CHAPTER I

INTRODUCTION

Many varieties of banana are cultivated in Thailand; these plants had been classified as Musa paradisiaca and Musa sapientum. Musa paradisiaca covers the cultivars Klue Klai, Klue Hakmuk; whereas Musa sapientum covers the cultivars Klue Kai, Klue Hom, and Klue Namwa.(1) Recently as a result of intensive research on banana plants in Trinidad,(2) it has been shown that most of the edible bananas cultivated throughout the world are hybrids of two wild species, Musa acuminata and Musa bulbisiana, and varieties of these hybrids. Consequently, all Thai banana plants, refered to in this thesis will be classified as Musa hybrids and will be named cultivars.

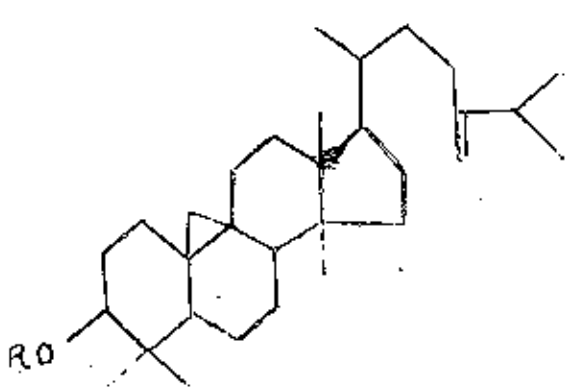
Musa-cultivar Namwa is a coarse herbaceous plant shooting from the perennial roctstock which is often stoloniferous. The trunk is erect, soft but stout which tapers towards the tip and is surrounded by the leaves. It is about 2-5 m. in height and is formed by the thickened closely imbricate red tinted pale green leaf sheaths. Leaves are large, oblong about 2m. long, midrib prominent blade with bases oblique or nearly equal; the upper surface is dark green, and the lower glaucous. The glaucous cover is covered with a waxy powder. Inflorescence is terminal

and later recurved. It is a stout bracteated spike. The bracts are dirty purple subtended the group of flowers and easily drop off. Flower at the lower finger is perfect, and the upper one unisexual. Fruit is formed in hands, there are 5-10 hands per bundle, and each hand consists of 5-12 fingers. The fruit is cylindrical, about 3-6 cm. in diameter, and 10-15 cm. long, and is ridged before maturing. Klue Namwa usually takes about 8-10 months to give a bundle of fruit, ready for harvesting.

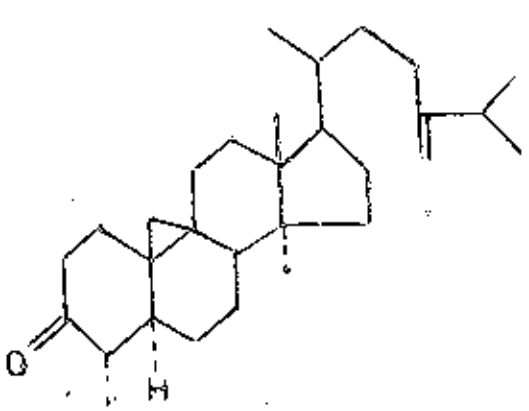
The banana has a nutritive value(3) similar to the potato, but it has a higher food value. With 75 % of water, it carries 22 % of carbohydrates, which are in the form of starch before the flesh is ripe, and as simple sugars when the flesh has ripened. While the carbohydrates are still chiefly in the form of starch, the unriped fruits can be dried. The resulting banana fig can be stored for a considerable time. The banana also yields a number of minor edible products including sweetmeats, flour (dried and powdered unriped banana) and powder (dried and powdered ripe bananas). The bunch of male flowers are eaten after they are cooked. The female flower can be eaten also as a salad. Very young fruits can be eaten cooked, and so can the interior tissue of the rhizome. It is also possible to make alcohol and alcoholic beverages from bananas. Banana pulp can be used with chemicals to dye wool, silk, cotton, leather and wood. Paper can be made from the stems

which can also be used as a pig-food. The leaf of the banana can make a wrapper and plate for food. The Siamese also wrap cigarettes in the leaves.

New uses for the banana plant other than as a source of fruit would be advantageous. Jewers has reported[4] an investigation of the wax of banana skins (Musa sapientum) from the British Cameroons with a view to finding chemicals of industrial importance. This work has revealed the presence of large quantities of methyl steroids which have been separated by chromatography over silica gel. An ester fraction, which accounts for about 40 % by weight of the wax and is composed mainly of 24-methylenecycloartanyl palmitate (I;R=$CH_3(CH_2)_{14}CO$), and a ketonic fraction, about 20 % by weight of the wax which has been shown to be cycloeucalenone (II), are the major components of the wax.



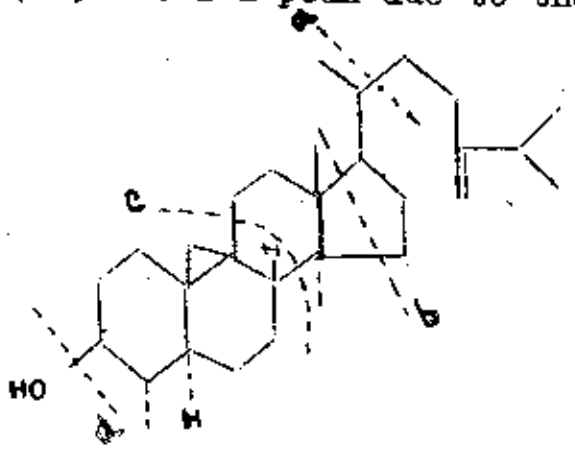
(I)



(II)

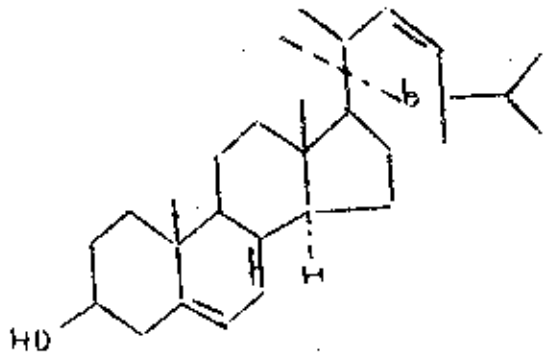
Chromatography of the ketonic fraction over alumina afforded cycloeucalenone (II), m.p. 80°-80.5°, which gave an oxime m.p. 175° - 176°. The infra-red spectrum of the ketone showed absorption peaks at 3050 $cm.^{-1}$ (C-H stretching of a cyclopropane ring), 1708 $cm.^{-1}$ (C = O stretching of a cyclohexanone), and 3010, 1638, 888 $cm.^{-1}$ (C-H stretching, C=C stretching, and C-H bending of a vinylidene group).

Ozonolysis of cycloeucalenone afforded formaldehyde, isolated as its dimedone derivative, which confirmed the presence of a vinylidene group in the molecule. Sodiumborohydride reduction of cycloeucalenone furnished an alcohol (III), m.p. 136° - 137°, which gave an acetate, m.p. 110°. The mass spectrum of the alcohol showed a splitting pattern as indicated by (III). A significant fragment of 97 mass units is observed in the mass spectrum which is suggested to result from fragmentation at (a). The spectrum of ergosterol[5] (IV) shows a peak due to the loss of the whole

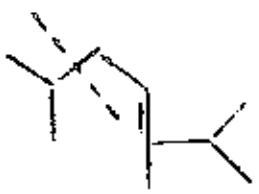


(III)

side chain, which is accounted for by weakening by the double bond of the bond attaching the side chain to the ring system. The production of the fragment of 97 mass units in the spectrum of cycloeucalenol would arise, in a similar way, from a side chain (V), thermal isomerization occuring before fragmentation. Appearance of a peak of 167 mass units due to fragmentation at (b) is in keeping with the mass spectra of steroids, which lose their side chains plus 42 mass unit.

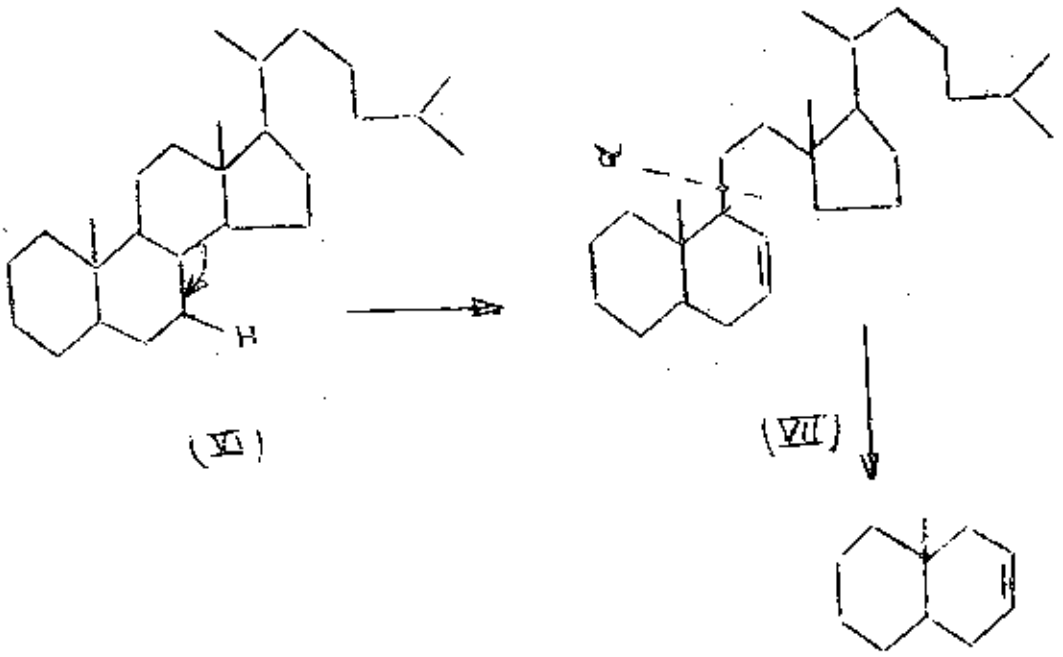


(IV)



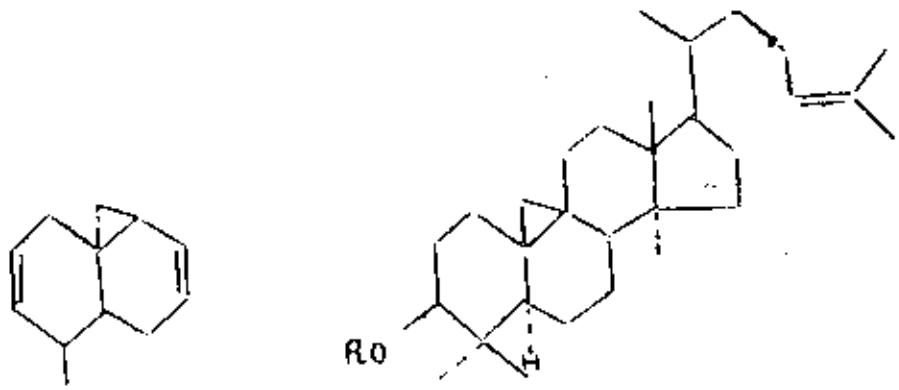
(V)

No reference spectra are available of compounds having a cyclopropane ring as found in cycloeucalenone. However, it is possible to compare the spectrum of this compound with a similar type of compound sitostane[6] (VI). This compound is known to produce an ion of mass 149 in its spectrum which is attributed to (VIII).



(VI) (VII) (VIII)

Cyclocucalenol would be expected by analogy to produce a fragment (IX) of mass 159; a strong ion of this



(IX) (X)

mass is found in its spectrum. Dehydration is known to occur in the determination of the mass spectra of many alcohols, which accounts for fission at (d).

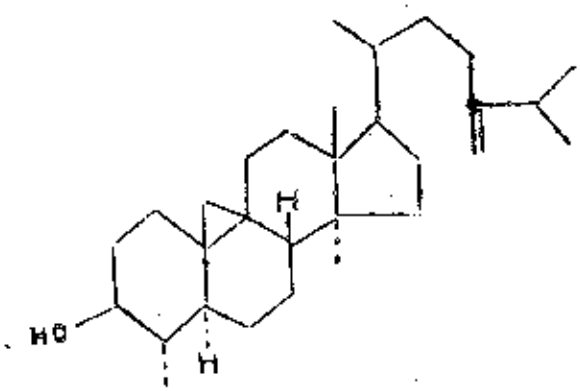
The N.M.R. spectrum of cycloeucalenol was also in agreement with the structure (III). The presence of two

non-equivalent protons on a cyclopropane ring was indicated by a quartet at 6.5, 10.5, 22, and 26 cps. These protons are shielded relative to those in cycloartenol (X, R=H; 18, 22, 32.5, and 36.5 cps.) and cycloartenyl acetate (X, (X, R=CH_3 CO; 18, 22.5, 33, and 37.5 cps). Nevertheless, the differences in chemical shift of the two protons and the coupling constants are very similar ($\delta\nu$=14 cps; J=4 cps). It would seem, therefore, that N.M.R. can be used effectively to differentiate cyclopropane triterpenoids of the cycloeucalenol and cycloartenol types. The presence of an equatorial hydroxyl group and a vinylidene group was also revealed by N.M.R.

The above physical evidence suggested that the ketonic component of banana skin wax was cycloeucalenone which had previously been prepared by King from cycloeucalenol isolated from Eucalyptus microcorys[7]. Comparison of the I.R. spectra of the ketone from banana skin wax with that of cycloeucalenone proved this to be the case.

24- methylenecycloartanol (I; R=H) could not be obtained in a pure state by chromatography over alumina of the alcohol derived from the ester fraction by hydrolysis. However, fractional crystallization of the acetylated alcohol furnished 24-methylenecycloartanyl acetate (I; R=CH_3 CO) m.p. 116°. The infra-red spectrum of this compound showed absorption maximum at 3050 $cm.^{-1}$ (C-H stretching of cyclopropane ring), 1725 and 1238 $cm.^{-1}$

(C=O stretching and C–O– C asymmetric stretching of acetate), and 3010, 1638, and 888 cm.$^{-1}$ (C=H stretching, C=C stretching, and C-H bending of a vinylidene group). Mass spectral study of the alcohol fraction, after chromatography over alumina, showed that the compound was heterogenous and consisted mainly of an alcohol having a molecular weight of 440, which is in agreement with that for 24– methylene-cycloartanol ($C_{31}H_{52}O$), together with a small quantity of a C_{30} alcohol, possibly cycloeucalenol (XI).



(XI)

The additional methyl group in this compound must be in the nucleus and not in the side chain as shown by the presence of a fragment of mass 173 in the mass spectrum. This corresponds to the fragment of mass 159 in the mass spectrum of cycloeucalenol, previously discussed, plus an additional methyl group. Fragments of mass 97 and 127 found in the spectrum of cycloeucalenol and attributed to fission in the side chain, were also observed in the

spectrum of this alcohol.

The information suggested that the alcohol might possibly be 24-methylenecycloartanol, which had previously been isolated from Rice Bran Oil by Ohta and Shimizu.[8] Confirmation of this structure was obtained by preparation of the dihydro acetate, m.p. 121°-122°, and comparison of the infra-red spectrum of the unsaturated acetate with a sample of 24-methylenecycloartanyl acetate provided by Dr. Ohta.

The above work has stimulated the author to investigate the chemical constituents of the Thai banana plant. The presence of large quantities of isolatable steroids in the wax of a Thai banana could be of economic importance to Thailand, as these compounds could be used in the manufacture of steroids of pharmaceutical interest. It is for this reason that the author has under taken the present work.