The Inter-relation of Utilin and Entandrophragmin

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UTILIN, $C_{41}H_{52}O_{17}$, has been isolated from the timber of *Entandrophragma utile*.[1] Entandrophragmin, $C_{43}H_{56}O_{17}$, has been isolated from the timber of the species *E. bussei*,[2] *E. caudatum*,[2] and *E. cylindricum*,[1] from some specimens of *E. utile*,[3] and from *E. spicatum*.[4] The n.m.r. spectra of the two compounds are identical except in the methyl region, and this, together with the analytical similarity suggested that they were esters of the same complex alcohol. This has been confirmed.

Methanolysis of either utilin or entandrophragmin gives the same two products, (A), $C_{22}H_{30}O_{10}$ m.p. 260—270°, isolated as the free alcohol, the other isolated after acetylation as a penta-acetate (B), $C_{37}H_{42}O_{16}$ m.p. 320—325°. Ammonolysis of either utilin or entandrophragmin gives 2,3-epoxy-2-methylbutyramide, alkaline hydrolysis and titration shows the presence of a lactone ring and gives three mol. of volatile acid and two mol. of non-volatile acid. One of these is already accounted for by the isolation of the epoxy-amide above, the other is a nuclear carboxyl group, present as a methyl ester in the original compounds (n.m.r. band at δ 3·60). The volatile acids have been identified by n.m.r.-spectroscopic examination of the sodium salts,[5] utilin gives one mol. of 2-methylbutyric acid and 2 mol. of acetic acid, entandrophragmin one mol. each of 2-methylbutyric, isobutyric, and acetic acids. The difference between utilin and entandrophragmin is therefore considered to be

that one is an acetate and the other an isobutyrate of the same complex, polyacylated nucleus.

On alkaline hydrolysis utilin and entandrophragmin give β-furfuraldehyde,[1] as do the compounds of the gedunin series. The bands characteristic of the β-substituted furan ring are present in the spectra of these two compounds, and are also shown by methanolysis product (B). They are not present in the spectra of methanolysis product (A) which has thus lost the furan ring.

Utilin, which gives two mol. of acetic acid on hydrolysis, shows only one CO·Me group in the n.m.r. spectrum. Similarly, entandrophragmin, which gives one mol. of acetic acid, shows no CO·Me group, while the integrated intensity of the acetate band in the penta-acetate (B) reveals only four CO·Me groups. It therefore seems that in each of these compounds one acetate group is concealed in some way, and does not appear in the usual place in the n.m.r. spectrum. In agreement with this, methanolysis product (A) shows three *C*-methyl groups, while methanolysis product (B) shows four *C*-methyl groups (at δ 0·76, 1·33, 1·53, and 1·64) one of which presumably represents the missing acetate.

Investigation of the structures of the compounds described is proceeding. The formulae are all based on elemental analysis and mass-spectral molecular-weight determinations.

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