Tetrahedron Letters No.51, pp. 4639-4643, 1965. Pergamon Press Ltd.
Printed in Great Britain.

REACTIONS OF PRIMULA GENIN A - Part I

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(Received 26 October 1965)

During an examination (1) of the extractives of the bark of the mangrove Aegiceras corniculatum which grows on the coast of New South Wales and Queensland, we isolated rapanone and a mixture of triterpenes similar to that previously reported by Rao and Bose, including genin A (2), aegiceradienol (3), and aegiceradiol (4). In one isolation of the triterpenes the mild acid hydrolysis of glycosides used by Barton *et al* (5) was employed and it was observed that a much improved yield of genin A was obtained with little if any of the aegiceradiol or aegiceradienol which were isolated when the usual hydrolysis conditions (2) were used. The suspicion that these compounds might be artefacts derived from the decomposition of genin A under acid conditions was strengthened by a micro scale experiment in which genin A was refluxed in ethanolic hydrochloric acid under the same conditions used for the original acid hydrolysis of the crude glycoside mixture from the bark. Thin layer chromatography (t.l.c.) of the recovered material on silica gel showed a series of spots of which three corresponded to authentic genin A, aegiceradiol, and aegiceradienol.*

Similar treatment of highly purified genin A (single spot on t.l.c.) on the preparative scale gave a crude solid which was chromatographed over alumina. The first eluted fractions were combined and recrystallised repeatedly to give a product, [Light absorption: $\lambda_{max.}$ 236, 243 and 251 mμ; log ε 4.19, 4.24, 4.05 (in alcohol)] which was converted into the acetate and identified as 28-noroleana-12,17-dien-3β-yl acetate, (5), (7) m.p. 179-181°, $[\alpha]_D$ + 62.8° (c, 2.37).** Later eluates from the column were combined (t.l.c. monitored) and the product recrystallised to yield oleana-12,15-dien-3β, 28-diol which was purified as its diacetate, m.p. 212-214°, $[\alpha]_D$ + 53° (c, 1.40) (4), (8). Both these compounds were identical, by mixed m.p., infrared, and t.l.c. comparison, with the corresponding derivatives of aegiceradienol (3) and aegiceradiol (4) isolated from _A. corniculatum_. It is thus confirmed that these compounds are artefacts derived from genin A during the fairly vigorous acid hydrolysis of the crude glycoside mixture and probably do not occur in the plant.

The isolation of oleana-12,15-dien-3β,28-diol (II) would seem quite unexceptional as this would be the product expected from acid catalysed dehydration of the axial 16α-hydroxyl

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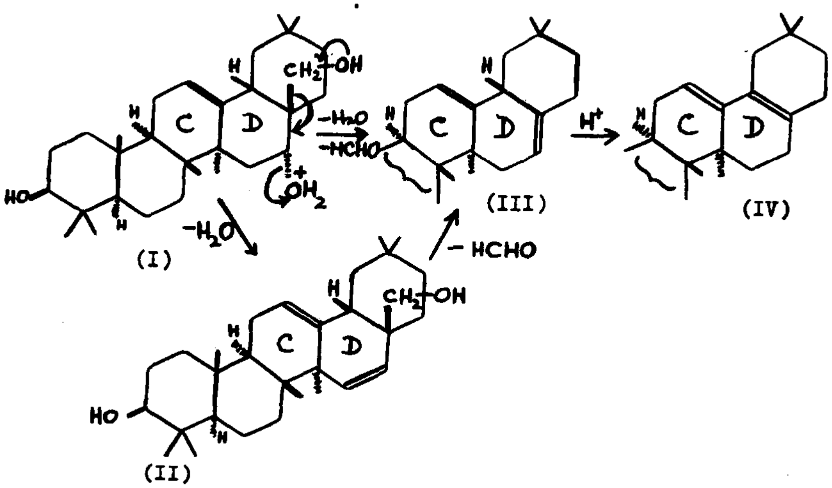
* At this stage of the work we became aware of the review by Halsall and Aplin (6) in which the suggestion was made that these products might be artefacts derived as above.

** Chloroform solutions were used for all rotations.

group of genin A (I). The conversion of genin A into 28-noroleana-12,17-dien-3β-ol (IV) is of greater interest. Two possible modes of elimination of the angular primary alcohol can be envisaged, both of which are reverse Prins type reactions. In one case elimination to form (II) would be followed by loss of formaldehyde in a similar fashion to that observed recently in the conversion of pre-senegenin into polygalic acid (9) and of "Triterpene A" into "Triterpene B" (10). The other possibility would involve the intact 1,3-glycol system and would require simultaneous loss of water and formaldehyde from (I) (see arrows). In both cases migration of the newly formed double bond of (III) into conjugation under the acid conditions would give the observed diene (IV). Preliminary experiments favour the concerted elimination, as treatment of the diol (II) under the usual acid conditions gave little indication of the formation of (IV),



most of the diol being recovered.

A similar elimination of formaldehyde from a 1,3-glycol system was observed recently with illudin-S by McMorris and Anchel (11) and it has been suggested (12) that this type of reverse Prins reaction would be favoured by a trans relationship of the eliminated groups. In the case of genin A the corresponding groups are trans 1,2-diaxial.

Further work on the minor products formed in the acid treatment of genin A is in progress. One of these is a substance, isomeric with 28-noroleanadienol, which was isolated as its acetate, m.p. 107-108°, $[\alpha]_D + 64^{\circ}$ (c, 1.24). It showed no conjugated absorption in its u.v. spectrum and was unaffected by treatment with hydrogen chloride in chloroform. This substance has also been isolated in small amount from the mangrove bark extract.

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