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SYNTHESIS OF 25-OXYGENATED D:A-FRIEDOOLEANANES FROM D:A-FRIEDOOLEAN-7β-OL

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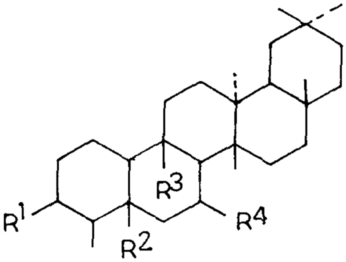
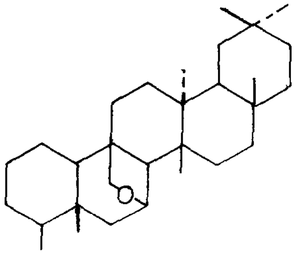
Summary : D:A-Friedoolean-25-ol(1) and 25-al(2) have been synthesised from D:A-friedoolean-7β-ol(3). Substituted tetrahydrofuran rings are opened up on treatment with lithium in ethylenediamine to yield the corresponding saturated alcohols.

Although a number of triterpenoids belonging to the D:A-friedooleanane group and containing oxygen functions at C-25 have been isolated and their structures suggested[1-7], but none of these compounds has been synthesised or directly correlated with any known compound as yet. Some of these compounds were converted[1,2] into D:A-friedoolean-25-ol(1) and 25-al(2) and their structures were also established on the basis of spectral data[1-4]. The present communication reports the first successful synthesis of these two compounds (1 and 2) from D:A-friedoolean-7β-ol(3), a compound of known[8] structure and stereochemistry.

7β,25-oxido-D:A-friedooleanane(4) synthesised from 3 by the procedure of Sengupta et al[9] on reduction with lithium in ethylenediamine afforded 1 and 3 in nearly 18% and 10% yields respectively. Unchanged 4 was however, recovered in ca 70% yield.



1, $R^1=R^4=H$; $R^2=CH_3$; $R^3=CH_2OH$
2, $R^1=R^4=H$; $R^2=CH_3$; $R^3=CHO$
3, $R^1=H$; $R^2,R^3=CH_3$; $R^4=OH$ (β)
6, $R^1=OH$(β); $R^2=R^3=CH_3$; $R^4=H$
7, $R^1=R^4=H$; $R^2=CH_2OH$; $R^3=CH_3$
8, $R^1=R^4=H$; $R^2=CHO$; $R^3=CH_3$



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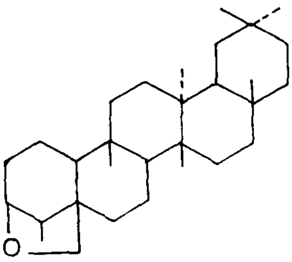

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In a typical procedure, a mixture of 4 (200 mg), lithium (200 mg) and dry ethylenediamine (20 ml) was refluxed under N_2 atmosphere for 6 hrs. The mixture was cooled, treated with NH_4Cl (2 g) and acidified with 5N HCl. Extraction with ether followed by chromatography (silica gel) yielded the products (1, R_f 0.95; 4, R_f 0.87 and 3, R_f 0.75). R_f values were measured on dried silica gel plates in petrol-benzene (9:1) . 1 on oxidation with CrO_3-pyridine complex[1] yielded 2 and 2 on reduction with $LiAlH_4$ and sodium in amyl alcohol yielded the same alcohol (1).

The poor yields of 1 and 3 were attributed to the steric hindrance rendered by the axial methyl groups at C-5 and C-14 that opposed the attack of the solvated electrons at the 7,25-oxide bridge in 4. To rationalise this, 3β,24-oxido-D:A-friedooleanane(5)[4] was synthesised from D:A-friedoolean-3β-ol(6)[10] and 5 having no such hindrance for attack of the solvated electrons at C-3 from the equatorial side when reduced under identical conditions yielded D:A-friedoolean-24-ol (7, 75%) and 6 (22%) and no unreacted 5 could be detected. 7 on oxidation with CrO_3-pyridine yielded D:A-friedoolean-24-al(8)[4].

Compounds 1,2,5,7 and 8 were identified by comparisons with their reported physical and spectral data[1-4] and 3,4,6 were identical with authentic samples[8-10].

In the present work the reagent lithium in ethylenediamine has been used for the first time to open substituted tetrahydrofuran rings to give the corresponding saturated alcohols.

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