and 0.7 cm. in internal diameter at the main part and 1.5 cm. in the upper part, equipped with a glass cock at the bottom. The lower end of this tube is combined with the measuring receiver by a rubber stopper. A side tube for suction is attached to the upper part of the receiver. At the bottom of the tube and upon the cock, glass wool is packed 5~6 mm. thick. A slurry of alumina in petroleum benzine is poured into the tube, until the height of the alumina reaches 7~8 cm. while the solvent flows down dropwise into the receiver.

Dissolve the residue from carbon tetrachloride solution in 1 cc. of petroleum benzine and pour it into the column before the solvent flow out entirely from alumina layer. As soon as the sample solution penetrates into alumina, add slowly the developing solvent, i.e. 10% acetone-petroleum benzine, into the tube so as to avoid the agitation of alumina layer. The filtrate from the column is fractionated into 2-cc. portions from the beginning of development and 20 fractions are sufficient for vitamin D to be eluted completely. Developing may be carried out with or without suction, but should be completed within 2 hours.

4. Vitamin D measurement. Evaporate each fractions to dryness at the pump, and to the residues add 0.2 cc. of chloroform and then 3 cc. of antimony trichloride reagent. Measure the optical densities at 500 mμ 2 minutes after the addition of the reagent. Calculate the weights of vitamin D in gamma from optical densities for each fractions, using a conversion factor, and sum them up over the vitamin D fraction. From this sum the amount of vitamin D in 1 g. of oil is calculated.

Summary

1) The optimum condition of digitonin precipitation reaction has been determined. The elimination of sterols seems to be satisfactory.

2) A method of the determination of vitamin D by means of the digitonin precipitation reaction followed by chromatography on alumina is proposed. This method applied to fish liver oils of medium potency results in good agreement with biological assays.

(Received May 15, 1953)

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47. Shojiro Uyeo and Junji Koizumi: Lycoris Alkaloids. XXV.[1] Studies on the Constitution of Lycoramine. (4).

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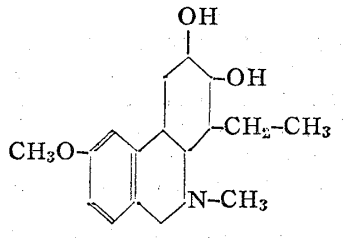
In the preceding paper[1] it was shown that catalytic reduction of lycoremine, a new alkaloid contained in *Lycoris radiata*, gave mainly lycoramine, a base first isolated from the same plant by Kondo, Tomimura, and Ishiwata[2]. Kondo and Ishiwata[3] assigned the formula $C_{17}H_{25}O_3N$ to lycoramine and subjected it to mild oxidation to obtain lycoramine lactam, which on distillation with zinc dust yielded 1-methylphenanthridine, and the skeleton of the molecule was established. Lycoramine lactam was then oxidized with chromic acid and yielded a ketone, which on further treatment with potassium permanganate furnished among others an *o*-dicarboxylic acid, "acid B", of the formula $C_{13}H_{13}O_6N$, m.p. 261~262°. The structure of the acid was proved by decarboxylation to the known 6-methoxy-N-methyldihydroisocarbostyril. This suggested that the rings A and B of lycoramine are represented by 6-methoxy-N-methyltetrahydroisoquinoline. Although Kondo and Ishiwata proposed, on the basis of this and other experimental findings, the structure (I) for lycoramine, they appear to have encountered some difficulties in the interpretation of the



(I)

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1) S. Uyeo, S. Kobayashi: This Bulletin, 1, 139 (1953).

2) H. Kondo, K. Tomimura, S. Ishiwata: J. Pharm. Soc. Japan, 52, 433 (1932).

3) H. Kondo, S. Ishiwata: *Ibid.*, 58, 1, 13 (1938); Ber., 70, 2427 (1937).

results obtained by the degradation of the C ring of the molecule. Since Cook and Loudon[4] have already discussed these respects in details, it may be superfluous to represent them in this instance. However, the reinvestigation of the work published more than fifteen years ago seemed evidently desirable not only on account of the controversies concerned but also in view of the facts shown in the preceding paper. The present report describes the experimental results obtained during these two years in the studies of the constitution of lycoramine which were carried out under the generous support of Professor H. Kondo.

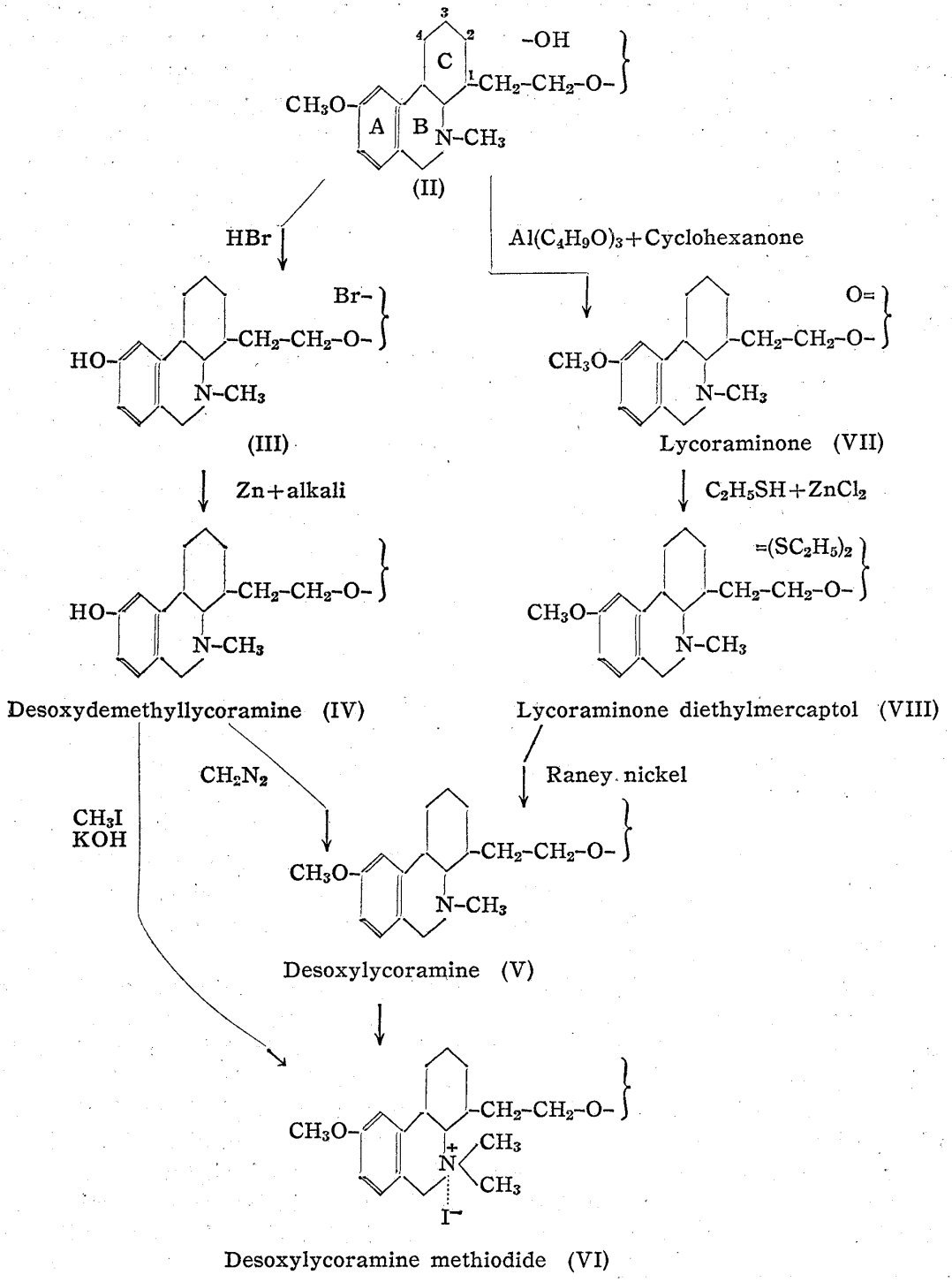
As has already been pointed out[1], lycoramine is best represented by the formula $C_{17}H_{23}O_3N$ rather than that reported previously. On acetylation of the base with acetic anhydride and sodium acetate an acetyl derivative was obtained which showed the same melting point as that which was previously described. An analysis of the compound disclosed, however, that it contained only one acetyl group, while the previous workers[3] found two acetyl groups in the molecule. An attempted oxidation of lycoramine with periodic acid was unsuccessful as was reported by Kondo and Ishiwata[3], the starting material being recovered unchanged almost quantitatively. By the C-methyl determination of lycoramine there were obtained figures which might suggest a negative result. These findings suggested that the C ring of lycoramine (II) may contain one hydroxyl group and that the remaining oxygen atom might belong to an oxygen bridge which connected the carbon atom situated at the position 2, 3, or 4 and the ethyl side-chain at 1-position of the hydrophenanthridine nucleus to form an oxide ring of a five-, six-, or seven-membered type. In order to open the postulated oxide ring, lycoramine was subjected to reaction with an excess of anhydrous hydrobromic acid in glacial acetic acid at 100°, whereby there was obtained a hydrobromide, m.p. 215~217° (decomp.), $C_{16}H_{20}O_2NBr \cdot HBr$, of a phenolic base containing a nonionizable bromine atom. The bromine atom of the base can readily be removed on treatment with zinc dust in aqueous alcoholic sodium hydroxide solution, yielding a crystalline product (III), $C_{16}H_{21}O_2N$, m.p. 228~229°. The base is soluble in aqueous alkali and gives a green coloration with ferric chloride but contains no C-methyl group as was shown by the Kuhn-Roth's determination. These results may indicate that the reaction with hydrobromic acid has failed to effect cleavage of the oxide ring of the molecule, changes being only the demethylation of the methoxyl group on the benzene ring and the replacement of an alcoholic hydroxyl group by a bromine atom which is capable of being reduced to hydrogen by zinc and alkali. The resulting base may therefore be designated desoxydemethyllycoramine (IV). Upon methylation with diazomethane, desoxydemethyllycoramine afforded an oily product, desoxylycoramine (V) which was unable to be crystallized, but yielded a crystalline perchlorate, m.p. 220~221°, and a methiodide (VI), m.p. 275~276°. The latter derivative was also obtained by direct methylation of desoxydemethyllycoramine with methyl iodide in the presence of potassium hydroxide in methanol solution.

An approach to the same degradation product by another route was eventually realized in the following way. Lycoramine was first oxidized according to the method of Oppenauer by the use of aluminum *t*-butoxide and cyclohexanone in toluene solution to yield lycoraminone (VII) which melted at 130~132°. Lycoraminone is a monoketone, giving a monosemicarbazone of m.p. 114~116° and showing a carbonyl absorption maximum at 5.80 μ in the infrared spectrum. It contains no hydroxyl group, since the OH band does not appear in the 2.7~3.0 μ region. These findings further afforded a supporting evidence for the presence of one rather than two hydroxyl groups in lycoramine molecule. When reacted with ethyl mercaptan in the presence of zinc chloride and sodium sulfate,

4) Manske, Holmes: "The Alkaloids", Academic Press, Vol. II, 331~352(1952).

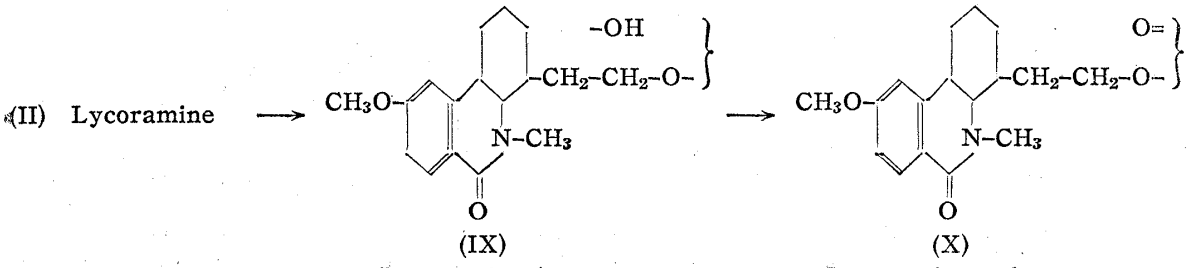
lycoraminone was converted into the diethylmercaptol (VIII), which was immediately desulfurized by means of Raney nickel in boiling alcohol to form desoxylycoramine (V). Thus a viscous oil was obtained which was characterized by conversion to its crystalline perchlorate and methiodide (VI). These salts showed the same melting points when alone and on admixture with those of the corresponding derivatives obtained above. Thus the identity was established.

The sequence of reactions may be summarized as follows:



Previously, Kondo and Ishiwata[3] obtained an evidence indicating the presence of an α-diketonic grouping in the oxidation product of lycoramine lactam with chromic acid. In view of the present results mentioned above, the formation of a diketone from the lactam is highly improbable, and so the reinvestigation was carried out with the following results.

Oxidation of lycoramine with diluted potassium permanganate solution in the cold readily afforded a neutral substance, lycoramine lactam (IX), $C_{17}H_{21}O_4N$, the properties of which were in good accord with those given in the original paper[3]. When this substance was oxidized either with chromic acid in the manner described previously or by the Oppenauer method in the similar way used in the case of lycoramine itself, the identical product was obtained for which the name lycoraminone lactam (X) would be proposed. Although the melting points, given in the literature to the carbonyl derivaties of this ketone lactam, were in most cases very close to the corresponding materials obtained in the present experiments, considerable discrepancies were found in the analytical values. Contrary to the previous report, it was observed that lycoraminone lactam formed a monoxime, mono-*p*-nitrophenylhydrazone, and a monosemicarbazone as were elucidated by the analyses. In addition to these derivatives, a phenazine derivative was reported in the previous paper.[3]. The authors also were able to isolate a crude product giving a similar melting point to that of the phenazine derivative when lycoraminone lactam and *o*-phenylenediamine were heated on a water bath in alcoholic solution, but the substance was too unstable to be recrystallized from alcohol. It is believed that the reaction product is not a phenazine derivative.



The authors are indebted to the Ministry of Education for the grant of a Scientific Research Fund, and to Messrs. Hozumi and Imaeda for the microanalyses.

Experimental

Lycoramine—The crude alkaloid, which was recovered from the perchlorate monohydrate, m.p. 132~136° (decomp.), by neutralization with alkali in aqueous solution, extraction with ether and removal of the ether, was recrystallized from acetone several times to yield colorless prisms or plates, m.p. 120~121.5°. *Anal.* Calcd. for $C_{17}H_{23}O_3N$: C, 70.58; H, 7.95. Found: C, 70.23, 70.36; H, 7.82, 7.40; C-CH_3, 1.07, 0.68.

Acetyl derivative of lycoramine—A mixture of 0.5 g. of lycoramine, 0.3 g. of anhydrous sodium acetate, and 7 cc. of acetic anhydride was heated on a water bath for 30 minutes. After cooling, 10 cc. of water was added to the reaction mixture and the aqueous solution was rendered alkaline with 20% K_2CO_3 solution. The precipitate was filtered off and when dried weighed 0.47 g. Recrystallization from 50% alcohol gave colorless needles melting at 93~95° after drying in vacuo for a long time. *Anal.* Calcd. for $C_{17}H_{22}O_3N\cdot COCH_3$: $COCH_3$, 12.99. Found: $COCH_3$, 13.00.

Lycoramine chloroaurate—Bright red rhombic crystals from hydrated methanol, m.p. 193° (decomp.). *Anal.* Calcd. for $C_{17}H_{23}O_3N\cdot HAuCl_4$: C, 32.43; H, 3.81; Au, 31.31. Found: C, 32.41, 32.51; H, 3.80, 3.91; Au, 31.33.

Attempted oxidation of lycoramine with periodic acid—A solution of 100 mg. of lycoramine in 50 cc. of water was added to 50 cc. of 0.1 mol. aqueous periodic acid solution. The solution was kept at 20° for 24 hours. 5 cc. of the solution was mixed with 10 cc. of a saturated $NaHCO_3$ solution, 15 cc. of 0.1 *N* sodium arsenite solution, and 1 cc. of 5% KI solution, and the excess of

sodium arsenite was titrated with 0.1 *N* iodine solution, no consumption of periodic acid being observed.

The same results were obtained when the solution was titrated after standing for 48 or 72 hours. The three titrated solutions were combined, made strongly alkaline with 20% NaOH and extracted with six 20-cc. portions of chloroform. Upon evaporation to dryness, 27 mg. (yield, 90%) of lycoramine was recovered as an oil, which was readily crystallized by the addition of a few drops of ether, and melted then at 114~116°. No depression in melting point was observed on admixture with an authentic sample.

The Oppenauer oxidation of lycoramine—A mixture of 2.5 g. of lycoramine, 3 g. of aluminum *t*-butoxide, 60 cc. of dry cyclohexanone, and 210 cc. of dry toluene was maintained at a reflux for 6 hours in an oil bath. After cooling, the reaction mixture was extracted six times with 20-cc. portions of 10% H_2SO_4. The combined acid solutions were washed five times with 25-cc. portions of ether to remove cyclohexanone, rendered alkaline with 50% NaOH solution, and then extracted seven times with chloroform. The chloroform solutions were combined, dried over K_2CO_3, and the solvent was removed by distillation, yielding 2.2 g. of a semisolid residue. This was dissolved in benzene and filtered through an alumina column to retain some unchanged lycoramine. Elution of the column with benzene and evaporation of the eluate afforded, after recrystallization from absolute alcohol, 0.65 g. of lycoraminone (VII) in colorless plates, m.p. 130~132°. Washing of the column with 50 cc. of acetone furnished, after evaporation, an additional 0.2 g. of the less pure ketonic base, m.p. 126~129°, while lycoramine still remained in the column. Total yield, 0.85 g. *Anal.* Calcd. for $C_{17}H_{21}O_3N$: C, 71.08, H, 7.31. Found: C, 71.23; H, 7.19.

Lycoraminone semicarbazone—A solution of 0.14 g. of semicarbazide hydrochloride and 0.3 g. of sodium acetate in 2 cc. of water was added to a solution of 0.1 g. of lycoraminone in the minimum amount of alcohol. After heating on a water bath for one hour and then cooling, the reaction mixture was made alkaline to litmus. The crystalline precipitate was collected by filtration and recrystallized from acetone-hexane to give the semicarbazone, m.p. 114~116° (decomp.). *Anal.* Calcd. for $C_{18}H_{24}O_3N_4$: C, 62.79; H, 6.97; N, 16.27. Found: C, 63.01; H, 6.69; N, 16.52.

Lycoraminone diethylmercaptol (VIII)—To a mixture of 3 cc. of dry ethyl mercaptan, 0.85 g. of freshly fused zinc chloride and 0.7 g. of anhydrous sodium sulfate was added with cooling 0.2 g. of lycoraminone dissolved in 4 cc. of dry mercaptan. The mixture was allowed to stand at 5° for 24 hours and then at room temperature for 4 hours. After the addition of 5 cc. of ice water, the oily layer which separated was taken up in chloroform. The chloroform solution was shaken with 10% sodium hydroxide solution, dried over potassium carbonate, and evaporated to dryness. The resulting viscous oil of mercaptol was used directly in the desulfurization reaction.

Desoxylycoramine (V)—The mercaptol obtained above was refluxed for 3 hours with 5 g. of Raney nickel in 40 cc. of 75% alcohol. The nickel was filtered and washed three times with 20-cc. portions of hot alcohol. The combined alcohol solutions were concentrated under a reduced pressure to yield 0.1 g. of oily desoxylycoramine, which distilled at 150~160° under 0.05 mm. Hg.

Desoxylycoramine perchlorate—A part of the oily product obtained above was dissolved in a small amount of methanol and acidified with 10% perchloric acid. The resulting crystalline precipitate was once recrystallized from methanol, giving the perchlorate as colorless leaflets, m.p. 219~220°. *Anal.* Calcd. for $C_{17}H_{23}O_2N \cdot HClO_4$: C, 54.61; H, 6.42. Found: C, 54.31; H, 6.40.

Desoxylycoramine methiodide (VI)—The remaining portion of the oily product mentioned above was heated with methyl iodide in methanol to obtain a white precipitate, which was collected on a filter, and recrystallized from methanol. The resulting white needles had m.p. 274~275° (decomp.) after drying in vacuo. *Anal.* Calcd. for $C_{17}H_{23}O_2N \cdot CH_3I$: C, 52.06; H, 6.28. Found: C, 51.88; H, 6.54.

Reaction of lycoramine with hydrobromic acid—A solution of 1 g. of lycoramine and 15 cc. of glacial acetic acid saturated with anhydrous hydrogen bromide was sealed in a glass tube and heated in a water bath at 100° for 3 hours. The reaction mixture was diluted with 15 cc. of water, transferred to a flask and evaporated to dryness under a reduced pressure. Excess hydrogen bromide was removed by standing over solid KOH in an evacuated desiccator to obtain a slightly brown oily residue. Addition of acetone to the residue precipitated crystalline powder which was recrystallized from absolute alcohol to give 0.9 g. of bromodemethyldesoxylycoramine (III) hydrobromide, m.p. 215~217°(decomp.). *Anal.* Calcd. for $C_{16}H_{20}O_2NBr \cdot HBr$: Br (ionizable), 19.09. Found: Br(ionizable), 18.82, 18.71.

The free base (III) was obtained by dissolving the hydrobromide in a small amount of water, neutralization with aqueous $NaHCO_3$, extraction with chloroform, and evaporation of the chloroform. The crude material was recrystallized from alcohol several times and melted slowly at 180~190°. *Anal.* Calcd. for $C_{16}H_{20}O_2NBr$: C, 56.80; H, 5.91. Found: C, 56.79, 56.60; H, 6.17, 5.95.

Debromination of bromodemethyldesoxylycoramine (III)—To a hot stirred slurry of 0.5 g. bromodemethyldesoxylycoramine (III) hydrobromide and 25 g. of zinc dust in 70 cc. of 95% alcohol was added dropwise 20 cc. of 20% NaOH solution. The mixture was stirred and refluxed for 1.5

hours and filtered while hot. The precipitate was refluxed with three 40-cc. portions of alcohol. The combined filtrates was acidified with acetic acid and the alcohol was removed by distillation under a reduced pressure. The residual aqueous solution was diluted with water, shaken with ether, neutralized with 15% Na_2CO_3 solution, and extracted with four 30-cc. portions of chloroform. The combined extracts was dried and evaporated to dryness, yielding 0.29 g. of demethyldesoxylycoramine (IV) in fine needles, which were recrystallized from absolute alcohol, m.p. 228~229°(decomp.). *Anal.* Calcd. for $C_{16}H_{21}O_2N$: C, 74.13; H, 8.10; C-CH_3, 0. Found: C, 73.85; H, 8.27; C-CH_3, 1.12.

Methylation of demethyldesoxylycoramine (IV) with diazomethane—An excess of diazomethane dissolved in ether was added to a solution of 0.1 g. of the debrominated product (IV) obtained above in 15 cc. of methanol and the mixture was allowed to stand overnight. The reaction mixture was evaporated to dryness, dissolved in 10% hydrochloric acid, filtered from an insoluble material, and rendered alkaline with aqueous NaOH. The alkaline solution was extracted with ether and the ether solution was concentrated to yield 0.05 g. of an oily material (desoxylycoramine (V)). From the aqueous alkaline solution, 0.03 g. of the starting material was recovered upon addition of NH_4Cl and extraction with chloroform. The perchlorate of the methylated product was prepared with 10% perchloric acid. After one recrystallization from methanol the white salt melted at 220~221° and did not depress the melting point of desoxylycoramine perchlorate obtained above. *Anal.* Calcd. for $C_{17}H_{23}O_2N \cdot HClO_4$: C, 54.61; H, 6.42. Found: C, 54.78, 54.94; H, 6.59, 6.78.

The methiodide (VI) was obtained, on heating of the above product with methyl iodide in methanol, in colorless needles, m.p. 275~276°(decomp.), and the melting point was undepressed on admixture with a sample of desoxylycoramine methiodide described above. The same product was also yielded when the debrominated product was reacted in methanol with methyl iodide in the presence of potassium hydroxide, the methiodide of the methyl ether being precipitated on cooling. This compound melted at 275~276° after recrystallization from methanol. *Anal.* Calcd. for $C_{17}H_{23}O_2N \cdot CH_3I$: C, 52.06; H, 6.28. Found: C, 51.80; H, 6.61.

Lycoramine lactam (IX)—This was prepared by the procedure of Ishiwata[3], but the yield was increased when 1 g. of lycoramine was oxidized with a smaller amount of $KMnO_4$ (1.8 g.), 0.6 g. of lycoramine lactam being obtained as colorless needles, m.p. 251~252°. *Anal.* Calcd. for $C_{17}H_{21}O_4N$: C, 67.32; H, 6.93. Found: C, 67.14, 66.88; H, 7.01, 6.98.

Lycoramine lactam acetate—A mixture of 0.45 g. of lycoramine lactam, 0.27 g. of anhydrous sodium acetate, and 6.3 cc. of acetic anhydride was heated on a water bath for 2 hours. After cooling, 12 cc. of water was added to the reaction mixture and it was made slightly alkaline by the addition of 20% K_2CO_3 solution. The crystals of the acetate which separated were collected on a filter. Two recrystallizations from 30% alcohol gave colorless fine needles, m.p. 130~131°. *Anal.* Calcd. for $C_{17}H_{20}O_4N \cdot COCH_3$: C, 66.08; H, 6.66; $COCH_3$, 12.46. Found: C, 65.96; H, 6.63; $COCH_3$, 12.45, 12.46.

The Oppenauer oxidation of lycoramine lactam—To a boiling solution of 0.5 g. of lycoramine lactam and 50 cc. of freshly distilled cyclohexanone in 50 cc. of dry xylene was added 5 g. of powdered aluminum phenoxide. The mixture was refluxed gently with mechanical stirring for 7 hours. The cooled reaction mixture was washed successively with three 20-cc. portions of 10% H_2SO_4 and two 20-cc. portions of 10% NaOH solution, and the organic layer was evaporated to dryness under a reduced pressure, leaving a brown viscous oil of the oxidized product contaminated with the starting material. From both the acidic and the basic aqueous layers, a small amount of the oxidation product was recovered by extraction with chloroform after neutralization. The combined oxidation products were dissolved in benzene and the benzene solution was poured through an alumina column. The benzene eluate was collected and evaporated to dryness. Recrystallization of the crystalline solid from absolute alcohol afforded 0.2 g. of colorless prisms melting at 218~219°. The melting point was undepressed on admixture with a specimen (X) prepared from lycoramine lactam by oxidation with chromic acid according to the method described previously. *Anal.* Calcd. for $C_{17}H_{19}O_4N$: C, 67.77; H, 6.31. Found: C, 68.14, 67.70; H, 6.60, 6.44.

Lycoraminone lactam semicarbazone—0.05 g. of lycoraminone lactam (X) was dissolved in 2 cc. of alcohol, water was added until the solution became faintly turbid, and the turbidity was removed by the addition of a few drops of alcohol. 0.1 g. of semicarbazide hydrochloride and 0.15 g. of sodium acetate were then added to the above solution. After heating on a water bath for 1.5 hours, the reaction mixture was cooled in an ice bath and the vessel was scratched until crystallization occurred. Recrystallization from alcohol afforded 0.03 g. of the semicarbazone as colorless needles, m.p. 238°(decomp.). *Anal.* Calcd. for $C_{18}H_{22}O_4N_4 \cdot H_2O$: C, 57.42; H, 6.42; N, 14.82. Found: C, 57.65; H, 6.32; N, 15.56.

Oxime—To a solution of 0.05 g. of lycoraminone lactam in 2 cc. of absolute alcohol, a solution of 0.02 g. of hydroxylamine hydrochloride and 0.046 g. of sodium acetate in 2 cc. of water was

added and heated under reflux on a water bath for 1.5 hours. After cooling, the reaction mixture deposited crops of white crystals, which were recrystallized twice from alcohol, affording colorless fine needles, m.p. 257°. *Anal.* Calcd. for $C_{17}H_{22}O_4N_2$: C, 64.55; H, 6.32; N, 8.86. Found: C, 64.43; H, 6.55; N, 8.69.

***p*-Nitrophenylhydrazone**—A mixture of 0.03 g. of lycoraminone lactam, 0.016 g. of *p*-nitrophenylhydrazine, 2 cc. of alcohol, and 2 drops of 10% acetic acid was heated under reflux for 1 hour on a water bath. Yellow fine needles which separated were collected on a filter after cooling and recrystallized three times from alcohol, m.p. 259~260° (reported m.p. 267~268°). *Anal.* Calcd. for $C_{23}H_{24}O_5N_4$: C, 63.30; H, 5.50; N, 12.84. Found: C, 62.98, 63.20; H, 5.80, 5.69; N, 12.51, 13.40.

Reaction of lycoraminone lactam (X) and *o*-phenylenediamine—To a solution of 0.1 g. of lycoraminone lactam in 3 cc. of absolute alcohol was added 36 mg. of *o*-phenylenediamine in 1 cc. of absolute alcohol. The solution was refluxed on a water bath for 3 hours and the alcohol was evaporated to dryness under a reduced pressure. The residue afforded, after trituration with ether, yellow powder, which was dissolved in 100 cc. of benzene and chromatographed over alumina to obtain three fractions on elution with benzene. The first fraction consisted of recovered *o*-phenylenediamine; the second one gave 10 mg. of colorless microcrystals, m.p. 180°, which were soluble in 10% hydrochloric acid, but less so in 3% hydrochloric acid. An attempted recrystallization from boiling alcohol was accompanied by gradual decomposition with discoloration to brown, and no crystals could be obtained pure. The third fraction furnished 20 mg. of brown resinous substance. Upon elution with methanol and evaporation of the solvent, 40 mg. of lycoraminone lactam was recovered unchanged.

Summary

The structure of lycoramine was reinvestigated and discussed. Contrary to the previous report, lycoramine, $C_{17}H_{23}O_3N$, was found to contain only one alcoholic hydroxyl group, which could be replaced by a hydrogen atom either by treatment with hydrobromic acid followed by reduction with zinc dust and alkali, or by reduction with Raney nickel of the mercaptol obtained by oxidation of the hydroxyl group by the Oppenauer method to a ketone and thioketal formation. The inert oxygen atom in the molecule appears to belong to an oxide ring fused to the C ring of the hydrophenanthridine skeleton.

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