protons respectively There is also a 12 proton singlet signal at $\delta = 1\ 43$ accounting for the four methyl groups in the molecule The remaining signals in the NMR spectrum must all be due to the olefinic protons in the side chain at C-3 and an *ABX* system is found in the olefinic zone with $\delta_A = 5\ 05$ (1H) $\delta_B = 5\ 08$ (1H) $\delta_X = 6\ 18$ (1H), $J_{AX} = 18$ Hz, $J_{BX} = 10$ Hz, and $J_{AB} = 1\ 0$ Hz This system is typical of a vinyl group attached to a quarternary carbon[6]

That double bond in the C-3 substituent is not in conjugation with the coumarin chromophore is further indicated by the Lemieux–Rudloff test[7] in which the production of formaldehyde showed the terminal position of the double bond This confirmed the structure of the side chain In the mass spectrum the parent peak appeared at 15 m u less than the molecular ion peak, which is very characteristic of α,α-dimethyl pyranocoumarins[8]

On these bases, the compound is assigned structure I The number of naturally occurring coumarins with 1,1-dimethylallyl substitution at C-3 is very limited, and all occur exclusively in the Rutaceae I is presumably formed from xanthoxyletin by *C*-isoprenylation at C-3, following standard mechanisms[9]

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IDENTIFICATION OF EBELIN LACTONE FROM BACOSIDE A AND THE NATURE OF ITS GENUINE SAPOGENIN*

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Key Word Index—*Bacopa monniera*, Scrophulariaceae, sapongein, bacogenin A_4, ebelin lactone

The acid hydrolysis of bacoside A yielded a mixture of four aglycones which were designated as bacogenins A_1, A_2, A_3 and A_4 in order of increasing R_fs on TLC[1] Recently structure I has been assigned[2] to bacogenin A_1

* Part V in the series "Chemical Examination of *Bacona monniera*" For Part IV see Ref 2 C D R I communication No 1782

[1] CHATTERJI, N , RASTOGI, R P and DHAR, M L (1965) *Indian J Chem* **3,** 24

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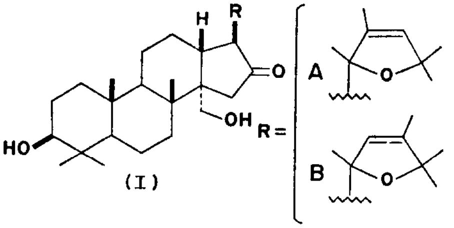
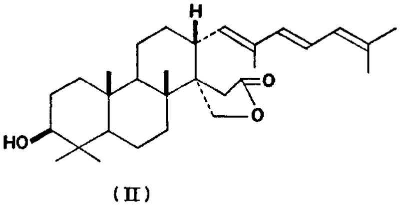
Bacogenin A_4, m p 175°, $C_{30}H_{46}O_3$ (M^+ 454), was found to be the major component in the aglycone mixture It showed λ_{max} 269, 279, 291 nm and formed a monoacetate, m p 212°, $C_{32}H_{48}O_4$ It has been identified as ebelin lactone (II) from its chemical and physico-chemical data and finally by the direct comparison (TLC, m m p , PMR and IR) of mono-*O*-acetyl bacogenin A_4 with mono-*O*-acetylebelin lactone which was obtained from zizyphoside [3]



(I)



(II)

Bacoside A did not show any UV absorption demonstrating that the triene system of ebelin lactone was absent in the genuine sapogenin and was generated under acidic conditions of hydrolysis The IR spectrum of bacoside A was also devoid of carbonyl absorption, and, therefore, it must carry a latent carbonyl group probably in the form of a ketal as in the case of cimigenol [4] A more interesting fact was that while ebelin lactone has a normal disposition of isoprene units in its side chain, bacogenin A_1 contained a rearranged side chain and both of these must have arisen from a common precursor

In order to explain the formation of two different side chains from a common precursor the presence of a cyclopropane ring in its side chain has been contemplated This possibility was put to test by recording the PMR spectra (in pyridine-d_5) of three ebelin lactone-yielding glycosides, viz bacoside A from *Bacopa monniera* Wettst (Scrophulariaceae),[1] zizyphoside from *Zizyphus rugosa* Lam (Rhamnaceae),[3] and the saponin from *Emmenospermum alphitoniodes* F Muell (Rhamnaceae)[5] and two other triterpenoid saponins namely asiaticoside from *Centella asiatica* L (Umbelliferae),[6] celsioside from *Celsia coromandeliana* Vahl (Scrophulariaceae) [7] The PMR spectra of the three ebelin lactone-producing saponins showed an identical narrow 4H multiplet centred at 0 5 ppm which could be assigned to the 4 protons of a cyclopropane ring Whereas no such signal was obtained in the last two saponins which yield the aglycones belonging to the α- and β-amyrin groups respectively. These results confirm the presence of a disubstituted cyclopropane ring in the side chain of the genuine precursor of ebelin lactone.

Since amongst the three ebelin lactone-producing saponins only bacoside A yielded bacogenin A_1, the genuine precursor in this case must be slightly different from the other two saponins, mentioned above In view of these facts tentative structures (III and IV) of both the precursors (genuine sapogenins) are being proposed as a working basis for future studies The possible course of derivation of bacogenin A_1 and ebelin lactone from III and the latter only from IV during acid hydrolysis could be visualized as shown in Schemes 1 and 2 respectively.

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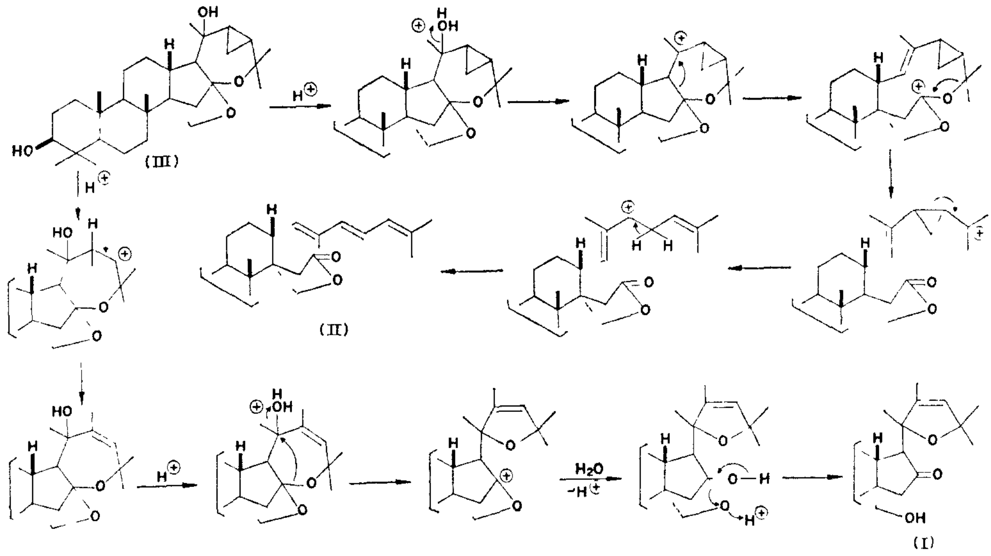
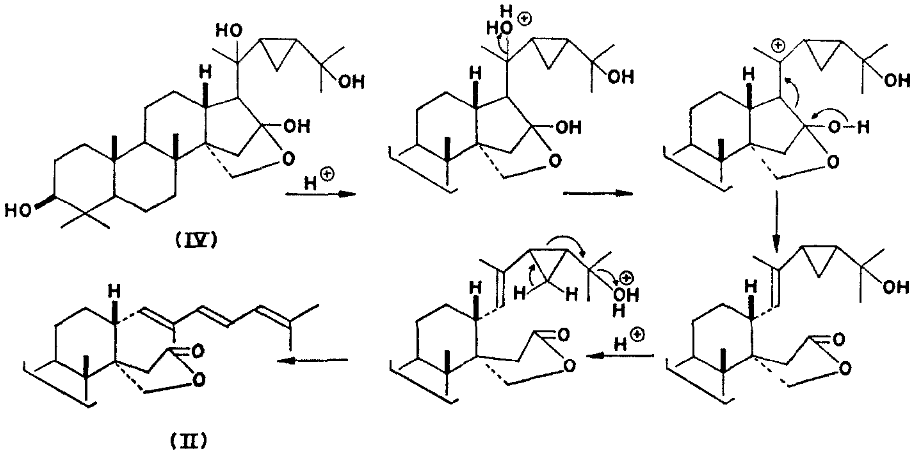
[7] Unpublished work of the authors



SCHEME 1 FORMATION OF BACOGENIN A_1 AND EBELIN LACTONE



SCHEME 2 FORMATION OF EBELIN LACTONE

Attempts have been made to obtain the true sapogenin by mild acid treatment of the bacoside, enzymatic hydrolysis or its degradation by Smith's periodate oxidation These procedures have so far yielded only intractable products

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