Structure of Evertetrose and Everninonitrose

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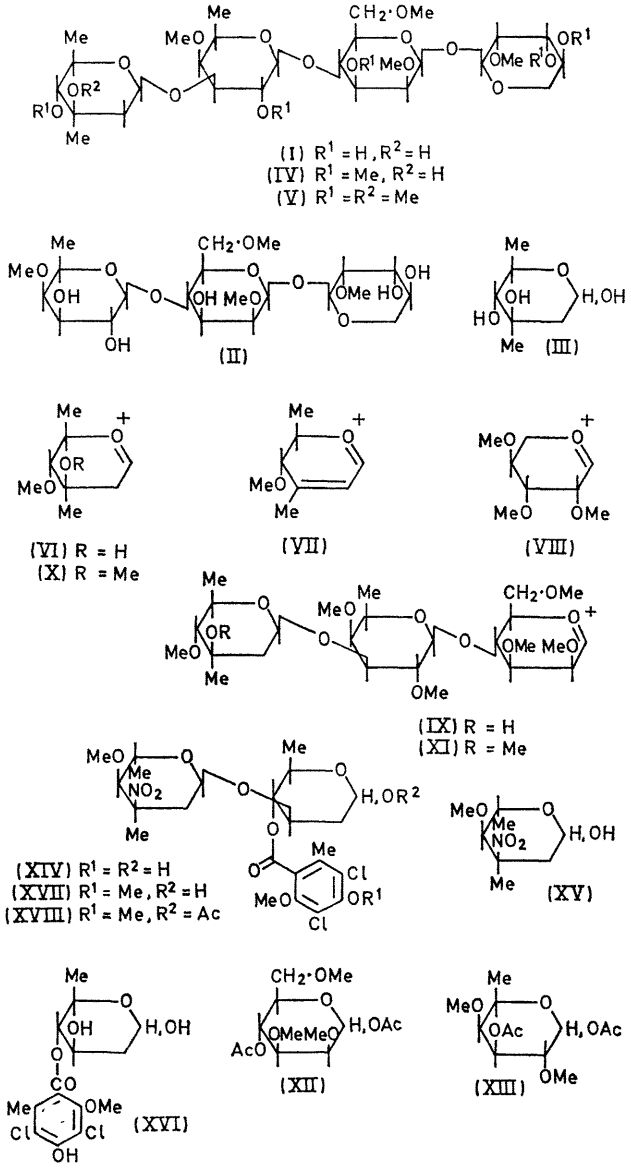
Summary The structure and absolute stereochemistry of evertetrose and everninonitrose, two degradation products of everninomicin "D", have been established.

EVERTETROSE (I) an amorphous, non-reducing solid, $[\alpha]_D$ −37·2°(H_2O,72h), shows no distinctive u.v. absorption and no carbonyl i.r. absorption. Its n.m.r. spectrum (D_2O) shows the presence of four methoxy-groups, two secondary methyl groups, a tertiary methyl group, and four anomeric protons at δ 5·3 (1H, d, *J* 2 Hz), 4·9 (1H, $J_{w/2}$ 1·5 Hz), 4·25 (1H, d, *J* Hz), and 4·85 p.p.m. (1H, q, *J* 2 and 7 Hz). On hydrolysis with aqueous acid (I) yielded evertriose (II)[1] and evermicose (III),[2] and on methylation[3] (I) yielded a mixture of (IV) and (V). The nonamethyl ether (IV) besides showing a small molecular ion peak at *m/e* 728 showed a stronger peak at *m/e* 696 (*M* − MeOH). Other prominent ions were at *m/e* 159 (VI), 141 (VII), 175 (VIII), and 537 (IX). In the decamethyl ether (V) the ions (X) and (XI) appeared at *m/e* 173 and 551 respectively. The mass spectra of (IV) and (V) established that (V) was methylated at the tertiary hydroxy-position which was free in (IV) and that evermicose was linked to the curacose part at C-2 or C-3. On prolonged hydrolysis with aqueous acid (V) gave a mixture from which the more polar fraction was isolated by preparative t.l.c. This was acetylated with pyridine–acetic anhydride and the crude acetate was separated into (XII) and (XIII) [δ 1·28 (3H, d, *J* 6 Hz, CMe), 2·1 (6H, s, MeCO), 4·85 (1H, q, *J* 3 and 10 Hz, 3-H), 5·5 (1H, d, *J* 8 Hz), and two methoxy-groups]. Isolation of (XIII) after acetylation of the hydrolysate of (V) established that the linkage of evermicose to curacose was at C-3.[1] The stereochemistry of the evermicose part of the anomeric linkage was deduced from the n.m.r. spectrum and was also confirmed by the application of Klyne's rule.[4] Thus the structure and absolute stereochemistry of evertetrose is established as (I) and the sequence of the four sugar fragment in everninomicin "D" is proven.

Everninonitrose (XIV) is also an amorphous solid, $[\alpha]_D$ −65·4°($CHCl_3$). Hydrolysis gave evernitrose (XV)[5] and everninocin[6] (XVI), and methylation with diazomethane gave (XVII) which formed a monoacetate (XVIII). The stereochemistry of the anomeric linkage was assigned from application of Klyne's rule.[4] Mass and n.m.r. spectra of (XIV), (XVII), and (XVIII) were consistent with the assigned structures and will be discussed in detail later.



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