°, $\nu_{max.}$ 3450 (OH), 1740 (δ-lactone), 1675 (αβ-unsat. carbonyl), 1500, and 875 cm^{-1} (β-substituted furan), τ 8·80 (6H), 8·83 (6H), and 8·90 (5 × CMe), 6·22 (m, 7-H), 5·46 (15-H), 4·36 (17-H), and peaks for the furan protons and 1H and 2-H.

Rearrangement of 7-*Deacetylgedunin*.—7-Deacetylgedunin (2·0 g) yielded a product which showed three compounds on t.l.c. besides the starting material. This was chromatographed on a silica gel column (2·5 × 40 cm), and fractions were eluted with ether–light petroleum mixtures.

30% Ether eluted a *compound* (0·6 g) of structure corresponding to (IV), m.p. 248—252° (from methanol), $[\alpha]_D$ −194·5° (Found: C, 73·8; H, 7·2%; *m/e* 422. $C_{26}H_{30}O_5$ requires C, 73·9; H, 7·2%; *M*, 422), $\nu_{max.}$ 3500 (OH), 1735, 1675, and 875 cm^{-1}, $\lambda_{max.}$ 243 nm (ε 12,000). 40% Ether eluted unchanged starting material (0·4 g). 45% Ether eluted a *compound* (0·6 g) of structure corresponding to (II), m.p. 160—165° (from methanol), $[\alpha]_D$ +85·8° (Found: C, 70·9; H, 7·3%; *m/e* 440. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%; *M*, 440), $\nu_{max.}$ 3400, 1735, 1675, and 875 cm^{-1}, $\lambda_{max.}$ (MeOH) 238 (ε 8000) and 260 nm (4400), $\lambda_{max.}$ (MeOH–NaOH) 235 and 298 nm. Only traces of the third compound were isolated.

Rearrangement of 7β-*Hydroxygedunin*.—7β-Hydroxygedunin (0·5 g) afforded *crystals* (VIII) (0·4 g), m.p. 274—275°, $[\alpha]_D$ −46° (Found: C, 70·7; H, 7·4%; *m/e* 440. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%; *M*, 440), $\nu_{max.}$ 3300 (OH), 1740, 1675, and 875 cm^{-1}; 15-O-*acetate*, m.p. 280—283° (Found: C, 69·6; H, 7·1%; *m/e* 482. $C_{28}H_{34}O_7$ requires C, 69·7; H, 7·1%; *M*, 482), $\nu_{max.}$ 1740, 1710 (δ-lactone and acetate), 1670 (αβ-unsaturated carbonyl), 1500, and 875 cm^{-1} (β-substituted furan); 15-*oxo-analogue*, m.p. 272—274° (Found: C, 70·9; H, 6·9%; *m/e* 438. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9%; *M*, 438), $\nu_{max.}$ 1740, 1690, 1680, 1500, and 875 cm^{-1}, τ 8·20, 8·82, 8·87, and 9·03 (6H) (5 × CMe), 6·68 (d, *J* 12 Hz, 8-H), 4·22 (17-H), and signals for the furan, 1-, and 2-protons. Sodium borohydride reduction of (VIII) gave a product which did not crystallise, τ 5·74 (15-H), and 8·53, 8·67, 8·76 (6H), and 8·87 (5 × CMe).

Rearrangement of 1,2-*Dihydro*-7β-*hydroxygedunin*.—1,2-Dihydro 7β-hydroxygedunin (obtained by catalytic hydrogenation of 7β-hydroxygedunin) was rearranged in a similar manner to give a compound which crystallised from methanol and which was found to be 1,2-dihydro- (VIII), m.p. 265—269°, $\nu_{max.}$ 3300 (OH), 1735 (δ-lactone), 1700 and 1670 (C-7 and C-3 carbonyls), and 1500 and 875 cm^{-1} (furan), τ 2·58, 2·61, and 3·64 (m) (furan), 4·60 (17-H), 5·82 (15-H), and 8·43, 8·86 (6H), 8·92, and 9·03 (5 × CMe).

The same compound was obtained by catalytic hydrogenation of the rearrangement product of 7β-hydroxygedunin.

Rearrangement of 7-*Deacetyl*-1,2-*epoxygedunin*.—7-Deacetyl-1,2-epoxygedunin (2·0 g) gave a crude product which on t.l.c. showed a mixture of two major compounds and one minor and very polar compound which could not be isolated. The major compounds were isolated by chromatography on silica gel, yielding a *compound* with structure corresponding to (IV), *i.e.* a $\Delta^{7,9(11)}$-compound, m.p. 272—273° (Found: C, 71·3; H, 7·1. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9%), $\nu_{max.}$ 3450 (OH), 1740, 1680, 1500, and 875 cm^{-1}, τ 2·56, 2·58, and 3·62(m) (furan), 3·77 (m, 7-H), 4·28 (m, 11-H), 4·62 (17-H), 5·49 (15-H), 6·24(d) and 6·56(d) (*J* 4 Hz, 2-H and 1-H, respectively), and 8·80, 8·84, 8·93, 8·98, and 9·03 (5 × CMe).

The second fraction eluted was a *compound* of structure corresponding to (II), *i.e.* a 15-oxo-compound, m.p. 144—148° (Found: C, 68·1; H, 7·2. $C_{26}H_{32}O_7$ requires C, 68·4; H, 7·1%), $\nu_{max.}$ 3400 (OH), 1725, 1700, 1500, and 875 cm^{-1}, τ 2·56, 2·58, and 3·68(m) (furan), 4·94 (17-H), 5·17 (7-H), 6·56 (dd, *J* 10 Hz, 1-H and 2-H), and 8·72, 8·76, 8·90, and 8·98 (6H) (5 × CMe).

14,15-*Deoxy*-1,2-*epoxygedunin*.—14,15-Deoxygedunin (2·0 g) was dissolved in dioxan (25 ml) and a 1 : 1 mixture of 30% hydrogen peroxide and N-sodium hydroxide (10 ml) was added. The mixture was set aside overnight at room temperature, then filtered. The filtrate on dilution with water slowly deposited crystals of 14,15-*deoxy*-1,2-*epoxygedunin* (1·8 g), m.p. 301—305° (Found: C, 69·6; H, 7·1. $C_{28}H_{34}O_7$ requires C, 69·7; H, 7·1%), τ 8·70, 8·78, 8·96 (6H), and 9·02 (5 × CMe), 8·00 (OAc), 4·80 (7-H), 4·31 (15-H), 5·03 (17-H), 6·53 (dd, 1-H and 2-H, *J* 5 Hz), and signals for furan protons.

Treatment of 14,15-*Deoxy*-1,2-*gedunin with Boron Tri-*

fluoride–Ether Complex.—To a solution of the 1,2-epoxide (0·5 g) in dry benzene (25 ml), boron trifluoride–ether (15 drops) was added. The initially colourless mixture became yellow during 4—7 days. When no further change was noticeable, it was poured into aqueous sodium hydrogen carbonate and extracted with chloroform. The crude product obtained on evaporation of the extract showed a major and a minor compound on t.l.c., the former having the lower R_F value. On crystallisation from chloroform–benzene, it gave *crystals* of the major product (X) (0·3 g), m.p. 253—256° (Found: C, 67·2; H, 7·2%; *m/e* 500. $C_{28}H_{36}O_8$ requires C, 67·2; H, 7·25%; *M*, 500), $\nu_{max.}$ 3400 (OH), 1735 (acetate), 1675 (αβ-unsat. carbonyl), 1500, and 875 cm^{-1} (β-substituted furan). Acetylation yielded *compound* (XI), m.p. 285—287° (Found: C, 68·6; H, 6·9%; *m/e* 524. $C_{30}H_{36}O_8$ requires C, 68·7; H, 6·9%; *M*, 524), $\nu_{max.}$ 1760 (vinyl acetate), 1715 (acetate), and 1675 cm^{-1} (αβ-unsat. carbonyl). Sodium borohydride reduction of (X) gave a non-crystalline product, τ 6·00(m), 6·22(m), and 6·42(m) (1-H, 2-H, and 3-H) and 8·72, 8·77, 8·83, 9·03, and 9·08 (5 × CMe).

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