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SYNTHESIS OF BIVITTOSIDE C GENINE

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Summary: Starting from the readily available[2] 3β,7β,18-trihydroxy-lanostane the aglycon of bivittoside-C is synthetized in a six step sequence.

In 1981 Kitagawa and co-workers[1] reported the isolation and the structure of the glycosides from the seacucumber *Bohadschia bivittosa*. Enzymatic hydrolysis furnished two lanostane-type sapogenols, differing only in a 12α-hydroxy moiety.

We now wish to report the partial synthesis of the bivittoside C genine,the 3β-hydroxy-9(11)-en-lanost-18,20-lactone in an overall yield of about 6%. Starting from the recently described[2] (I) selective acetylation resulted in compound (II), m.p. 188-189°C; yield up to 75%. By means of the Heusler-Kalvoda photoreaction we obtained a mixture of four cyclic ethers (III-VI) which could be separated by preparative HPLC (n-hexane:ethylacetate= 3:1) and identified by n.m.r. The yield of the desired compound (III) was, depending on the nature of the substituent at C-7, between 15% (keto) and 25% (acetate). Treatment of (III) with $NaIO_4/RuO_2$ in water-acetone-CCl_4[3] at room temperature produced the lactone(VII), m.p. 223-225°C, yield 72-80%; ν 1755 (lactone), 1740 (acetate); δ 2.92 (t, 1H, C-8), 4.39-4.56 (m, 1H, C-3), 4.64-4.94 (m, 1H, C-7). Alkaline hydrolysis followed by reacetylation gave (VIII), m.p. 228-229°C; δ 2.57 (t, 1H, C-8), 3.32-360 (m,1H, C-7), 4.39-4.56 (m, 1H, C-3) and the lactone (III), respectively.

X-ray crystallography of compound (VIII) verified the structure of 3β-acetoxy-7β-hydroxy-lanostane-18,20(S)-lactone.

Reaction of (VIII) with the inner salt A, obtained by the procedure of Burgess et al.[4] in benzene, did not result in the expected compound (IX), but in the already rearranged product (X), m.p. 221-223°C, Lit.[1] 225-226°C, yield 37%; δ 1.41 (s, 3H, C-21), 4.39-4.56 (m, 1H, C-3), 5.27-5.32 (m, 1H, C-11). The yield could not be increased by use of other reagents like $POCl_3$ or $SOCl_2$, instead we obtained the 7α- and 7β-chloro substituted compounds.

Hydrolysis with potassium carbonate in methanol gave the desired genine (XI), m.p. 228-229°C, Lit.[1] 231-233°C, yield 85%; δ 3.18-3.33 (m, 1H, C-3), 5.27-5.32 (m, 1H, C-11).

All n.m.r. data were measured in $CDCl_3$, i.r. data in KBr, and all compounds gave satisfactory analytical figures.

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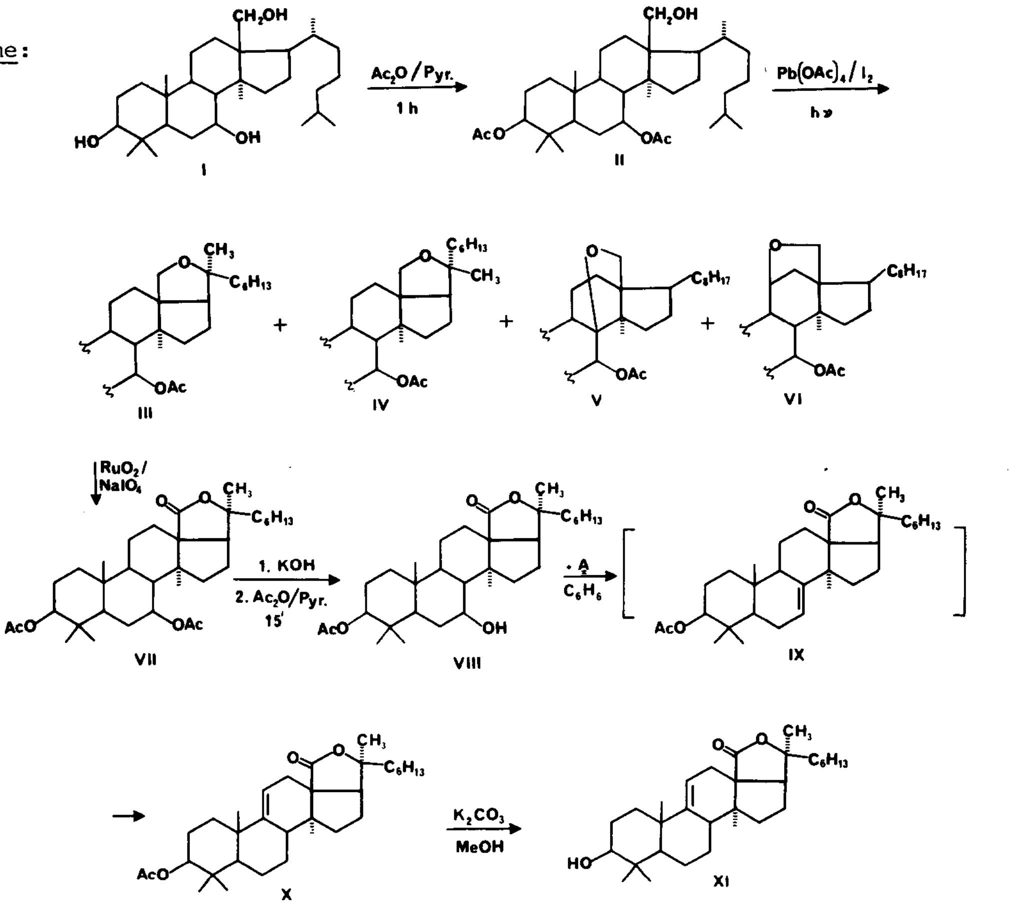
Scheme:



A = $C_2H_5OC(=O)\bar{N}SO_2\overset{+}{N}(C_2H_5)_3$

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