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CHEMICAL STUDIES OF MARINE INVERTEBRATES VI.(1) TERPENOIDS LXV. PRASLINOGENIN, A NEW HOLOTHURINOGENIN FROM THE INDIAN OCEAN SEA CUCUMBER Bohadschia koellikeri

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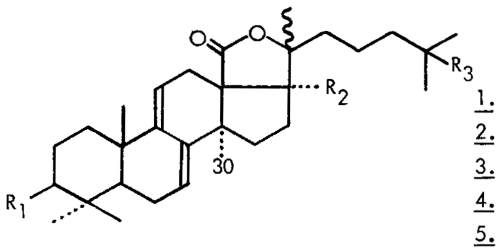
The isolation of three triterpenoid sapogenins, seychellogenin (1), koellikerigenin (2) and ternaygenin (3), from the aglycone mixture resulting from acid hydrolysis of the glycosides of the sea cucumber Bohadschia koellikeri has been reported recently.(1) The present communication deals with a minor constituent of that mixture, praslinogenin, m.p. 290–291.5° to which structure 4 can be assigned on the following evidence.



1. R_1 = OH R_2 = H R_3 = H
2. R_1 = OH R_2 = H R_3 = OH
3. R_1 = OH R_2 = H R_3 = OCH_3
4. R_1 = OH R_2 = OH R_3 = OCH_3
5. R_1 = OAc R_2 = OH R_3 = OCH_3
6. R_1 = OAc R_2 = H R_3 = OCH_3

The ir spectrum of praslinogenin, showing bands at 3490 (γ_{OH}) and 1760 cm^{-1} (γ-lactone), as well as its uv spectrum displaying the typical lanostadiene triple absorption at 237, 244 and 252 nm, indicates that the compound belongs to the group of the holothurinogenins (1,3,4,5). The mass spectrum shows a molecular ion at m/e 500 (in agreement with a formula $C_{31}H_{48}O_5$) and intense fragment ions at m/e 468, 435, 381, 299. All occur 16 mass units higher than the corresponding ions (m/e 452, 419, 365 and 283) in the mass spectrum of ternaygenin (3) (M^+, m/e 484). In both cases the base peak at m/e 73 can be attributed to the ion $(CH_3)_2\overset{+}{C}=OCH_3$.

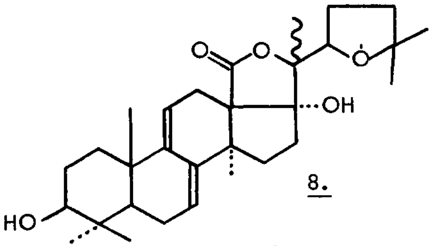
Praslinogenin forms a monoacetate 5 (m.p. 271–274°, M^+, m/e 542 (corresponding to $C_{33}H_{50}O_6$), whose ir spectrum still shows the presence of a hydroxyl group. The tertiary nature of this hydroxyl function is further confirmed by the presence of only one proton of the H-C-O type in the nmr spectra of 4 and 5. These nmr spectra are practically identical with those of ternaygenin (3) and ternaygenin acetate (6) with the exception of the chemical shift of one methyl group (see Table 1).

Table 1

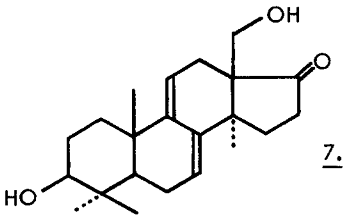
	δ Values for Methyl Group Signals							
Ternaygenin (3)	0.90	1.01	1.01	1.11		1.15	1.15	1.41
Praslinogenin (4)	0.93	1.02		1.12	1.16	1.16	1.16	1.42
Ternaygenin acetate (6)	0.90	0.98	1.00	1.12		1.15	1.15	1.40
Praslinogenin acetate (5)	0.90	0.96		1.11	1.15	1.15	1.15	1.41

These data indicate that praslinogenin is an x-hydroxyternaygenin, in which the tertiary hydroxyl group can only be attached at 5α or 17α. The last location is favored because the nmr chemical shift of one methyl group absorbing at 1.00 ppm in the ternaygenin series is shifted to 1.15 ppm in the praslinogenin derivatives (see Table 1). This is precisely the value observed for the C-30 methyl group in the 17α-OH derivatives 22, 25-oxidoholothurinogenin (8)[3] and griseogenin.[4]

It was hoped that $LiAlH_4$ reduction of praslinogenin (4), followed by periodate reduction, would afford the known[3] 17-ketone 7 and thus demonstrate the postulated structure by direct correlation with 22,25-oxidoholothurinogenin (8). Whereas ternaygenin (3) is easily reduced by $LiAlH_4$ in dioxane to the corresponding triol 9, praslinogenin (4) afforded an amorphous compound which did not react with periodate as would be expected for the normal reduction product 10. Uv , ir, nmr and mass spectral data indicate structure 11 for the reduction compound, which thus results from further cyclization of 10 by loss of the elements of methanol.



8.



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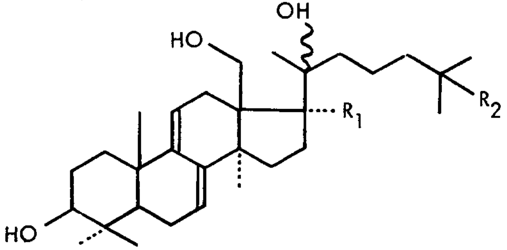
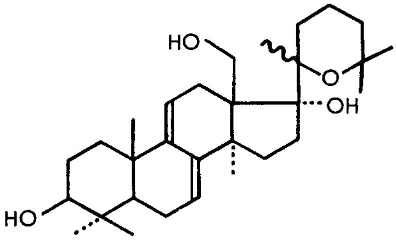


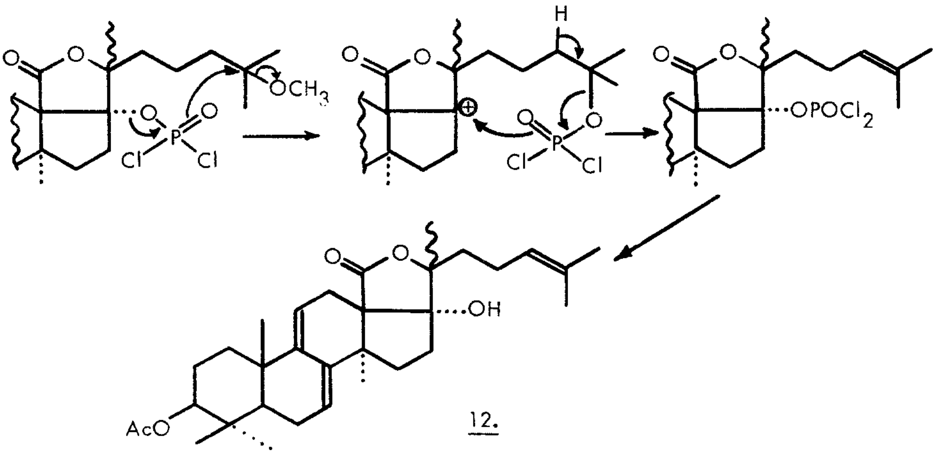
9. $R_1 = H$ $R_2 = OCH_3$

10. $R_1 = OH$ $R_2 = OCH_3$



11.

The 5α position for the tertiary hydroxyl group could be eliminated by the fact that praslinogenin acetate (5) was very resistant to dehydration (in agreement with the behavior observed for 17α-OH compounds (such as 8). No dehydration was observed on exposure of 5 to phosphorus oxychloride or thionyl chloride in pyridine at room temperature, to iodine in refluxing benzene, to sulfuric acid in refluxing THF or to p-toluenesulfonyl chloride in pyridine. Under forcing conditions (phosphorus oxychloride in pyridine at reflux for 4 hours) praslinogenin acetate (5) yields a compound m.p. 232–239°, whose ir spectrum still indicates the presence of OH, γ-lactone and acetate functions. Its uv spectrum shows the persistence of the typical lanostadiene triple absorption at 237, 244 and 252 nm. Important features of the nmr spectrum are the absence of a methoxyl signal and the presence of methyl singlets at 0.90, 0.98, 1.13, 1.15, 1.41, 1.58, and 1.70 ppm, the latter two being assigned to methyls on double bond. The mass spectrum shows a molecular ion at m/e 510 ($C_{32}H_{46}O_5$), but no peak at m/e 73 and no M-CH_3OH ion. Instead, an intense ion at m/e 69, assigned to the fragment $(CH_3)_2C{=}CHCH_2^+$ is present. The reaction product thus must be formulated as 12, a conceivable mechanism being illustrated below.



12.

In view of the demonstrated[1] ease of methylation of the tertiary hydroxyl group in the side chain of koellikerigenin (2) during acid treatment in methanol, it appears probable that praslinogenin (4) is an artifact produced from a hypothetical 25-OH precursor during the hydrolysis of the glycosides.

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REFERENCES

(1) For preceding paper, see P. Roller, C. Djerassi, R. Cloetens and B. Tursch, J. Am. Chem. Soc., **91**, 4918 (1969).

(2) The name "praslinogenin" is derived from the island of Praslin, in the Seychelles group, where much of our material was collected.

(3) J. D. Chanley, T. Mezzetti and H. Sobotka, Tetrahedron, **22**, 1857 (1966).

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