Acid-catalysed Rearrangements of Trevoagenin A and B

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Summary Acid treatment of trevoagenin A (**1**; 20*R*,24*R*) or B (**1**; 20*S*,24*R*) in aqueous alcohol gives a mixture of the lactone (**2a**) and its *Z* isomer.

IN a recent communication[1] structures are proposed for sapogenin, not yet isolated, from a number of saponins obtained from certain species of Rhamnaceae and Scrophulariaceae which on acid hydrolysis all give ebelin lactone. We now report the acid-catalysed rearrangement of trevoagenin A and B, isolated from *Trevoa trinervis* Miers (Rhamnaceae).[2]

By refluxing trevoagenin A (**1**; 20*R*,24*R*) or B (**1**; 20*S*, 24*R*)† with 2N-HCl in aqueous alcohol for 5h a mixture of the *E* (**2a**) and *Z* isomers of 16,17-seco-3β-hydroxy-24-oxo-5α-dammar-17(20)-ene-16,30-lactone is obtained.‡

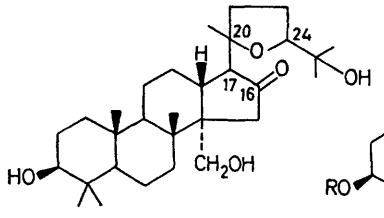
E isomer (**2a**)§ (75%), $C_{30}H_{48}O_4$, m.p. 212—214° (MeOH), $[\alpha]_D$ 0° ($CHCl_3$); M^+ 472 (100%); ν_{max} (KBr) 3555, 1765, 1700 cm^{-1}; n.m.r. ($CDCl_3$) τ 5·05 [d, J 10 Hz, H-C(17)], 5·68 br [s, $W_{1/2}$ 3 Hz, 2H-C(30)], 6·8 [m, $W_{1/2}$ 18 Hz, H-C(3)], 8·35 [s, $W_{1/2}$ 3 Hz, Me-C(20)], 8·91 [d, J 7 Hz, 2Me-C(25)], 8·98 [s, Me-C(8)], 9·01 [s, Me-C(10)], 9·14 [s, αMe-C(4)], and 9·22 [s, βMe-C(4)]. Acetylation gave the monoacetate (**2b**), m.p. 156—158° (MeOH), $[\alpha]_D$ + 7° ($CHCl_3$). Confirmation of the isopropyl ketone in the side chain was obtained by the presence of ions at *m/e* 71 (80%) and 429 (10%) in the mass spectrum of (**2a**).

† The determination of the stereochemistry of these compounds will be reported elsewhere.

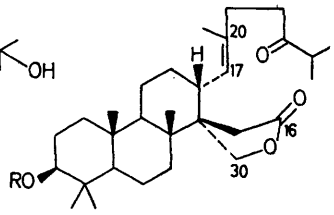
‡ Very minor quantities of other products are formed during the reaction and are being studied.

§ All new compounds gave satisfactory analytical results.

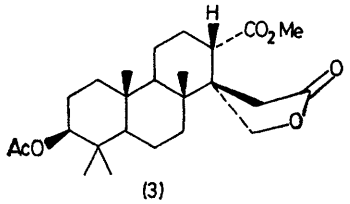
Z isomer (25%), $C_{30}H_{48}O_4$, m.p. 203—205° (MeOH), $[\alpha]_D$ — 13° ($CHCl_3$); ν_{max} (KBr) 3505, 1765, 1700 cm^{-1}. Its n.m.r. spectrum is nearly superimposable with that of (**2a**) except for the following signals: τ ($CDCl_3$) 8·33 [d, *J* 1 Hz, Me-C(20)], 8·89 [d, *J* 7 Hz, 2Me-C(25)], and 8·96 [s, Me-C(8)]. The compound gave an amorphous monoacetate.



(1)



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



(3)

These data are in accord with the structures shown. Chemical confirmation was obtained by converting the acetates, by ozonization and cleavage of the ozonide with Jones reagent, into the same octanor-acid methyl ester (**3**), m.p. 212–214° (MeOH), $[\alpha]_D$ — 2° ($CHCl_3$), identical (m.m.p., t.l.c., i.r., n.m.r.) with the compound obtained by Eade *et al.*[4] on degrading ebelin lactone.

Either trevoagenin A or B under the acidic conditions used for the rearrangement, but for a shorter time (2h), yield an approximately 1 : 1 mixture of A and B. Since the *Z* isomer of (**2a**) is not converted into (**2a**) under the conditions of the rearrangement it seems plausible that (**2a**) and the *Z* isomer are formed stereospecifically from trevoagenin A and B produced by previous equilibration.

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