SUMMARY

The work embodied in the present thesis has been divided into two parts.

PART-I

INVESTIGATION OF THE BARK OF SAPIUM BACCATUM ROXB. : ISOLATION AND STRUCTURE ELUCIDATION OF A NEW NOR-TRITERPENE, $C_{29}H_{46}O_4$, m.p. 228-9°, $(\alpha)_D$ + 9.09°.

Chapter I :

In this chapter the morphological features of the plants of the Euphorbiaceae family, Sapium species and Sapium baccatum Roxb. are described.

Chapter II :

This chapter gives a short review on steroid and terpenoid peroxides.

Chapter III :

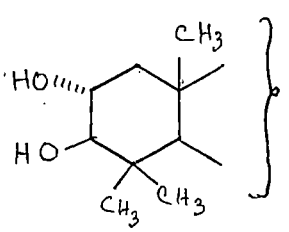
The isolation of taraxerone, taraxerol, β-sitosterol, 1-hexacosanol, 3,3'-di-O-methyl ellagic acid, 3-acetoxy aleuritolic acid and a new nor-triterpene, $C_{29}H_{46}O_4$, m.p. 228-9°, $(\alpha)_D$ +9.09° is described in this chapter.

Chapter-IV :

In this chapter the structure elucidation of a new nor-triterpene, $C_{29}H_{46}O_4$, m.p. 228-9°, $(\alpha)_D$ - 9.09° isolated from the benzene extract of Saplum baccatum Roxb. is described.

Section A :

In this section, the nature of two of the four oxygen functions of the nor-triterpene has been discussed. The nor-triterpene formed a diacetate. The NMR spectra of the nor-triterpene and its diacetate showed that the two hydroxyl groups are present in the diequatorial $2\alpha, 3\beta$-configuration as shown in the partial structure 1.



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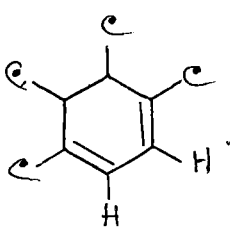

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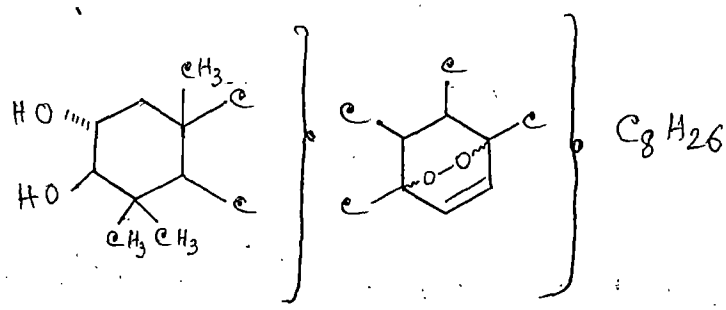
Section B :

This section deals with the nature of the remaining two oxygen functions. The nor-triterpene and its diacetate liberated one atom of iodine for one atom of oxygen when treated with potassium iodide in glacial acetic acid. This indicated that the two oxygen functions are

present either in a peroxide linkage of the type -C-O-O-C- or two epoxide linkages of the type  . When treated with methanolic alkali, both the nor-triterpene and its diacetate gave a homoannular conjugated diene 2 which on eosin-sensitised photooxidation gave back the original nor-triterpene. This suggested the presence of a peroxide linkage in the nor-triterpene. The presence of an abundant peak at m/e 426 (M^+ -32) in the mass spectrum of the nor-triterpene gave additional support to the above conclusion. The NMR spectra of the nor-triterpene and its diacetate showed an AB type of quartet arising from a disubstituted double bond of the type  which must be placed in the same ring as the peroxide moiety. The partial structure of the nor-triterpene can now be written as in 3 :



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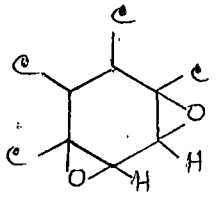
When the nor-triterpene diacetate was adsorbed on a column of basic alumina, it rearranged to a new product. The NMR, IR and mass spectral

data of the rearranged compound and its hydrolysis product suggested it to have a dioxide structure as shown in 4.



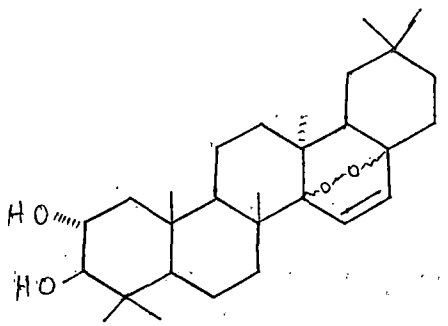
4

This observation is in accordance with the partial structure 3 for the nor-triterpene.

Section C :

This section deals with the nature of the skeleton of the nor-triterpene. From an analysis of the molecular formula of the nor-triterpene and the homoannular conjugated diene 2, the nor-triterpene was shown to be pentacyclic in nature. From an analysis of the NMR and mass spectra of the nor-triterpene, its diacetate and the various degradation products, the presence of hopane, lupane and friedolane type of skeleton were excluded. Since the nor-triterpene was found to occur with other Δ^{14} - taraxerenes, e.g., taraxerone, taraxerol and 3-acetoxy aleuritolic acid, it appeared from biogenetic considerations that the same Δ^{14}-taraxerene type of nucleus might be involved in the formation of the nor-

triterpene in the plant. On the basis of these considerations, structure 5 has been proposed for the nor-triterpene.



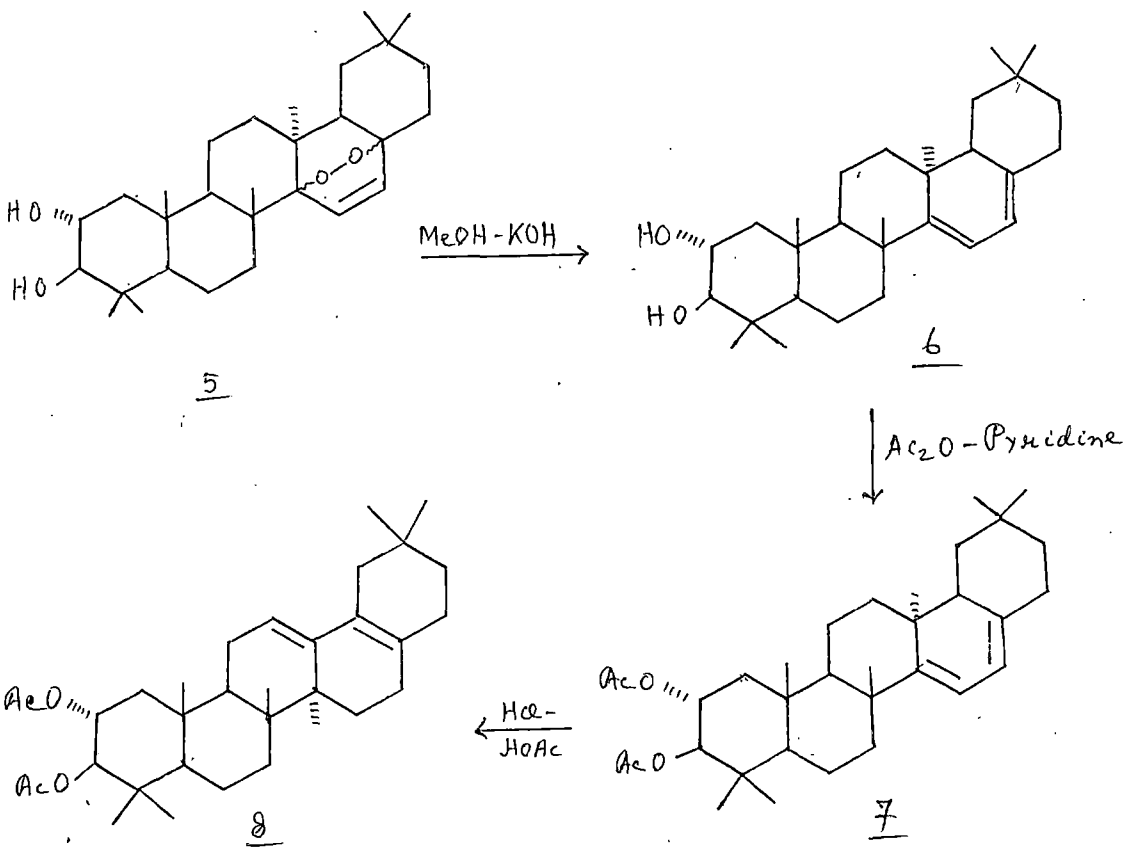
5

This structure can explain all the reactions of the nor-triterpene in a very satisfactory manner.

Section B :

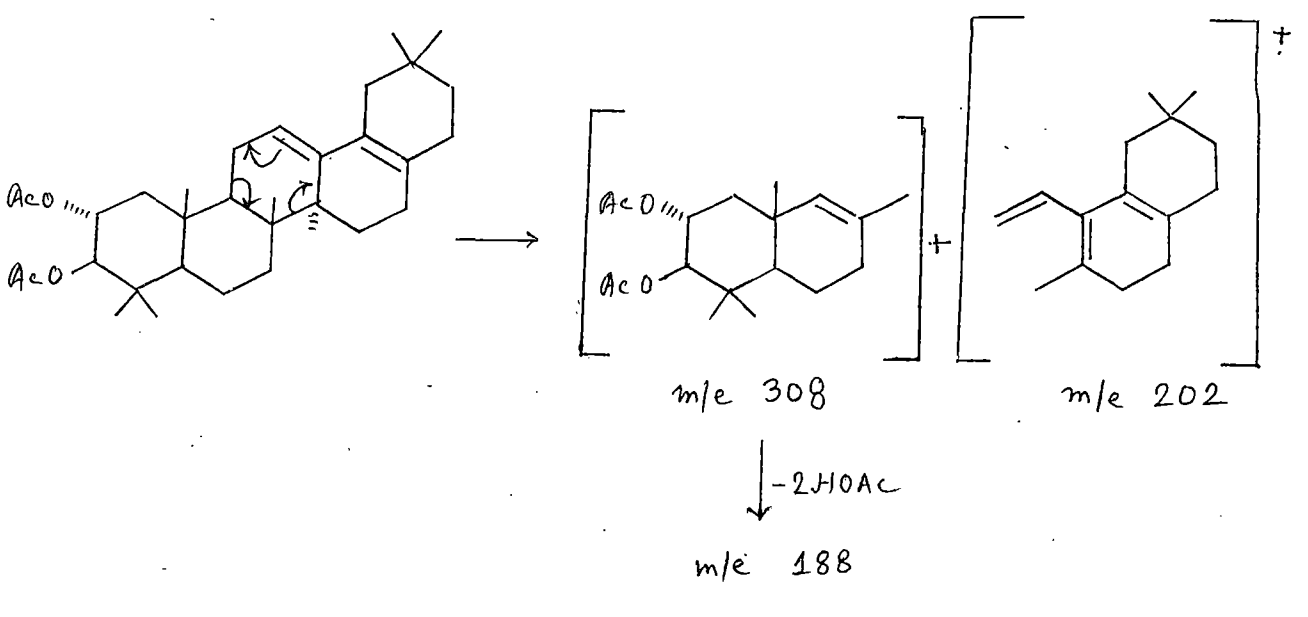
In this section, the experimental results which confirmed the proposed structure 5 have been discussed. Treatment of the nor-triterpene 5 with methanolic alkali gave the homoannular conjugated diene 6 and this on acetylation afforded the diacetate 7. When the diacetate 7 was treated with HCl - HOAc mixture it rearranged to a product, the UV spectrum of which showed the presence of a hetero-annular conjugated diene system. The NMR spectrum showed the presence of only one vinyl proton and the mass spectrum showed peaks at m/e 510 (M^+), 495 (M^+-CH_3), 450 (M^+-HOAc), 435 ($M^+-HOAc-CH_3$), 390($M^+-2HOAc$), 375 ($M^+-2HOAc-CH_3$), 309, 203 and 189. On the basis of these

spectral data, the rearranged product has been assigned structure 8.



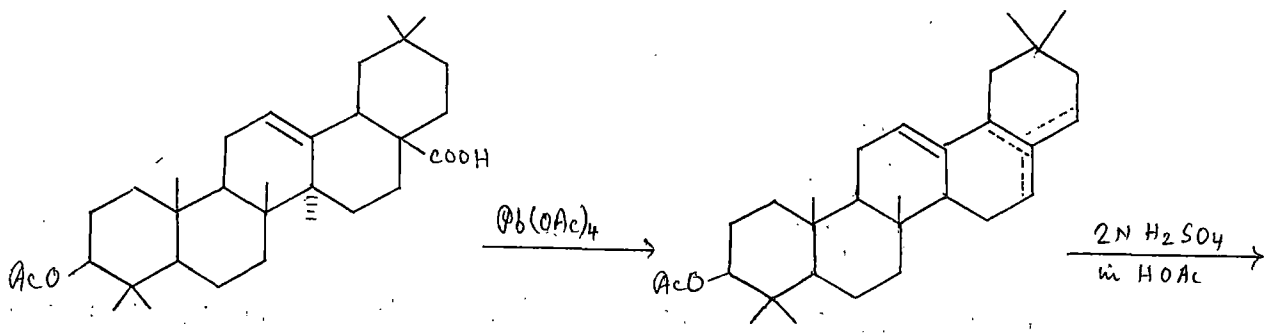
5 6 7 8

The mass fragmentation pattern of the rearranged product 8 can be explained as follows:



The fragments at m/e 202 and 133 are diagnostic of the system shown in 5.

In order to correlate the above observation, a similar diene system 11 have been prepared starting from acetyl oleanolic acid 9. Oxidative decarboxylation of acetyl oleanolic acid 9 with lead tetraacetate gave among other products the diene mixture 10 which on acid isomerization afforded the heteroannular conjugated diene 11.



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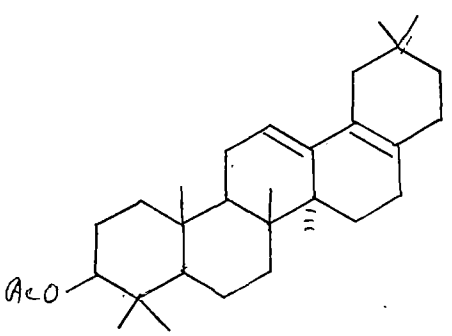
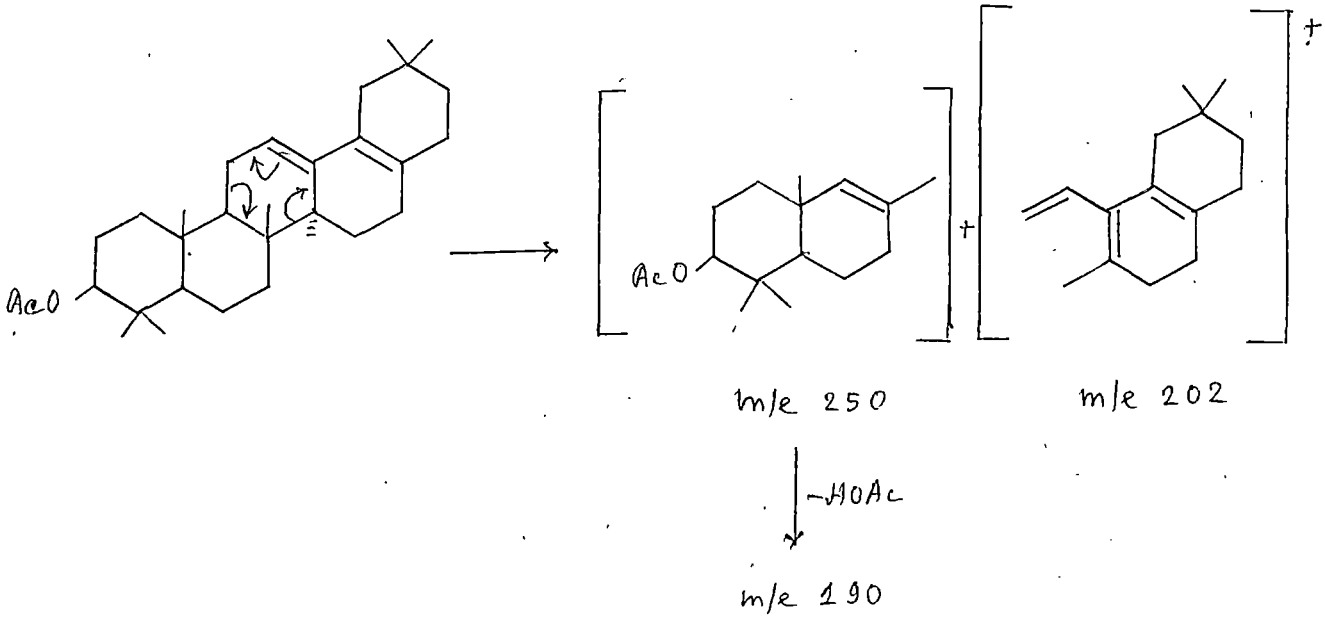
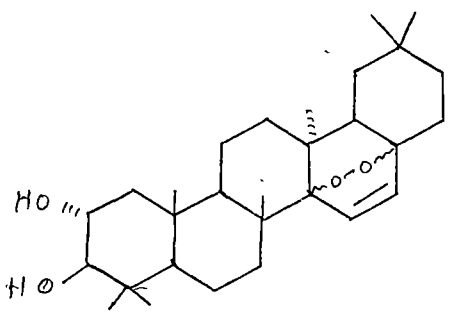


11

If the peaks at m/e 202 and 190 are indeed diagnostic of structure 8, it is expected that 11, which has the same skeleton as that of 8 should exhibit peaks at m/e 202 and 190 corresponding to the following fragmentation.



In fact, the mass spectrum of 11 showed prominent peaks at m/e 452 (M^+), 437 (M^+-CH_3), 392 (M^+-HOAc), 377 ($M^+-HOAc-CH_3$), 202 and 190. Hence the structure 9 for the rearranged diene diacetate is confirmed, which in turn confirms structure 6 for the homoannular conjugated diene. The nor-triterpene isolated from the plant must therefore have the structure 5 and the double bond must be placed in ring D in accordance with the NMR results.



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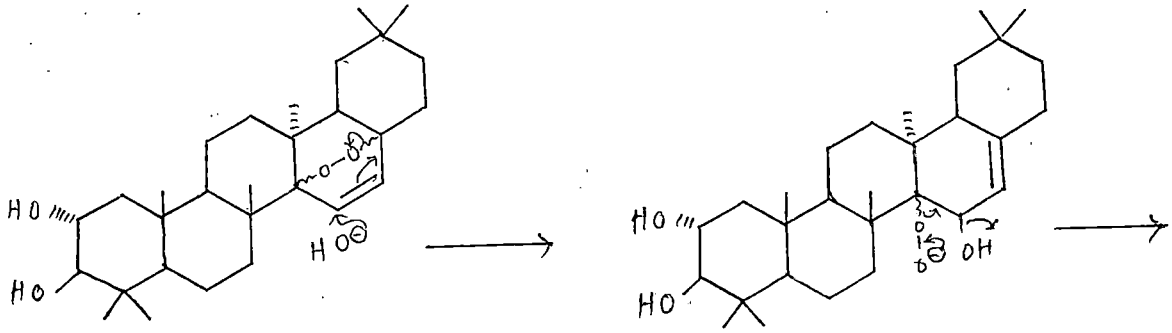
The formation of the homoannular conjugated diene 6 from the nor-triterpene peroxide 5 can be explained by the following mechanism:



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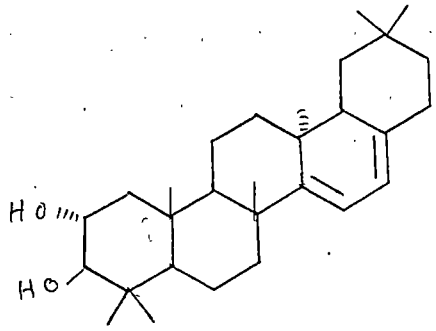

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Chapter V :

Experimental portion has been described in this chapter.

PART - II

CHEMICAL INVESTIGATION OF AILANTHUS GRANDIS PRAIN. : ISOLATION OF TWO NEW QUASSINOIDS GRANDILACTONE A AND GRANDILACTONE B AND STRUCTURE ELUCIDATION OF GRANDILACTONE A.

Chapter I :

In this chapter the morphological features of the plants of the Simaroubaceae family has been described.

Chapter II :

An up-to-date brief review on quassinoid bitter principles isolated from Simaroubaceae family plants has been incorporated in this chapter.

Chapter III :

This chapter describes the isolation of two new quassinoids Grandilactone A and Grandilactone B from the benzene extract of Ailanthus Grandis Prain. The structure elucidation of Grandilactone A is also discussed.

Section A :

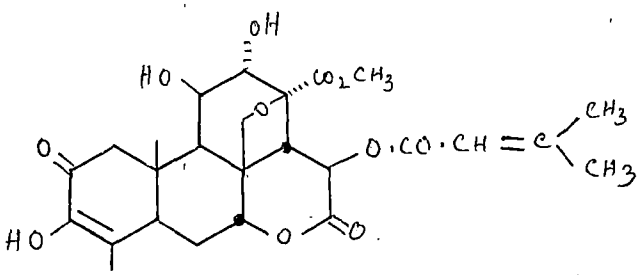
This section deals with the extraction of Ailanthus Grandis Prain. The benzene extract of Ailanthus Grandis Prain on concentration

gave two solids: solid (A) and solid (B).

Section B :

This section describes the investigation on the structure of a new quassinoid Grandilactone A.

Solid (A) (Section A) on crystallisation gave crystals of Grandilactone A, $C_{25}H_{32}O_9$, m.p. 253°C, $(\alpha)_D$ +195.7°. Grandilactone A formed a triacetate. A careful inspection of the I.R. spectra of Grandilactone A and its triacetate revealed that of the nine oxygen atoms present in Grandilactone A, three are present as hydroxyl groups, two are involved in a δ-lactone group, two in a α,β-unsaturated ester group, one is present as a α,β-unsaturated carbonyl function and the ninth oxygen atom is involved in an ether linkage. The U.V. spectrum of Grandilactone A disclosed the presence of an α,β-unsaturated carbonyl group and an α,β-unsaturated ester group. The mass spectra of Grandilactone A and its triacetate showed peaks at m/e 55 and 83. By analogy with Brusatol 12, which also showed peaks at m/e 55 and 83, the partial structure 13 was advanced for Grandilactone A. This assignment was further supported by the observation of peaks at m/e 393 ($M^+-C_4H_7CO$) and at m/e 375 ($M^+-C_4H_7COOH$) in the mass spectrum of Grandilactone A and at m/e 502 ($M^+-C_4H_7COOH$) in the mass spectrum of Grandilactone A triacetate.



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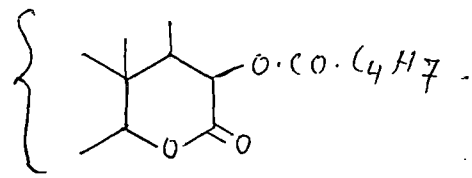

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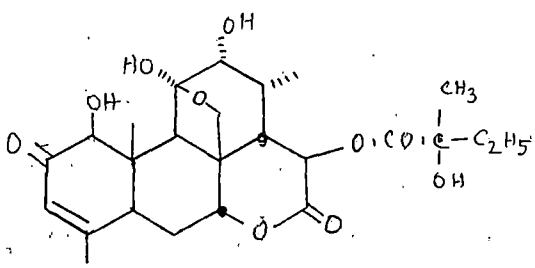
The striking similarity of mass fragmentation pattern of Grandilactone A to those of Glaucarubinone 14 and Ailanthinone 15 suggested that these three quassinoids might have the same basic



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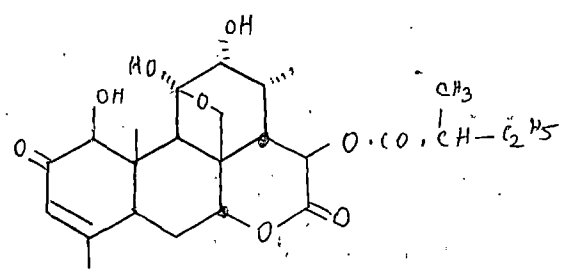

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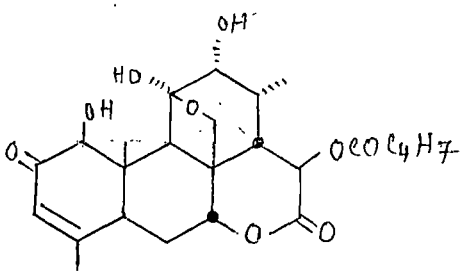
skeleton. On this basis the structure of Grandilactone A was extended to 16. The U.V., I.R. and N.M.R. data of Grandilactone A and its



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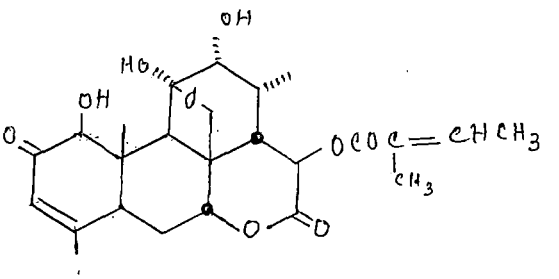

17

triacetate are in complete agreement with this structure. Moreover, the NMR spectrum of Grandilactone A showed that the ester group was present as $-O.CO.C(CH_3)=CHCH_3$. On this basis the structure of Grandilactone A was extended to 17. Further work is in progress to characterise the ester part.

Section C :

In this section the isolation of another new quassinoid, Grandilactone B is described.

Solid (B) (Section A) on crystallisation gave crystals of Grandilactone B, $C_{25}H_{34}O_9$ m.p. 273°C, $(\alpha)_D$ + 200°. The I.R. spectrum

of this compound showed the presence of -OH group (free), -OH group (H-bonded), δ -lactone group, α,β -unsaturated carbonyl function and conjugated C = C. The U.V. spectrum of the compound confirmed the presence of an α,β-unsaturated carbonyl chromophore. Work on the structure elucidation of Grandilactone B is in progress.

Chapter IV :

This chapter describes the experimental part pertaining to the above work.