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# CHEMOTAXONOMICAL ALKALOID STUDIES III.

# FURTHER STUDIES OF LIPARIS ALKALOIDS.

Kunisuke Nishikawa and Yoshimasa Hirata

Chemical Institute, Faculty of Science
Nagoya University, Chikusa, Nagoya, Japan

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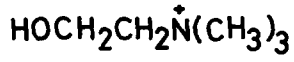
Recently, we reported the structures of new glycosidic alkaloids isolated from Liparis species of Orchidaceae. (1) (2) From the point of chemotaxonomical interests, we studied the isolation of Liparis alkaloids from other species, Liparis bicallosa Schltr., and its variant, Liparis hachijoensis Nakai and Liparis auriculata Blume.

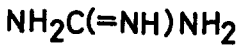
In this communication, we wish to report the successful isolation and the results of structural elucidation of these Liparis alkaroids.

L. bicallosa Schltr. and L. hachijoensis Nakai contain the same mixture of alkaloids which were choline( I ), guanidine( II ), laburnine( III )(3), malaxin( IV )(4) and a new crystal ( V ).

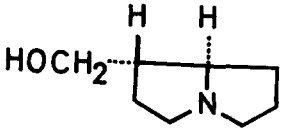
The procedure of extraction was described below.



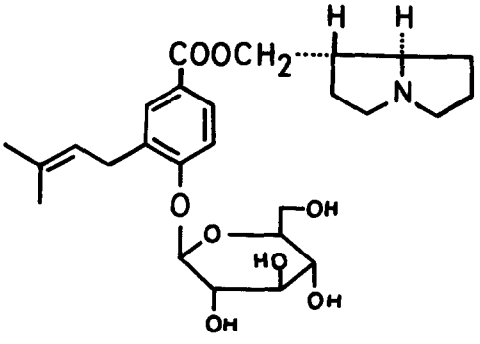
( I )



( II )



( III )



( IV )

Methanolic extracts which were obtained by soak the fresh plants in hot methanol ( about 60° ) were concentrated under reduced pressure. After the residual water layer was washed with ether several times, saturated aqueous solution of ammonium tetrathiocyanoammonochromate was added to this extracts ( water layer ).

Thus obtained reinecke salt was dissolved with as small volume of acetone as possible and the reddish purple acetone solution was filtered. Warmed saturated aq. soln. of silver sulfate was dropped to the filtrate until the reddish color was disappeared and the formed precipitate was removed by centrifugation. The supernatant was concentrated and dried in vacuo. Methanolic soln. of the residue gave a crystal( V ) and furthermore, the mother liquid was separated into choline, guanidine, laburnine and malaxin by chromatography on paper with the mixture of n-BuOH, AcOH, $H_2O$ ( 4 : 1 : 1 ). The alkaloid ( V ), $C_{27}H_{42}O_8N_4 \cdot H_2O - H_2SO_4$, m.p. 180-182°, pKá=9.8 ( 66 % MeOH ), is a main alkaloidal component of these plants and has some points of similarity to malaxin in physical properties as follows: $\nu_{max}^{KBr}$ ( $cm^{-1}$ ) 3400, 3200 ( shoulder ), 2700, 1710, 1660 ( very strong ), 1605; $\lambda_{max}$ ( $\varepsilon$ ) 255 mμ ( 16000 ) in methanol; N.M.R.* ( $D_2O$-$H_2SO_4$ ) 1.77 ( 6H, broad singlet ), 7.34 ( 1H, doublet, J=9 cps ), 7.80 ( 1H, singlet ), 7.96 ( 1H, doublet, J=9 cps ).

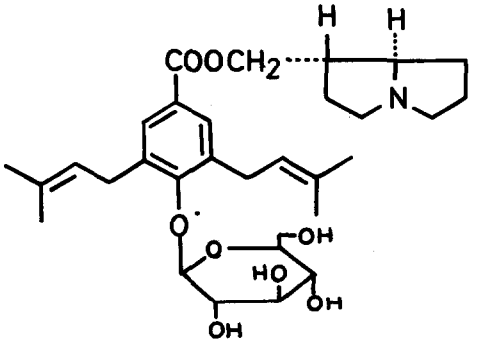
Such physical data and the degradation products are very similar to those of malaxin, but in any acidic or alkaline condition, nonsubstituted guanidine was obtained from V quantitatively.

Moreover, on paper chromatography it decomposed to malaxin and guanidine in any solvent.

Now, we concluded that V must be malaxin-guanidine complex, in fact, when malaxin ( free base ) and guanidine sulfate were mixed in adequate ratio ( about 1 : 1.5 mol. eq. ), completely same crystal as V was obtained.

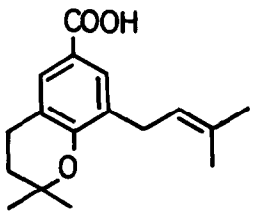
From the L. auriculata Blume, a new glycosidic alkaloid ( VI ), a main alkaloidal component of this plant, was isolated. The methanolic extracts were obtained by same method as previously described above, which were concentrated under reduced pressure and the remained aq. layer was washed with ether. The saturated solution of picric acid was added to the extracts and the precipitate was collected by filtration. Paper chromatography of the picrate with the mixture of n-BuOH, AcOH, $H_2O$ ( 4 : 1 : 1 ) gave a free base, auriculine( VI )( amorphous solid ), which was named by us.

This alkaloid was reconverted into picrate but its crystallization was unsuccessful. ( m.p. 97-100° ).

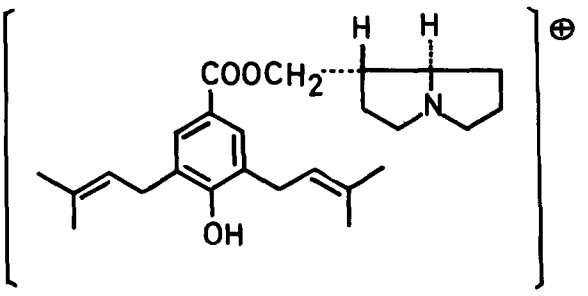



( VI )

Physical properties: $\lambda_{max}$ 246 mμ ( methanol ); $\nu_{max}^{KBr}$ ( $cm^{-1}$ ) 3400, 1715, 1605, 1100-980, $(\alpha)_D^{20°}$=-19.1° ( in methanol ), indicate that auriculine ( VI ) seems to have same chromophore as Kumokirine or Kuramerine(2). Exactly, it gave a glucose, laburnine and VII by treatment with 2N Hcl at 100° for several hours.




( VII )




( VIII )

These results show that VI should be constructed by glucose, 3,5-dimethylallyl-4-hydroxy benzoic acid (1), (2) and laburnine (3), because the calculated molecular weight of VI is in well agreement with the combined formula of these three components.

The fragment peak( m/e 397 ) which is interpreted by the ion of VIII provided the evidence of the structure VI for auriculine.

* Easily assighed signals were only described. All other signals were broad or complex multiplet.

## REFERENCES

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